

APPLICATION OF NANOTECHNOLOGY IN WATER RESEARCH

Edited By
Ajay Kumar Mishra

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Preface

The science of nanotechnology holds possibilities which will benefit the fields of science, technology and engineering. Increasing interest in the research and development of nanotechnology raises questions about its future prospects and possible consequences. Numerous studies have focused on the potential risks of nanotechnology to human health and the environment, since the properties of nanomaterials have always provided a sufficient case for ecotoxicological investigations. At present, limited knowledge and a number of major uncertainties exist regarding the behavior, chemical and biological interactions and toxicological properties of engineered nanomaterials.

An overview of what constitutes ethical and lawful conduct in the application of nanotechnology is provided in this book. Reasons are offered for the significance of nanotechnology in the context of water, along with the benefits and risks of this technology. National and international nanotechnology regulatory documents and their application to water are outlined, elaborating the complexities regarding the establishment of regulations and laws. This book therefore looks into the generation of new basic knowledge, which is crucial for the assessment of the fate and behavior of nanotechnology-based materials, and reviews current efforts concerning their possible impact.

Water pollution is a severe environmental problem. In recent years, various methods for the removal of inorganic and organic pollutants from water have been extensively studied. The removal of heavy metals from water always becomes the burning issue in research, and nanomaterials provide high surface area and a specific affinity for heavy metal adsorption from aqueous systems. They have better adsorption capacity, selectivity and stability than the nanoparticles used, and are also very effective for the removal of both organic and inorganic pollutants from water.

There has been an increasing amount of research attention directed towards the application of nanotechnology in water, including organic, inorganic and microbial pollutants. Described in this book are nanotechnology

applications for various water-related research areas of the environmental sciences such as remediation and speciation, membranes, nanomaterials and water treatment. There is also a comprehensive discussion about the advancements in water research.

Researchers working in a similar domain and those involved in water and environmental research applications will benefit from the fundamental concepts and advanced approaches described in the content of this book. Also benefiting are those who are working towards their graduate and postgraduate degrees in the area of nanotechnology. A platform is provided in this book for all researchers, as it covers an extensive amount of background information provided in recent literature, along with abbreviations and summaries. The broader research areas of chemistry, physics, materials science, polymer science, and engineering and nanotechnology are also presented in an interdisciplinary approach.

In brief, this book contains fundamental knowledge of the recent research and development advancements in the application of nanotechnology for water-related research fields.

Ajay Kumar Mishra
Editor

Part 1

GENERAL

Nanotechnology and Water: Ethical and Regulatory Considerations

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Abstract

This chapter provides an overview of what constitutes ethical and lawful conduct in the application of nanotechnology in the context of water in South Africa. It initially focuses on the ethical issues raised by the application of nanotechnology to water. Reasons are given for the significance of water-related nanotechnology and the benefits and risks of the technology are discussed. An outline of national and international nanotechnology regulatory documents and their application to water nanotechnology is presented along with a discussion of the complexities regarding the establishment of regulations and laws concerning nanoscience and nanotechnologies. The assistance of soft laws in the context of regulatory vacuums is highlighted. Differing perspectives of research involving people as research subjects in the context of nanotechnology and water are discussed.

Keywords: Ethics, regulation, nanotechnology, water

1.1 Introduction

This chapter provides an overview of what constitutes ethical and lawful conduct in the application of nanotechnology in the context of water in South Africa. The chapter initially focuses on the ethical issues raised by the application of nanotechnology to water. Reasons are offered for the significance of nanotechnology in the context of water and the benefits and risks of the technology are discussed. National and international nanotechnology regulatory documents and their application to water

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nanotechnology are outlined and the complexities regarding the establishment of regulations and laws related to nanoscience and nanotechnologies are described. The assistance of soft laws in the context of regulatory vacuums is highlighted. Differing perspectives of research involving people as research subjects in the context of nanotechnology and water are discussed.

The purpose of this chapter is not to take policy positions or to suggest solutions but merely to raise some of the important societal and ethical issues associated with nanotechnology, with a focus on its research and development in the water sector. In so doing, it is hoped that this section will form the basis of discussion on the policy ramifications of nanotechnology, from which positions and solutions can begin to emerge. Moreover, it is hoped that recognition of the ethical issues associated with nanotechnology will enable future ethical reviews of proposed nanotechnology research in order for the appropriate development to be carried out.

1.2 Ethics and Nanotechnology

1.2.1 What Is Ethics?

Before considering some of the main ethical issues generally related to nanotechnology and those concerning its application in the water sector, it is necessary to provide the reader with some idea of what “ethics” is and to describe our understanding of what “ethical issue” means. We therefore begin by doing so, before discussing some of the main ethical principles that should be taken into consideration in making ethical decisions.

Ethics is a branch of moral philosophy concerned with the moral choices people make. It includes the study of right and wrong, good or bad actions and/or policies. As a study of morality, it involves a careful systematic reflection on and analysis of actions and policies. It involves clarifying concepts, justification and analyzing or evaluating arguments.

Although it is closely related to the law, ethics is not identical to law. For example, prior to 1994 in South Africa, even though apartheid was law, it was certainly not ethical. In many countries, however, ethics is incorporated into aspects of the law. For example, in South Africa the Bill of Rights makes it unlawful to unfairly discriminate against other people on the basis of, among other grounds, race.

Ethical judgments are not just people expressing their opinions or personal preferences or stating the legal position on an issue. In ethics it is

not enough to say that an action or policy is right or wrong, good or bad, without explaining why and without providing defensible reasons for one's position. Ethics is an exercise of reason and not merely a recital of the law or a set of ethical codes that have been developed to apply to a select group of people. In ethics, our judgments must be justified, i.e., backed by good reasons grounded in ethical principles. The ideas that should come out on top are the ones best supported by the best reasons.

1.2.2 What Is an Ethical Issue?

We can simply understand an “ethical issue” to mean an issue on which disputants’ differences in judgment or belief stem from differing assessments of the matter made from an ethical perspective [1]. An “ethical perspective” is one in which action assessments hinge on the assessor’s beliefs about its likely consequences for the well-being of parties affected or likely to be affected by it, or on the belief that the action (or practice or policy) is intrinsically good or right, evil or wrong, or obligatory [1]. An ethical perspective is to be understood here as a perspective of ethics and to be contrasted with, say, a legal perspective. An ethical dilemma is a situation in which no solution seems completely satisfactory. Opposing courses of action may seem equally desirable, or all possible solutions may seem undesirable [2].

Issues such as, for example, torture, abortion and physician-assisted suicide are ethical issues because agreement over what is right or best does not exist and because moral support is possible for more than one course of action. To designate them as ethical issues is, however, not to judge them as “ethical” in the positive sense that is the opposite of the negative sense connoted by “unethical.” Rather, it is to claim that matters thus designated fall within the domain of ethics. Hence, ethical issues are ones in which it is appropriate to bring to bear the concepts and principles of ethics in order to make judgments about the moral acceptability of related actions, practices or policies around controversial issues.

1.2.3 Basic Principles in Ethical Decision Making

Ethical judgments must be supported by principles. However, ethical decision making is almost never a matter of automatically applying principles and generating an answer, for two main reasons:

- The right thing to do often depends on the facts of the case which may be unknown, and

- The principles being applied may conflict with one another as well as with other values or goals.

Ethical principles derive from ethical theories or perspectives that expound different conceptions of what it means to live morally, in other words, that seek to tell us what is right and wrong. These principles provide insight into a range of important considerations that should be taken into account in ethical decision making. However, it is important to bear in mind that no single ethical principle can be applied individually. Instead, each ethical principle represents a partial contribution to an extraordinarily complex reality. So, even if we could decide which ethical principle is the “correct” one, how the principle is applied to specific practical issues will often be controversial because there is no consensus about the right or superior ethical principle. For example, one might argue that the right thing entails doing one’s duty, whereas someone else might argue it is to promote the public welfare, even at the expense of individual rights. Some of the main principles of ethics include utility, fairness, justice, proper human excellences and beneficence.

1.2.3.1 Utility

One of the most well-known general principles in ethics, the principle of utility (also known as the greatest happiness principle) tells us to produce the greatest balance of happiness over unhappiness, making sure that we give equal consideration to the happiness and unhappiness of everyone who stands to be affected by our actions. The principle of utility, whether it is applied to acts or rules, is certainly a reasonable principle, because how our behavior affects others should be of ethical concern to us. If we want our ethical rules to make our society a good society, then it is hard to argue against the claim that a happy society is better than an unhappy society. Thus the effect of our actions and ethical rules on the happiness and unhappiness of people should remain an important ethical consideration.

1.2.3.2 Fairness

Fairness is another important ethical consideration. However, knowing what the fairest thing to do is not always easy. Various conceptions of fairness have been offered, notably the Golden Rule and respect for persons. Many take the Golden Rule, to do unto others as we would have them do unto us, to be the best standard of fairness. If we are to act ethically, we must, in terms of the Golden Rule, follow the same ethical rules in our

dealings with others that we expect them to follow in their dealings with us. Thus the same ethical standards must apply to all of us.

Another conception of fairness is grounded in the principle of respect for persons, where fairness entails treating other people with respect. This kind of respect is quite distinct from the kind of respect exemplified by calling people by their appropriate titles. It is a special kind of respect, which is captured by the ethical standard to never use other people merely as means to your own ends. Respect for persons is closely tied to the notion that persons are autonomous beings. Our behavior is the product of our choices and our choices are the product of what we take to be the best reasons for acting. And that is what makes us autonomous. As rational beings, we have our own goals and aspirations, we are capable of evaluating and weighing them against one another, we can reject or change them as we see fit, and we can determine how best to achieve those goals and then act accordingly. To respect persons, then, is to recognize that they have their own reasons for acting and to give those reasons the same respect we feel our reasons warrant from others. Thus on this conception, fairness requires that we never use other people merely to serve our own ends, but rather that we treat others as persons who have their own ends in life. Typically we fail to respect others when we coerce, manipulate or deceive them to act in certain ways.

1.2.3.3 *Justice*

Most, if not all, people want to live in a just society, but while they may agree that we are ethically required to be just, they are as likely to disagree about what justice requires. For some being just means respecting individual rights, for others, it means protection from harm and exploitation, i.e., that no one has an unfair advantage over others. Still for others it means treating people equally, giving equal treatment and distributing society's limited resources in an equitable manner—be it on the basis of need, merit, or ability to pay, for example. What makes society a just one is therefore a controversial matter. In research, justice is usually understood as fair distribution of benefits and burdens.

1.2.3.4 *Proper Human Excellences*

Whereas the other principles already described provide general guidelines for how we ought to act toward one another, and focus on individuals' duties towards one other, another important aspect of ethics does not focus on duties but on the character traits and activities that are distinctively human, and which taken together, constitute the good life for human

beings. According to this approach to ethics there are certain excellences, what are often called virtues, uniquely proper to human life. In terms of this approach to ethics, the full ethical or good life involves the development of these excellences in the fulfillment of our social roles.

Human excellences are usually tied to our various social roles, be it as children, as parents, friends, educators, physicians, lifeguards, citizens and so on. Some people might therefore, for example, argue that responsible stewardship is a proper excellence of the government and its officials, which posits a duty on them to demonstrate concern for both those who are not in a position to represent themselves and for the environment in which future generations would either flourish or suffer. Some excellences, such as compassion, loyalty, generosity, honesty, kindness and the like are, however, thought proper to us all.

1.2.3.5 Beneficence

Beneficence emphasizes the ethical importance of doing good to others by, for example, promoting or maximizing what is best for them—individuals and groups—while simultaneously minimizing harm to individuals and the general public. The principle requires that the potential benefits and harms and their probabilities be weighed up at the same time to decide what overall is in an individual or group's interests. In a research setting, the principle finds expression in a favorable risk/benefit assessment or ratio. This means that the research must have social value or utility, in other words, that the research aims are worthwhile, and that the potential risks of research are reasonable in light of the expected benefits.

1.2.4 Significance of Nanotechnology in the Water Sector

Throughout the world, countries are faced with growing challenges of access to clean and safe drinking water. In 2002, 1.1 billion people did not have access to a reliable water supply and 2.6 billion people lacked access to adequate sanitation [3]. A common problem in developing countries is drinking water that is contaminated with bacteria and viruses, which are the main cause of waterborne diseases. Recent statistics indicate that more people are dying annually from unsafe water than from all forms of violence combined, including war [4].

In South Africa, an estimated 5.7 million people lack access to basic water services, and about 17 to 18 million people lack basic sanitation services [4]. These figures are likely to increase due to industrial explosion, rising population and climate change, which is set to drastically affect sub-Saharan Africa. Finding new ways to address the challenge of providing clean water

has become a global priority. One of the approaches being explored in many countries, including South Africa, is the application of nanotechnology.

1.2.5 Benefits of Nanotechnology

Nanotechnology is among the most revolutionary technologies in human history. It has the potential to provide innovative solutions to technological problems that have been with us for some time [5]. According to the United Nations Educational, Scientific and Cultural Organization (UNESCO), nanotechnology could do a great many good things for society because of its potential to change things such as increase the speed of memory chips, remove pollution particles in water and air, find cancer cells quicker, alleviate world hunger, clean the environment, cure cancer and spur economic development through spin-offs from research [6]. Nanotechnology-driven capabilities have dramatically revolutionized the way doctors' treat their patients, the way clean energy is generated, how contaminated environmental ecosystems can be remediated, and how very clean water will likely be provided in the most rural human settings. These applications, among other things, have great relevance to South Africa, particularly in addressing some of the Government's challenges such as poverty alleviation, rural development, health and sanitation. In South Africa, water is one of six focus areas highlighted in the country's National Nanotechnology Strategy [7] in which nanotechnology can offer the most significant benefits for the country.

The water sector can apply nanotechnology to develop cost-effective and high-performance water treatment systems, as well as instant and continuous ways to monitor water quality, among other things. Nanotechnology provides an opportunity to refine and optimize current techniques, and offers new methods for treating domestic, industrial and mining wastewater. Essentially, nanotechnology can offer solutions that are tailor-made to remove a specific contaminant or solutions that "multi-task" using different nano-based techniques. This is ideal for water pollution because water contains different forms of contamination at different locations such as heavy metals (e.g., mercury, arsenic), biological toxins including waterborne-disease causing pathogens (e.g., cholera, typhoid), as well as organic and inorganic solutes [4].

In South Africa, the applications of nanotechnology being investigated and applied in the water sector include:

- Nanofiltration membranes which act as a physical barrier and selectively reject substances smaller than their pores, removing harmful pollutants and retaining useful nutrients present in water.

- Nanocatalysts and magnetic nanoparticles that can chemically break down pollutants right where they are, avoiding the need to transport them elsewhere.
- Sensing and detection of biological and chemical contaminants at very low concentrations in the environment, including water [8].

Some developments in the use of nanotechnology in the water sector in South Africa include the “tea bag water filter” that can be placed in the neck of a bottle to kill disease-causing microbes as water passes through the filter, making the water safe to drink¹, and a water treatment plant incorporating ultrafiltration membranes to clean brackish groundwater (i.e., water that is salty, but less so than sea water) or borehole water [9]. These developments may provide cheap solutions to purify water in South Africa’s remote areas. It could also potentially be used worldwide in areas where clean water supplies are threatened by waterborne diseases such as cholera as a result of natural disasters such as earthquakes and floods. The potential for global impact is therefore huge [4].

Nanotechnology offers a number of benefits to the water sector, for instance by enabling more effective removal of contaminants at lower concentrations due to increased specificity and “smart filters” tailored for specific uses. Novel reactions at the nanoscale due to increased numbers of surface atoms may also enable the removal of contaminants that were previously very difficult to treat. The number of treatment steps, the quantity of materials, as well as the cost and energy required to purify water could be radically reduced using nanotechnology—making it easier to implement in rural remote communities. Nanotechnology could therefore potentially lead to cost-effective and high-performance water treatment systems because it has the scope and performance potential to generate technically and environmentally appropriate solutions to water-related problems over a wide spectrum. In addition to improved treatment technologies, it offers the promise of cleaning up historic pollution problems and the potential for instant and continuous monitoring of water quality. Because nanotechnology has the potential to solve water quality challenges, research efforts in this field could serve to ameliorate many of the world’s water problems.

¹The inside of the tea bag is coated with a thin film of biocides encapsulated with nanofibers, so as the filter traps bacteria they are killed by the biocide coating. At the time of writing this chapter, the “tea bag water filter” was to be tested by the South African Bureau of Standards (SABS), before it is considered for introduction to various communities.

1.2.6 Ethical Issues and Concerns Related to Application of Nanotechnology in the Water Sector

Because ethics also involves clarifying concepts, it is important to recognize that although the term nanotechnology is widely used, there is a range of definitions of what nanotechnology is or could be; and it is important to recognize that none has been agreed upon [6]. Definitions vary around the world depending on what countries hope it will achieve—whether that relates to the body and human medicine, the environment, new materials or new biological objects—for the interests of nations and social actors interested in nanotechnology [6].

A broad definition defines nanotechnology as research conducted at the nanoscale, i.e., one billionth of a meter² [6]. A more specific definition defines nanotechnology as involving “research and technology development at the atomic, molecular, or macromolecular levels, in the length scale of approximately 1 to 100 nm range, to provide fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices, and systems that have novel properties and functions because of their small and/or intermediate size” [10].

Another definition sees nanotechnology as representing a new kind of science that emerges at the nexus of biology, information technology and cognitive sciences at the nanoscale [11]. In South Africa, the South African Agency for Science and Technology Advancement (SAASTA) defines nanotechnology as the manipulation of materials at a very tiny scale—essentially the atomic and molecular levels [4].

Nanotechnology-related ethical issues are ethical issues related to nanotechnology research and development (R&D) or manufacturing activity, or to the diffusion, regulation, or use of nanotechnology materials and final products [1].

Nanotechnology has the potential to benefit the public health and welfare. However, like other technologies such as biotechnology, nuclear technologies and computer technologies, the introduction and implementation of nanotechnology raise serious societal and ethical issues, both for scientists who are developing this technology and for members of the public. Many of the issues are the same as those that affect a wide range of other technologies. So, while the technology is new, the issues it gives rise to have been faced before by researchers and society.

²For reference, a human hair is roughly 20,000 nm in diameter. Molecules, viruses and atoms are objects that range from less than 1 nanometer (atoms) to about 100 nanometers (e.g., large molecules like DNA).

1.2.6.1 *Issues of Safety, Toxicity and Environmental Impact*

One of the most pressing issues related to nanotechnology are toxicity and exposure to humans and the environment because of our current poor understanding of the fate and behavior of nanoparticles in humans and the environment. There are two main concerns related to nanotechnology: the hazardousness of nanoparticles and the exposure of risk [6]. The first concerns the biological and chemical effects of nanoparticles on humans or the environment; the second concerns the issue of leakage, spillage, circulation, and concentration of nanoparticles that would cause a hazard to humans or the environment [6]. There are concerns that the same properties (size, shape, reactivity, etc.) that make nanomaterials so useful could also make them harmful to the environment and toxic to humans, for example, if they enter and build up in drinking water supplies and the food chain [9]. Additionally, although nano-enabled technology can significantly improve the quality of water, nanoparticles are likely to interact with and destroy beneficial bacteria, which play an important role in wastewater treatment plants [9].

It is, however, important to distinguish between three types of nanoparticles when discussing safety considerations: “engineered” nanoparticles (such as buckyballs and gold nanoshells); “incidental” nanoparticles (such as those found in welding fumes, cooking and diesel exhaust) and “naturally occurring” nanoparticles (such as salt spray from the ocean or forest-fire combustion). Only engineered nanoparticles constitute an entirely new class of particles and thus might pose new forms of hazards or exposure risks, and therefore new questions about how to deal with them [6]. It is also important to note that buckyballs are the only engineered nanoparticles that have, at least up until 2006, been seriously studied, whereas incidental nanoparticles (which are often also referred to as “ultrafine particulate matter”) have been studied more extensively [6]. Studies conducted on the toxicity of nanoparticles such as fullerenes have shown it to be hazardous³. However, there are considerable difficulties in assessing the environmental and ecological impact of nanotechnology because of uncertainties and knowledge gaps, largely due to the natural complexity of ecological cycles, and the impossibility of directly experimenting with the natural environment. Knowledge about the hazard and exposure risk of nanoparticles to the ecology is therefore slim [6]. Thus, the proper question for regulators

³ For example, one study demonstrated oxidative damage to the brain in the largemouth bass (Oberdöster, E. 2004. Manufactured nanomaterials [fullerenes, C 60] induce oxidative stress in brain of juvenile largemouth bass. *Environmental Health Perspectives*, 112(10): 1058–1062).

and policy makers to ask of nanotechnology is not, “Is it safe?” but rather, “How can we make nanotechnology safer?” [6].

The social, economic and environmental benefits of nanotechnology are beyond debate, however, because there are uncertainties and knowledge gaps and consequently a lack of data on possible risks associated with nanoparticles to humans and the environment, risk assessment and management is crucial [4, 9]. It is necessary to identify the acceptable risk threshold and to balance the potential benefits as well as the potential harms, respecting the values at stake. Challenges that need to be resolved before nanoparticles could be successfully used on a large scale in water treatment include safety evaluation, large-scale production facilities, safe disposal of wastes and energy efficiency. These are major challenges that may cause major delays in the large-scale application of nanotechnology in water treatment [12].

1.2.6.2 Distributive Justice Issues

Some of the important issues concerning nanotechnology relates to the question of a knowledge gap and the degree to which the kinds and direction of nanotechnology research will benefit all nations equally. Nanotechnology could be less accessible to developing countries compared to developed countries due to barriers effectively being imposed by financial costs required for the development of nanotechnology. At the same time, however, it is often citizens of developing countries that are most likely to be involved as research participants for nanotechnology development, and therefore who bear the potential burden or risks associated with nanotechnology. Additionally, there is the concern that focusing on nanotechnology may divert funding from tackling diseases that affect developing countries. While nanotechnology can create new opportunities for people, the overall goals of research in this area must be seen in the context of fair distribution and the improvement of the health and welfare of people. If public funds are to be used to conduct nanotechnology research, there must be fair sharing of burdens and benefits. When research and technological developments are funded by public money, it must benefit citizens.

1.2.6.3 Intellectual Property Rights Issues

One of the troubling issues that nanotechnology gives rise to concerns the very structure of science itself [6]. Typically we believe that science should serve the needs of society, that research must have social value, and that scientific knowledge is a common good. However, technological practices often do not. The concept of intellectual property rights (IPR) poses a problem because on the one hand it can be seen as an incentive for

invention and innovation, while on the other hand it can equally be seen as a barrier to universal acceptability of products emanating from research; thus making science a means for corporate profitability rather than a public good. Because of the nature of nanoscience, over-patenting is a definite foreseeable risk which could adversely affect transactional costs. This would impact further on the nano-divide (developed-developing world).

1.2.6.4 Public Involvement and Consumer Awareness

Public and civil society groupings should be involved early on in interdisciplinary discussions on intellectual property and safety and toxicity issues that emanate from nanotechnologies. Consumer awareness and participation in the formulation of nanotechnology policy is requisite. Nowadays one of the core questions concerning the development of any scientific or technical product is the degree of trust and reliability that consumers and citizens put in the information they are given [6].

In the context of lack of knowledge and uncertainties it is challenging to provide adequate information and to obtain informed consent. In addition, the information sharing should go beyond informing the public as if it is a prerequisite for effective marketing of commercial products. What is needed is transparency and openness, not only on the possible benefits but also on the harms and risks, even if uncertain and unknown. In so doing, public trust is earned.

Thus far we have outlined some of the important considerations that we can bring to bear when deciding how we should act, whether individually or collectively. Basing our judgments on ethical principles is necessary if we are to deal with the ethical issues raised by nanotechnology. It is, however, important to note that principles point only to the direction of an argument and are not a substitute for argument. Thus we must make sure that debates on these issues are thoughtful, careful and, importantly, well-reasoned. Moreover, these debates should inform pertinent laws and regulations in the field.

1.3 Legal and Regulatory Issues and Concerns Related to the Application of Nanotechnology in the Water Sector

While nanoscience and its resultant technologies progress at a rapid rate, laws and regulations have lagged behind. Nanotechnology has created its own set of legal and regulatory complexities. New laws and clarification

of uncertainties are now required. In addition, challenges to aspects of existing laws will emerge [13]. Currently, nanotechnology specific regulations and laws have not been established in South Africa. This is because this technology is still in its infancy in the country and scientific evidence and data to demonstrate the impact of products already in use is lacking. Moreover, for these reasons, national regulations developed around the world are also relatively “loose” [8]. In addition, because this is an emerging technology, there is a huge and persistent lack of clarity about nanotechnology risks, which in turn creates profound dilemmas for regulators and lawmakers alike. Profound uncertainties about the adequacy of existing risk assessment and management frameworks and about rapidly progressing scientific and commercial developments now confront regulatory systems. Rapid commercialization and overwhelmingly complex future generations of nanotechnologies underscores the limitations of existing regulatory frameworks to deal with emerging risks. Needless to say, this has also impacted negatively on international governance of nanotechnology [14]. Hence, proper and appropriate regulatory action is complex and protracted. In the absence of hard regulations in the field, some countries like South Africa have opted for soft regulations to guide the processes in the interim. Currently, South Africa has developed a Draft Code of Conduct which has drawn significantly from the European Commission’s (EC) Code of Conduct for Responsible Nanoscience and Nanotechnology Research [15].

1.3.1 The EC’s Code of Conduct for Responsible Nanoscience and Nanotechnology Research and Other Initiatives

The EC’s Code of Conduct is voluntary and offers a set of general principles and guidelines for actions to be taken by all stakeholders. The Code sets out to facilitate and underpin regulatory and non-regulatory approaches. The general principles are as follows:

- a. **Meaning:** Research activities should be comprehensible to the public and their design, implementation, dissemination and use should be in the interest of the well-being of individuals and society and with respect to fundamental human rights.
- b. **Sustainability:** Safe and ethical research should be conducted. Research should contribute to sustainable development as well as the United Nations’ Millennium Development Goals and should not harm or create a biological, physical or moral

- threat to people, animals, plants or the environment currently or in the future.
- c. **Precaution:** The precautionary principle should underline research activities. Potential environmental, health and safety impacts should be anticipated. Due precaution, proportional to the level of protection should be taken while progress for the benefit for science and society is encouraged.
 - d. **Inclusiveness:** The principles of openness to all stakeholders, transparency and respect for the legitimate right of access to information should guide governance of research activities. All stakeholders should participate in decision-making processes.
 - e. **Excellence:** Research should be conducted in accordance with best scientific standards, including standards that underpin research integrity and Good Laboratory Practices.
 - f. **Innovation:** Maximum creativity, flexibility and planning ability for innovation and growth should be encouraged.
 - g. **Accountability:** Researchers and research organizations should remain accountable for the social, environmental and human health impacts of their research on present and future generations.

While there are several drawbacks to the Code itself, there has been unambiguous agreement on its principles by the EU Member States [16].

Other initiatives include the World Health Organization's Dakar Statement on Nanotechnology and Manufactured Nanomaterials which requests governments to apply the precautionary principle as one of the general principles of risk management. It also calls for more international cooperation in information sharing and risk assessment [18]. While these initiatives play an important coping role in the current climate of regulatory and legal uncertainties, their voluntary nature is a substantial disadvantage.

1.3.2 The Precautionary Principle

Because of scientific uncertainties with regard to risks, states have responded in different ways with a "wait and see" approach at one end of the spectrum, where regulatory action is delayed until sufficient knowledge about risks becomes available, to a precautionary response where

regulatory action to limit or prevent potential harm from uncertain risks is enacted. In both instances competing values of technology promotion versus harm prevention are weighed up [14].

The Precautionary Principle is a philosophical approach allowing for decision making by policy makers when uncertainties and risks result in potential for harm to humans and the environment. It is a concept that was born in Germany in the 1970s and drives the implementation of environmental policies that aim to bridge the gap between science, society and the environment. It has been widely adopted by the EU in its policies and codes [18]. In 2011, the Wingspread Statement on the Precautionary Principle was adopted. It states that when activities threaten harm to the environment or human health, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically [19]. Because of the possibility of the Principle serving to inhibit research and development, it has not been widely adopted in some countries, including the US. However, the cost of not exercising appropriate caution when the potential implications of an action are uncertain must be borne in mind, and while the Principle has been the subject of much debate it does provide the opportunity to balance scientific knowledge with uncertainties. It is for these reasons that a product could be banned in one country but not in another [18]. South Africa, in adopting the guiding principles in the EU Code of Conduct, has opted for the precautionary route to steer its policies when it embarks on developing regulations for nanoscience and nanotechnologies.

1.4 Nanotechnology, Water and Human Health Research

Because considerable uncertainty exists on the potential for threats to the environment and human health by nanomaterials, it is possible that human subjects' research may be embarked upon at some stage. International and most national norms demand high standards of ethics to maximize participant protections and benefit sharing in research. Respecting autonomous decision making means that enrollment can only be effected by the participant making an informed choice. Informed consent is regarded as a process that starts at recruitment and is reinforced throughout the study. Respecting autonomy also entails protecting participants' privacy and confidentiality. The benefits of research should always outweigh its potential harms, and individuals and communities should be better off, or at least

no worse off, as a result of the research. In addition, the risks and benefits must be distributed equitably in society and vulnerable groups should not be made the subjects of research and should not be disproportionately exposed to risks for the benefit of privileged groups.

In South Africa, the National Health Act (No 61 of 2003, chapter 9) makes it mandatory for all health research to be reviewed and approved by a Research Ethics Committee registered with the National Health Research Ethics Council before the research is undertaken.

1.5 Conclusion

In this chapter we provided an overview of what constitutes ethical and regulatory conduct in the application of nanotechnology in the context of water. We described some of the main ethical principles and issues raised by the application of nanotechnology and explored the benefits and risks of the technology. We discussed how national and international regulatory documents apply to water nanotechnology, mindful of the complexities regarding the establishment of regulations and laws in the situation of nanoscience and nanotechnologies.

Nanotechnology is generally regarded as a new generation of technology with the potential to revolutionize most facets of the world we live in. This includes virtually all aspects of our daily lives, including health and health care, the materials and equipment we use and the way they are manufactured, and our environment and protection thereof. Nanotechnology can be used to develop new products, and also to work towards clean water, renewable energy, safe food and smart medicines for the growing number of people on our planet [12]. However, nanotechnology brings with it old and new ethical dilemmas and profound regulatory complexities because of uncertainties regarding risks, both in the present and the future. As with earlier technological advances, regulatory and legal responses have lagged behind. Because of the many cross-national regulatory challenges, the extremely fundamental nature of the challenges, and the lack of harmonization in responses between states, international coordination and cooperation are essential. In addressing the potential benefits and risks of nanotechnology, it is critical to engage diverse stakeholders at various levels of nanotechnology research and development.

Findings of an investigation into nanoscale research in South Africa suggest that it is driven by individual researchers' interests, that it is still in its early stages of development, and that South Africa's nanoscale research is below what one would expect [20]. Therefore we need research in the

areas of safety, toxicity, health and environmental effects, and the ethical issues related to the production of nanotechnology.

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Nanoparticles Released into Water Systems from Nanoproducts and Structural Nanocomposites Applications

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Abstract

The increasing research and production of nanomaterials raise questions about their fate and behavior. The manufacturing of nanocomposites for engineering applications or everyday goods is omnipresent. Consequently, numerous studies have focused on studying the potential health risks of nanoparticles and nanomaterials on human health and the environment. To do so the properties of different nanoparticles must be characterized and a sufficient amount must be sampled for ecotoxicological investigations. At present, limited knowledge and a number of major uncertainties exist regarding the behavior, chemical and biological interactions, and toxicological properties of engineered nanomaterials. This chapter will therefore look into the generation of new basic knowledge which is crucial for the assessment of the fate and behavior of nanotechnology-based materials, and review current efforts related to the possible impacts that occur during the whole life cycle of nanomaterials.

Keywords: Polyurethane nanofoam, layered silicates, nanodust, generated nanoparticles

2.1 Introduction

Attention has been focused on nanoreinforced polymers because of their potential to exhibit impressive enhancements of material properties compared to pure polymers [1]. For lightweight constructions, among various

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nanocomposites, much attention has been paid to polymer/silica nanocomposites because of their enhanced mechanical properties, high thermal stability and high flame retardancy. Nanoclays account for approximately 70% of the total volume of nanomaterials commercially used [2, 3]. Nanoclays are widely used in the automotive and packaging sector, mainly due to their low cost and availability. PMMA-epoxy-nanoclay composites [4], polypropylene-nanoclay composites [5], polyvinylidene fluoride-nanoclay nanocomposites [6] and nanoclay-modified rigid polyurethane foam [7] have exhibited improved properties when compared to their bulk polymer constituents and conventional macro-composite counterparts. Numerous studies have reported the improvement of energy absorption of nanoclay/polymer nanocomposites [8–11]. For example, John *et al.* [12] have shown that the incorporation of 2 and 4 vol% of nanoclay, respectively, improves the tensile modulus of cyanate ester syntactic foams by 6 and 80%.

On the other hand, increasing research and production of nanomaterials raise questions about their fate and behavior. Consequently, numerous studies have focused on studying the potential health risks of nanoparticles and nanomaterials [13–15]. The European Union funded several projects dealing with the toxicological effect of nanoparticles. The NANOTOX (Investigative support for the elucidation of the toxicological impact of nanoparticles on human health and the environment) [16] and NEPHH (Nanomaterial related environmental pollution and health hazard throughout their life cycle) [17] Projects both deal with the toxicological impact of nanoparticles on human health and the environment. To do so the properties of different nanoparticles must be characterized and a sufficient amount must be sampled for toxicological investigations. In relation to toxicological studies, investigation of all physical and chemical parameters would be ideal, but represents a major workload. A significant number of parameters can therefore be retained as a minimum for successfully conducting meaningful toxicological studies [18]. These would include: particle size, particle distribution, specific surface area, crystalline structure, surface reactivity, surface composition and purity. Limited knowledge and a number of major uncertainties exist at present regarding the behavior, chemical and biological interactions, and toxicological properties of engineered nanomaterials.

The evaluation and understanding of these properties require the collection of the nanoparticles released and their analyses. Three different techniques are, at present, used to collect nanosized particles [19]: electrostatic precipitation [20], impingement [19, 21] and filtration; and the placement of the particles onto a water-based medium in preparation is

often necessary for the analyses [19]. In this work, we used a water solution and filtration method in order to collect and characterize the nanosized particles released from low-velocity impact testing. Various researches have already studied nanoparticle properties with similar methods, as well as the efficiency of different filtration techniques [22–24]. Akbulut *et al.* [25] showed that rate-zonal centrifugation using an aqueous multiphase system as media is an efficient method in order to separate and classify gold nanoparticles of different shapes and sizes.

2.2 Case Study on Polyurethane/Organically-Modified Montmorillonite (PU/OMMT) Nanofoam Nanoparticles in Water Suspension

The generation of new basic knowledge is crucial for the assessment of the fate and behavior of nanotechnology-based materials. At present, existing research about the potential environmental and health risks of nanoparticles [26–31] has focused on the hazard of pristine engineered nanoparticles, such as nanoclay or SiO₂. However, as shown in Figure 2.1, nanoparticles released into the environment during the nanocomposites life cycle are very likely to have different physicochemical properties than nanoparticles introduced in the matrix during the manufacturing process [32, 33]. So, the whole life cycle of nanomaterials must be conceded to ensure that possible impacts can be discovered systematically.

In the literature, we can find different cases of nanosized particles released from nanocomposites which have already been studied. The investigations [35–39] have tried to simulate the dust generation from nanocomposites during some mechanical stress situations, which concerns many processes such as dry or wet drilling, sanding, abrasion, shredding, etc.

Therefore this study will investigate the behavior of nanoclay/polyurethane foam nanocomposites intended for lightweight construction and the dust generation in water during low-velocity impact tests. Indeed, polyurethane sandwich structures are commonly used in structural applications in the aerospace, automotive or building sectors, due to their high specific strength and stiffness, low weight, excellent thermal insulation, acoustic damping or fire retardancy. However, their applications are limited because of sensitivity to impact loading damage [40]. In order to solve this problem, the addition of nanoparticles (in particular, nanoclay) into the polyurethane foams was found to enhance the material properties [41–47]. Failure strength and energy absorption capabilities were

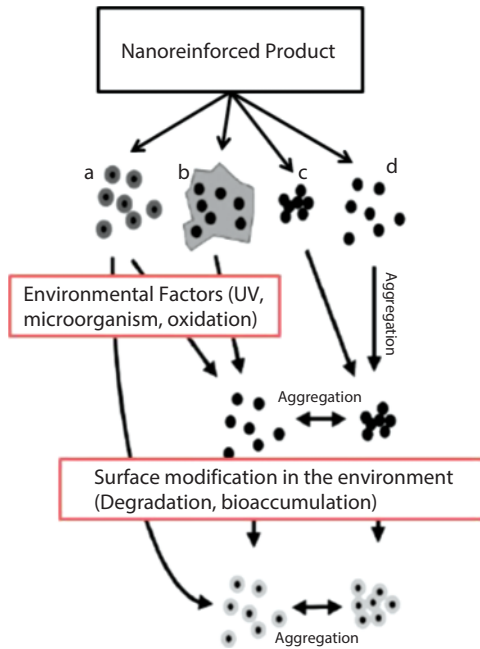


Figure 2.1 Release of nanoparticles from products and (intended or unintended) applications: (a) release of functionalized nanoparticles, (b) release of nanoparticles embedded in a matrix, (c) release of aggregates of nanoparticles and (d) release of free nanoparticles. Moreover, surface modifications (e.g., coating with natural compounds) can affect the aggregation behavior of the nanoparticles [34].

improved. It was also shown [42, 43] that the material became more brittle, which can involve a more important amount of dust generated during impact testing.

Nanoparticles were generated by impacting polyurethane/montmorillonite (PU/MMT) nanocomposites via drop-weight impact testing. The released particles were sampled and extracted by suspending them in solution. The solution was filtrated in several steps and the physical and chemical properties were characterized by means of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) measurements and Dynamic Light Scattering (DLS) technique. The results showed that two types of dust particles were generated during impact testing of the nanofoams. Single elliptical MMT layers (350 x 120 nm) and nanoparticles of composite material PU/MMT could be found in the suspension. The results clearly showed that the nanomaterial which was intergrated in the polymeric matrix could be re-founded in the fracture of the nanofoam; furthermore, a hybrid particle of PU/MMT could be detected. These

results illustrate a new insight into nanoparticle behavior and advice on a new dimension for nanomaterial risk assessment.

2.3 Methodology

2.3.1 Material Synthesis of Nanophased Composites

Polyurethane foam with different weight percentages (up to 10%) of nanoclay was manufactured in four steps at the Department of Chemistry and Technology of Polymers (Cracow University of Technology, Poland). Polyol blend (polyether RF-551) and polyester (T-425R) mixture from Alfasystems, Brzeg Dolny, Poland, was stirred with powdered MMT (Optibent 987, Süd-Chemie AG, Moosburg, Germany). Catalyst (N,N-dimethyl cyclohexylamine) water and surfactant (SR-321, Union Carbide, Marietta, GA) were added in order to prepare the polyol premix (component A), and n-pentane was added as a physical blowing agent to component A. Component B was polymeric 4, 4'-diphenylmethane diisocyanate (PM 200). It was added to component A and the mixture was stirred for 10 seconds with an overhead stirrer. Prepared mixtures were dropped into a mold. All the experiments were performed at ambient temperature of ca. 20°C.

2.3.2 Drop-Weight Impact Test and Fracture Particle Extraction

Low impact tests were conducted using an instrumented falling weight impact device (drop tower). The device was equipped with data acquisition system to acquire force versus time data. Using this machine, impact energy and velocity can be varied by changing the mass and height of the dropping weight. The velocity of the falling drop mass is measured just before it strikes the specimen. It is also fitted with pneumatic rebound brake, which prevents multiple impacts on the specimen. The dimensions of the utilized specimen were height 50 mm, width 35 mm and depth 25 mm.

Figure 2.2 shows the location of the specimen in the crash chamber. The crash test occurred against foam growth direction. The samples were placed and adjusted according to the Striker in the crash chamber. The samples were fixed vertically at the basin of the crash chamber by the two beams. The specimens were impacted with 20J impact energy level.

By impacting, the specimen fracture was obtained and sampled in the used crash chamber. After removing the chamber from the drop tower, the entrance of the chamber was sealed to minimize the possibility of

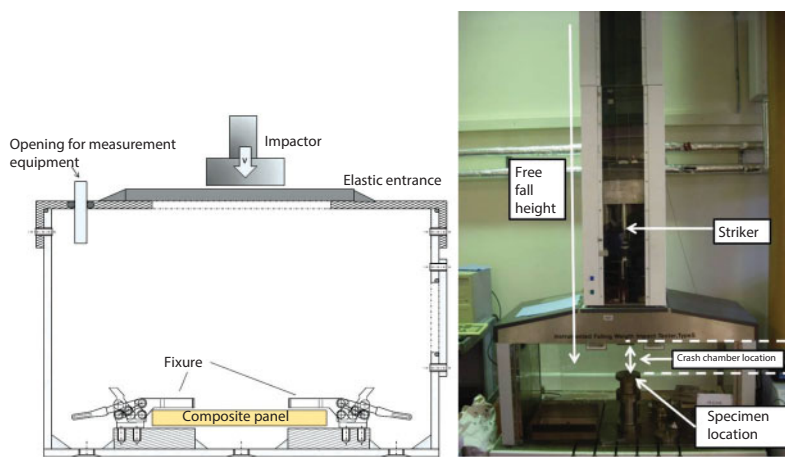


Figure 2.2 Position of the sample in the chamber and installation of the experiments.

contamination. The chamber was filled with 250 ml of double dionized water to suspend the particles in solution. The solution was then removed by means of a sterile syringe through the designed opening and stored in a glass vial. The solution was first filtered with general purpose filtrater paper (Whatman Standard Grades 11 μm). In addition, this filtered solution was placed in a sintered disk filter funnel (Duran 1.0–1.6 μm) and let filter due to gravitation.

2.3.3 Characterization

2.3.3.1 *Scanning Electron Microscopy (SEM)*

The morphology of the fracture samples was investigated by using a FEI XL30 field emission scanning electron microscope. The operating voltage was in the range of 10–20 kV to minimize charging of the sample. Specimens were prepared by sonicating the solution for 15 min at 35 kHz and dropping a drop of the solution on a Silicon Chip Specimen Substrate (SPI substrate). The silicon substrate was sonicated for 5 min at 35 kHz and then cleaned first with acetone and then with ethanol. The specimen was then left to dry in the air.

2.3.3.2 *Transmission Electron Microscopy (TEM)*

A JEOL–200CX transmission electron microscope was used to investigate the morphology of the samples. For TEM studies, solution was diluted in dionized water and sonicated for 2 hours. After centrifugation (6000 g for

10 min), the final separated slurry was sonicated for approximately 5 min to better disperse the nanoparticles. A drop was placed on a carbon-coated copper TEM grid (200–300 mesh) and then left to dry in air.

2.3.3.3 X-ray Diffraction

Powder X-ray diffraction (XRD) θ – 2θ studies were performed with q ranging between 0° and 90° using nickel-filtered Cu $K\alpha$ ($\lambda = 0.154$ nm) radiation at a scan rate of $1^\circ/\text{min}$. The XRD pattern of the PU/MMT indicates the presence of predominantly montmorillonite Na-Mg-Al-Si₄O₁₁ crystals.

2.3.3.4 Dynamic Light Scattering (DLS)

Particle size distribution was measured by Dynamic Light Scattering technique (Zetasizer Nano ZS, Malvern Instruments Ltd.). The solutions were sonicated 15 min at 35 kHz prior to investigation. With a sterile syringe, 1.5 ml of the solution was extracted and inserted into the appropriate vials for DLS.

2.4 Results and Discussion

2.4.1 Synthesized Nanocomposites

The synthesized PU/MMT nanocomposites have been characterized by means of SEM and XRD investigations. Figure 2.3A shows the powdered MMT (Optibent 987, Süd-Chemie AG, Moosburg, Germany). The arrows indicate the layer thickness d , which was measured to be approximately 5 nm. The synthesized nanocomposite can be seen in Figure 2.3B. The incorporation of MMT resulted in a higher number of cells with smaller

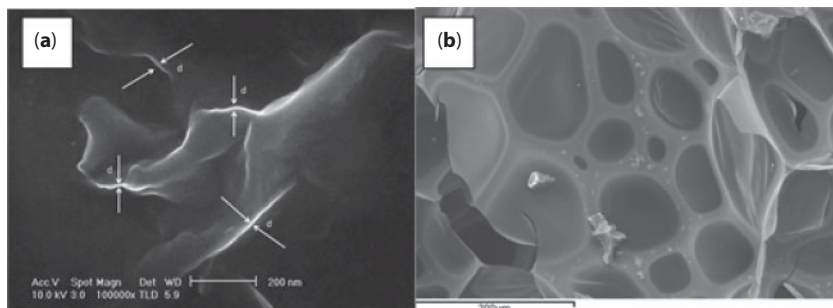


Figure 2.3 SEM image of (a) powdered MMT and (b) PU/MMT nanocomposite.

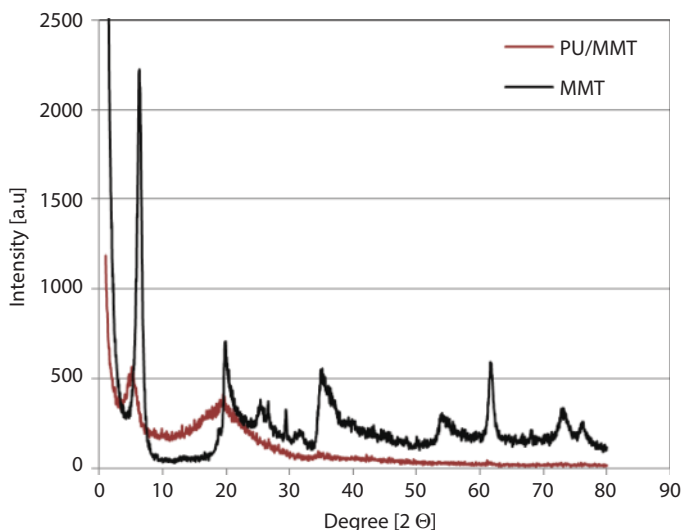


Figure 2.4 The X-ray diffraction (XRD) pattern of a pure polyurethane of PU/MMT with 10% MMT.

dimensions and higher anisotropy index. The nanolayers (observed as small spots) were approximately 3–5 nm thick and well dispersed on the surface of the polyurethane. The SEM results indicate that the MMT particles are completely disordered and dispersed relatively homogeneously on the nanoscale in the PU matrix.

The XRD curves of MMT powder and the PU/MMT composites are presented in Figure 2.4. The discernible peaks which can be clearly identified in the scan in Figure 2.4 can be matched to the (6.9), (13.5), (19.7), (21.5), (27.0), (35.0), (48.5), (54.0), (61.76), (73.13), and (76.68) planes of a cubic MMT unit cell. It was observed that the regular arrangement of MMT layers was maintained in PU foams and diffraction peaks were displayed at about 5.2 deg and 19.3 deg (Figure 2.4). The interlayer distance in PU materials increased slightly as compared with neat MMT (peak 6.9 deg and 19.7 deg) due to intercalation of polymeric component [11, 48].

2.4.2 Generated Nanocomposite Dust from Impact Test

2.4.2.1 Morphology Studies

Figure 2.5 shows the SEM images of un-filtrated solution obtained by diluting the PU/MMT fractures. An overview of the substrate surface is given in Figure 2.5A. Characteristic for the surface area were particles, which

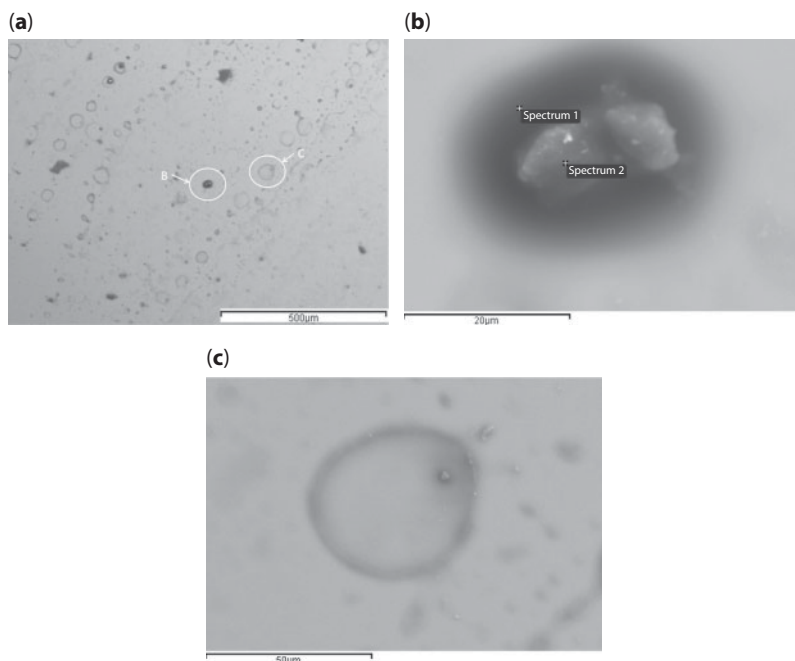


Figure 2.5 SEM images of un-filtrated solution (a) surface, (b) particle, and (c) particle and MMT atoll.

were enclosed by a black matter as shown in Figure 2.5B. Via EDX the particles' elements were detected to be the same as from the bulk PU/MMT nanocomposites, so that it can be assumed that the particles were fractures parts. The black matter could be identified by means of EDX to concisely the same elements as MMT, so that it can be assumed that it is MMT. The MMT has a highly hydrophilic nature, so it dissolves in water. This means that the MMT nanophase which was set free during impact dissolved and agglomerated due to favorite bonding to other MMT particles, and then to the surface with high surface tension, while drying. Figure 2.5C shows a particle surrounded by an atoll of MMT. It can be assumed that the surface tension is high while dropping the solution on the substrate. While drying, larger particles will be deposited on the surface due to sedimentation. This will reduce the surface tension of the substrate, and thus agglomeration is promoted.

Figure 2.6 shows the images made from the solution after the first filtration step $< 11 \mu\text{m}$. Similar to the images obtained from the unfiltered solution (Figure 2.5A), particles which were enclosed by black matter could be

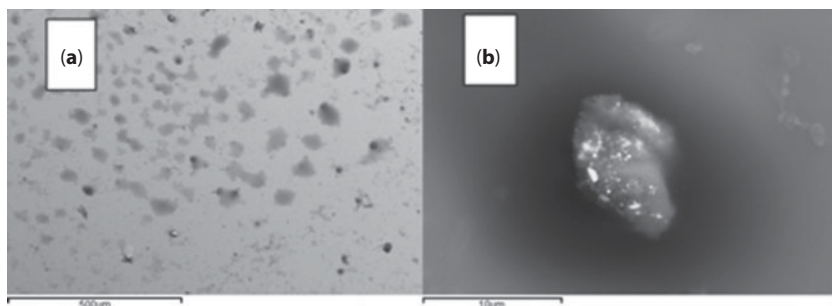


Figure 2.6 SEM images of filtrated solution < 11 μm : (a) surface and (b) particle.

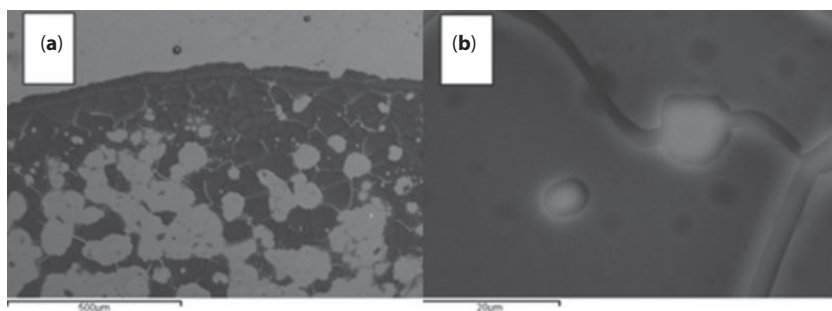


Figure 2.7 SEM images of filtrated solution < 1 μm : (a) surface and (b) aggrandisement of surface.

found. The concentration of these particles increased, as shown in Figure 2.6A, in comparison with Figure 2.5A. The particles were smaller in size (Figure 2.6B) and consisted of the same material as the bulk PU/MMT nanocomposite before impact. The same assumptions as for the unfiltered solution can be made. However, an increase in concentration and decrease of particle size could be detected.

The SEM images obtained from the solution after the second filtration step < 1 μm are shown in Figure 2.7. The surface image in Figure 2.7A shows that the substrate has been coated by a layer of black matter. The layer shows cracks and pores, which split up the layer throughout the whole coating. The EDX analysis has shown that the black matter consists of the same elements as MMT powder, therefore it can be assumed that it is the MMT which was incorporated in the nanocomposite. An aggrandisement of the MMT coating shows black spots on the coating. As their mean size was approx. 5 μm , it can be excluded that those are particles at any

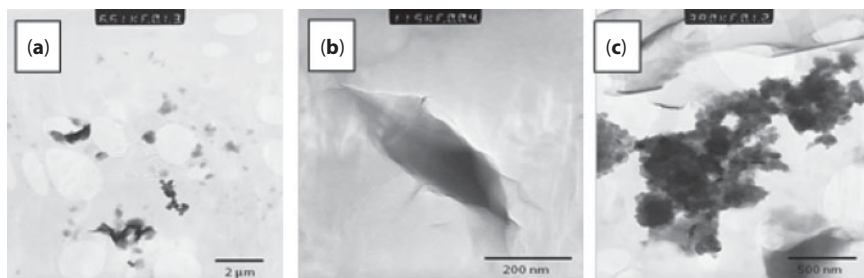


Figure 2.8 TEM images of PU/MMT fractures : (a) surface overview, (b) MMT particle, and (c) PU/MMT particle.

origin. However, it can not be excluded that smaller particles are imbedded in the matter.

The TEM images shown in Figure 2.8 indicate that through diluting, sonification and centrifugation, particles could be found that could not be seen in the SEM images. An overview of the surface can be seen in Figure 2.8A. As previously shown in SEM investigations, this image shows black matter. However, the aggrandisement of the matter shows two types of particles, as shown in Figure 2.8B and C. Single MMT particles could be found, and those kept their layered pattern and had an elliptical form with a mean semimajor axis size of 360 nm and a mean semiminor axis of 120 nm (Figure 2.8B). This indicates that some of the incorporated MMT does not bond or interact with the matrix material so that it can be released during impact testing.

Besides raw MMT particles, composite particles could be found, as shown in Figure 2.8C. This indicates that through impact testing fractures of the composites are formed. Furthermore, it shows that the intercalated structure of PU/MMT nanocomposites endures impact testing.

2.4.2.2 *Size Effect*

Dynamic Light Scattering analysis was conducted to analyze the particles in a suspension, as imaging of the particles without diluting, ultrasonification and centrifugation was not possible. The DLS analysis could size particles in the size range of 255–458 nm, as shown in Figure 2.9. The results indicate that by filtration of the solution the frequency of smaller particles increases. By filtration of the origin solution, the 255-nm-sized particles could be increased from 1.1% to 9.9%. The results of the DLS correlate well with the investigations obtained via SEM. Furthermore, the DLS results show that the highest frequency can be found for a particle size of 342 nm

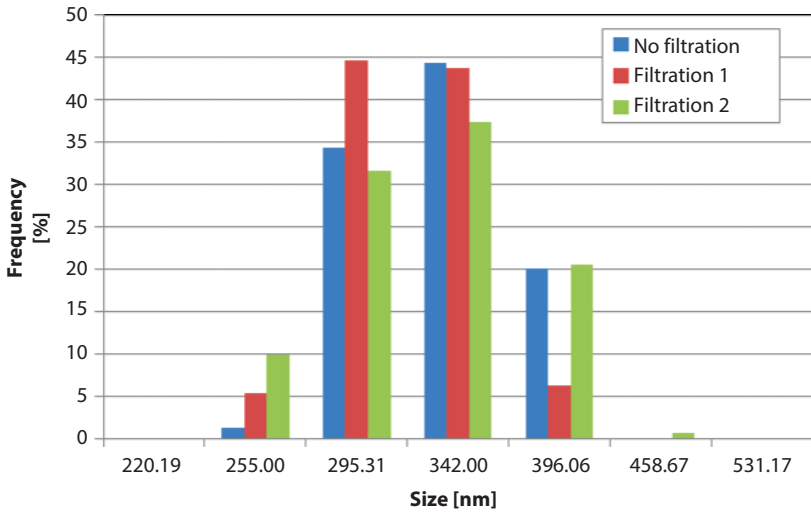


Figure 2.9 DLS analysis of suspensions.

within all solutions. However, it has to be kept in mind that DLS analysis is based on the theory that the investigated particles are perfect spheres.

2.5 Conclusion

This study has shown that by impacting polyurethane/montmorillonite (PU/MMT) nanocomposites via low-energy impact test, nanoparticles can be generated. Through filtration steps the concentration of particles in a smaller size range was increased. The SEM images show that after the second filtration step $< 1 \mu\text{m}$, mostly agglomerated MMT could be found on the substrate. However, through further dilution, ultrasonification and centrifugation of the suspension, two types of particles could be detected on TEM images, elliptical (350 x 120 nm) MMT layers and hybrid PU/MMT particles. This result indicates that although the nanocomposites had an intercalated structure, not all of the MMT integrated with the polymer was bound to the matrix, and therefore could be released during drop-tower impact testing. Furthermore, composite nanoparticles could be detected to be released during impact testing. While further toxicological studies on MMT powder can be made rather easily, the toxicological assessment of the random hybrid particles will need further investigation. Therefore, adequate sampling and measurement strategies and techniques must be considered to assess the fate and behavior of PU/MMT nanocomposites.

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Part 2

REMEDIATION

Prospects for Immobilization of Microbial Sorbents on Carbon Nanotubes for Biosorption: Bioremediation of Heavy Metals Polluted Water

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Abstract

There is growing consideration to abandon the conventional water treatment methods because of their high cost and environmental impact. Alternative methods investigated nowadays present the advantages of being cheaper and ecofriendly.

Among the biosorbents used for the bioremediation of heavy metal pollution of water are microorganisms, which have an inherent ability to uptake heavy metals from solutions.

In order to render microbial biosorbents suitable for process applications, immobilization on adequate supports is required. Apart from their large specific surface area and hollow structure, carbon nanotubes (CNTs) present a number of features making them attractive for immobilization of microbial sorbents to be used in biosorption processes.

This chapter elaborates the potential of microorganisms as biosorbents used in the bioremediation of toxic heavy metals pollution of water systems and explores the possibility of enhancing their performance through immobilization on adequate support matrices, namely carbon nanotubes.

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3.1 Dispersion of Metal Pollutants in Water Sources

Metals are inorganic constituents of the soil unevenly distributed around the world. Natural events leading to exposure of the inner part of the ground often contribute to the dispersion of metals in the environment. However, the growing number of inhabitants on earth as well as the exponential increase of industrial activities has mainly resulted in deforestation and erosion of soils, washing away the metals. Direct anthropogenic actions, which are the major sources of toxic heavy metals, consist of the mismanagement of solid and liquid wastes coming from industries such as electroplating, metal finishing, electronics, metallurgy, and mainly mining. For the scope of this study our discussion will mainly focus on metal pollution related to mining activities.

Effluents arising from mining activities may contain potential pollutants. Polluted water effluents may be produced directly during mineral processing or indirectly when heavy rain comes into contact with sulphide-bearing materials in tailings dumps, resulting in acidic effluents following oxidation. Underground and open pit mining operations always channel processed water into the nearby streams or rivers; however, mining-induced fracture in the collapsed strata promotes contamination of underground water by mine effluents. The main types of water pollution from mining operations could be identified as heavy metal contamination (from processed and acidic effluents); processing chemical pollution (from processed effluents) and acidification (from acidic effluents). Processed mine water and acidic water may contain toxic elements such as heavy metals and reagents (cyanide, sulphuric acid and mercury, used to separate valued metals from ores) that could affect the ecosystem when discharged in the environment. Mining pollution has an obvious impact on biodiversity affecting the wildlife; few terrestrial and aquatic species are known to be naturally tolerant of heavy metals, although some have adapted over time. Salmon species, for example, are particularly sensitive to increased concentrations of copper [1].

In 1989, it was estimated that about 19300 km of streams and rivers, and about 72000 ha of lakes and reservoirs worldwide had been seriously affected by mine effluents [2]. It has also been reported [3] that mining activities have led to the contamination of water in the dolomitic regions of Wonderfontein spruit (South Africa) with excessive sulphate, nitrate,

N-compounds, toxic heavy metals, including radioactive elements such as uranium, and occurrence of acid mine drainage.

Although mostly found in any soil, toxic heavy metals are abundant in mining areas, where metal rich ores have been exposed to the atmosphere. Oxidation of the sulphur content of these rocks by rain water leads to acidic water and dispersion of toxic heavy metals in the surface and groundwater systems.

3.2 Removal of Metal by Conventional Methods

Conventional techniques are used industrially to recover valuable metal or to remediate water pollution; numerous processes are currently used to remove dissolved heavy metals, among which are chemical precipitation and sludge separation, ion exchange, reverse osmosis, filtration, chemical oxidation or reduction, adsorption using activated charcoal or coagulation and electrodialysis [4–9].

Precipitation is the most commonly used removal method, particularly when metal recovery is not a consideration. This process is based on the fact that most metal hydroxides are only slightly soluble and that some metal carbonates and sulphides are also only sparingly water soluble [10]. Metal precipitation from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. The precipitate can then be removed from the treated water by physical methods such as clarification and/or filtration. The typical precipitation process using sodium hydroxide or lime as reactant is generally applicable to copper, zinc, iron or nickel removal with no special modification; well-sized reverse osmosis (RO) can then be used after prefiltration (following precipitation) to ensure that dilute solutions are totally clean.

For metal removal using ion exchange, chelated resin, for example, serves as a matrix for adsorption of target ions from the effluent system. The most efficient uses are for removing lead, copper and nickel. They exchange sodium for the target metal and pass the hardness ions, calcium and magnesium. They are effective on industrial water rinse without any preconditioning and are very effective in the direct replacement of sludge generating systems. In hydrometallurgy, after leaching process, ion exchange is used for the purification and concentration of dissolved values. Regeneration is very efficient and the target metal is usually recovered in relatively small volumes of regenerant [11].

Recovery of heavy metals by electrodialytic method consists of placing electrodes in separate compartments, where electrolyte solutions are

circulated; electrolyte solutions ensure that a good contact between the electrode surface and the surroundings is maintained [12]. Electrolysis (electro-winning or electro-refining) is used for the recovery of valuable metals after purification in hydrometallurgical plants. Ion exchange membranes determine the passage of anions or cations in the direction of anode or cathode electrodes respectively; this prevents the waste of current [12]. When an electrical potential is applied across the ion-exchange membranes, cations in solution begin to migrate toward the cathode, anions toward the anode. Metal removal in this process occurs through electroosmosis mechanism due to electrical, temperature, concentration and mechanical pressure gradients that exist across the membrane [13].

The first report of laboratory experimentation of electrodialytic remediation was done by Jakobsen *et al.* [12], who reported the removal of cadmium from wastewater sludge; the remediation process allowed the reduction of two-thirds of the total cadmium from the wastewater sludge. The recovery of valuable metals by electrolysis is technically challenging and probably not cost effective at a low production rate [14]. Furthermore, these techniques are likely to generate toxic sludge or other waste products that require careful disposal [15].

3.3 Microbial Sorbents for Removal of Toxic Heavy Metals from Water

3.3.1 Biouptake of Metal

The limitations of conventional methods present an opportunity to explore the possibility of considering a biological approach for the recovery or removal of metal from solutions. Biological methods are more effective for large volume and diluted solutions; they are cheaper and ecofriendly. Various types of biomasses such as seaweeds, molds, yeasts, crabshells and bacteria have been tested for metal biosorption with very encouraging results. However, microorganisms, especially bacteria with high growth rates, are favorable for biosorption purposes. The bacteria biosorption process involves a solid phase (biosorbents or cells) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). The affinity of the sorbent for the sorbate species promotes the attraction of the latter and binding with different mechanisms. Mechanisms involved in metal ions uptake by bacteria mainly depend on

non-metabolic and metabolic phenomena [16]. Two major mechanisms could therefore be identified as biosorption (passive binding of metal on cell surface) and accumulation (active sequestration of metal ions inside the cells) [17].

3.3.2 Factors Affecting Microbial Adsorption Capacity

3.3.2.1 Cell Age

According to Alcamo [18], bacteria growth can be separated in different stages, mainly as the lag phase, the log phase and the stationary phase. At each of these phases bacteria exhibit different morphology and the intensity of metabolic activities may vary. As demonstrated in the previous sections, heavy metal uptake by bacteria is dependent on bacterial morphology (surface availability and cell wall structure) and metabolism. It could therefore be predicted that bacteria adsorption capacity will be affected by cell age. Younger cells (24 h old) of an industrial strain of *S. cerevisiae* have been reported [19] to exhibit Ag^+ uptake capacity twice that of older cells (96 h old).

3.3.2.2 Physicochemical Effect

Conditions of the microenvironment such as pH, temperature and initial metal concentration are likely to influence metal removal by microorganisms.

The pH value of the solution is related to the amount of hydrogen ion (H^+) or hydroxyl group present and therefore influences metal uptake through hydrogen ion competition at the cell surface and changes of the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, the speciation and the biosorption availability of the heavy metals [20, 21]. In fact, at acidic pH there are hydrogen ions in solution which compete with metals for anionic functional group on cell surface, therefore reducing biosorptive capacity of metal cations [22, 23]. On the other hand, there is dissociation of metal complexes with both organic and inorganic ligands at low pH, promoting the release of aquo ion [24, 25]. Optimal pH for metal biosorption varies for almost each biosorbent; it is reported that the optimal pH value is 5–9 for copper biosorption by *S. cerevisiae*, and 4–5 for uranium [26]. In the study done by Mapolelo and Torto [27], they found that the optimal pH value for Cd and Zn biosorption is 5.8, while for Cr(III) and Pb it is 5.2. This implies that the influence of pH value on metal biosorption varies

among metal species and biosorbent, therefore requiring further studies to classify specificity.

The function and cell structure of microbial sorbents can be affected by temperature changes [28]; high temperature to a certain extent may lead to the increase of metabolic activity and energy of the system (metal solution), which could promote the active uptake or attachment of metal to cell surface respectively [29, 30]. Goyal *et al.* [29] found that the metal biosorption of Cr(VI) by *S. cerevisiae* increases with increasing temperature in the range of 25–45°C, which they explained was as a result of the increased affinity of cell surface sites for metal at higher temperature. The decrease of biosorption capacity at higher temperature may be due to the damage of active binding sites in the biomass [31]. Most of the researchers have concluded that the change of temperature in the range of 30–40°C has a small influence on metal adsorption.

3.3.2.3 *Cell Biomass*

Metal adsorption capacity is also a function of surface availability, which is related to the concentration of biomass. High concentration of biomass provides more surfaces available for metal binding, reducing the adsorption time as well as promoting passive adsorption. However at low concentration of biomass, metal ions are likely to be sequestered inside the cells.

3.3.2.4 *Initial Concentration of Metal*

Initial metal concentration in solution may affect metal biosorption in two ways: firstly on a physiological aspect and then on a physical aspect. High initial concentration of metal is likely to inhibit metabolic activities and hinder active accumulation of metal; while the surface available for metal binding on bacterial cell could be quickly saturated at higher concentration of metal. Wang and Chen [32] reported that the uptake rate of the metal ion will increase along with increasing its initial concentration if the amount of biomass is kept constant; implying that biosorptive capacity of metal ions is related to the ratio of the concentration of initial metal ions to the concentration of biomass.

3.3.2.5 *Metals Competition*

The presence of multi-metals in solution could also affect the adsorption of the metal ion of interest. In fact, the degree of removal of heavy metal ions from wastewater by biosorption depends on the multi-metal competition for the binding sites on the surface of sorbent [33]. When various metals

are present in solution, the tendency is that the surface available on bacterial cell for binding of specific metal ions will be reduced for each metal ion, as co-ions are likely to interact with functional groups on the surface. Goksungur *et al.* [34] observed that the competitive biosorption capacities of the ethanol-treated yeast for all metal ions of Pb, Cu and Cd were lower than that under the non-competitive conditions. There was a decrease of metal uptake in competitive conditions between same charged species for binding sites of the ethanol-treated yeast cells.

3.3.2.6 Exposure Time

When exposed to heavy metals in solution, bacterial cells can immediately interact with metals and in a few minutes metal uptake can result through the passive mechanism. Kefala *et al.* [30] reported maximum removal of cadmium ions by biomass of *Actinomyces* after 5 minutes exposure time, which was in agreement with the findings by Sadowski *et al.* [35]. However, metabolic uptake of heavy metals by microbial biomass required longer exposure time. For example, Kim *et al.* [36] observed an increase of lead uptake by *Bacillus* sp over 48 hours exposure. Metal uptake is thus influenced by the exposure time and could allow determination of the mechanism involved in metal removal by bacteria.

3.3.3 Isothermic and Kinetic Equilibrium of Biosorption

Most of the experiments on heavy metals biouptake by microorganisms have only been performed at laboratory scale and very few have been implemented at an industrial level due to limited understanding of the interaction between microbial sorbent and heavy metals. For this reason recent works have focused on investigating the affinity of biomass for metal through the determination of biosorbent adsorption capacity, study of isotherm and kinetic equilibrium of the biosorption process.

The affinity of a microorganism for a given metal determines its ability to uptake a certain amount of the metal from solution. That ability is recognized as metal adsorption capacity, which is defined as the amount of heavy metal adsorbed onto the unit amount of the dry or wet biomass as expressed in mg/g.

Isotherm refers to a relation holding true at a constant temperature. The study of isotherm is important for the fact that adsorption isotherm can be used to describe how metals interact with biosorbent, and therefore is critical in establishing optimal use of biosorbent as well as the design of the bioremediation plant [37]. Various isotherm models are available but

the Langmuir and Freundlich models are the most widely accepted surface adsorption models for the single-solute systems. The Langmuir isotherm model assumes that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The model illustrates a nonlinear and saturated adsorption process that can allow the determination of the equilibrium constant, hence estimation of biosorption affinity [38].

The Freundlich isotherm model establishes the relationship between the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact. The Freundlich model is based on sorption on a heterogeneous surface [39, 40].

The rate equation for the biosorption process usually determines the rate of metal adsorption by biosorbent. Various kinetic models have been used to test experimental data, including pseudo-first, pseudo-second order and intraparticle diffusion, to examine the mechanism involved in the biosorption [38]. Among the kinetic models, pseudo-first order and pseudo-second order kinetics are the most widely used models to describe the adsorption process [41, 42]. Important parameters considered for pseudo-second order kinetics are: i) the equilibrium rate constant; ii) the equilibrium adsorption amount, and iii) the adsorption amount at a given time.

3.3.4 Drawbacks Due to Inhibition

Microorganisms use some metals as substrate required for metabolic functions; but most of the metals are likely to be toxic, especially at high concentrations. Metal removal through both passive (biosorption) and active (bioaccumulation) mechanisms can be affected by the toxicity of metal species, which affect microbial biological functions and morphology (reduces cell surface availability) [43].

The cell wall of bacteria contains some functional groups (phosphoryl, carboxyl and amino groups) responsible for binding metals present in the environment. These groups give the cell surface a negative charge density [44], therefore conferring them the ability to bind metal cations [45–48]. It is suggested that the binding of cations by the walls of many Gram-positive bacteria is a function of peptidoglycan-associated teichoic acid [49]. It therefore ensues that the Gram-negative bacteria cell wall could not have the same binding ability as with Gram-positive bacteria, owing to the fact that they possess a much thinner peptidoglycan shielded by an outer membrane [50, 51]. Nevertheless, Gram-negative bacteria possess anionic lipopolysaccharides (LPS) extended beyond the outer membrane proteins and facilitate attachment of metal to cell wall [52–54]. In some cases metals

can be sequestered into bacterial cells through two mechanisms: the first is quick and unspecific, driven by chemiosmotic gradient across the cell membrane. The second one is through an active transport requiring the hydrolysis of ATP and is slower than the previous one. Various heavy metals can easily cross the cell membrane through the first mechanism and become toxic once present in high concentrations inside the cell [55]. Most of the light metals are used in bacterial metabolic functions, but the heavy metals are essentially toxic, especially at high concentrations.

The inhibitory effect of metal, whether bacteriostatic or bactericidal, affects the morphology or the metabolic function of bacteria (Figure 3.1). For example, copper can change bacterial rods into spherical form [56]. Toxicity of metal is reported to be related to the strength of the covalent binding of the metal ion to various ionic groups on the cell surface. However, the strength of binding increases with electronegativity of each metal [57, 58]. Metal may affect oxidative phosphorylation and membrane permeability, as seen with vanadate and mercury [59]. In fact, mercury and silver ions are reported to act on cell membrane through precipitation of cellular proteins [60]. Heavy metal ions can strongly bind sulphhydryl groups of proteins and so doing change the structure and enzymatic activities of proteins and cause malfunctioning of metabolic pathways [61, 62]. For example, silver ions denature enzyme of the target cell or organism by binding to reactive groups, resulting in their precipitation

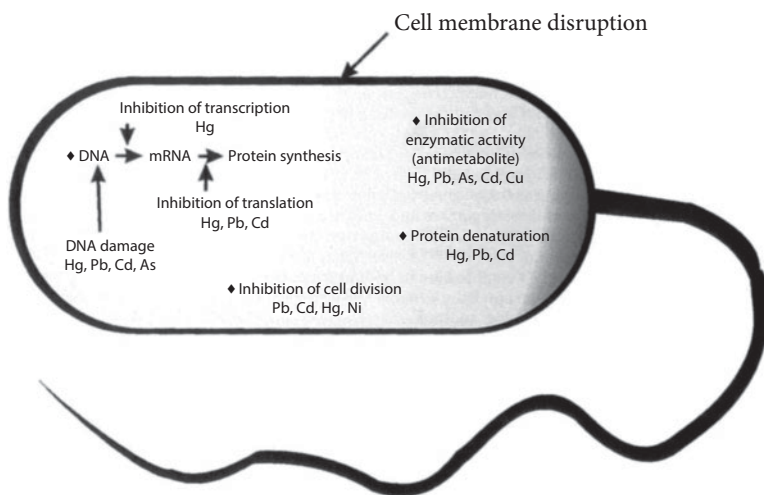


Figure 3.1 Summary of the various toxic influences of metals on the microbial cell demonstrating the ubiquity of metal toxicity (From [59]).

and inactivation; by reacting with the thiol groups on the enzymes and proteins, silver significantly inhibits the growth of bacteria [63]. However, silver also reacts with the amino-, carboxyl-, phosphate-, and imidazole-groups and diminishes the activities of lactate dehydrogenase and glutathione peroxidase.

Heavy metal cations may bind to glutathione and the resulting bis-glutathiono-complexes tend to react with molecular oxygen to oxidize bis-glutathione GS-SG [64], the metal cation and hydrogen peroxide H_2O_2 . The metal cations will then catch two glutathione molecules once the oxidized bis-glutathione is reduced again in a NADPH-dependent reaction; this process causes a considerable oxidative stress [62]. Cell mutation can also arise as an interaction of the bacteria gene with heavy metals. Khan and coworkers [65] studied the nuclease activity of nickel (II), cobalt (II) and copper (II) complexes and found that they were responsible for DNA cleavage. According to the explanation of Aruoma *et al.* [66], copper ions bound to DNA react with peroxide and ascorbic acid to generate hydroxyl radicals, which then react with DNA bases in a site-specific manner causing DNA strand breakage.

Bacteria metabolism could also be disturbed as a result of heavy metal competition with cofactor for the binding sites on enzymes. Studying the effect of metal ions (inserted at sulphur-rich sites) on the activity of sulfite oxidase, Neumann and Leimkuhler [67] found that heavy metal caused the inhibition of the enzyme and through this mechanism could become toxic to *Escherichia coli*.

The performances of microbial sorbents in some instances are unsatisfactory and pretreatment of biomasses are undertaken to increase the surface area and/or the number of active groups or to overcome challenges of inhibition, therefore improving the metal binding capacity. Pretreatment methods are either chemical or physical.

3.3.5 Metal Tolerance Mechanisms of Microbial Sorbents

Microorganisms living in an environment contaminated with a high concentration of heavy metals generally develop mechanisms allowing them to adapt to the milieu. These indigenous microorganisms can tolerate relatively high concentrations of heavy metals and are therefore suitable for use as biosorbents for metal uptake processes. Various types of metal resistance mechanisms are developed by microorganisms; these mechanisms include the efflux of metal ions outside the cell, accumulation and complexation of the metal ions inside the cell, and reduction of the heavy metal ions to a less toxic state [62]. In resistant bacteria these mechanisms can occur singly or

in combination [68, 62]. Genes conferring these resistance mechanisms mostly reside on plasmids [69–71] but also on the chromosomes [72, 73]. Efflux pumps are the major currently-known groups of plasmid resistance systems supported by proteins acting as metal-transporters (ATPases) or the chemiosmotic system across cell membrane.

Cloning of genes and expression in bacteria allows for the providing of bacteria with traits such as gene resistance, making them improved biosorbents for the biosorption process. The genetically modified bacterium can then tolerate high concentrations of a given metal, increasing its ability to uptake the metal from solutions. For example Siddiqui *et al.* [74] cloned the pMOL28-encoded nickel resistance genes in *Pseudomonas* spp and observed an increase of the ability of the conjugated species to resist higher concentrations from 0.5 to 1.5 mM NiCl_2 .

3.3.6 Pretreatment of Microbial Sorbent

Various methods have been used by researchers to pretreat biomass in order to modify the functional groups on the cell surface, therefore enhancing the metal binding capacity. Modifications can be introduced either during the growth of a microorganism or in the pregrown biomass. Modifications done during the growth generally consist of changing the composition of the culture medium. *Aspergillus niger* biomass grown in the presence of large amounts of potassium hexacyanoferrate from citric acid fermentation plant was reported [75] to exhibit very high biosorption due to change in cell wall composition.

Pretreatment of pregrown cells, consists to affect through a physical or chemical method the number of sites in the biosorbent material, the accessibility of the sites and the chemical state of the sites (i.e., binding strength) [76]. Physical methods include vacuum and freezing/thawing, boiling/heating, autoclaving and mechanical disruption. The various chemical methods used for biomass modification include treatment with various organic and inorganic reagents, such as acid and caustic, methanol and formaldehyde among others. Alkali pretreatment of *Mucor rouxii* biomass contributed to a significant increase in its bioadsorption capacity when compared to autoclaving, while pretreatment of biomass with acid resulted in decreased bioadsorption of heavy metals [77, 78].

However, microbial biosorbents in planktonic form are dispersed and could not ensure optimum mass transfer; furthermore, they may be degraded when exposed to harsh environmental conditions. Immobilization of microbial biosorbents is therefore needed for effective application of biosorption.

3.4 Immobilization of Microbial Sorbents on CNTs

The immobilization of microorganisms on carbon nanotube (CNT) is an approach that is beneficial in the implementation of various techniques. The stability of the complex microorganism-CNTs is crucial for the success of each application and is often dependent on the binding strength or features of both microorganism and CNT. In such an interaction, the nature of microbial cell membranes and the physical characteristics of CNTs play very important roles.

3.4.1 Possible Interaction between Microorganisms and CNTs

3.4.1.1 *Microbial Cell Membranes and Functional Groups*

Microorganisms are mainly divided into eukaryotic and prokaryotic cells. Eukaryotic microorganisms encompass algae, fungi and protozoa, while only two groups, namely bacteria and archaea, constitute prokaryotes. As opposed to eukaryotes, prokaryotes do not have a membrane-enclosed nucleus as well as few membranous organelles. The cytoplasmic content of these microorganisms is protected by a cell wall or cell membrane, which is the point of contact with the environment. There exist chemical differences between eukaryotic and prokaryotic membranes. Cell wall structure is also the basis of division of bacteria into Gram-positive and Gram-negative groups. The cell wall of algae is mainly composed of a network of cellulose supplemented with a variety of polysaccharides; the cell of fungi is as rigid as for the algae but mainly contains polysaccharides. Gram-positive bacteria cell wall is comprised of a thick layer of peptidoglycan which is responsible for the negative charge of the wall. The overall negative charge of the Gram-negative cell wall is due to the dominant presence of lipopolysaccharides, which are highly charged in nature.

The components of the cell surface of the microorganism also include ligands such as OH^- , HPO_4^{2-} , CO_3^{2-} , R-COO^- , $=\text{C=O}$, CN^- , R-S^- , $-\text{SH}^-$ and NH_2^- , which are active groups involved in the interaction with the environment.

3.4.1.2 *Characteristics of CNTs*

Carbon nanotubes have unique physical properties, making them attractive material for various applications. The CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) depending on the number of carbon atom layers. Each type

of CNT is based on the principle of hybridized carbon atom layers in the walls of CNT and represents a hollow, concentric cylindrical structure that is closed at both ends [79]. The SWCNTs consist of one layer with diameters ranging from 0.3–3 nm, whereas MWCNTs are composed of more than one layer that form concentric tubes and can reach diameters of up to 100 nm or more. Depending on the adsorbate present, the features of CNTs influencing their adsorption properties include their high porous and hollow structure, light mass density, affinity to adsorbates and large specific surface area [80, 81]. The size of surface area is dependent on the extent of pore aggregation due to the entanglement of a certain number of individual tubes [82–85]. Adsorption on CNTs mainly occurs at four regions: at hollow interiors of nanotubes they are open ended, at interstitial pore spaces between the tube bundles, at groves present at the boundary of nanotube bundles or at the external surface of the outermost CNTs [86, 87]. According to Upadhyayula *et al.* [87], the interior space of CNTs cannot serve as adsorption because CNTs have closed caps, and secondly, the smaller diameter of the tubes does not accommodate a typical macromolecular-sized contaminant; while only a few low-molecular-weight, small-sized adsorbates can be adsorbed in the interstitial spacing formed between the bundles of nanotubes [82]. The groves at the boundary of nanotube bundles and the external surface of the outermost CNTs are therefore the most suitable regions for adsorption, providing large pore spaces for microorganisms.

The adsorption of microorganisms on carbon nanotubes results from physical-chemical mechanisms. The structures of microorganisms and CNTs as described above are susceptible to the promotion of chemical interactions such as ionic and covalent binding as well as physical binding, including electrostatic or London-van der Waals forces. During an exercise aiming to systematically compare the adsorptive interactions between CNTs and organic pollutants with significantly different physical-chemical properties, Chen *et al.* [88] found that the adsorption affinity correlated poorly with hydrophobicity but increased in the order of nonpolar aliphatic < nonpolar aromatics < nitroaromatics for CNTs, and the adsorption affinity increased with the number of nitrofunctional groups within the group of nitroaromatics. According to Arepalli *et al.* [89], SWNTs generally have strong van der Waals forces that may cause them to aggregate into microscopic bundles or ropes, which in turn agglomerate loosely into small clumps. The van der Waals forces of MWCNTs are said to be less effective than those of SWCNTs [90], leading to less tight interactions between cells and MWCNTs within the aggregates. In a separate study, Akasaka and Watari [91] found that apart from the effect of van der Waals forces, the diameter of CNTs affect the way in which they precipitate and capture cells;

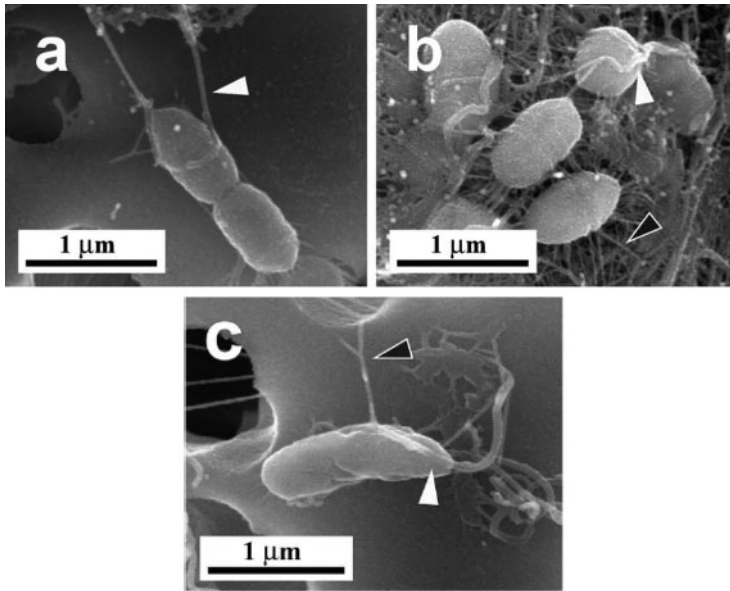


Figure 3.2 SEM images of *S. mutans* adhered to CNTs: (a) bundles of CNTs wound around *S. mutans* ; (b) the bacteria adhered to the meshwork comprising bundles of SWCNTs; (c) 30-MWCNTs wound around bacteria (from ref. [91]).

CNTs that captured pathogens by winging ensured stronger adhesion and inhibited the release and budding of captured bacteria (Figure 3.2).

Arias and Yang [90] reported that surface groups on the CNTs coupled with different buffer conditions would affect the interactions between CNTs and cells as well as formation of cell-CNTs aggregates due to either charge-associated effects or reaction environments.

Overall, according to Ren *et al.* [80] a number of factors likely to influence adsorptive interactions between CNTs and organic matters include: CNT properties (size, shape, surface areas, large average pore diameter and volume, morphology, functional groups, impurity), organic matter (hydrophobicity, electron polarizability, polarity, size, functional groups) and environmental conditions (pH, ionic strength).

3.4.2 Adsorption of Microorganisms on CNTs for Bioremediation

The biosorption process has been attractive and considered as an alternative to conventional methods because of the lower cost of the technique. However, the need to culture biosorbent after each cycle of biosorption

may render the process costly, hence the need to immobilize the biosorbent to diminish dispersion, loss and degradation which impact on the adsorption capacity. A couple of support materials have been used for the immobilization of biosorbents in bioremediation processes; these include alginate, polyacrylamide, polyvinyl alcohol, polysulfone, silica gel, cellulose and glutaraldehyde [21]. A few basic features have to be considered when selecting the support material; material used as a carrier should have chemical, physical and biological stability during processing as well as in the reaction conditions, sufficient mechanical strength and should have adequate function groups for binding biosorbent and high loading capacity [92]. Binding of microbial sorbent on support matrix can be done using reversible (adsorption, disulphide bonding, chelation) or irreversible (covalent bonding, entrapment, encapsulation, crosslinking) methods.

The discovery of carbon nanotubes in the 90s has led to development of several applications. A few of these applications include: the role of sensors in the detection of pathogens after surface modification of CNTs [93, 94], pristine and modified CNTs have shown antimicrobial activities [95, 96], CNTs have been used for the detection of toxic contaminants upfront in a wastewater treatment plant [97, 98], CNTs have been used for the concentration of bacterial pathogens from contaminated water systems [99, 100], CNTs can be used as filters for seawater pretreatment to remove bacteria from raw seawater, thereby reducing the biofouling problems of reverse osmosis membranes [101], and recently CNTs have been used as support for microbial sorbents for the removal of toxic heavy metals from solutions [102].

The potential of CNTs to adsorb microorganisms has been thoroughly studied, and it has been found that microbial adsorption capacities on CNTs are higher than any other commercially available adsorbent media; CNTs express selective adsorption of bacteria and the adsorption kinetics of bacteria on CNTs is almost instantaneous [87]. Akasaka and Watari [91] showed that both the SWCNTs and MWCNTs can effectively adsorb microorganisms, although the better performance was recorded with the MWCNTs; they also found that the diameter of CNTs played a role in microbial adsorption efficiency.

Bacteria in biofilm state are more bioavailable, protected from adverse conditions in the environment, and the lipopolysaccharides and EPS produced at the surface of biofilm may serve as metal chelators. Therefore, materials that facilitate a higher degree of bacterial colonization are suitable for metal biosorption processes. According to Salah *et al.* [103], desirable qualities of such materials include: a highly porous structure on which microorganisms can easily colonize, the ability to provide modulating

effect by adsorbing high concentrations of the toxicant from the bulk but regulate its availability to the microbes, and the ability to contribute to the buffering capacity of biofilm consortium.

Some researchers [94, 104, 105] have functionalized CNTs using carbohydrate ligands in order to modify their adsorption capacities.

Using *P. aeruginosa* immobilized multiwalled carbon nanotubes for biosorption of heavy metals, Tuzen *et al.* [102] showed that such biosorbent could be used for at least 50 cycles without losing its adsorption capacity; furthermore, the biosorbent was successfully used to reduce the level of toxic heavy metals in tap water and spring water below the recommended limit. These results are encouraging for the continued investigation of the use of CNTs as support matrices for microbial sorbents in bioremediation of heavy metals polluted effluents.

3.5 Conclusion

The potential of microorganisms for removal of metals has been convincingly demonstrated by researchers over the years; however, the biosorption process can not yet be considered as a total replacement for the conventional methods for several reasons. Issues related to the availability of biosorbent at low cost, the sustainability of the process and the recovery of toxic metals following adsorption, are still to be effectively addressed. Immobilization of microbial sorbents that allows control and reuse of microbial sorbents may be a solution to these problems. Support matrices previously used for immobilization are not resistant; the carbon nanotubes could therefore be a good alternative given their attractive features. However, the major concern when using CNTs in the bioremediation of water could be their relative toxicity to humans.

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Plasma Technology: A New Remediation for Water Purification with or without Nanoparticles

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Abstract

One of the most serious problems facing billions of people today is the availability of fresh water. The conventional water recycling methods like chemical oxidation processes and advanced oxidation processes (AOP) are effective but have problems such as high cost, secondary pollution and production of chlorinated species. To overcome these problems nanoparticles are increasingly used. The conventional methods of nanoparticle production usually requires a long time and have a high cost, which render them ineffective for large-scale production of nanoparticles. Nanoparticle production using the plasma technique overcomes these shortcomings. Additionally, the plasma itself acts as a perfect method for water purification due to the formation of various reactive chemical species such as radicals ($\text{OH}\cdot$, $\text{H}\cdot$, $\text{O}\cdot$, $\text{HO}_2\cdot$) and molecular species (H_2O_2 , H_2 , O_2). Hence, the use of the combined action of nanoparticles and plasma is a new method for solving water treatment problems.

Keywords: Water purification, plasma technique, nanoparticles, reactive chemical species, molecular species, chemical oxidation processes

4.1 Introduction

Water is an indispensable requirement for life as well as industries. Water is a resource that is becoming increasingly scarce and needs to be sustained,

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globally and locally. Water pollution added to the scarcity of water has become an acute problem in recent times. Groundwater, river, and lakes are polluted by human activities and industrial wastes. One of the most serious problems faced by billions of people today is the availability of fresh water. It has been estimated that 1.2 billion people have no water within 400 m of their dwelling [1]. Purifying and reusing wastewater has been thought of as a solution due to the adverse effects of the discharge pollutants on human and aquatic life. For the treatment of wastewater, traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process have been used. But these methods cannot be successfully employed in the complete destruction of pollutants [2], and have the further disadvantage of potential secondary pollution [3]. A water treatment process has been developed using chemical oxidation processes (COPs). The most commonly used oxidants are chlorine, chlorine dioxide, chloramines, ozone, and potassium permanganate, which have high oxidation potential and hence prove to be an effective oxidant for water treatment. However, their use for destructive treatment of wastes has been limited because such reagents have usually been expensive, and the addition of large quantities of oxidizing agents to a waste solution may result in a new waste treatment problem involving the reduced products of the oxidizing agents. For example, halogenated organic by-products can form if chlorine or ozone (in the presence of bromide ion) are used, which can have possible health effects [4, 5].

4.2 Water Purification Using Advanced Oxidation Processes (AOP)

There has been a continuing need for the development of effective, cheap and environmentally friendly processes for the disinfection and degradation of organic pollutants in water. Great attention has been focused on the so-called advanced oxidation processes (AOP) that are based on generation of highly reactive species, especially hydroxyl radicals. This is because the hydroxyl radical is a very powerful, non-selective oxidant that has the oxidation potential to completely oxidize organics to carbon dioxide and water [5]. There are a number of methods for generating hydroxyl radicals that may be applied in AOP, such as photochemical and electrochemical oxidation, photolysis of hydrogen peroxide and ozone, Fenton-type reactions, TiO_2 photocatalysis, wet oxidation, sonolysis, and irradiation of water by high energy electron beams or γ -rays. Further, work with the combination of other catalysts, including alumina [6] and zeolites [7], has

also been conducted. However, a common feature of AOP is that the radical production involves a significant expense of energy (either chemical, electrical or radiative). The need for an energy efficient method for production of highly reactive transient species has motivated research on the application of high voltage electrical discharges for water purification. In general, strong electric fields applied to water initiate both chemical and physical processes as ultraviolet radiation, overpressure shock waves and, especially, formation of various reactive chemical species such as radicals ($\text{OH}\cdot$, $\text{H}\cdot$, $\text{O}\cdot$, $\text{HO}_2\cdot$) and molecular species (H_2O_2 , H_2 , O_2).

4.3 Nanoparticle Synthesis Using Plasma and Its Application towards Water Purification

Water purification using nanoparticles is currently an area of intense scientific research. Traditionally, nanoparticles have been produced only by physical and chemical methods. Some of the commonly used physical and chemical methods include ion sputtering, solvothermal synthesis, reduction and sol-gel technique. Iron nanoparticles have attracted considerable interest because of their potential applications in water purification, special magnetic properties in micro- and nanoelectronics, and so on. However, traditional processes usually need a long time or have a high cost. The new method for the preparation of nanoparticles is to use the plasma technique for nanoparticle production. Plasma methods effectively combine the contributions of ultraviolet (UV) radiation, active chemicals and high electric fields that contain free charges (electron, ions), free radicals, excited molecules and UV photon, and generate transient electric fields (Figure 4.1).

Plasma is obtained when gases are excited into energetic states by radio-frequency (RF), MW, or electrons from a hot filament discharge. Plasmas can be categorized into two main groups, i.e., high-temperature plasmas and low-temperature or gas discharge plasmas. A typical classification and parameters of different kinds of plasmas are given in Table 4.1. High-temperature plasma implies that all species (electrons, ions and neutral species) are in a thermal equilibrium state; while low-temperature plasma has been further subdivided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal equilibrium (LTE) state, and non-thermal plasma (NTP), also called non-equilibrium plasma or cold plasma (8–11).

Dielectric barrier discharge (DBD) plasma may be a good method to produce iron nanoparticles, but the system needs to be heated. A simple method of producing Fe nanoparticles based on the dissociation of

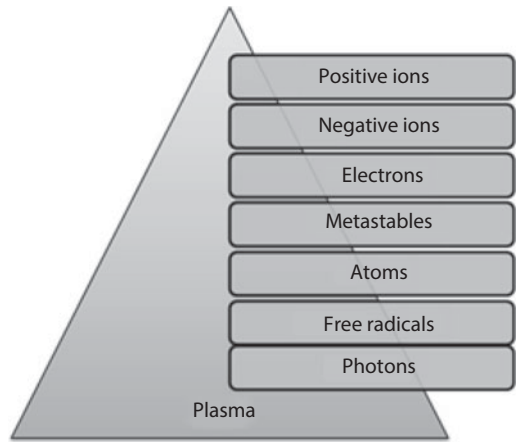


Figure 4.1 Constituents of plasma.

Table 4.1 Classification of plasma.

Plasma	State	Example
High-temperature plasma (Equilibrium plasma)	$T_e \approx T_i \approx T_g, T_p = 10^6\text{--}10^8\text{K}$ $n_e \geq 10^{20}\text{ m}^{-3}$	Laser fusion plasma
Low-temperature plasma		
Thermal plasma (Quasi-equilibrium plasma)	$T_e \approx T_i \approx T_g \leq 2 \times 10^4\text{ K}$ $n_e \geq 10^{20}\text{ m}^{-3}$	Arc plasma, plasma torches, RF inductively coupled discharges
Non-thermal plasma (Non-equilibrium plasma)	$T_e \gg T_i \approx T_g = 300\text{.....}$ 10^3 K $n_e \approx 10^{10}\text{ m}^{-3}$	Glow, corona, APPJ, DBD, MHCD, plasma needle, etc.

ferrocene by a simple single electrode atmospheric cold argon plasma jet has been described by Yu-Tao *et al.* [12]. The system has been driven by a sinusoidal ac-supply with a peak voltage of 0–30 kV and a frequency of 50 kHz. The average size of iron nanoparticles analyzed by scanning electron microscopy has been found to be about 10–30 nm for the gas phase samples, and 30–100 nm for the liquid phase samples. This method has been assumed to be competitive for metal nanoparticle synthesis due to its simplicity and low cost [12].

4.4 Application of Plasma for Water Purification

In addition to the nanoparticle preparation for water purification systems, plasma itself serves as an independent remediation for water purification. Plasma treatment of contaminated water appears to be a promising alternative method in this direction. It has a characteristic feature that all kinds of organic materials, including recalcitrant matter, are decomposed due to active species produced by plasma. Dyes have been one of the major pollutants in water. Due to their high solubility in water, they can be transported over large distances once they are discharged in streams and rivers. Most of the dyes have been found to be resistant to normal wastewater treatment processes. Biotreatment of effluents containing organic dyes has not been effective due to their resistance to aerobic degradation, while by anaerobic degradation carcinogenic aromatic amines have been formed as by-products [13]. An AOP based on the generation of plasma at the gas-water interface has been studied for the degradation of water-bound pollutants like dyes [14]. In a dielectric barrier discharge (DBD) reactor, the electrical discharges take place between electrodes, where at least one of the electrodes is covered with a thin layer of dielectric material such as glass or quartz [15]. Dielectric barrier discharge has been an effective way to produce low-temperature plasma. Media can cover the electrode surface or place between the two electrodes, two electrodes with a high enough voltage, electrode gap of air generated by the breakdown discharge. The discharge forms a large number of fine discharge fast pulse discharge channels, the performance being uniform, diffuse and stable. Dielectric also plays a role in energy storage during the discharge process to delay discharge stability and produce very short pulses, while it can inhibit the production of spark discharge. In the case of the water treatment application of DBD reactors, a layer of water around one of the electrodes acts as a dielectric [16]. Decomposition of the azo dye methyl red in aqueous solution has been performed using a pulsed dielectric barrier discharge in coaxial configuration. The solution has been made to flow as a thin layer on the surface of the inner electrode of the DBD reactor, so that the oxidizing species formed in the discharge can easily penetrate the solution, react with the dye molecules and decompose them. After plasma treatment for 10 minutes, 93% removal of the dye has been found to reach 50 mg/L initial concentration of methyl red in solution and the corresponding removal yield has been found to be 52.5 g/kWh. Lower concentrations of the dye could be removed faster, however, the efficiency has been found to be lower in that case [17]. A DBD reactor has also been designed and tested for the degradation of a model aqueous pollutant crystal violet (CV).

It has been observed that the major reactive species involved in the degradation process include hydroxyl radical, hydrogen peroxide, and ultraviolet, which might cause strong oxidizing effects in the degradation of CV. The effect of various parameters like applied voltage, gas flow rates, concentrations of dye, addition of Fe^{2+} or H_2O_2 , and change in pH has been studied on the synergistic effect during degradation. Mineralization of the dye has been confirmed by total organic carbon (TOC) analyzer and infrared gas analyzer. It has been observed that both degradation efficiency and TOC removal increases with increasing the input energy; however, the energy yield decreases. Formation of H_2O_2 has been confirmed, and it increases with treatment time. The degradation process of the model dye, CV, has been found to obey first-order kinetics, and the rate of degradation strongly increases with the addition of Fe^{2+} due to the catalytic formation of hydroxyl radicals via Fenton-type reactions. The specific advantage of the present process is found to be the mineralization of CV, the highest energy yield up to 86.3 g/kWh [18].

Another method for the removal of dye is contact glow discharge electrolysis (CGDE). Contact glow discharge electrolysis is a novel type of electrochemical process in which plasma is sustained by dc glow discharges between an electrode and the surface of the electrolyte. In CGDE, a continuous dc voltage of around 0.5 kV is applied to a thin wire anode in contact with the water surface while the cathode is dipped in water and isolated from anode through porous glass [19, 20]. Also, H_2 is formed in the gas phase and H_2O_2 in the aqueous phase [20]. A sheath of vapor forms around the anode through which current flows as a glow discharge. Charged species in the plasma (present in the discharge gap or sheath of vapor around the anode) are accelerated due to the steep potential gradient and enter the liquid phase with an energy that may be as high as 100 eV. In the case of contact glow discharges, almost all the species in the discharge zone, i.e., anions, cations and neutrals, heat up, so the plasma generated in the reactors can be called a hot plasma [21]. In the case of both CGDE and DBD reactors, the electrical discharges take place in the gas phase in close proximity to the water surface. They require an intense electric field of the order of 1 MV cm^{-1} for electrical discharge to take place in water. Such a high electric field has been made possible by applying high-voltage pulses of 15–100 kV, usually of positive polarity, with a sharp rise time (a few nanoseconds) and short duration (nano- to microseconds) in a pulsed corona discharge reactor [22]. Oxidative degradation of eight kinds of dyes induced by plasma in aqueous solution has been investigated with contact glow discharge electrolysis (CGDE). It has been demonstrated that these eight dyes (Acridine Orange [AO], Methyl Blue [MB], Rhodamine B [RhB],

Table 4.2 The decolorization rate of different dyes after different discharge times.

Dyes solution	MB	FG	RB	MO	AO	CAS	RhB	GTL
Decolorization 2 min	97.49	92.84	93.63	99.11	97.99	93.86	95.13	94.93
Rate (%) 5 min	99.46	94.41	94.11	99.34	98.47	93.94	97.20	96.55

weak Acid Flavine G [FG], Weak Acid brilliant Red B [RB], Cationic Red [GTL], Chrome Azurol S [CAS], Methyl Orange [MO]) underwent degradation in CGDE, where Fe^{+2} could be utilized to raise the efficiency of the degradation of the dyes. The concentration of Fe^{+2} has been taken as $1\ \mu\text{M}$ and the value of pH has been controlled to 2.14. The decolorization rates of single dyes after degradation are listed in Table 4.2 [23].

Further, another important waste to be purified was the wastewater from the paracetamol factory. Atmospheric pressure plasma in gaseous media was utilized to decompose organic materials in environmental water and kill bacteria in wastewater. Non-thermal plasma combined with activated carbon has been developed to purify wastewater from the paracetamol factory. The effect of discharge time, discharge voltage, initial pH value of wastewater, velocity of the air flow and whether adding activated carbon on the chemical oxygen demand (COD) degradation and decolorization ratio have been investigated. It has been seen that as discharge time was prolonged, the decolorization ratio decreased but the COD degradation ratio increased at first and then reached to a constant value. The ratios of COD degradation and decolorization decreased when the initial pH value increased. With the increase of inputting air flow, it has been found that the COD degradation ratio went up and had an optimal peak value, and then the decolorization ratio declined. The ratio of decolorization and the COD degradation could be improved significantly with the addition of activated carbon [24]. Non-thermal plasma generated in a pulsed dielectric barrier discharge in coaxial configuration has been investigated for the removal of three β -lactam antibiotics (amoxicillin, oxacillin and ampicillin) from water. The discharge was generated at the gas-liquid interface at room temperature and atmospheric pressure, in oxygen. Solutions of concentration $100\ \text{mg/L}$ were made to flow as a film over the surface of the inner electrode of the plasma reactor, so the discharge was generated at the gas-liquid interface. The electrical discharge was operated in pulsed regime, at room temperature and atmospheric pressure, in oxygen. Amoxicillin has been found to degrade after 10 min plasma treatment, while the other two antibiotics required about 30 min for decomposition. The evolution of the

degradation process was continuously followed using liquid chromatography-mass spectrometry (LCeMS), total organic carbon (TOC) and COD analysis [25].

In addition to this, the effect of these discharges on bacteria has been studied using water contaminated with *Escherichia coli* or *Bacillus subtilis*, the latter in both the vegetative and spore state. The strongest effect was obtained on *E. coli*. The concentration of *E. coli* was reduced by three orders of magnitude after applying eight corona discharges to the water. The corresponding energy expenditure has been found to be 10 J/cm^3 . The decontamination rate had the largest values at the beginning, and decreased considerably after 15 electrical discharges, reaching a constant residual concentration value of 10^{-4} of the initial concentration. For *B. subtilis* in the vegetative state, it took almost 30 discharges to reach the same result, corresponding to an energy expenditure of 40 J/cm^3 . It has been found that there was no effect on *B. subtilis* spores. Comparisons with the pulsed-electric field (PEF) method indicated that the decontamination efficiency of the PWC method has been found to be slightly higher than that of the PEF method [26]. Atmospheric non-thermal plasma of the gliding-arc type (Glidarc) [27, 28] has been found to be efficient against microorganisms for treatments performed under burning discharge [29, 30], and the inactivation of cells in water continued after the discharge had been switched off [29]. Microbial cells have been found to be killed by contact with water that had first been activated by electric discharges (and so-called plasma-activated water [PAW]) without themselves being subjected to the plasma plume [31]. It has been reported that water treated by various plasma discharges becomes acidic, which leads to antimicrobial effects [32, 33]. Oehmigen *et al.* [34] suggested that the acid created in water is nitric/nitrous acid and the antimicrobial properties observed were due to the result of the synergetic action between H_2O_2 and nitric/nitrous acid [34]. Similar results were obtained by Ikawa *et al.* [35]. The major role of nitrites has been evidenced together with a synergistic effect of nitrates and H_2O_2 and matching acidification. It has been found that reactive nitrogen- and oxygen-based species play an important role in the lethal effect of non-equilibrium atmospheric air-based plasma [36, 37]. The main radical species present in the Glidarc plasma plume were identified as $\text{OH}\cdot$ and $\text{NO}\cdot$ when humid air is the working gas [38]. These radicals are precursors of other active species in water, such as nitrates, nitrites, and hydrogen peroxide [39]. Acidified nitrites and H_2O_2 are known to be less efficient versus yeast than versus bacteria [40, 41], and PAW was found to be more efficient against *H. alvei*, *Staphylococcus epidermidis*, and *Leuconostoc mesenteroides* than against *Saccharomyces cerevisiae* [42].

Water purification by streamer discharge using a stacked Blumlein line pulsed power generator under the water containing pollutants has been investigated. The pulsed power generator consisted of six stacked Blumlein lines to generate high voltage with low charging voltage. The output voltage was applied to a wire electrode to generate streamer discharge in the water and the wire electrode was set on an array of small size holes of an air tube. The air bubbles were injected into the water through the holes to assist the discharge development. Acid Blue 64 solution was employed as a specimen. It was found that the number of discharges increased with the increasing number of holes. Energy efficiency for decolorization of the solution was found to improve by increasing the number of discharges produced simultaneously at the same input energy, whereas the degradation efficiency and energy transfer from the pulsed power generator to the reactor decreased when a streamer-to-arc transition occurred. The solution of 2000 $\mu\text{S}/\text{cm}$ conductivity has been successfully decolorized using the wire electrode placed in the air tube to reduce ohmic loss with high-conductive solution [43]. One single bubble whose average diameter was 2.4 mm was produced in water and the electrical discharge phenomena was observed by both electrical and optical measurements. The experiments were carried out using a pulse-shaped circuit by a Blumline-type pulse forming network (PFN). For the experiments, first the pure water whose conductivity was 2.33 $\mu\text{S}/\text{cm}$ was used [44]. A new type of discharge method (i.e., discharge inside bubbles in water operating in bubbled water) has been proposed in order to use not only ozone but also atomic oxygen, OH, and other radicals generated for effective water treatment [45]; this method was applied to decolor the indigo solution whose original color is blue. The discharge of this method has been thought to begin at the crossing points of mesh electrode, acrylic resin spacer, and bubbling gas (i.e., called a triple junction, where there is a weak point for the electrical breakdown in the electrical power devices). This weak point for the electrical breakdown has been very actively used for the surface discharge [46].

Recently, liquid-phase electrical discharge reactors have been investigated, and it has been found that strong electric fields applied to water (electrohydraulic discharge) initiate both chemical and physical processes. Three types of electrohydraulic discharge systems (pulsed corona electrohydraulic discharge [PCED], pulsed arc electrohydraulic discharge [PAED] and pulsed power electrohydraulic discharge [PPED]) have been employed in numerous environmental applications, including disinfection, chemical oxidation, and the decontamination of sludge [47]. The types of electrohydraulic discharge systems differ in several operational characteristics, as summarized in Table 4.3, due to their different configurations as well as the

Table 4.3 Characteristics of different electrohydraulic discharges¹.

Parameter	Pulsed Corona (PCED)	Pulsed Arc (PAED)	Pulsed Power (PPED)
Operating frequency [Hz]	$10^2\text{--}10^3$	$10^{-2}\text{--}10^2$	$10^{-3}\text{--}10^1$
Current (peak) [A]	$10^1\text{--}10^2$	$10^3\text{--}10^4$	$10^2\text{--}10^5$
Voltage (peak) [V]	$10^4\text{--}10^6$	$10^3\text{--}10^4$	$10^5\text{--}10^7$
Voltage rise [s]	$10^{-7}\text{--}10^{-9}$	$10^{-5}\text{--}10^{-6}$	$10^{-7}\text{--}10^{-9}$
Pressure wave generation	weak	strong	strong
UV generation	weak	strong	weak

¹Data taken from [48].

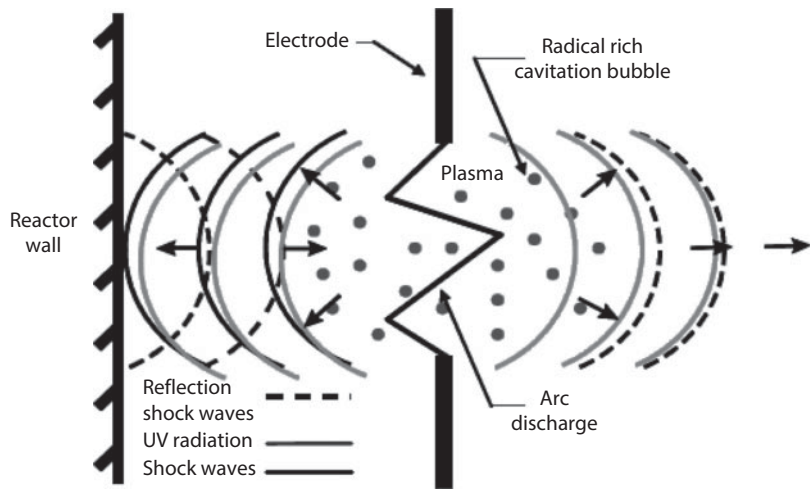


Figure 4.2 Water treatment mechanisms initiated by PAED [49, 58].

different amounts of energy injected into each type of system [48]. Direct plasma technologies (i.e., electrohydraulic discharge) have the potential to be more efficient than either indirect or remote plasma technologies as they capitalize, to some degree, on all of these mechanisms due to the direct application [49, 50].

Figure 4.2 shows the treatment mechanisms initiated by PAED. Preliminary research has indicated that PAED offers advantages over indirect plasma methods in that it can provide comparable or superior

Table 4.4 Comparison of Plasma and Conventional Water Treatment Processes [49, 50].

Target Compounds	Cl/ClO ₂	Ozone	Electron Beam	PCED	PAED	UV-C
Microorganisms	Adequate	Good	Adequate	Good	Good	Good
Algae	None	Partial	None	Partial	Good	Adequate
Urine Components	Adequate	Good	Good	Good	Good	None
VOCs	None	Adequate	Good	Good	Adequate	None
Inorganics	None	Partial	Partial	Adequate	Adequate	None

treatment of microorganisms, algae, volatile organics, nitrogenous municipal waste compounds, and some inorganics [51–57]; these observations are qualitatively summarized as in Table 4.4 [49, 50].

4.5 Combined Action of Nanoparticles and Plasma for Water Purification

The combination of plasma and nanoparticles also proves to be a methodology for water purification. For example, TiO₂ has been extensively used for advanced water treatment and water purification process due to its stable and non-toxic nature, insolubility in water, high photocatalytic activity and abundance. The synergistic effect of pulsed discharge plasma and TiO₂ nanoparticles, and the relation of decoloration efficiency of Acid Orange 7 (AO7) dye wastewater with an amount of TiO₂ particles added into the reaction system, as well as the electric parameters of the discharge system have been investigated. The results obtained further confirm that streamer produced by pulsed discharge plasma induced the photocatalysis of TiO₂ and there has been an optimal TiO₂ amount in the pulsed discharge system for achieving a higher decoloration efficiency of AO7. The synergistic decoloration efficiency of AO7 has been found to be higher in the case of higher input power [59]. Recently, isolated nanoparticles of TiO₂ were deposited over substrates providing larger surface area for the photocatalytic process. Nanoparticles of TiO₂ were deposited using microwave-assisted Electron Cyclotron Resonance (ECR) plasma. Hydrogen plasma has been used to deposit the nanotitanium with the help of chemical sputtering. This nanocrystalline film of TiO₂ has then been used to study the photocatalytic

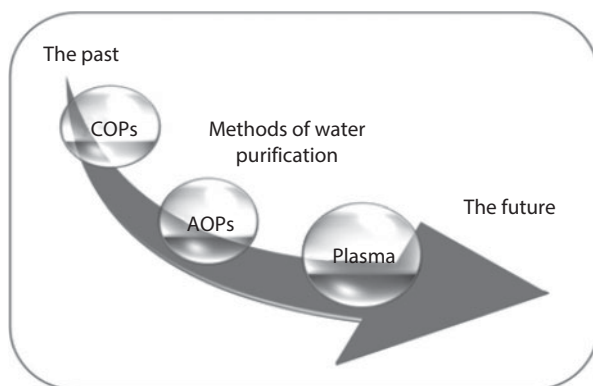


Figure 4.3 Plasma — a promising future approach for water purification.

degradation of methylene blue (MB) in aqueous solution. It has been found to be successful in immobilizing TiO_2 nanoparticles on glass substrate, shows strong adhesion consequently easy for repeated use for photocatalytic degradation, and thus is suitable for water purification [60].

All of these methods have been successfully employed for the complete decomposition of pollutants with the potential to stop further secondary pollution, but plasma has a characteristic feature that can decompose all kinds of organic materials, including recalcitrant matter, due to the active species produced by plasma. Compared to its fellow AOP approaches, non-thermal plasma can achieve greater output and more efficiency. However, applying non-thermal plasma technology in organic wastewater cleaning remains an interesting research area. To enhance the efficiency of bacteria inactivation in the wastewater various methods have been used, such as electrochemical and photocatalytic disinfections, chlorinations, ozonations, Fenton reaction, UV irradiation and electrohydraulics. The use of plasma in water purification attracts attention because of the possibility of obtaining gas jets with a high oxidizing power in compact devices at reasonably low energy inputs. New applications of plasma (Figure 4.3) and nanoparticles in the field of water purification systems have emerged as a promising future approach.

4.6 Conclusion

Many problems that have arisen due to water pollution seem to have been solved by using nanoparticles which have been synthesized at low cost using the plasma technique (such as Fe nanoparticles). Additionally, the

plasma itself acts as a perfect method for water purification due to the formation of various reactive chemical species such as radicals ($\text{OH}\cdot$, $\text{H}\cdot$, $\text{O}\cdot$, $\text{HO}_2\cdot$) and molecular species (H_2O_2 , H_2 , O_2). Further, advanced water treatment problems have also been solved by using a combination of the nanoparticle and plasma approach, where the synergistic effect of pulsed discharge plasma and TiO_2 nanoparticles leads to decoloration of Acid Orange 7 (AO7). Hence, we hereby conclude that all these parameters help in wastewater treatment and in preserving water, which has always been a valuable resource for the growing population.

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Polysaccharide-Based Nanosorbents in Water Remediation

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Abstract

Heavy metals is a general collective term usually applied to elements such as Hg, Pb, Cr, Cu, Ni, Cd and Co. These metals are major pollutants of water, industrial effluents, marine water and even treated wastewater. Environmental contamination by these heavy metals is a widespread problem arising from ever-growing industrial activities. Intake of polluted water is well known to cause various types of diseases like muscle pain, weakness, abdominal pain, and diarrhea, and can even cause cancer and death in many cases. Hence it is mandatory to remove these and other similar toxic metal ions from water and, therefore, appropriate treatments and measures need to be employed in polluted waters to attain the required acceptable environmental standards. In recent years, many approaches have been developed, including adsorption, ion exchange, reverse osmosis, nanofiltration, coagulation, membrane permeation and oxidation.

The present chapter deals with the role of polysaccharide-based nanoparticles for the removal of inorganic metal toxicants from drinking water. The chapter covers an introduction to polysaccharides, their metal ion binding properties, non-toxic nature, various methods of nanoparticles synthesis and their characterization by different analytical techniques, along with various studies pertaining to the application of these polysaccharide nanostructures in water remediation. There is also a brief account of recent studies involving these nanosorbents in water decontamination.

Keywords: Biopolymers, nanoparticles, metal ions, toxicity, remediation

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5.1 Introduction

Environmental pollution is a worldwide problem and can be defined as the introduction of contaminants into a natural environment that cause instability, harm or discomfort to the ecosystem. In other words, environmental pollution is “the unfavorable alteration of our surroundings. It is the introduction of contaminants into the environment that causes harm or discomfort to humans or other living organisms or that damage the environment.” Pollution can be in the form of chemical substances or energies such as noise, heat or light. There are many types of environmental pollution, but four of them have the most perilous effects on our lives, i.e., air, soil, thermal and water pollution (Figure 5.1).

The first type is air pollution, which is a major environmental risk to health in many developed and developing cities of the world. The air pollution levels are usually determined by concentrations of air pollutants such as nitrogen dioxide, sulfur dioxide, carbon monoxide, ozone and suspended particulate matters (PMs). The U.S. Environmental Protection Agency defines PMs as “very small pieces of solid or liquid matter, such as particles of soot, dust, fumes, mists, or aerosols” [1]. Among the major sources of pollution are power and heat generation, the burning of solid wastes, industrial processes, and especially transportation. Long-term exposure to air pollutants can result in chronic respiratory and cardiovascular diseases, including cancers [2, 5].

The second type is soil pollution, which is due to contamination from the release of harmful substances into the soil. Soils polluted with heavy metals pose a health hazard to humans as well as plants and animals. This

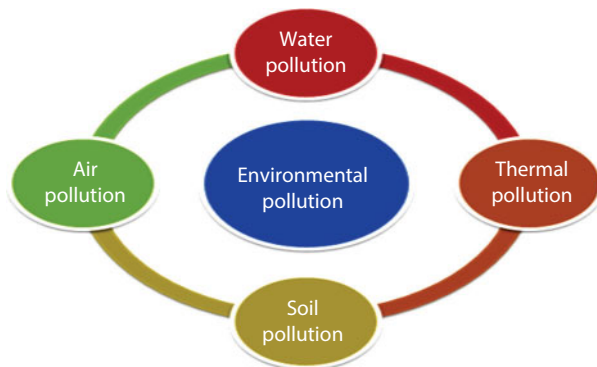


Figure 5.1 Diagrammatic representation of the major types of pollution.

is because plants, are the producers of the food chain and, take up their nutrients, which are essential for their life, from the soil. The nutrients taken up by the plants are then transferred to the consumers that depend on these plants. Hence soil consisting of contaminants will not only affect the plants growing in the soil but will also indirectly harm the entire food chain. Soil pollution is mainly caused by industrial activities such as chemical works, service stations, metal fabrication shops, paper mills, tanneries, textile plants; waste disposal sites and intensive agriculture are particularly guilty of polluting the environment. Thus, heavy metals need to be removed from the soil for agro-ecological sustainability and human benefit [6–9].

The third type is thermal pollution, which can be defined as the increase in atmospheric temperature because of the discharge of waste heat into the environment. The major sources of thermal pollution are fossil-fuel and nuclear electric-power generating facilities and, to a lesser degree, cooling operations associated with industrial manufacturing, such as steel foundries, other primary-metal manufacturers, and chemical and petrochemical producers. The increased temperature accelerates chemical-biological processes and decreases the ability of the water to hold dissolved oxygen. Thermal changes affect the aquatic system, thus rapid and dramatic changes in biologic communities often occur in the vicinity of heated discharges. Thermal pollution is directly linked with global warming. A temperature increase of about 0.8 degrees was observed within the last 15 years as mentioned in EPA 2001 [10].

The fourth type is water pollution, which can be defined as the introduction of chemical, physical, or biological material that degrades the quality of the water and affects the organisms living in it. In other words, “water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities, such as fish.” Let us discuss water pollution in detail, as water is a basic need for human life, and the existence of life on earth without water is not possible.

5.2 Water Pollution

Water is an essential natural resource for sustaining life and the environment that we have always thought to be available in abundance and a free gift of nature, and is under constant pressure as a resource. Due to population growth, economic development, rapid urbanization, large-scale

industrialization, and environmental concerns, water stress has emerged as a real threat [11]. Water covers about 70% of the earth's surface; out of this 97.5% of water is present in seas and oceans and 1.73% is present in the form of glaciers. Only 0.77% of fresh water is available on the earth's surface for human and agricultural use. This limited available quantity of water is also polluted by a variety of pollutants. The major sources of water contamination are domestic, industrial and agricultural, as well as solid waste pollution, thermal pollution, shipping and radioactive wastes [12–14].

At present, the world is facing formidable challenges in meeting the rising demand for clean water as the available supplies of fresh water are decreasing due to extended drought, population growth, and competing demand from a variety of users. Rapid industrialization and population growth have increased water demands but the supply of water is limited. This available limited quantity of water is also polluted by a variety of pollutants. Different types of pollutants are present in water and can be chemical or biological, as discussed below.

5.2.1 Microbiological Contamination

Microorganisms like *Escherichia coli* (*E. coli*), *Sarcina lutea* (*S. lutea*) and *Staphylococcus aureus* (*S. aureus*) are responsible for waterborne diseases such as diarrhea, dysentery, worms, typhoid, jaundice, polio, etc., and are transmitted through contaminated water; whereas chemical pollutants include ionic contaminations (anionic and cationic). Some examples of organic pollutants are discussed below.

5.2.2 Natural Organic Matter

The presence of natural organic matter (NOM) and organic pollutants in water pose a challenge for municipalities and water treatment industries. Currently the removal of organic pollutants from water is negatively impacted by the presence of natural organic matter (NOM). Natural organic matter occurs in all natural water sources when plant and animal materials break down. Natural organic matter adversely affects the quality of water since it imparts color, causes odor and taste, and increases corrosion and biofilm in the water distribution network. It has also been reported that NOM has complexing properties that include an association with toxic elements and micropollutants. Moreover, it serves as a precursor for the formation of chlorinated compounds, and these are potentially carcinogenic. Most importantly, recent studies have revealed that NOM

blocks pores of activated carbon and render it ineffective in the removal of other micropollutants [15–17].

5.2.3 Organic Pollutants

In many industries, process or wastewater streams may contain organic compounds which need to be removed from the stream before they are discharged or recycled. Organochlorine pesticides (OCPs) are one of the most important persistent organic pollutants (POPs), and have been of great concern globally for their toxicity and environmental persistence. Usually high and even low concentrations of these compounds have a detrimental impact on non-target organisms and high bioaccumulation in animals and humans via the food chain; these compounds pose a great threat to ecosystems and human health [18–20]. Most of these organic compounds under conditions of high pressure and temperature will be dissolved in the water; thus traditional treatment methods like gas stripping, solvent extraction and activated carbon adsorption may not be efficient or even economical. The removal of organic contaminants from aquatic systems is difficult. Even when not toxic they often produce aesthetically undesirable problems such as color, odor and taste. Most of these organic compounds are toxic and pose a threat to human health, even at very low levels.

5.2.4 Anionic Pollutants

Anionic pollutants such as phosphate, chromate, cyanide, nitrate and fluoride have threatened the environment and human beings because they pose a significant health risk. Phosphate, nitrate, chromate, and cyanide-iron complex are the most common pollutants in groundwater.

Phosphorus is the eleventh most abundant element on the surface of the earth and is most commonly found in the form of phosphate. The main sources of pollution with phosphate ions are: waters from the fertilizer industry, municipal waters, the use of detergents containing phosphate, waters resulting from agriculture and animal husbandry, etc. Many phosphorus compounds cause serious health problems. On the other hand, it plays an important role in biochemical processes and it is a key factor in the eutrophication of surface water. Phosphorus exists in a wide variety of physicochemical parameter forms in natural waters, and they are highly mobile within the aquatic ecosystem.

Nitrate can be fatal to infants under six months of age at concentrations greater than 10 mg NO_3/L . In infants, nitrate is reduced to nitrite, which combines with hemoglobin in the blood to form methemoglobin and leads

to a condition commonly known as blue baby syndrome [21]. For this reason the maximum permissible limit was reduced to 25 mg/L from 50 mg/L.

Chromate, a species of hexavalent chromium, induces acute allergy and becomes carcinogenic after long exposure. Its widespread industrial applications as a metal corrosion inhibitor and high mobility are the two primary reasons why chromate is frequently found in contaminated sites and groundwater [22, 23]. The most commonly used cyanide form, hydrogen cyanide, is mainly used to make the compounds needed to make nylon and other synthetic fibers and resins.

Fluoride has a recognized role in the prevention of tooth caries via topical application and in dental toothpastes. However, chronic excessive fluoride intake may result in fluorosis, which can result in damage to teeth and bones [24, 25]. It is a widespread endemic disease in China covering 29 provinces, municipalities and autonomous regions. Damaged teeth are characterized by the appearance of yellowish to brownish striations and/or mottling, whereas skeletal fluorosis can result in osteosclerosis, osteoporosis, ligamentous and tendinous calcification, and extreme bone deformity [26–29].

5.2.5 Metallic Contamination (Heavy Metal Toxicity)

“Heavy metal” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4000 kg m^{-3} , or 5 times more than water [30]. Heavy metals are natural constituents of the earths’ crust. Human activities have drastically altered the biochemical, geochemical cycles and balance of some of the heavy metals. Heavy metals are stable and tend to persist and accumulate in the environment. They cannot be degraded or destroyed [31]. In other words, heavy metal can be defined as a member of an ill-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides and actinides [32].

Although some of them act as essential micronutrients for living beings, at higher concentrations they can lead to severe poisoning. The most toxic forms of these metals in their ionic species are the most stable oxidation states (e.g., Cd^{2+} , Pb^{2+} , Hg^{2+} , Ag^{2+} , As^{3+}) in which they react with the body’s biomolecules to form extremely stable biotoxic compounds which are difficult to dissociate [33]. The contamination of the environment with toxic metals has become a worldwide problem. Metal toxicity affects crop yields, soil biomass and fertility. Heavy metal poisoning can result from drinking-water contamination (e.g., Pb pipes, industrial and consumer wastes), intake via the food chain or high ambient air concentrations near

emission sources. Use of contaminated water for drinking purposes can cause various types of diseases, some of which are discussed below. There are several metals which are studied mainly due to their toxicity and pollution concerns [34].

5.3 Hazardous Effects of Toxic Metal Ions

5.3.1 Chromium

Chromium, Cr(III), is an essential trace element needed for glucose metabolism in humans, plants and animals. It is relatively innocuous and immobile when compared to Cr(VI) compounds. The maximum concentration limit for chromium (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L. The U.S. Environmental Protection Agency (EPA) has set a Maximum Contaminant Level (MCL) in drinking water at 0.1 mg/L or 100 µg/L [35–37]. Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage and respiratory problems [38]. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma). Injection may affect kidney and liver functions. Skin contact may result in systematic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes [39–41].

On the basis of the above problems, there is an urgent need for developing a cost-effective technique to remove contaminants from drinking water and to safeguard the health of affected citizens.

5.3.2 Cadmium

Cadmium in nature exists mainly in the +2 oxidation state, which gives stable compounds. The major sources of Cd(II) in most water bodies include mining through acid mine drainage and battery manufacturing industries. Cadmium is a non-essential element and is one of the most hazardous trace elements, which is classified as a “priority metal” from the standpoint of potential hazard to human health and plant life [38]. Cadmium is listed by the U.S. Environmental Protection Agency as one of 126 priority pollutants. The most dangerous characteristic of cadmium is that it accumulates throughout a lifetime. Cadmium accumulates mostly in the liver and kidneys and has a long biological half-life of 17 to 30 years in humans [42–44]. Cadmium can cause osteoporosis, anemia, non-hypertrophic emphysema, irreversible renal tubular injury, eosinophilia, anosmia and

chronic rhinitis. Cadmium is a potent human carcinogen and has been associated with cancers of the lung, prostate, pancreas, and kidney. [45] A disease known as “Itai Itai” in Japan is associated with cadmium poisoning, which results in multiple fractures in the body.

5.3.3 Arsenic

Arsenic (As) is a toxic semi-metallic element that can be fatal to human health. Arsenic contamination in natural waters is a worldwide health concern [46]. Elevated concentrations of As(V) and As(III) are found in groundwater in many regions around the world. It is naturally present in groundwater in the form of different chemical species; some anthropogenic activities contribute artificially to arsenic pollution in groundwater [47–49]. Arsenic can have a significant adverse impact on the environment. Elevated concentrations of arsenic, i.e., As(V) and As(III), are found in many [50, 51] parts of the world, especially in developing countries such as Bangladesh, India, Nepal, and Vietnam. Due to its high toxicity and carcinogenic effect, the World Health Organization (WHO) has recommended a maximum contaminant level for arsenic in drinking water of $10 \mu\text{g L}^{-1}$. Prolonged use of arsenic contaminated water may cause numerous diseases of the skin and internal organs. The diseases caused due to intoxication of arsenic through arsenic contaminated drinking water are liver damage, and peripheral vascular disease, leading to gangrene of the lower limbs. This condition is commonly known as “black foot disease” in Taiwan, “*Kai Dam*” in Thailand and “*Bell Ville*” in Argentina. Other diseases caused due to arsenic toxicity include cancers of the lungs, skin, and bladder, tummy bug leukemia, kidney and bladder cancers, dermatitis, hyperpigmentation, and arsenical keratosis. Arsenic acts as a non-genotoxic carcinogen and it also affects DNA methylation and repair [52, 53].

5.3.4 Mercury

Mercury has received extensive exposure because of its toxicity to humans. In 1953, people died in the fishing villages along Minamata bay in Japan due to mercury poisoning. High levels of mercury were discharged by the nearby plastics factory and were accumulated in the shellfish eaten by the villagers [54].

In the environment, humans and animals are exposed to numerous chemical forms of mercury, including elemental mercury vapors (Hg), inorganic mercurous (Hg(I)), mercuric (Hg(II)) and organic mercuric compounds [55]. Environmental mercury is ubiquitous and consequently

it is practically impossible for humans to avoid exposure to some form of mercury. All forms have toxic effects in a number of organs, especially in the kidneys [56]. Elemental, inorganic, and organic forms of mercury exhibit toxicological characteristics including neurotoxicity, nephrotoxicity, and gastrointestinal toxicity with ulceration and hemorrhage.

Pollution occurs from mining activities and smelting operations of some other metals, like lead, and is of concern because inorganic and organic lead is considered extremely toxic as it causes physiological, biochemical, and behavioral dysfunctions in laboratory animals and humans, including central and peripheral nervous systems, haemopoietic system, cardiovascular system, kidneys, liver, and male and female reproductive systems. Nickel, molybdenum and zinc are other metals whose growing levels in the environment has caused major concern [54].

In general, heavy metal toxicity can cause chronic, degenerative conditions. General symptoms include: headache, short-term memory loss, mental confusion, sense of unreality, distorted perception, pain in muscles and joints, and gastrointestinal upsets, food intolerances, allergies, vision problems, chronic fatigue, fungal infections, etc. Sometimes the symptoms are vague and difficult to diagnose [55]. On the basis of the above problems, there is an urgent need for developing a cost-effective technique to remove contaminants from drinking water and to safeguard the health of affected citizens.

5.4 Technologies for Water Remediation

The major water remediation technologies include precipitation-coagulation, membrane separation, ion exchange, lime softening and adsorption on iron oxides or activated alumina, some of which are discussed in detail below.

5.4.1 Oxidation and Reduction

In oxidation, contaminated water is treated with oxidizing agents like chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, manganese oxides and Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), which can be employed to accelerate oxidation [57]. Chlorine is used as a rapid and effective oxidant, but many times it reacts with organic matter, producing toxic and carcinogenic trihalomethanes as by-products. Potassium permanganate effectively oxidizes arsenite, and it is an easily available low-cost chemical suitable for developing countries. Hydrogen

peroxide can also be used as an effective oxidant if the raw water contains dissolved iron, which often occurs in conjunction with arsenic contamination, allowing the occurrence of Fenton reactions.

5.4.2 Coagulation and Filtration

Conventional coagulation/filtration is a common water treatment methodology used to remove suspended and dissolved solids from source water. The coagulation process promotes aggregation of the suspended solids to form flocks, which then can be removed through sedimentation or filtration. Coagulation is typically described as a process consisting of three steps: coagulant formation, particle destabilization, and interparticle collisions. The first two steps, coagulant formation and particle destabilization, occur during rapid mixing, and the third step occurs during flocculation. Alum and iron(III) salts, such as ferric chloride, are the most common coagulants used for drinking water treatment.

Coagulation using alum and iron(III) salts can be used to remove dissolved inorganic drinking water contaminants, such as arsenic. Removal mechanisms for dissolved inorganics consist of two primary mechanisms: adsorption and occlusion. During the adsorption process, the dissolved contaminant attaches to the surface of a particle or precipitate. Occlusion occurs when the dissolved contaminant is adsorbed to a particle and then entrapped as the particle continues to agglomerate. Several factors affect the coagulation process, including coagulant dosage, pH, turbidity, natural organic mater (NOM), anions and cations in solution, zeta potential, and temperature [58, 59].

5.4.3 Lime Softening

Lime softening is commonly used to reduce hardness in source waters. Hardness is due primarily to the presence of calcium and magnesium ions. The lime provides hydroxide ions that increase pH, which results in calcium arsenic removal; however, competition between arsenic and carbonate for sorption sites on the iron hydroxide reduced the removal efficiency to levels below those normally achieved with a conventional coagulation/filtration process using iron(III) salts [60].

5.4.4 Membrane Processes

Membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED).

In each of these processes, membranes pass or retain dissolved species based on the size, shape, or charge of the compound. Both MF and UF exclude water constituents based on size, which is 0.8–10 μm for MF and 0.09–10 μm for UF [61, 62].

In RO, influent water is forced through a membrane in the opposite direction from natural osmosis, at a specified operating pressure [63]. The range of particles that RO membranes can retain is 0.005–0.5 μm , including ions. In electrodialysis (ED), ions are transported from a lesser to a higher concentrated solution through ion permeable membranes under the influence of a direct electric current. The efficiency of the technique is similar to that of RO, mainly in treating water with high total dissolved solids (TDS). The membrane operation is a chemical-free process and maintenance consists of only ensuring a reasonably constant pressure, and periodically cleaning of the membranes.

5.5 Shortcomings of the Technologies Used for Water Remediation

The oxidation reduction method can remove toxic contaminants, but the only disadvantage is that it increases chemical load in treated water. Coagulation with metal salts and lime softening removal have been the most commonly used technologies in the past. Coagulation processes are sometimes unable to remove metal ion to levels below the permissible limit. These treatment techniques are not appropriate for small systems and disposal of sludge may be a problem. Though conventional coagulation and lime softening removal could significantly remove toxic ions, the processes have several complications and hence are not that simple. Membrane processes are more expensive than other treatment methods. The main disadvantages, especially for RO, are the low water recovery rates around 10–20%, which could be a problem in water-scarce areas, high electrical consumption, relatively high capital and operating costs (expensive membranes), and the risk of membrane fouling. High concentrations of suspended solids, organic matter, humic acids, hardness, sulfides, ammonium, nitrite, methane, etc., interfere with the purification process [64].

Hence, on the basis of the above discussion effective technologies are needed, and many investigations have described methods to improve water treatment such as nanobioremediation. Nanobioremediation can be defined as the removal of toxic contaminants from water using nanomaterials, they can be polymeric (polysaccharide, proteins, etc.) or

non-polymeric (metallic, carbon nanotubes, etc.) nanoparticles. Before studying nanotechnology in water remediation, information about nanotechnology is needed.

5.6 Nanotechnology

Nanotechnology has become the fastest growing field with enormous potential applications in areas ranging from electronics to cosmetics. Richard Feynman introduced the concept of nanotechnology in his pioneering lecture, “There’s plenty of room at the bottom,” at the meeting of the American Physical Society in 1959.

The term “nanotechnology” varies greatly based on the specific definitions that are normally used. The National Science Foundation and the National Nanotechnology Initiative define nanotechnology as the understanding and control of matter at dimensions of 1–100 nanometers, where the term nanometer means one billionth of a meter; by comparison, a human hair is 80,000 nm thick. On the basis of origin, there are three types of nanomaterials:

- Natural: such as a tiny particle from a volcanic eruption.
- Incidental: such as emission from engine combustion.
- Engineered: purposely manufactured [65].

Another classification of nanomaterials is shown in Figure 5.2.

Nanotechnology is a field of applied science, focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. This branch of knowledge is a sub-classification of technology in colloidal science, biology, physics, chemistry and other scientific fields, and involves the study of phenomena and manipulation of materials in the nanoscale. Also, a unique aspect of nanotechnology is the “vastly increased ratio of surface area to volume,” present in many nanoscale materials, which opens new possibilities in surface-based sciences [66–69].

5.6.1 Approaches for the Preparation of Nanomaterials

There are two main approaches for the synthesis of nanoengineered materials. They can be classified on the basis of how molecules are assembled to achieve the desired product.

Nanoscale materials and devices can be prepared using either “bottom-up” or “top-down” fabrication approaches, as shown in Figure 5.3. In

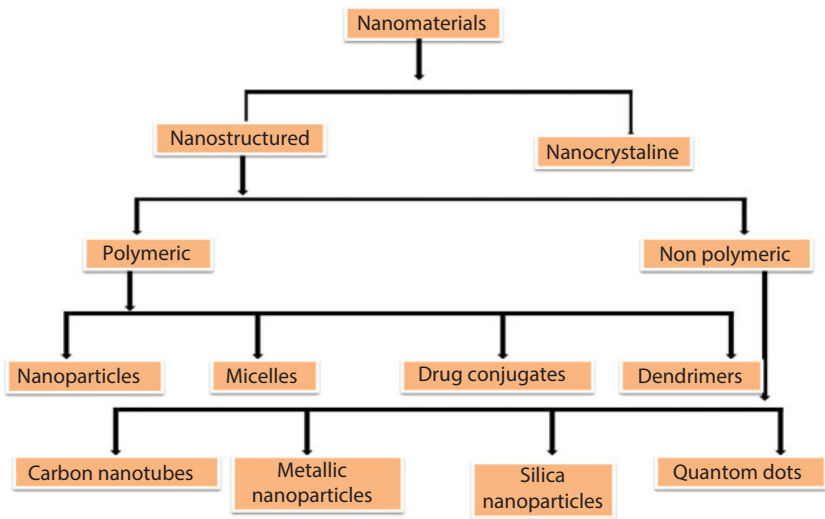


Figure 5.2 Classification of nanomaterials.

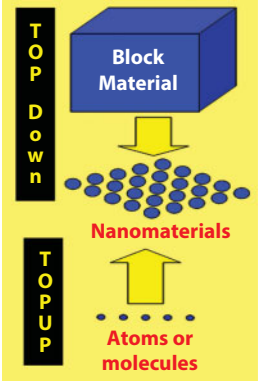


Figure 5.3 Top-down and bottom-up approaches to the synthesis of nanoparticles.

bottom-up methods, nanomaterials or structures are fabricated from the buildup of atoms or molecules in a controlled manner that is regulated by thermodynamic means such as self-assembly [70]. Alternatively, advances in microtechnologies can be used to fabricate nanoscale structures and devices. These techniques, referred to as top-down nanofabrication technologies, include photolithography, nanomolding, dip-pen lithography and nanofluidics [71, 72].

5.6.2 Composition of Nanomaterials

Nanomaterials include clusters of atoms (quantum dots, nanodots, inorganic macromolecules), grains that are less than 100 nm in size (nanocrystalline, nanophase, nanostructured materials), fibers that are less than 100 nanometers in diameter (nanorods, nanoplatelets, nanotubes, nanofibrils, quantum wires), films that are less than 100 nanometers in thickness, nanoholes, and nanocomposites that are a combination of these. In a broad definition, nanomaterials are divided into one, two and three dimensions.

One-dimensional nanomaterials include thin films and engineered surfaces, which have been developed and used for decades in fields such as manufacturing electronic devices, chemistry and engineering. Nanofilms are also used in eyeglasses, computer displays and cameras to protect or treat the surfaces [73].

Two-dimensional nanomaterials such as tubes and wires have generated considerable interest among the scientific community in recent years. In particular, their novel electrical and mechanical properties are the subject of intense research.

Three-dimensional nanomaterials such as fullerenes, dendrimers, and quantum dots have been finding new approaches for drug delivery, medical diagnosis and cancer treatments, which are supposed to have a huge future market. Examples of one-, two- and three-dimensional nanoparticles are shown in Figure 5.4.

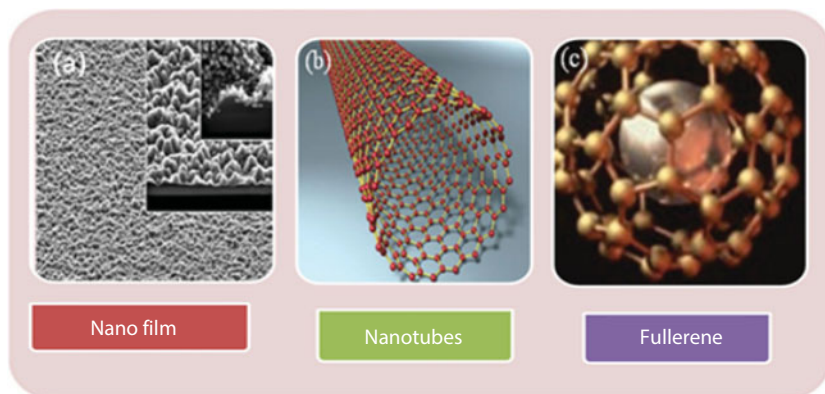


Figure 5.4 Diagrammatic representations of (a) one-, (b) two- and (c) three-dimensional nanomaterials.

5.6.3 Nanotechnology in the Field of Water Remediation

Nanotechnology affects each and every area of our life; some fields of application are shown in Figure 5.5. In recent years, nanoremediation has become the main focus of research and development. This technology has great potential for use in cleaning up contaminated sites and protecting the environment from pollution.

5.6.3.1 Carbon Nanotubes

Carbon nanotubes are hexagonal networks of carbon atoms, 1 nm in diameter and 1–100 nm in length, as a layer of graphite rolled up into a cylinder. There are two types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), which differ in the arrangement of their graphene cylinders. Carbon nanotubes have exceptional thermal, electrical, and mechanical properties, allowing for wide potential applications in numerous industries [74, 75].

The unique properties of carbon nanotubes would allow water molecules to pass through the interior of the cylinders, while chemical and microbial contaminants could not. This is a filtration process called size exclusion. This could be accomplished at a high rate of flow with very little energy (pressure) input to “push” the water through the nanotubes—thus it is a big advantage over current membrane technologies. Additionally, research has shown carbon nanotubes have a strong ability to adsorb many types of chemical and microbial contaminants [76–79].

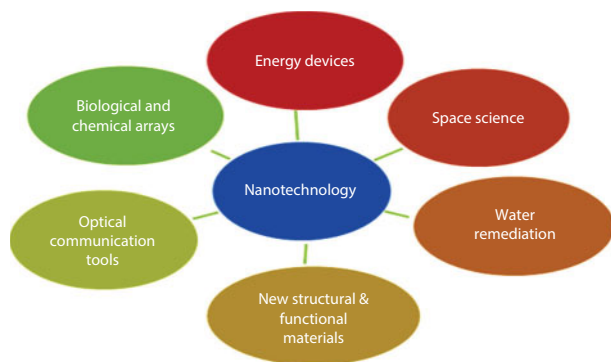


Figure 5.5 Pictorial presentations of applications of nanotechnology.

5.6.3.2 *Dendrimers*

Another example of environmental treatment and remediation-related application of nanomaterials includes dendritic nanoscale chelating agents for polymer-supported ultrafiltration (PSUF). Dendrimers are highly branched polymers with controlled composition and an architecture that consists of nanoscale features. In other words, dendrimers or cascade molecules have branching construction similar to a tree, in which one trunk forms several large branches; each forming smaller branches, and so on. The roots of the tree also have the same branching mode of growth. The environmental applications of dendrimers were first explored by Diallo *et al.* [80]. Rether and Schuster made a water-soluble benzoylthiourea modified ethylene diamine core-polyamidoamine dendrimer for the selective removal and enrichment of toxicologically relevant heavy metal ions. They studied complexation of Co(II), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) by the dendrimers ligand and using the polymer-supported ultrafiltration process. Dendrimers are hyperbranched, tree-like structures and have compartmentalized chemical polymer. Dendrimers contain three different regions: core, branches, and surface.

5.6.3.3 *Polysaccharide-Based Nanoparticles*

Polysaccharide-based nanoparticles provide an alternative to the above-mentioned nanosystems due to some inherent properties like biocompatibility and biodegradability, and therefore are environmentally safe; and because of the presence of functional groups, they are capable of binding metal ions even at low concentrations. Polysaccharide as adsorbents are known to bind metal ions strongly, so they have been widely investigated for the removal of heavy metals in water treatment. These advantages have led to increasing interest in biosorption [81].

The term “biosorption” refers solely to the technological application of natural systems that have existed for thousands of years. Due to the high polluting capacity of modern society in recent years these processes have been used to the benefit of mankind. In other words, “biosorption” can be defined as the removal of metallic ions by means of passive adsorption or complexation by live biomass or organic waste [82]. In recent years there has been considerable interest in the use of sorbent materials; particularly biosorbents such as wheat straw, agricultural by-products, microbes and biopolymers including cellulose, pectin, carrageen, lignin, chitosan and cellulose alginic acid. Sorption by biomass is now recognized as an alternative method for the treatment of wastewaters containing heavy metals [83]. The biosorbents, unlike monofunctional ion exchange resins, contain a

variety of functional sites including carboxyl, imidazole, sulfhydryl, amino, phosphate, and sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties. Use of biopolymers has several advantages in the field of water treatment, including heavy metal removal. The biopolymers are biodegradable macromolecules.

There has been fast growth in the research of nanoparticles of polysaccharides such as chitosan, alginate, and glucomannan, which are biocompatible and nontoxic, hence used for different applications in the medical, food, water purification, wastewater treatment and cosmetic industries. On the basis of structural characteristics, the polysaccharide nanoparticles are prepared mainly by four mechanisms, namely covalent crosslinking, ionic crosslinking, polyelectrolyte complexation, and self-assembly of hydrophobically-modified polysaccharide. Use of polysaccharide has several advantages in the field of water treatment, including heavy metal removal.

5.7 Polysaccharides

Polysaccharides are polymers of monosaccharide joined by glycosidic bonds. These highly abundant molecules are from various origins including algal origin (e.g., alginate and carrageenan), plant origin (e.g., cellulose, pectin and guar gum), microbial origin (e.g., dextran and xanthan gum), and animal origin (e.g., chitosan, hyaluronan, chondroitin and heparin) [84]. Polysaccharides can be either homopolysaccharides or heteropolysaccharides and occur in algae (e.g., alginate), plants (e.g., pectin, guar gum), microbes (e.g., dextran, xanthan gum), and animals (chitosan, chondroitin). They are highly stable, safe, non-toxic, hydrophilic and biodegradable. Polysaccharides have a large number of reactive groups, a wide range of molecular weight, varying chemical composition, etc. Polysaccharides can also be divided on the basis of charge into cationic polysaccharides (chitosan), anionic polysaccharides (alginate, heparin, hyaluronic acid, pectin, etc.), nonionic polysaccharides (starch, dextrans, guar gum), amphoteric polysaccharides (carboxymethyl chitosan, N-hydroxy-dicarboxyethyl-chitosan, modified potato starch) and hydrophobic polysaccharides.

5.7.1 Classification of Polysaccharides

The following section briefly describes the major classification of polysaccharides.

5.7.1.1 *Storage Polysaccharides*

Storage polysaccharides are energy storage polysaccharides which are present in seeds, stems, tubers, rhizomes (starch) and liver (glycogen), etc.

5.7.1.2 *Structural Polysaccharides*

Structural polysaccharides are used to provide protective walls or lubricative coatings to cells. Cellulose, chondroitin sulphates, hyaluronic acids and chitin are examples.

5.7.1.3 *Heteropolysaccharides*

Heteropolysaccharides contain two or more different types of monosaccharide units and occur in both straight-chain and branched-chain forms. The major heteropolysaccharides include the connective tissue polysaccharides, the blood group substances, glycol proteins and glycol lipids, particularly those formed in the central nervous system of animals, and a wide variety of plant gums like pectin, lignin, and mucopolysaccharides, etc.

5.7.1.4 *Homopolysaccharides*

Homopolysaccharides have one type of monosaccharide and are subdivided into straight-chain and branched-chain, depending upon the arrangement of the monosaccharide units. These homopolysaccharides are further classified into plant polysaccharides, animal polysaccharides (e.g., chitin, glycogen), microbial polysaccharides (fungal [e.g., pullulan] and bacterial polysaccharide [e.g., xanthan gum, gellan gum, dextran and curdlan]), and seaweed polysaccharides (e.g., agar, carrageenan, furcellaran and alginate).

5.7.2 **Preparation of Polymeric (Polysaccharide-Based) Nanoparticles**

On the basis of structural characteristics, the polysaccharide nanoparticles are prepared mainly by four mechanisms, namely, covalent crosslinking, ionic crosslinking, polyelectrolyte complexation, and self-assembly of hydrophobically-modified polysaccharides.

5.7.2.1 *Covalent Crosslinking*

In a covalently crosslinked NP, the network structure is permanent since irreversible chemical links are formed unless biodegradable or

stimuli responsive crosslinkers are employed [85]. The rigid network allows absorption of water and bioactive compounds without dissolution of the NP even when the pH drastically changes. Chitosan is frequently used to prepare nanoparticles using the covalent crosslinking method. Covalent crosslinkers are molecules with at least two reactive functional groups that allow the formation of bridges between the polymeric chains [86]. The most common covalent crosslinkers used with polysaccharides are dialdehydes such as glutaraldehyde. However, dialdehydes are highly toxic and therefore biocompatible alternatives have been tested. For example, natural di- and tricarboxylic acids have been used for intramolecular crosslinking.

5.7.2.2 *Ionic Crosslinking*

Ionic crosslinking represents a simple alternative to covalent crosslinking for charged polysaccharides. This method enables the preparation of NPs by the formation of reversible ionic crosslinking, and since no harsh preparation or toxic crosslinkers are used, these NPs are generally considered biocompatible [85]. For charged polysaccharides, small molecules of polyanions and polycations could act as ionic crosslinkers for polycationic and polyanionic polysaccharides, respectively. Charged polysaccharides can form ionic crosslinked NPs with oppositely charged ions or small ionic molecules. For example, the polyanion tripolyphosphate (TPP) has been widely used to crosslink the CS, and divalent cations such as Ca^{2+} have been used to crosslink alginate [87].

5.7.2.3 *Polysaccharide Nanoparticles by Polyelectrolyte Complexation (PEC)*

Polyelectrolyte complexes (PEC) are formed by direct electrostatic interactions of oppositely charged polyelectrolytes in solution. These complexes resemble ionic crosslinking since non-permanent networks are formed that are more sensitive to changes in environmental conditions [88]. However, unlike ionic crosslinking, in which ions or ionic molecules react with the polyelectrolyte, in PEC the interaction is between the polyelectrolyte and larger molecules with broad Mw range [85]. Polysaccharide-based polyelectrolyte complexation nanoparticles can be obtained by means of adjusting the molecular weight of component polymers in a certain range.

5.7.2.4 *Self-Assembly of Hydrophobically-Modified Polysaccharides*

When hydrophilic polymeric chains are grafted with hydrophobic segments, amphiphilic copolymers are formed. Upon grafting hydrophobic

moieties onto a hydrophilic polysaccharide, an amphiphilic copolymer is created. In aqueous solutions amphiphilic copolymers tend to self-assemble into NPs in which the inner core is hydrophobic and the shell is hydrophilic. The hydrophilic shell serves as a stabilizing interface between the hydrophobic core and the external aqueous environment.

5.7.3 Some Examples of Polysaccharides

5.7.3.1 Alginate

Alginates (Figure 5.7a) consist of a linear chain of (1–4)-linked residues of β -D-mannuronic acid and α -L-guluronic acid in different proportions and sequential arrangements. The most common arrangement is a block copolymer, in which long homopolymeric sequences of guluronic acid residues (G–G blocks) and similar sequences of mannuronic acid residues (M–M blocks) are intercalated between sequences of mixed composition (M–G blocks) (1). According to the “egg-box” model as shown in Figure 5.6, the metal binding mechanism of alginates is provided by the formation of the covalent bonds between polysaccharide carboxyl groups and two valence metal ions. The presence of carboxylic group in the alginate moiety helps to form complexes with cationic metal ions and has drawn tremendous attention in the scientific community for concentrating metal ions in the alginate beads [90]. Especially chain segments containing oligopolymeric blocks of guluronic acid exhibited selectivity for metal cations, and the sorption of Cu from aqueous solution by calcium alginate was studied.

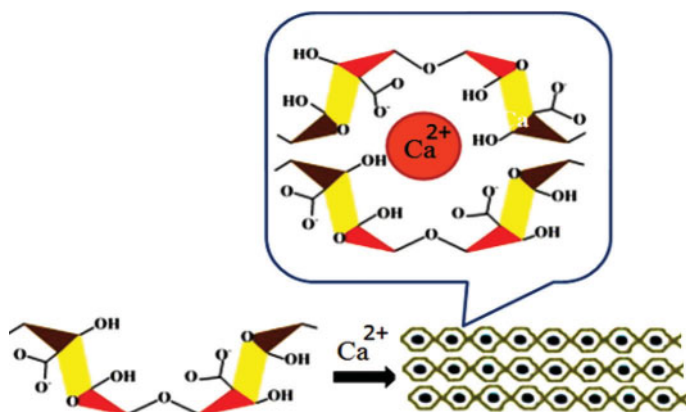


Figure 5.6 Schematic representation of “egg box” model of alginate.

Usually sodium and calcium salts are used in experiments. In this case chelation is presented by ion exchange process between sodium/calcium ions and ions of heavy metals. As sodium and calcium possess quite different properties and form water soluble and insoluble alginates, respectively, it is of interest to compare these two types of alginate salts regarding their metal binding capacity.

5.7.3.2 Chitosan

Chitosan is transformed polysaccharide obtained by the de-N-acetylation of chitin, which makes up the shells of crustaceans such as crabs and shrimps [91]. It is biodegradable, biocompatible, hydrophilic, harmless to living things and nontoxic, making it an environmentally friendly substance [92]. The free amino groups of chitosan can serve as coordination sites for binding metals. Several metals are preferentially adsorbed in acidic media, while chitosan can dissolve in acidic condition. To overcome such a problem and to increase physical and chemical strength, some crosslinking agents such as glutaraldehyde, epichlorohydrin and ethylene glycol diglycidyl ether are used to stabilize chitosan in acid solutions. The amino and two hydroxyl groups on each glucosamine in the repeating unit of chitosan can act as a reactive site for chemical modification. In order to increase the adsorption ability of chitosan, and to improve the adsorption selectivity of metal ions, several chemicals have been used to modify chitosan such as glycine, polydimethyl siloxane, thiourea and maleic anhydride. The chemical structure of chitosan is shown in Figure 5.7b.

5.7.3.3 Guar Gum

Guar gum is also known as cluster bean (*Cyamopsis tetragonoloba* [L.]) obtained from leguminous crop. Chemically, guar gum is a straight-chain galactomannan, and has a chain of (1→4)-linked-β-D-mannopyranosyl

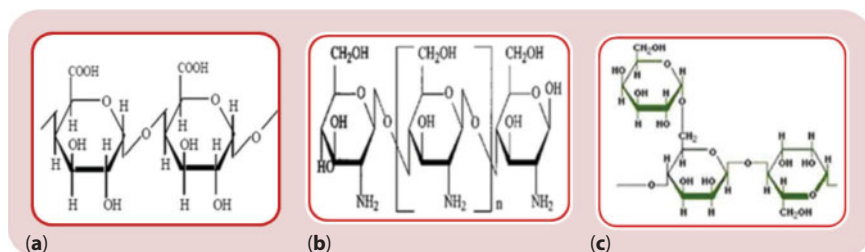


Figure 5.7 Chemical structures of (a) alginate, (b) chitosan, and (c) guar gum.

units with single α -D-galactopyranosyl unit connected by (1 $\rightarrow$ 6) linkages. D-mannopyranosyl to Dgalactopyranosyl units are present in fixed ratio of 1.8:1. The average molecular weight of guar gum is in the range of $1-2 \times 10^6$ Dalton. The cis-position is important since adjacent hydroxyl groups reinforce each other in hydrogen bonding reactions. The chemical structure of guar gum is shown in Figure 5.7c.

5.7.3.4 Poly- γ -Glutamic (γ -PGA)

Poly- γ -glutamic acid (γ -PGA) is a water-soluble, biodegradable, edible and nontoxic biopolymer [93] that consists of repetitive glutamic acid units connected by amide linkages between α -amino and γ -carboxylic acid functional groups. Naturally produced γ -PGA is an anionic polypeptide usually containing nearly equal amounts of D and L units, and the molecular weight of the polymer is generally high [94]. Poly- γ -glutamic and its derivatives have been utilized in a wide range of industrial fields, including cosmetics, food, medicine and water treatment. As γ -PGA is a polyacid with good flocculating activity and high affinity and tightly binds toxic heavy metal ions such as Pb^{2+} , it may therefore be useful for treating wastewater.

5.7.3.5 Starch

Starch, naturally occurring polymer of glucose, is a group of polysaccharides, composed of glucopyranose units joined together by glycosidic linkages. The largest source of starch is corn (maize), with other commonly used sources being cereals (e.g., corn, wheat, rice, oat, barley) containing 60% to 80%, legumes (e.g., chickpeas, beans, peas) containing 25% to 50%, tubers (e.g., potatoes, cassavas, cocoyams, arrowroot) containing 60% to 90%, and some green or immature fruit (e.g., bananas, mangos) containing 70% starch in dry base. Starch and its derivatives represent a cheap and environmentally safe source of raw material for the preparation of low-cost adsorbents that may be useful for the removal of pollutants from wastewater. This biopolymer represents an interesting alternative as an adsorbent because of its particular characteristics (abundant, renewable and biodegradable raw resource) and properties such as its chemical stability and high reactivity, resulting from the presence of chemically reactive hydroxyl groups in its polymer chains [95].

Starch products themselves are hardly suitable as sorbents, since they lack controllable particle size and certain wear resistance, hardness, and porosity. However, the biomaterial has been used for the removal of heavy metal ions in various modified [96] forms, e.g., poly(acrylamide)-starch

graft copolymer carbamoylethylated starch and starch carbamate. Water-insoluble starch phosphate [97] carbamate has been reported for Cu(II) removal. The effectiveness of insoluble starch xanthate [98] for the removal and recovery of heavy metals (Cd[II], Cu[II], Hg[II], and Ni[II]) from simulated wastewater has also been evaluated. Among various modifications, crosslinked starch microspheres show high stability towards swelling, high temperature, high shear and acidic conditions [99], and have been used as good adsorbent due to their total biodegradability, biocompatibility, non-toxicity, stability during storage, cost effectiveness, as well as their simple fabrication method [100].

5.7.3.6 *Tamarind Xyloglucan*

Xyloglucans are members of a group of polysaccharides typically referred to as hemicelluloses. Xyloglucan is found in the plant cell wall that is cross-linked with load-bearing cellulose microfibrils, and affects wall mechanical properties and cell wall enlargement. Xyloglucan is a major structural polysaccharide in the primary cell walls of higher plants. Tamarind xyloglucan is obtained from the endosperm of the seed of the tamarind tree, *Tamarindus indica*. These are also present as storage products in some seeds as a resource for the embryo after germination. Xyloglucan is expected to have new applications in food, serving as a thickener and stabilizer, gelling agent, ice crystal stabilizer, and starch modifier. Tamarind xyloglucan has a (1→4)- β -D-glucan backbone that is partially substituted at the O-6 position of its glucopyranosyl residues with α -D-xylopyranose. Some of the xylose residues are β -D-galactosylated at O-2 [101–103].

5.7.3.7 *Cellulose*

Cellulose (Figure 5.8a) is the most abundant biopolymer resource in the world, and is widely considered as a nearly inexhaustible raw material with fascinating structures and properties. Cellulose consists of β -1, 4-D-linked glucose chains, in which the glucose units are in 6-membered rings (i.e., pyranoses), joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Four different polymorphs of cellulose are known, including cellulose I, II, III, and IV. Cellulose I and II are the most studied forms of cellulose. In living plants, cellulose I is the most widespread crystalline form, which consists of an assembly succession of crystallites and disordered amorphous regions.

Cellulose nanocrystals have been produced from different cellulose sources and observed by a variety of techniques with dimensions ranging from several nanometers to several micrometers. Cellulose nanocrystals

exhibit exceptional product characteristics such as nanoscale dimension, high aspect ratio, high specific strength and modulus, low density, and biodegradability. Due to their unique physical and chemical properties, cellulose nanocrystals can be potentially applied to various fields, such as the material science, electronics, catalysis, biomedical, and energy fields. For instance, various cellulose nanofibrils, nanocrystals and whiskers have been incorporated into polymer matrices to produce reinforced composites that significantly improve mechanical strength [104–108].

5.7.3.8 *Murein*

Murein, also named ‘peptidoglycan,’ is an aminosugar polymer consisting of two β -(1, 4)-linked hexoses, *N*-acetylglucosamin (GlcNAc) and *N*-acetyl-D-muraminic acid (NAMA), the latter differing from GlcNAc in that the 3-position is substituted with an *O*-lactic acid group. The carbohydrate moieties are linked to short oligopeptides, which crosslink the polysaccharide chains. Murein is the structural component of the cell wall of all bacterial species. There are also other kinds of carbohydrates found in the bacterial cell wall, but it is murein that is the major unifying structure.

5.7.3.9 *Pectins*

Pectins are polysaccharides occurring in all plants, primarily in their cell walls. They act as intracellular cementing material that gives body to fruits and helps them keep their shape. When fruit becomes overripe, the pectin is broken down into its monosaccharide constituents. As a result, the fruit becomes soft and loses its firmness. One of the most prominent characteristics of pectins is their ability to form gels. All pectins are composed of D-galactopyranosyl uronic acid units, which are α (1, 4)-linked. They contain methyl esters and acetyl groups to various degrees and show a typical average molecular size of 100,000 Da [109]. The structural formula of pectin is shown in Figure 5.8b.

5.7.3.10 *Dextrans*

It has long been known that sucrose solutions convert into viscous solutions, gels, or flocculent precipitates. The material that produced such changes in sucrose solutions was isolated and found to be a polysaccharide that was called dextran. The enzymes capable of synthesizing polysaccharides from sucrose are produced by Gram-positive bacteria of the type *Leuconostoc* and *Streptococcus*. It is a polysaccharide composed of straight chain and consists of α -1, 6 glycosidic linkages between glucose molecules, while branches begin from α -1, 4 linkages and there are three hydroxyl

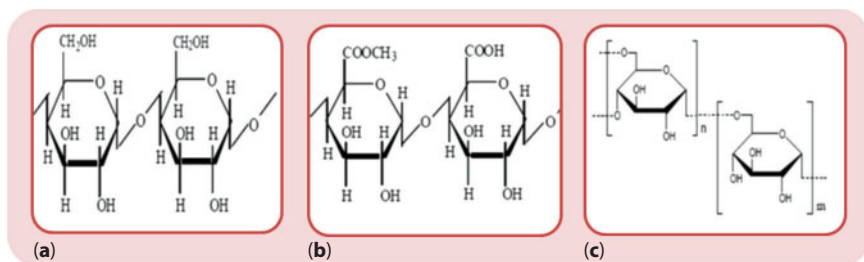


Figure 5.8 Chemical structures of (a) cellulose, (b) pectin, and (c) dextran.

groups per anhydroglucose unit, which makes it very soluble in water. Dextran is glucose polymers which have been used as a plasma expander for five decades to reduce blood viscosity [110–112]. Dextran contains a large number of hydroxyl groups which can be easily modified and ready to form hydrogel by either direct attachment or through a crosslinker. Structural formula of dextran is shown in Figure 5.8c.

5.7.3.11 Glycogen

Glycogen serves as the secondary long-term energy storage in animals that can be quickly mobilized to meet a sudden need for glucose. Glycogen is made primarily by the liver and the muscles by glycogenesis. Glycogen is the analogue of starch, a glucose polymer in plants, and is sometimes referred to as animal starch, having a similar structure to amylopectin but more extensively branched and compact than starch. Glycogen is a polymer of α (1–4) glycosidic bonds linked with α (1–6)-linked branches. It plays an important role in the glucose cycle. In the liver hepatocytes, glycogen can compose up to eight percent of the fresh weight (100–120 g in an adult) soon after a meal. Only the glycogen stored in the liver can be made accessible to other organs. In the muscles, glycogen is found in a low concentration (one to two percent of the muscle mass). It is insoluble in water. Its structure is similar to that of amylopectin, but it is more branched and each branch contains from 8 to 12 glucose units. It is a more compact molecule with a molecular weight of several millions [113, 114].

5.7.3.12 Gellan gum

Gellan gum is an exocellular anionic heteropolysaccharide produced by the aerobic fermentation of the bacterium *Sphingomonas elodea* (formerly known as *Pseudomonas elodea*). There are two chemical forms of gellan gum: native or natural form, which has high acyl contents, and low or deacetylated form. Both forms have a similar linear structure made up of

the repeating units of tetrasaccharide which is composed of β -D-glucose, β -D-glucuronic acid and α -L-rhamnose residues in the molar ratio of 2:1:1. The native form contains two acyl substituents, namely acetate and glycerate, both being located on the same glucose residue and, on average, there is one glycerate and a half acetate group per every tetrasaccharide repeating unit (Figure 5.6). This difference in substitutions leads to a difference in the gelling potential [115]. Some investigators have elucidated the gelation mechanism of gelan gum in the presence of various monovalent and divalent cations [116–119]. The gelling of gellan gum is inducible by cations and is temperature dependent. Gellan gum forms gels in the presence of mono- and divalent cations; however, its affinity for divalent cations such as Ca^{2+} and Mg^{2+} is much higher than for monovalent ones such as Na^{+} and K^{+} . This difference in efficiency has been attributed to the difference in their gel-inducing mechanisms. In the case of monovalent cations, the gelation is mainly contributed by the screening of the electrostatic repulsion between the ionized carboxylate groups (COO^{-}) on the gellan chains [120].

5.7.3.13 Xanthan

Xanthan is a microbial polysaccharide. According to its chemical structure [121], xanthan can be classified as stereoregular copolymeric polyelectrolyte. Xanthan gum is a high molecular weight extracellular polysaccharide produced by the fermentation of the gram-negative bacterium *Xanthomonas campestris*. The primary structure of this naturally produced cellulose derivative contains a cellulose backbone (β -D-glucose residues) and a trisaccharide side chain of β -D-mannose- β -D-glucuronic acid- α -D-mannose attached with alternate glucose residues of the main chain. The terminal D-mannose residues may carry a pyruvate function, the distribution of which is dependent on the bacterial strain and the fermentation conditions. The nonterminal D-mannose unit in the side chain contains an acetyl function. The anionic character of this polymer is due to the presence of both glucuronic acid and pyruvic acid groups in the side chain [122].

5.8 Advantages of Using Polysaccharides for Removal of Toxic Metal Ions

Adsorbents used for adsorption processes of pollutants should contain the following properties: (i) efficient for removal of a wide variety of target (hydrophobic) pollutants; (ii) high capacity and rate of adsorption; (iii) important selectivity for different concentrations; (iv) granular type

with good surface area; (v) high physical strength; (vi) able to be regenerated if required; (vii) tolerant for a wide range of wastewater parameters; and (viii) low cost. Sorption using polysaccharide-based materials as adsorbents has several advantages.

- The polysaccharide-based sorbents are low-cost materials obtained naturally, whereas the majority of commercial polymers and ion-exchange resins are derived from petroleum-based raw materials using processing chemistry, which is not always safe and environmentally friendly. In the present scenario, there is a growing interest in developing natural low-cost sorbents as an alternative to synthetic polymers.
- The use of polysaccharide-based biosorbents is cost-effective. Crosslinked materials are easy to prepare with relatively inexpensive reagents (low operating cost). The amount of sorbent used is, in general, reduced as compared to conventional sorbents since they are more efficient. Much lower quantities of biopolymer are required to build the hybrid materials. Activated carbon, synthetic ion exchange resins and others are quite expensive, and with increasing quality cost increases. Moreover, the volume of sorbent material required increases proportionately with the solute load, so that at higher solute concentrations, equipment size makes such conventional adsorption processes economically unfeasible, even on a small scale.
- These materials are versatile. This versatility allows the sorbent to be used under different forms, from insoluble beads, to gels, sponges, capsules, films, membranes or fibers. Materials are available in a variety of structures with a variety of properties. The utilization of crosslinked beads or hybrid materials has many advantages in terms of applicability to a wide variety of process configurations and reusability for repeated runs [123]. Different analytical methods including the batch method, sorption columns, dynamic tests or reactors can be used. In general, conventional sorbents are commonly operated in fixed-bed processes.
- Polysaccharide-based nanosorbents are very efficient for the removal of pollutants at different concentrations. They possess a high capacity and high rate of adsorption, and a high efficiency and selectivity in detoxifying both very dilute

and concentrated solutions. In general, activated carbon and synthetic resins suffer from a lack of selectivity and applications are typically limited to levels of contaminants in the ppm range.

- Presence of multiple functional groups in biopolymers provides excellent chelating and complexing materials for a wide variety of pollutants including dyes, heavy metals and aromatic compounds. Although polysaccharides are highly efficient in the removal of toxic metal ions in natural state, their adsorption capacity can still be improved by the substitution of functional group onto the polymeric chain.
- Regeneration of polysaccharide-based sorbents is easy. The sorbents can be regenerated by desorption at low cost if required. They can be easily regenerated by a washing solvent because the interaction between the pollutant and sorbent is mainly electrostatic, hydrophobic and ion-exchange interactions.

5.9 Brief Review of the Work Done

A recent study by Dambies *et al.* [124] showed that chitosan beads removed about 60% of Cr(VI) ions from aqueous solution. Ngah *et al.* and Gylieue *et al.* [125, 126] stated that chitosan could be effective adsorbent for collection of Cu(II) ions from aqueous solutions. Panday *et al.* [127] have used calcium-alginate microcapsules with or without humic acid for the removal of various metals. Various alginate gel-based adsorbents were investigated by Park and Chae [128] for the removal of Pb(II). Alginic acid has been also shown to be effective at removing many cationic metals from solutions including Pb(II), Cu(II), Cd(II), Zn(II) and Co(II). Dhakal *et al.* and Banerjee *et al.* [129, 130] worked on iron doped calcium alginate beads and reported that Fe-CA beads are highly effective in removing As(V) over a wide concentration range (20–250mg kg⁻¹) with 30 min exposure time. Tiwari and his coworkers [131] have reported in their paper that alginate and carboxymethyl cellulose beads can be used as an efficient adsorbent for the removal of arsenic from aqueous solutions. Crosslinked starch xanthate and carboxyl-containing starch products have been shown to remove heavy metal cations effectively from wastewater. Kim and Lin [132] worked on crosslinked starch xanthate and carboxyl-containing starch products and reported that it can remove heavy metal cations effectively from wastewater. Chan and Wu

[133] reported the mass transport process for the adsorption of Cr(VI) onto crosslinked cationic starch, as well as the adsorption of Cu^{2+} and Ga^{2+} onto insoluble amphoteric starch containing quaternary ammonium and phosphate groups. Xu *et al.* [134] also worked on removal of Pb(II) using crosslinked amphoteric starch.

Numerous other researchers worked on natural biosorbents for the removal of toxic metal ions. Agrawal *et al.* [135] worked on gelatin-based nanocomposites for the removal of chromium ions. Alginate nanoparticles were used by Singh *et al.* [136] as an efficient adsorbent in arsenic remediation from aqueous solutions. Bajpai *et al.* and Shrivastava *et al.* [137, 138] studied the removal of Ni^{2+} and chromium ions using alginate and alginate-gelatin crosslinked nanoparticles, respectively.

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Part 3

MEMBRANES & CARBON NANOTUBES

The Use of Carbonaceous Nanomembrane Filter for Organic Waste Removal

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Abstract

Nanotechnology has great impact on the present scenario of wastewater treatment because of their particle size and surface area. Nanomaterials such as metals, metal oxide, low cost adsorbent, nanocatalyst, organic macromolecules composite, and other compounds such as natural organic matter, fullerenes, dendrimers, dyes, chitosan, enzyme, various shaped nanostructures such as nanorods, nanowires and nanotubes (both organic and inorganic) ultrathin films and nanomembrane are used in wastewater treatment. Nanotechnology is an advanced technology used for the cleanup of contaminated water by nanocatalysts, nanofiltration or membrane filtration, and the adsorption of pollutants via nanoscale materials. The use of carbonaceous nanomaterial membranes can serve as high capacity and selective sorbents for organic solutes in aqueous solutions, which can solve wastewater treatment problems. The present chapter initially describes the possible application areas of nanomaterials in wastewater treatment as well as its uses as nanomembrane filter.

Keywords: Wastewater, carbonaceous nanomembrane, nanofiltration organic/inorganic composite materials, low-cost adsorbent

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6.1 Introduction

A large number of metal, metal oxides, carbonaceous and composite nanomaterials have a broad range of properties compared to the bulk metal/metal oxide materials. These materials are more attractive and have great advantages for use in consumer products and medical applications [1]. Among various nanomaterials, Ag, TiO_2 and ZnO nanoparticles are increasingly used to improve water quality and microbial control activities [2, 3]. Silver nanoparticles directly destroy pathogens from drinking water by using impregnated bacterial paper and ceramic filter [4–6]. The metal oxide nanoparticles can be prepared by employing several methods such as chemical vapor deposition (CVD), spray pyrolysis, ion-beam-assisted deposition, laser ablation, and sputter deposition [7–10]. Among various methods, nanostructures can also be obtained by very simple and effective chemical routes such as sol–gel, chemical precipitation, co-precipitation, sonochemistry, and hydrothermal techniques which are used for the large-scale production of magnesium oxide (MgO), iron oxide (Fe_3O_3), and tin oxide (SnO_2) [11–13]. For long-range preparation procedures of zero, single and two-dimensional nanostructures such as nanoparticles, nanorods, nano and micro-flowers, nanobelts, nanosheets, spheres. etc., the solidification process also works for the formation of metal matrix nanocomposites (MMNCs) such as $\text{Al-B}_4\text{C}$, Mg-SiC , Al-CNT , Cu-CNT , Ti-SiC , Al-SiC , Mg-SiC , $\text{Al-Al}_2\text{O}_3$, Al-CNT , $\text{Mg-Y}_2\text{O}_3$, Al-Diamond , and Zn-SiC [14]. In this context, Talapin *et al.* reported that the TiO_2 and SnO_2 nanoparticles anisotropic self-assembly chain-like nanostructure exhibited semi-conducting properties with crystallography orientations used for tailoring the grain boundaries and enhancing charge transport [15].

Apart from the metal, metal oxide and composite nanomaterials, a new class of carbonaceous materials such as fullerenes, carbon nanotubes (CNTs) and their chemical derivatives play an important role in wastewater treatment [16]. Fullerenes are a class of closed-cage carbon molecule or carbon spherical molecules, C_n characteristically containing 12 pentagons and a variable number of hexagons. Fullerenes are commonly known as “buckyballs” (less than 300 carbon atoms) and giant fullerenes (more than 300 carbon atoms) with single- or multi-shelled carbon structure; for example, (60) Bingel adduct, (60)bis-PCBM and (60)PCB- C_{12} (lipo-soluble for skincare and nutrition), etc. The family of carbonaceous material fullerenes is also used for the adsorption of organic compounds and is very efficient in the removal of organometallic compounds and weak sorbents for a wide variety of organic compounds (e.g, phenols, PAHs, amines).

Adsorption of fullerenes depends on number of carbon atoms, such as C_{60} , which are not soluble in water and form carbon clusters have interstitial spaces for adsorption of various molecules [4]. Fullerenes and their derivatives are well-defined chemical compounds containing a given number of atoms, and nanotubes made under different conditions afforded by a given process, usually produce a range of diameters, lengths and physical properties [17, 18]. In this context the long-chain polymeric compounds, such as dyes and dye-doped nanoparticles, are used for biological applications because many dyes (e.g., rhodamine, cyanine, fluorescein, Alexa dyes) and inorganic molecules incorporate and modify various functional groups with silica matrix [19–21].

These long-chain organic compounds enhance detection of chemical and biological sensitivity and have high magnitude for use in many different applications. There is a new class of fluorescent probe for bioapplications in cellular imaging and labeling using surface-functionalized small molecule organic dye nanoparticles (NPs) for targeted cell imaging. The consequence of dye nanomaterials applications in water treatment has been studied by many researchers due to the fact that dyes are used in large amounts in many textile industries and can easily react with other species and form complexes. These complexes are highly stable and difficult to decompose. Organic dyes consist of various chemical compositions and these chemicals are toxic in nature with suspected carcinogenic and mutagenic effects; for example, chemicals such as p-phenylenediamine and aminophenyl have been suggested as possible carcinogens or mutagens as shown in experimental studies. Mostly dyes are used as coloring agents; current evidence has proved that hair dyes, which are toxic at very low concentrations, cause human cancer [22]. The organic dye (2-*tert*-butyl-9, 10-di(naphthalen-2-yl) anthracene, TBADN) is fabricated into NPs and is followed by surface modification with an amphipathic surfactant poly(maleic anhydride-*alt*-1-octadecene)-polyethylene glycol(C18PMH-PEG) by hydrophobic interactions to achieve good water dispersibility and bioenvironmental stability [23]. Various nanocomposites-based dye materials used as filling materials in photonic crystal synthetic opal, porous silicon, porous aluminum oxide, sol-gel silica films and other solid structures show photophysical properties. The dye Rhodamine 6G nanocomposites based on synthetic opal and porous aluminum oxide exhibit monomer-like luminescence spectrum, and interaction between dye molecules and dangling bonds on the surface of SiO_2 balls and Al_2O_3 affects the native PL matrices [24–32].

This chapter describes various ways in which metal, metal oxides, composites and carbonaceous materials are used for the treatment of

wastewater. The chapter also designates how recent techniques such as reverse osmosis, nanofiltration and ultrafiltration are used in wastewater treatment.

6.2 Organic Wastes and Organic Pollutant

The chemical compounds of living things are known as organic compounds because of their association with organisms. Among numerous types of organic compounds, four major categories are found in all living things: carbohydrates, lipids, protein, and nucleic acids. The largest and most significant class is the organic compounds known as hydrocarbons, chemical compounds whose molecules are made up of nothing but carbon and hydrogen atoms only. There are many linking molecules, which are bonded with nitrogen, sulfur and oxygen are also known as donor atoms. Generally, donor atom are arranged side chain, ring or directly to the carbon atom of the heterocyclic compounds (Figure 6.1a, b) and acting as basic center because each donor atom have electron pairs responsible for interaction with metal ions or any other species [33] (Figure 6.1c).

The determination of complex compounds in analytical chemistry, formed by metals with organic ligands, established in three stages. Initially, it develops new organic reagent, which approved for metal ions, after that it analyses the effect of reagent, structure and their reactivity. The reactivity counted by functional group, which present in reagent and calculated their complex formation constant (K_f) with the help of their mechanism. Over the past decades, organic reagents with metals ions are appropriate for the pre-concentration and loaded on absorbents. The varieties of organic compound are biologically active and used in medicine. Numerous number of organic compounds, which have found extensive applications in medicine, technology, analytical chemistry, etc. The derivatives of hydrazone are prospective

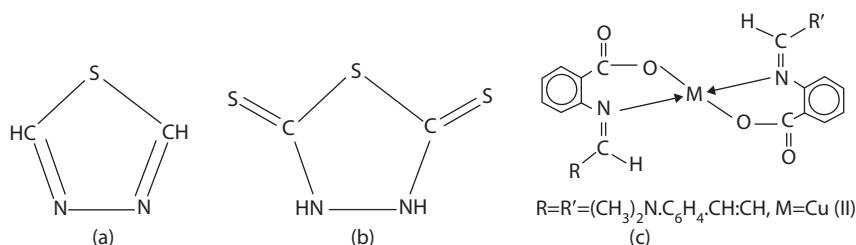


Figure 6.1 (a) and (b) show the heterocyclic compounds, whereas (c) presents the interaction with metal ions through the ligand's electron pairs.

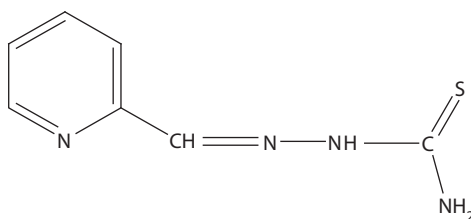


Figure 6.2 Pyridine-2-carboxaldehyde thiosemicarbazone.

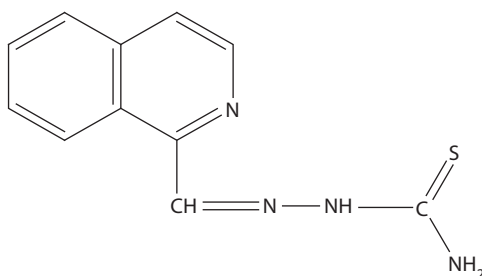


Figure 6.3 Isoquinoline-1-carboxaldehyde thiosemicarbazone.

applications in analytical chemistry [34]. It can be formed from the condensations process of hydrazides and a carbonyl compound. For examples: these compounds contain an azomethine nitrogen atom and are responsible for their reactivity with a number of metal ions, formed colored complexes [35].

Mostly the anticancer compounds/drugs contain sulfur and nitrogen atoms such as pyridine-2-carboxaldehyde thiosemicarbazone (Figure 6.2) and isoquinoline-1-carboxaldehyde thiosemicarbazone (Figure 6.3) [36].

Flavonoids compounds are extensively disseminated in nature, which shows the different characteristic properties such as chemical, physical and biological properties in 2'-hydroxy chalcones [37-39], because it has α : β unsaturated carbonyl group, 2'-hydro-xylchalacones, which have ability of chelates formation [40]. The synthetic property is much more superior to ketones and benzaldehydes from originally manufactured compounds. The spectrophotometric investigations revealed the efficiency of 2'-hydroxychalcones of various metal (iron, aluminum, Uranium) cations [41].

Phenol and its derivatives are invariably present in the effluents from industries engaged in manufacturing a variety of chemical compounds such as plastics, dyes and plants used for coal gasification, and petrochemical units [42].

In organic pollutants, unlike in metals, all organic molecules are ultimately decomposable. Persistent organic pollutants (POPs) include: PAHs, PCBs, PCDDs (dioxins), PCDFs (furans), phenols, chlorophenols, benzene, toluene, ethylbenzene, xylene and insoluble pesticide residues (e.g., aldrin, dieldrin, DDT, malathion, toxaphene) [43].

The analysis of organic pollutants is generally much more time-consuming and expensive than for other metals, and this often limits the number of samples which can be analyzed. Indirect methods, including total organic carbon (TOC), soil color and odor, are sometimes used as alternates to determine the presence of high concentrations of organic molecules such as petroleum hydrocarbons. Petroleum is a complex mixture of many thousands of compounds. These can be divided into four major categories:

- Alkanes
- Aromatics
- Resins
- Asphaltenes

In general, the alkane fraction is the most biodegradable, whereas the polar fraction (i.e., the resins and asphaltenes) is resistant to biological degradation. The aromatic compounds, particularly polycyclic aromatic

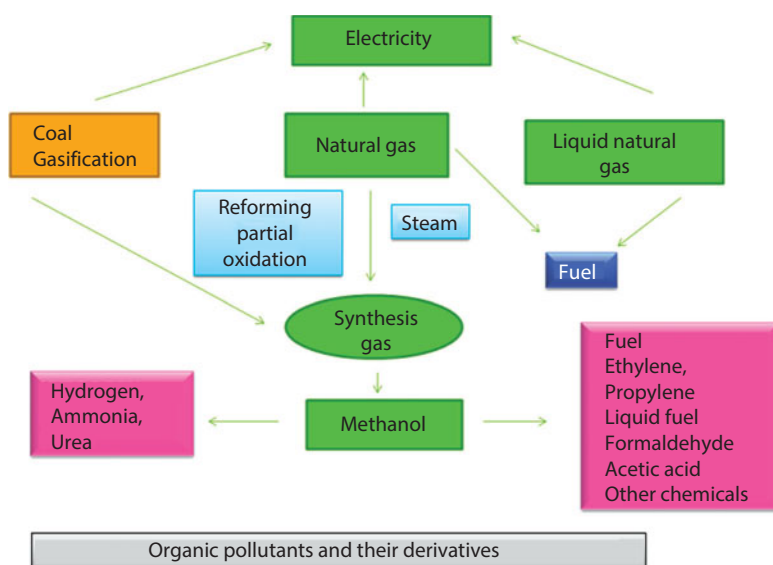


Figure 6.4 Schematic conversion process of organic pollutants.

hydrocarbons (PAHs), exhibit intermediate biodegradability, but these are of most concern owing to their toxicity and tendency to bioaccumulate (Figure 6.4) [44].

6.3 Low-Cost Adsorbents

Adsorbents, which have a very small diameter and arise in nanoscale, have great advantages due to their larger surface area and high reactivity; this leads to the availability of high numbers of atoms, ions and molecules of gas, liquids or dissolved solids to a surface for adsorption of contaminants. Various nanomaterial adsorbents such as activated alumina, activated carbon, polymeric resins, chitosan beads, carbon nano-tubes (CNTs), fullerenes, and zeolites are used in water purification to remove organics, inorganics and metals (Figure 6.5). Activated alumina is frequently used as an adsorbent for water treatment in rural as well as in urban areas. Nanomaterial adsorbents exhibit unique characteristics of physical and chemical textural properties, making them better than other transitional inorganic oxides. Alumina coating is a good adsorbent because it has high surface area maximum uptake capacity and high affinity for water. Metallic composites containing nanoparticles or carbon nanotubes could offer distinct advantages over polymeric composites due to their inherent high temperature stability, high strength, high modulus, wear resistance, and thermal and electrical conductivity of matrix. Aluminum nanocomposites predicted the weight reduction, currently realized through the use of polymer-based nanocomposites

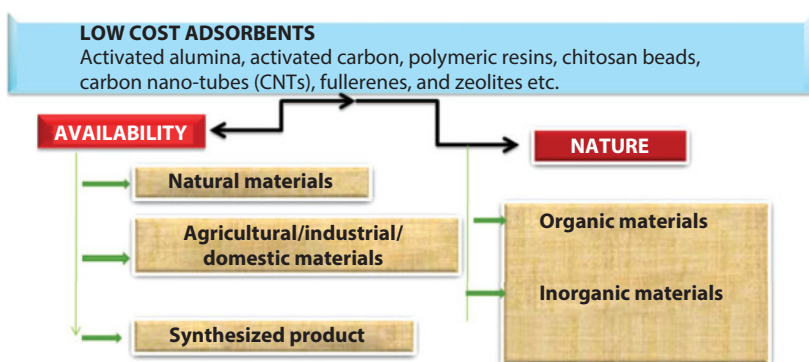


Figure 6.5 Schematic flow chart of low-cost adsorbents.

and polymer-based fiber composites in aerospace applications, primarily because the matrices have higher strength and stiffness. They also have much better thermal stability [45–47]. Various aspects of the wide range of potential nanoparticle adsorbents employed in the purification of water are presented in the following examples: Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanopowders adsorbent materials are used for adsorption studies in wastewater treatment, which are obtained from iron salts with NaOH by co-precipitation methods. The general morphology and dimension of particle elucidates via transmission electron microscopy (TEM) and a scanning electron microscope (SEM) equipped with energy dispersive system (EDS). Nassar investigated Fe_3O_4 nanoparticles adsorbents have been employed for the removal of Pb(II) ions from aqueous solutions via batch-adsorption technique. The effects of contact time, initial concentration, temperature, solution pH and coexisting ions on the amount of Pb(II) ions have been studied. Species of hexavalent chromium (Cr(VI)) nanoparticle were used for adsorption and separation in wastewater treatment; Cr(VI) nanoparticles acted as a carcinogen, mutagen and microtoxic in the biological system. The nanoparticles were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopic techniques which included various factors, e.g., temperature, initial concentration, and coexisting common ions such as Na^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , NO_3^- , and Cl^- , maximum adsorption obtained at pH 2.5 [47–49]

6.4 Heavy Metals

Commonly, heavy metals are most essential elements for human beings, they can take through diet while others are toxic even at very low concentrations. Heavy metals are released in the environment as industrial and waste effluents, which causes health hazardous problems [50–56]. The existence of heavy metals (i.e., copper [Cu], nickel [Ni], zinc [Zn], lead [Pb], mercury [Hg], chromium [Cr], cadmium [Cd]) is at the top of the wastewater toxicity list, and is significant in several areas such as chemical manufacturing, paint pigments, plastics, metallurgy and nuclear industry [57]. Metal ions has tendency to bio-accumulate, toxicity and persistency in microorganisms, aquatic flora and fauna. Food chain is a common pathway for to enter into organism, if they are present in excess amount are harmful for animals at higher tropical level. By this pathway, heavy metals in soil arise and it is the main source of plants and human's nutrition. Although plants acquire a trace amount

of heavy metals for growth and development, lead (Pb) and cadmium (Cd) may cause a great health and environmental risk, even at lower concentration. The deleterious effects of lead (Pb) on neurobehavioral development and brain cell function have been investigated [58, 59]. The maximum allowable limit of Pb^{2+} concentration in drinking water was restricted to 20 ng/ml [60] according to international regulations on water quality by the World Health Organization (WHO) [61] and the European Commission Directive (ECD) [62]. Hence, easy, effective, economical and eco-friendly techniques are required for fine tuning of effluent wastewater treatment. The search for a low cost and easily available adsorbent has led to the investigation of materials applicable to most treatment systems. The main pollution sources of heavy metals are waste residue, waste water and exhaust gas from industry and traffic [63–66], etc. Heavy metal-containing dyes, which are used extensively in the textile industry, are toxic and potentially carcinogenic; they cause serious environmental pollution because the complex of organic aromatic dyes is resistant to light, biological activity and other degradative environmental conditions [67–69]. Materials of biological origin have been studied and used as adsorbents for the removal of heavy metals from water industrial effluents: a white rot fungus species, *Lentinus sajor-caju* biomass, adsorbs Cd(II) [70]; chitosan, coffee, green tea, aloe, and Japanese coarse tea adsorb Cd(II) and Pb(II) [71]; barley straw adsorbs Cu(II) and Pb(II) ions [72]; chitosan-coated PVC beads adsorb Cu(II) and Ni(II) ions [73]; wheat straw adsorbs Cd(II) and Cu(II) [74]; acid-washed crab shells remove Ni(II) from electroplating industrial effluents [75]; and rhizopus arrhizus, a filamentous fungus, adsorbed Pb(II) ions in wastewater from a storage battery factory [76].

6.4.1 Iron

Fe is an integral part of many proteins and enzymes, which is an essential component of proteins involved in oxygen transport and regulation of cell growth. Iron deficiency limits oxygen delivery to cells, leading to fatigue, poor work performance, and decreased immunity. A recommended dietary allowance (RDA) of 8–18mg of Fe/day has been recommended for the average 19–50 year old males and females, respectively [77].

6.4.2 Nickel

Ni is generally obtained in drinking water at concentrations less than $10\mu\text{g L}^{-1}$. It assumed that in a 1.5 L of water contains 5– $10\mu\text{g Ni/L}$, the average

daily intake of nickel from water for adults are between 7.5–15.0 μg . Below 20 $\mu\text{g L}^{-1}$ concentrations of Ni present 97% in drinking water sample whereas 80% of samples had less than 10 $\mu\text{g L}^{-1}$. In exceptional cases, values up to 75 $\mu\text{g L}^{-1}$ are found, those as high as 200 $\mu\text{g L}^{-1}$ were recorded only in the nickel ore mining areas [78-79].

6.4.3 Copper

Copper is mainly used for pulp and paper board, wood and leather preserving, petroleum refining and for copper coatings and fittings. The excessive amount of copper shows adverse effect, which creates health problem such as gastrointestinal and liver toxicity. The EPA MCLG recommends the quantity of copper 1.3 milligrams per liter (mg/L) in drinking water which depends against adverse gastrointestinal effects [80].

6.4.4 Chromium

The role of adsorption in the removal of chromium ions Cr(VI) and Cr(III) from an aqueous solution and their removal mechanisms with biological species such as *L. hexandra*, *Sw. biomass*, *tamarind seeds*, *Posidonia oceanica* (*L.*) *fibers*, *Sargassum sp. algae* and a laboratory-cultivated microalgae (*Chlorococcum sp.*) have been studied [81–86]. A tanning effluent was characterized from a mycological point of view [87]; two fungal strains (*Fusarium solani* and *Mucor circinelloides*) were isolated from the effluent, and 3 strains (*Cunninghamella elegans*, *Rhizomucor pusillus* and *Rhizopus stolonifer*) were investigated for dye biosorption via batch experiments.

6.4.5 Cadmium

The cadmium (II) removal from wastewater reported that the biosorption kinetics were fast and indicated a high affinity for the carboxylic groups. The CSRT and fixed-bed studies showed that both systems can be used to continuously remove cadmium ions Cd(II) in aqueous solution. Although, the immobilization technique has great advantages such as high biomass loading, high reusability and minimal clogging in continuous flow systems [88, 89].

6.4.6 Lead and Mercury

Lead and mercury metals are highly toxic and have adverse effects throughout the body. They are present in the wastewater of a number of industrial products such as batteries, pigments, printing products, chlor-alkali materials, and explosives. These metals directly affect the kidneys, nervous system, and reproductive system, and can also cause high blood pressure. Lead is primarily damaging to fetuses and young children, whose brains are in the developing stage. The heavy metal mercury can cause severe problems such as pain, pinkness, and peeling of the hands, irritation, sweating, persistently faster-than-normal heart beat and loss of mobility, which is termed as acrodynia [90, 91].

6.4.7 Gold, Silver and Palladium (Au, Ag and Pd)

A low level of noble metals Au and Pd was removed from wastewater using surface-modified MCM-41 and MCM-48 mesoporous silica [92]. Additionally, the silver, gold, cadmium sulphide and uranium metals played an important role in the synthesis of metallic nanoparticles. A vast collection of biological resources available in nature, including plants and plant products, algae, fungi, yeast, bacteria, and viruses, could all be employed for synthesis of nanoparticles [93–103].

6.5 Composite Materials

Composite materials formed by the combination of organic and inorganic polymer materials are attractive for the purpose of creating high-performance or high-functional polymeric materials, termed as “organic-inorganic hybrid materials.” Organic-inorganic polymer-based hybrid ion exchangers showed an improvement in a number of properties, viz chemical, mechanical, radiation stability, ion-exchange, and also a selective nature for the heavy toxic metal ions [104].

6.5.1 Inorganic Composite Materials

Recently, inorganic, synthetic organic and organic-inorganic hybrid materials have been used for heavy metals adsorption. These include tantalum arsenate [105], iron (III) antimonate [106], antimony (V) silicate [107], zirconium (IV) phosphosilicate [108], alkali metal ions on iron (III) antimonate [109], and α -cerium phosphate [110].

6.5.2 Synthetic Organic Composite Materials

The synthetic organic ion-exchange resins have various anionic and cationic ion exchangers such as -SO_3^- , -COO^- , PO_3^{2-} , AsO_3^{2-} , NH_3^+ , NH_2^+ , -N^+ , -S^+ , etc., which are responsible for matrix carriers [111].

6.5.3 Organic-Inorganic Hybrid Composite Materials

The organic-inorganic hybrid composite ion exchange materials are pyridinium-tungstoarsenate [112], poly-o-toluidine Th(IV) phosphate [113], poly-o-anisidine Sn(IV) phosphate [114], and poly-o-toluidine Zr(IV) phosphate [115]. Polypyrrole/polyantimonic acid [116] is used for the selective separation of Pb^{2+} , Cd^{2+} , and Hg^{2+} . In many hybrid polymeric adsorbent materials, solvent-impregnated resins are used for the separation of metal and organic compounds from water [117]. Hybrid polymeric composites, namely nano-hydroxyapatite/chitin (n-HApC) and nano-hydroxyapatite/chitosan (n-HApCs), are used for the removal of Fe(III) from drinking water [118].

6.5.4 Mesoporous Organic-Inorganic Hybrid Materials

A review article explained mesoporous organic-inorganic hybrid materials, which is obtained through the coupling of inorganic and organic components by template synthesis. The main focus was on periodic mesoporous organosilicas (PMOs) for enantioselective chromatography, and a new heterogeneous catalysis has been developed [119]. Thiol-functionalized mesoporous silicas show interesting adsorption properties and high affinity for heavy metals, especially toxic Hg^{2+} ions, and have been demonstrated by several authors [120–122]. Additionally, 3-chloropropyl-functionalized silicas showed that all cyclam units were localized on the pore surface and were freely accessible to complexation by Cu(II) and Co(II) ions [123].

6.6 Carbonaceous Materials

The carbonaceous materials are in the form of biomass. Processing methods consist mainly of hydrogenation, pyrolysis, thermal, catalytic cracking, gasification and bioconversion. The process gives the polymeric structure, which is broken down into smaller intermediate species. These mixtures

produce hydrocarbon molecules, liquids and gases, which are generally used as chemical raw materials for several industries.

Carbonaceous materials can be categorized in three forms, which generate heat, electricity and liquid fuel. The most important characteristic properties of carbonaceous materials are involved in various processes such as biomass combustion, thermal gasification, pyrolysis, anaerobic digestion of agricultural wastes, straw utilization, environmental systems, and production/utilization interface. According to Zeng *et al.*, carbonaceous materials are largely used in the adsorption process for the removal of NO due to its high surface and high porosity properties. The removal of NO was also studied at room temperature. Carbonaceous material in the form of liquid exhibits higher heating value (20–25 MJ/kg), greater than the original material [124].

Various organic compounds such as benzene, polycyclic aromatic hydrocarbons (PAHs), and nitroaromatic compounds (NACs) adsorbed on carbonaceous material surfaces in the form of gas phase in water solution at room temperature. The carbonaceous materials are composed by graphite, glassy carbon, acetylene black, diamond, carbon nanofibers and carbon nanotubes [125].

6.6.1 Graphite

As we know, graphite is an allotrope of carbon, and single sheets of graphite are known as graphene. Graphene is the basic structural element of all carbon allotropes including graphite, carbon nanotubes and fullerenes. The sheets of graphene are highly applicable for electrical, thermal, 2-dimensional strength, and extremely springy. Different sizes of graphite were prepared and calculated by density of state (DOS) and experimental data calculated by the near edge x-ray absorption fine structure (NEXAFS) [126]. Fischer *et al.* combined all calculation results and observed that both the experimental and computational data exhibited high qualitative results [127].

6.6.2 Glassy Carbon

Glassy carbon (GC) is prepared via polymeric resin (e.g. polyacrylonitrile or phenol/formaldehyde) at high temperatures between 1000–3000°C and at low temperatures (~700°C), which allows doping with heteroatoms in polymers. The graphitic structure exhibited two planes: 1) the basal plane and 2) the edge plane. The basal plane of graphite is more reactive for

chemical reaction than the edge plane. There is no information related to the structure of GC and it is still under debate due to lack of experimental data. Some researchers describe GC as a network of randomly-oriented graphitic carbon or ribbons. It can also give electrochemical and reproducible electrode surface [128–134].

6.6.3 Acetylene Black

Calcium carbide and combustion of acetylene in air under pressure produce acetylene carbon black. The most important characteristic properties of carbon black are degree of aggregation, crystallization and orientation, which have high conductivity, dispersion, good thermal conductivity, and are employed as the positive and negative electrode. The small amount of acetylene black can increase the recycle times of battery [135, 136].

6.6.4 Diamond

Diamond and graphite are two allotropes of carbon, they vary from each other in structure. It exhibits properties such as an extremely hard, transparent with tetrahedral bonding of carbon, very high thermal conductivity, very low electric conductivity. The unit diamond crystal used for gem stones, crystals are used for grind/cut, hard surface of diamond coatings are used for cutting tools as well as it also used in medical devices [136–138].

6.6.5 Carbon Nanofibers

Carbon nanofibers are a major component of nanotechnology, which can be used as gas adsorbents, templates, actuators, composite reinforcements, catalysts, probes, chemical sensors, nanopipes, nanoreactors, etc. Several metals such as Fe, Co, Ni, Cr, V, and Mo are catalyzed in the synthesis of carbon nanofibers decomposition by carbonaceous gases such as ethylene [139].

Both the absorption and decomposition processes are accomplished on the free metal surface. There are so many applications of carbon nanofibers in various fields such as:

- Electronics: lithium-ion batteries and fuel cell electrode
- Additive polymers: enhanced polymer conductivity for composites materials
- Hydrogen gas storage
- Catalyst uptake materials

6.6.6 Carbon Nanotubes

The discovery of carbon nanotubes (CNTs) by Iijima [140] has attracted many researchers to CNTs, and till date a huge number of studies have piled up. Carbon nanotubes were first synthesized as a by-product of the arc-discharge method and are currently being prepared by many kinds of methods including arc-discharge [141], laser ablation [142], catalytic decomposition, hydrocarbon/chemical vapor deposition, plasma-enhanced chemical vapor deposition, thermal chemical vapor deposition, vapor phase growth [143], etc. In addition to this, electrolysis [144] and solar energy [145] methods have also been proposed. The nanotubes of carbon can be categorized into two types: one is multi-walled CNT (MWCNT) and the other one is single-walled CNT (SWCNT) [146]. The multi-walled carbon nanotubes are comprised of 2–30 concentric graphitic layers, with diameters which range from 10–50 nm and length of more than 10 μm . On the other hand, SWCNTs are much thinner, with diameters from 1.0–1.4 nm.

6.6.6.1 *Chemical Modification/Functionalization of Carbon Nanotubes*

Functionalization or chemical modification of carbon nanotubes is widely used in the chemical approach using strong oxidizing agent such as nitric acid and sulfuric acid. These strong acids preferentially disrupt the aromatic ring structure at the caps of the CNTs and lead to the introduction of the carboxylic acid groups at the open ends. This functionality can undergo further reactions to produce a large family of tailored materials. The approach has been proved to be applicable to various functionalities. However, the solubilization of CNTs in aqueous solutions is a prerequisite for use in many biological applications and is a more challenging task because of the hydrophobic nature of CNTs [147–149].

6.6.6.2 *Interaction and Functionalization of Carbon Nanotubes with Biological Molecules*

The interaction of biologically active molecules with CNTs such as DNA, proteins and lipids, efficiently happens due to noncovalent modification. Covalent chemistry, which takes place via modifications of the CNTs' side walls, disturbs the extended π -network, leading to a localization of electrons at the defect sites that are generated at the point of attachment. However, covalent chemistry at the ends of the SWNTs retains the SWNTs' electronic properties and provides a robust linkage to the biological molecule [150].

6.6.6.3 *Application of Biofunctionalized Carbon Nanotubes*

Biofunctionalization of CNTs can potentially facilitate the use of these materials in functional structure and for the bottom-up design of nanodevices if it is possible to make use of the powerful self-assembly properties of natural substances; because CNTs are promising building blocks for molecular electronics, the nanofabrication of electronic devices utilizing CNTs based on self-assembly principles of biology has been attempted. An example is the fabrication of a field effect transistor (FETs) based on CNTs by using DNA-mediated self-assembly. Long chain of DNA can be used as a scaffold onto the functionalized CNTs. Electrical contact to the nanotubes may be obtained by metallization of the scaffold DNA molecule because the nanotubes are usually a mixture of metallic and semiconducting constituents [151].

6.6.6.4 *Biosensing*

Carbon nanotubes offer a unique combination of quasi-1D structure and excellent electronic properties, which can dramatically improve the miniaturization prospects for electronic biosensor devices. Additionally, CNTs offer new opportunities for rapid, sensitive and label-free detection of biological agents, with the selectivity of detection provided by biofunctionalization of the CNTs. Furthermore, the nanotubes can clearly serve both as the transducer and as the platform where the biological recognition event occurs. These prospects make CNTs one of the most promising materials for advanced biosensors.

Electronic detection of biological species is very attractive because it offers a fast and direct, label-free detection, while sampling data in real time. Additionally, it does not require preparation steps and multiple reagents, making the use of these sensors quite simple [152–154].

6.7 Experimental

6.7.1 Material Synthesis of Different Types of Wastes

This section describes various syntheses of materials for wastewater treatment at the nanoscale level by many authors, which are given point-by-point below.

- The synthesis of metal nanoparticles for the reduction of metal salts using kinetic parameters such as diffusion distance, nature of solvent, slow-acting reducing agent and

controlling surface reactivity and their mechanism has been studied by Pradeep and Anshup [155]. They also investigated different sized gold nanoparticles, and the surface plasmon resonance band for citrate-reduced silver nanoparticles appears at 420 nm with broad features pointing to high polydispersity. This method enables the hindered diffusion of growth species from the solution to the nuclei and consequent formation of monodisperse nanoparticles.

- Huwe and Froba [156] have studied the transition metal oxides manganese, iron, cobalt, nickel, copper and zinc synthesized inside the pore system of mesoporous carbon (CMK-3); using nitrogen physisorption and high temperature treatment under reduction conditions leads to a better structural order as was confirmed by using the techniques of powder X-ray diffraction (PXRD), Raman spectroscopy, and transmission electron microscopy (TEM). To improve the synthesis procedure and as references for the XAFS investigations, bulk metal oxides have been synthesized in the same way.
- Jovanovic *et al.* [157] suggested the selection of zeolite (Z), natural clay minerals, bentonite (B) and sepiolite (S), and natural metal oxide minerals, limonite (L) and pyrolusite (P), as the natural materials, while waste iron slag (WIS) and waste filter sand (WFS) were the waste materials tested within the scope of the investigations and analyzed by scanning electron microscopy (SEM); BET specific surface areas were determined by nitrogen adsorption technique.
- Kulbat *et al.* [158] investigated the removal of heavy metals (Zn, Cu, Pb, Cd, Cr, Ni, Ag) from sewage; the concentrations of heavy metals conceded without preliminary separation of total suspended solids. The volume (250cm³) of sewage samples evaporated to dryness and complemented with 0.1 mol/dm³ nitric acid to adequate volume. The samples of sludge were dried to constant weight and mineralized with aquaregia.
- Zak *et al.* [159] employed two-stage precipitation and coagulation for the reduction in heavy metals (Cd, Cu, Cr, Ni, Sn, Zn) with the help of hydrogen peroxide. It separated the precipitated and thickened solid pollutants from wastewater obtained from the most effective system (the reduction of

80.5–99.1%) to eliminate heavy metals which occurred in the pretreatment system.

- Kundra *et al.* [160] employed titanium as a working electrode, which is stable, energy efficient and can effectively treat a variety of effluents. This technique can also be engaged for other heavy metal ions, viz Cr, Cd, Hg. The efficiency of the electrode can be improved by using carbon aerogel on titanium electrode, but detailed experimentation and their mechanism and economics are not extensively incorporated.
- Onundi *et al.* [161] synthesized CNT on GAC to form a composite material, CNT-GAC. They studied the adsorption mechanism of the nanosized composite in the removal of copper, nickel and lead ions from aqueous solution, and observed that the filtrate, after the adsorption experiment showed clear solution, which had no visible CNT-GAC remaining in the solution. This indicates that the macro-sized composite CNT-GAC retained the CNT on the GAC surface after adsorption, reducing membrane fouling; the separation problems were solved by using thermal chemical vapor deposition (CVD) technique.
- Singanan [162] determined the effectiveness of activated biocarbon derived from a traditional medicinal plant, *Tridaxprocumbens* (Asteraceae), when used to remove cadmium and lead from synthetic wastewater, and investigated the mechanisms of adsorption onto activated biocarbon by performing a batch experimental process.
- Benavente [163] studied the removal of Cu, Zn, Hg and Pb from aqueous solution using chitosan from waste shrimp shells and its application in the removal of heavy metals from gold mining effluents. The experimental data were tested with the Langmuir, Freundlich, Redlich-Peterson and SIPS isotherm equations, and simplified kinetic models were applied to determine the rate-controlling mechanisms for the adsorption process and desorption studies, which were carried out using different eluent solutions.
- Kosińska and Miśkiewicz [164] used biological sulfate reduction by *Desulfovibrio desulfuricans* source of HS^- and/or S^{2-} anions, which react with heavy metal cations and precipitate as sulfides decontamination of the wastewater from leather tanning, electroplating, organic dye production and

non-ferrous metallurgy, which were examined by flame atomic absorption spectrometer.

- Chorom *et al.* [165] have studied the Ni concentrations in wastewater, drainage water and industrial wastewater on the basis of phyto-remediation processes, using atomic absorption.
- Chowdhury and Yanful [166] have investigated arsenic and chromium removal from different water samples using commercially available nanosized magnetite, characterized as a mixture of magnetite and maghemite, in a batch experiments process. Redox potential and pH data helped to infer possible dominating species and oxidation states of arsenic and chromium in solution. Maximum uptake efficiencies of 99% and 96% were found at pH 2 and adsorbed amounts of As(V) species were 3.71 and 7.2 mg/g for initial arsenic (V) concentrations of 1.5 and 3 mg/L, respectively.
- The removal of Cu(II) onto carbonaceous materials sorbents such as activated carbon, CNT_s and carbon-encapsulated magnetic nanoparticles, have been studied by Bystrzejewski and Pyrzyńska [167]. The approaching equilibrium factors point out that CEMNPs and CNTs adsorb the Cu(II) ions faster than activated carbon at base pH, whilst at acidic pH the sorption kinetics display a completely reverse trend. The sorption kinetics in the case of CEMNPs and CNTs were limited by film diffusion, whilst the most typical was intra-particle diffusion for activated carbon.

6.7.1.1 Waste Materials for Environment or Pollutants

Pollution is any type of substance which exhibits a harmful effect on the flora and fauna, and is a risk for every organism. These substances/materials are present in our environment in the form of wastes. Some wastes are of use to us and are employed in waste reduction and recycling processes. The whole world is facing problems with contaminated water and the current challenge is to purify water. The development of novel nanomaterials (e.g., metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers at nanoscale) enters at the waste stage. They are cost effective, environmentally friendly and employed in various processes for treatment of surface water, groundwater and industrial wastewater contaminated by toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses [168].

6.8 Nanomaterials

There are several classes of nanomaterials such as metals and metal oxides, clays, polymers, chemicals, nanotubes and dendrimers, which can provide a higher ratio of surface area of particle size at the nanoscale level, and these materials are characterized by different morphology and structure. There is a large range of applications of nanomaterials in different areas such as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires and electronics, which make them advantageous for commercial or medical applications used for purposes of diagnosis, imaging and drug deliver. Nanocoatings and nanocomposite materials show great performance in UV rays protection, while engineered nanoparticles (EN) and nanostructures are used as catalyst for reactions in liquids and gases [169].

6.8.1 Importance of Nanomaterials and Their Characterizations

Nanomaterials at nanoscale are highly attractive and have great potential benefits for the reduction or prevention of pollutants from environmental sources, and impart increased affinity, capacity, and selectivity for pollutants. As we know, nanoscale materials have various shapes and structures such as spheres, needles, tubes and plates with amorphous pore sizes in nanometer range. Characterized on the basis of their size and shape, nanomaterials can directly affect the kinetics of deposition and absorption in the body. The nanomaterials' characteristic properties are potentially significant for their size, shape, agglomeration, surface area, surface chemistry, surface charge (providing supports for cells in more numbers) and porosity (isothermal gas adsorption) [170].

6.8.2 Importance of Inexpensive Nanomaterial in Wastewater Treatment

The purification of wastewater and maintenance of its quality is a current crucial issue because hazardous materials are present in larger amounts, which are not suitable for the health and environment. Generally, wastewater is highly contaminated (over 90–95%) and directly presents a high amount of micro and pathogenic organism [171].

All impurities can be removed with the use of various methods such as filtration, microfiltration, nanoadsorbents, carbonaceous materials, etc.

The extensive and advanced approach can overcome some inherent limitations.

Nanoscience technology is the most significant technology of the 21st century in science and engineering, and makes functional nanostructured materials and devices on the order of nanometer scale. In scientific terms, “nano” means 10^{-9} , where 1 nanometer is equivalent to one billionth of a meter. In other words, nanotechnologies are the body of theories and techniques that allow the production and manipulation of minute objects that measure a little as one billionth of a meter (a nanometer). The term nanotechnology includes many different fields such as engineering, chemistry, physics, biology, electronics, medicine, etc. Typically, nano-sized materials refer to the production of a “collection of distinguishable units,” each made up of a limited number of atoms (although this number would be fairly large). These units have a specific shape and have at least one of their dimensions ranging over the order of a few nanometers. In contrast to bulk materials, the nanosized materials have a distinctive size and shape, surface chemistry and topology. One can think of various types of nanosized materials, and these include nanodots, nanoparticles, nanotubes, nanowires, nanorods, and nanoribbons, nanofibers, nanopores, etc. [172]. The research activity in the area of nanomaterials thus really started gaining momentum, and soon there was an explosion of research interest in this field. The inventions of newer and newer types of nanomaterials, their properties and concepts of exploring their applications have now become a key factor of “materials technologies.” In fact, the worldwide scientific community is considered to be in its most creative, penetrating, self-correcting and divergent period of the last century. These nanosized configurations include nanoparticles, nanodots, nanowires, nanoribbons, and so on. Recently, nanomaterials have been used in various types of biological applications such as sensors, cancer treatment, drug delivery, nanomedicines, etc. [173].

Over the larger application areas of nanotechnology, the purification of water is a current priority due to public health concern and to provide clean water. Wastewater can be treated with nanotechnology to provide high-quality purified water.

6.8.3 Wastes for Wastewater Treatment

There are so many wastes which are present in the environment that greatly affect it such as agricultural waste, animal by-products, biodegradable waste, biomedical waste, chemical waste, domestic waste, electronic waste, gaseous waste, hazardous waste, heat waste, household waste, human

waste, sewage sludge, industrial waste, nuclear waste, recyclable waste, residual waste, hazardous waste, etc. [174].

6.8.4 Technology Used for Wastewater Treatment

6.8.4.1 Reverse Osmosis

Reverse osmosis is a type of membrane used for water purification. The principal of reverse osmosis is based on the separation of solvent from solution; by using a semi-permeable membrane, pure water can flow in either direction without restraint, but the route of salt or other dissolved impurities is reserved. Reverse osmosis is capable of eliminating calcium, magnesium, sodium ion, chloride ion, copper ion, as well as bacteria, and a vast majority of the industrial organic chemicals that are not ionized; and strong oxidizing agents such as chlorine and ozone will immediately wipe out the standard, polyamide type from RO membranes. Water containing these substances must be pretreated to remove them. Certain cationic polymers that are used in water treatment and wastewater treatment will also adhere to the reverse osmosis membranes, thereby reducing productivity [175, 176].

6.8.4.2 Nanofiltration

The nanofiltration (NF) process is similar to that of reverse osmosis (RO). The small difference between the two is that the reverse osmosis removal of monovalent ions is at 98–99% level at 200 psi, but nanofiltration membranes removal of monovalent ions varies between 50–90% depending on the material. It is an eco-friendly way to treat all kinds of water including ground, surface, and wastewater, or is used as a pretreatment for desalination. For this reason, NF membranes have a talent for removing turbidity, microorganisms and resistance, with a little of the dissolved salts [177, 178].

6.8.4.3 Ultrafiltration

Ultrafiltration (UF) membranes are characterized by high-molecular-weight substances such as emulsified oils, metal hydroxide dispersed materials, suspended solids, colloidal materials, and organic and inorganic polymeric molecules. The materials mostly used in UF are polymeric polysulfone (PS), polyethersulfone (PES), polypropylene (PP), or polyvinylidene fluoride (PVDF), and naturally hydrophobic and other molecular weight materials from water. The ultra membrane is potentially applicable

in many areas such as high water flux, high water purity, membrane fouling, and high mechanical, chemical and thermal stability [179].

6.8.4.4 Microfiltration

Microfiltration is a process which permeates micrometer-sized particles present in water. Microfiltration separates larger-sized particles such as fixed suspended solids and microorganisms. The membranes exhibit high porosity and have distinct pores. The separation is based on size of the particles. Microfiltration membranes are usually made up of ceramics, teflon, polypropylene, or other plastics. Microfiltration shows the best performance in fermentation, biomass clarification and anaerobic process with a cross-flow microfiltration (CFMF) unit. It can reduce membrane fouling and works at lower pressure, >100 psig, than nanofiltration and reverse osmosis. The wastewater is processed via a microfiltration system designed to separate the precipitates from the water. It has various applications such as sterilization of beverages and pharmaceuticals, elucidation of fruit juices, wines and beer, separation of bacteria from water, effluent treatment, and oil and water separation [180, 181].

6.9 Summary and Future Directions

In summary, nanotechnology has an enormous role in wastewater treatment. It is the main research thrust of the present era and the future. With the use of this technology one can fabricate novel devices for the filtration of pure quality water. In the filtration process, nanorange particles, which have high surface, enhanced porosity, and extraordinary reactivity, can give pure and recycled water. Several techniques have been adopted to purify wastewater, such as reverse osmosis, nanofiltration, ultrafiltration, microfiltration, etc. The aim of the present work has been to summarize and show concise information related to wastewater treatment with current technologies.

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Carbon Nanotubes in the Removal of Heavy Metal Ions from Aqueous Solution

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Abstract

Carbon nanotubes possess excellent electrical and mechanical properties. These excellent properties make CNTs promising materials for many applications. Because of their large surface areas and the ability to establish π - π electrostatic interactions, CNTs have become a new type of adsorbent due to their outstanding ability to remove various inorganic and organic pollutants from water. Moreover, after acid functionalization, the surface functional groups and hydrophobic surfaces of CNTs show strong interactions with both heavy metal ions and organic compounds. Studies have shown that CNTs possess great potential for removing heavy metal ions such as Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , etc. The adsorption of heavy metal ions from solution on CNTs has been proven mainly due to the surface functional groups on CNTs, and it is also strongly dependent on the pH of the solution. This chapter focuses on the adsorption capacity of carbon nanotubes. Factors that affect the adsorption process of Cd(II) , Cr(II) , Cu(II) , Ni(II) , Pb(II) and Zn(II) are reviewed.

Keywords: Carbon nanotubes, functionalization of carbon nanotubes, acid functional groups, removal of heavy metal ions, organic pollutants, competitive adsorption, polymer composites

7.1 Introduction

Heavy metals can be introduced into natural water systems by wastewater effluent from industries such as smelting, metal plating, phosphate fertilizer, mining, galvanizing, paints, pigments, cosmetics, alloy manufacturing, etc.

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However, unlike organic contaminants, heavy metals are not biodegradable and they can accumulate in living organisms for a long time, and most heavy metal ions are either toxic or carcinogenic. Metals that can be categorized under heavy metals are those with a higher density than 5 g/ml [1], but most importantly include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), vanadium (V) and zinc (Zn). Nevertheless, not all heavy metals are toxic, and some such as zinc, nickel and copper are essential for human health as trace elements; however, an excess amount can cause eminent health problems [2, 3]. Nowadays heavy metals pollution has drawn much attention and has become one of the most serious environmental problems.

There are many methods which have been used to remove heavy metal ions from natural water systems and industrial effluents. Examples of these methods include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. However, physical and chemical adsorption methods have been recognized as an effective and economically viable system for heavy metal wastewater treatment since the adsorption process offers flexibility in design and operation. Moreover, in many cases the adsorption process produces a high quality effluent treatment; and in most cases it is a reversible process and adsorbent can be regenerated by a suitable desorption process.

In this regard, activated carbon adsorbents have been most commonly used for the removal of heavy metal contaminants from either industrial effluents or natural water systems. They have high surface area because they contain large micropore and mesopore volumes, which are very important during the adsorption and desorption processes. In a recent study the use of activated carbon for removing heavy metals has been reported [4, 5]; also, activated carbon composite with additives such as alginate [6], tannic acid [7], and surfactants [8] have been studied for removal of heavy metals. Although activated carbon is the most used adsorbent, cost wise it is a relatively expensive adsorbent.

After the discovery of carbon nanotubes (CNTs) by Iijima [9], they have been widely studied for their excellent electrical and mechanical properties [10]. These excellent properties make CNTs promising materials for many applications, such as hydrogen storage [11], catalyst supports [12], chemical sensors [13], etc. Recently, large number of studies proved that CNTs possess great potential as relatively new adsorbents in removing heavy metal ions such as Cd^{2+} [14], Cu^{2+} [15], Ni^{2+} [16], Pb^{2+} [17], Zn^{2+} [18], etc. It has also been concluded that in most cases, the adsorption of heavy metal ions from solution on CNTs is mainly due to the surface functional groups on CNTs [18, 19], and is also strongly dependent on the pH of the solution.

However, one of the major drawbacks to the application of CNTs are their poor dispersion in solvents because of strong intermolecular van der Waals interactions between the tubes, which can lead to the formation of aggregates instead of dispersions, and the insolubility of CNTs in practically all solvents. Although the dispersion of CNTs in some solvents has been achieved by sonication, CNTs immediately precipitate when sonication is interrupted. On the other hand, it has been demonstrated that CNTs can interact either chemically or physically with different classes of compounds to form composites [20–28]. Therefore surface functionalization of CNTs is an important step towards the full utilization of the CNTs.

7.2 Synthesis of CNTs

There are two main methods or groups of synthesis of CNTs: sublimation of graphite with subsequent desublimation, and decomposition of carbon-containing compounds [29, 30]. The first group of processes is associated with high temperatures (up to 4000°C), which can be obtained in electric arcs [31–33], laser ablation [34–37], by focusing solar radiation [38, 39] or by resistive heating of graphite.

The second method is pyrolysis of carbon sources over inorganic catalyst of either mono- or bi-metals. Carbon source could be either gases such as carbon rich organic compounds (chemical vapor deposition, CVD process), solids (e.g., pyrolysis of polymers), or organic solutions (such as toluene) [40]. The advantage of the CVD method is that it can produce CNTs in large quantities and can be achieved at temperatures of 500 to 1300°C. Depending on the chemical composition of the carbon source, the pyrolysis method can be subdivided into disproportionation of CO [34, 41], the pyrolysis of hydrocarbons (CH_4 , C_2H_2 , C_6H_6 , etc., including polymers) [28, 42, 43] and pyrolysis of heteroatomic $\text{CH}_x\text{A}_y\text{B}_z$ compounds (such as B, N, O, ...) [44–49], in-order to tune the electronic property of the CNTs by replacing the carbon atoms with heteroatoms in the graphitic structure of the CNTs.

7.3 Functionalization of Carbon Nanotubes

The reactivity of CNTs towards the functional groups largely depends on the curvature-induced pyramidalization of p-orbitals of carbon atoms, which induces misalignment of the p-orbitals of carbon atoms in SWNTs [20–22]. As a result, the sidewall of a SWNT should be more reactive

than a flat graphene sheet; a SWNT of smaller diameter having larger p-orbital pyramidalization and misalignment angles suffers more severe curvature-induced weakening of p-conjugation and hence, is more reactive. However, due to the different bending patterns, nanotubes have less curvature compared with fullerenes with comparable diameters [50]; accordingly nanotubes are generally less reactive than fullerenes, and harsher experimental conditions are required to functionalize carbon nanotubes.

By utilization of the misalignment of the p-orbitals of carbon atoms that is induced by the curvature of the sidewall of the CNTs, CNTs can undergo surface chemical modifications that make them more dispersed in a solvent for integration into inorganic, organic, and biological systems [51]. The main approaches for surface modification falls generally into two categories: (1) the covalent attachment of chemical functional groups through reactions with the π -conjugated skeleton of CNT; (2) the non-covalent surface adsorption or wrapping of various functional molecules around the CNTs.

7.3.1 Attaching Acid Functional Groups

Acid functionalization of CNTs can be achieved by either heating or refluxing in a concentrated HNO_3 or mixtures of H_2SO_4 with HNO_3 , H_2O_2 , or KMnO_4 , depending on the degree of functionalization. This method of functionalization has been widely used for attaching acidic functional groups to CNTs [52, 53]. The main acidic functionalities include the $-\text{COOH}$, $-\text{C}=\text{O}$, and $-\text{OH}$ groups [54]. These functional groups exist on the sidewall of the CNTs in roughly estimated 4:2:1 proportions [55]. Similarly, acid functional groups can be attached to the sidewall of CNTs by the oxidative method via ozonolysis of the CNTs [56]. Acid-functionalized CNTs can be dispersed in water by sonication [57].

7.3.2 Fluorination

The sidewall fluorination of CNTs has been achieved using elemental fluorine in the range between room temperature and 600°C [58–65]. Nakajima *et al.* [41] studied the fluorination of CNTs under a wide range of temperatures and found that covalently fluorinated CNTs could be made between 250°C and 400°C . On other hand, Mickelson *et al.* [60] indicated that the best results for fluorination reactions on the sidewall of CNTs was between 150 and 400°C , because at higher temperatures the graphitic network decomposes.

7.3.3 Hydrogenation

Hydrogenation of CNTs has been reported by Pekker *et al.* [46] by reducing pristine CNTs with Li metal and methanol dissolved in liquid ammonia (Birch reduction). The hydrogenated material was found to be stable up to 400°C. Moreover, CNTs have been functionalized with atomic hydrogen using a glow discharge [67–69] or by proton bombardment [70].

7.3.4 Cycloadditions

The Haddon group was the first to apply carbene [2+1] cycloadditions to pristine CNTs [71–75]. During the reaction, carbene was generated *in situ* using a chloroform/sodium hydroxide mixture or a phenyl(bromodichloromethyl) mercury reagent. The [2+1] cycloadditions reactions then took place on the sidewall of the CNTs.

Hirsch *et al.* [76–78] performed studies that showed that the nucleophilic addition of carbenes to CNTs preferably produced zwitterionic 1:1 adducts rather than cyclopropane systems. Another possible [2+1] cycloaddition reaction was the thermal functionalization of CNTs by nitrenes. During this reaction, the first step was initiated by thermal decomposition of an azide, which produces alkoxy carbonyl nitrene via nitrogen elimination, followed by the [2+1] cycloaddition of the nitrene to the sidewalls of the CNTs, affording alkoxy carbonyl aziridino-CNT [76–81]57. Another example involved the irradiation of a photoactive azidothymidine in the presence of CNTs, which resulted in the formation of very reactive nitrene groups in the proximity of the carbon lattice. In a cycloaddition reaction, these nitrene groups coupled to the CNTs and formed aziridine adducts.

The amino-functionalized CNTs were particularly suitable for the covalent immobilization of molecules or for the formation of complexes based on positive/negative charge interaction [82–84]. Various biomolecules have also been attached onto amino-CNTs, such as amino acids, peptides, and nucleic acids [82–91]. Alvaro *et al.* [67] have studied modified CNTs obtained by the thermal 1, 3-dipolar cycloaddition of nitrile imines. Photochemical studies showed that, by photoexcitation of the modified tubes, electron transfer took place from the substituents to the graphitic walls [92, 93].

7.3.5 Amidation/Esterification Reactions

A carboxylation reaction is an oxidation reaction with an oxidizing acid, or a combination of acids such as a mixture of concentrated nitric and sulfuric acids [94–96]. This method is widely used for the purification of raw

CNTs [97–99]. This is achieved by inducing the opening of the tube caps as well as the formation of holes in the sidewalls. Liu *et al.* [100] demonstrated that carboxylate groups generated by the acid-cut nanotubes could be derivatized chemically by thiolalkylamines through an amidation reaction. In addition, Chen *et al.* [73] were the first to treat oxidized nanotubes with long-chain alkylamines via acylation, with the result that the functionalized material was soluble in organic solvents. Direct thermal mixing of oxidized CNTs and alkylamines to produce functionalized material through the formation of zwitterions has also been reported [101].

Esterification reactions can produce soluble functionalized nanotubes [100]. Condensation reaction of a carboxylate and other oxygenated functional groups has produced perfect rings at the ends of the oxidized SWNT [102]. Using similar methodology, Sun and coworkers [103–110] were able to attach lipophilic and hydrophilic dendrimers to oxidized CNTs via mediation or esterification reactions. More recently, Shi *et al.* [111] have studied multifunctional dendrimer-modified CNTs for *in vitro* cancer cell targeting.

7.3.6 Grafting of Polymers

The covalent surface reaction of CNTs with polymers is an important reaction since long polymer chains could attach to CNTs this helps to dissolve the CNTs in a wide range of solvents. Generally, there are two main routes for the covalent attachment of polymers to the surface of functionalized CNTs, namely “grafting to” and “grafting from” methods. The “grafted to” method is the synthesis of a polymer with a specific molecular weight, followed by end group transformation. Subsequently, this polymer chain will attach to the graphitic surface of either pristine or functionalized CNTs. On the other hand the “grafting from” method is based on covalent immobilization of polymer precursors on the surface of functionalized CNTs and subsequent propagation of the polymer in the presence of monomeric species.

Chemical reaction of CNTs and poly(methyl methacrylate) (PMMA) using the ultrasonication method of “grafting to” was reported by Koshio *et al.* [112, 113]. Similarly, Wu *et al.* [114] studied the nucleophilic reaction of polymeric carbanions with CNTs. In their studies organometallic reagents, such as sodium hydride or *n*-butyllithium were mixed with poly(vinylcarbazole) or poly-(butadiene), and the resulting polymeric anions were grafted to the surface of functionalized CNTs. An alternative approach was reported by Blau *et al.* [115, 116] which used CNTs functionalized with *n*-butyllithium and subsequently coupled with halogenated

polymers Qin *et al.* [117] also reported a grafting of functionalized polystyrene to CNT via a cycloaddition reaction.

Jia *et al.* [118] have reported the “grafting from” of CNT-polymer composites by an *in situ* radical polymerization process. They further claimed that the CNTs surface could play the role of grafting agent by opening the double bonds of the CNTs surface with initiator molecules. Qin *et al.* [119] also studied the grafting of polystyrenesulfonate (PSS) by *in situ* radical polymerization. In their study, they reported that due to the negative charges of the polymer chain the resulting material dispersed in aqueous media. In a subsequent study [120] they have reported polyvinyl pyridine (PVP)-grafted polymers from SWNTs by *in situ* polymerization. Carbon nanotubes grafted with poly(methyl methacrylate) have been prepared by emulsion polymerization of the monomer in the presence of a radical initiator [121] or a crosslinking agent [122]. Petrov *et al.* [123] have studied the modification of CNTs with polyacrylonitrile chains by applying electrochemical polymerization of the monomer. More recently, Che *et al.* [124] reported the “grafting-from” approach to the synthesis of dendritic poly(amidoamine) (PAMAM) on SWNTs, and they demonstrated the good dispersion and high reinforcement efficiency of these functionalized CNTs in an epoxy matrix. Finally, Yan *et al.* [125] recently reported a novel approach to graft polyamide 6 (PA6) onto the surface of CNTs. In their report the CNTs were covalently functionalized with copoly (styrene-maleic anhydride) (SMA) via free radical polymerization, then followed by a ring-opening polymerization of ϵ -caprolactam to graft PA6 onto the surface of functionalized CNTs. They claimed that the resulting product had good dispensability in many organic solvents such as formic acid and melted ϵ -caprolactam.

7.3.7 Other Reactions

Radical addition is another form of covalent sidewall functionalization of CNTs. This type of reaction has been intensively studied [76–78, 126–130]. The formation of aryl radicals is triggered by an electron transfer between CNTs and the aryl diazonium salts in a self-catalyzed reaction [131–143]. A similar reaction was later described, utilizing water-soluble diazonium salts, which have been shown to react selectively with metallic CNTs [134–137].

Nucleophilic addition to CNTs has been studied by Basiuk *et al.* [144]. Their approach involved the use of a solvent-free amination of the closed caps of CNTs with octadecylamine. It has been suggested that the addition took place only on the five-membered rings of the graphitic network of

the nanotubes, and that the benzene rings were inert to direct amination. Lastly, to covalently modify CNTs with both alkyl and carboxylic groups, Chen *et al.* [145] treated pristine material with *sec*-BuLi and subsequently with carbon dioxide.

7.4 Adsorption of Heavy Metal Ions on Carbon Nanotubes

The mechanisms by which the metal ions are adsorbed onto CNTs are not fully understood. However, recent studies [18, 19, 146, 147] have suggested that the adsorption mechanism is a combination of electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and, more importantly, surface functional groups of CNTs. There are several factors that affect the sorption of heavy metal ion on the surface of CNTs such as surface charge of CNTs, the interest of heavy metal ions, speciation of heavy metal ions in solution and finally the experimental conditions (such as ionic strength of the solution, pH of the solution, competition among ions in the solution, amount of CNTs, sorbent during the adsorption process to remove the analytes from a given solution quantitatively, contact time, initial metal ion concentration, and temperature during the sorption process, and whether the process is endothermic or exothermic).

In a number of studies [148, 149] it has been reported that the metal ion adsorption capacity of CNTs increases when the CNTs functionalized with acid functional groups, which leads to a rise in the amount of surface total acidity on the surface site of CNTs. Moreover, acid functionalization causes the opening up of tube ends [150] and generation of defects on the sidewall of nanotubes [151]; as a result more sp³ bonds are introduced to the surface structure of CNTs.

Although acid-functionalized CNTs have more surface total basicities than the pristine CNTs, surface charge of the CNTs depends on the pH of the surrounding electrolyte. The pH value at which the net surface charge is zero is called point of zero charge (PZC) isoelectric point [152]. For instance, the pH of PZC of unfunctionalized (as produced) CNTs is in the range of pH 4–6 [153, 154]. On the other hand, the pH of PZC of carboxylic-functionalized CNTs is expected to be more negative due to the presence of acid functional groups such as –COOH and –OH. These carboxylic functional groups make the pH of PZC of CNTs negative in solution and as a result the electrostatic attraction between the heavy metal ions and the negative surfaces of CNTs increases, and this boosts the

sorption of heavy metal ions on CNTs compared with that of as-produced CNTs [155, 153, 156]. During the adsorption process, when the pH of the solution is lower than the pH of PZC, the surface charge of CNTs becomes more positive and divalent heavy metal ion species in solution predominantly exist as M^{2+} ; this facilitates the adsorption of divalent metal ions and a competition takes place on the surface sites (CNT-OH) that will only be between H^+ and M^{2+} [157]. However, when the pH of the solution is higher than the pH of PZC, the surface charge of functionalized CNTs will be negative and the divalent metal ions predominantly exist in $M(OH)_n^{2-n}$ species [158–160]. Therefore, the removal of divalent metal ions is possibly the adsorption process accompanied by the precipitation reaction at high pH values.

7.4.1 Adsorption of Cd(II)

The adsorption capacity of pristine CNTs and HNO_3 -oxidized CNTs for the removal of Cd^{2+} from aqueous solutions at different pH values was investigated by Gao *et al.* [161]. The carboxylic-functionalized CNTs showed a higher adsorption capacity than the pristine CNTs. Furthermore, Xu *et al.* [160] and Yang *et al.* [159] have reported similar results in their study on carboxylic-functionalized CNTs as an adsorbent for the uptake of Pb^{2+} and Ni^{2+} , respectively. Cadmium(II) adsorption capacity of carbon nanotubes (CNTs) has been studied by functionalizing the CNTs using three different oxidizing agents, H_2O_2 , $KMnO_4$ and HNO_3 , and their adsorption capacities were compared with pristine CNTs [162]. According to the results, adsorption capacity of the pristine CNTs was 1.1 mg g^{-1} and for the H_2O_2 , HNO_3 and $KMnO_4$ oxidized CNTs was 2.6, 5.1 and 11.0 mg g^{-1} , respectively. Interestingly, the adsorption is strongly pH dependent and adsorption capacities were higher for HNO_3 and $KMnO_4$ oxidized CNTs than that of the pristine CNTs.

Vuković *et al.* [163] studied the sorption of Cd^{2+} ions onto a variety of CNT-based adsorbents, pristine CNTs, carboxylic-functionalized CNTs and ethylenediamine-functionalized CNTs. In their study they investigated the influences of the pH of the solution, contact time, initial metal ion concentration and temperature. The adsorption of Cd^{2+} ions by carboxylic-functionalized CNTs and ethylenediamine-functionalized CNTs was strongly influenced by the pH of the solution. According to the results, ethylenediamine-functionalized CNTs show the best sorption capacities when the pH is between 8–9, and acid-functionalized CNTs performed better when the pH was in the range of 6–10. Interestingly, there was a noticeable increase of Cd^{2+} sorption when the pH was in the range of

4–6. The sorption of Cd^{2+} on pristine CNTs, however, was observed to be relatively not dependent on pH variation.

The sorption of Cd^{2+} ions on amino-functionalized multiwalled carbon nanotubes (CNTs), 1, 6-hexanediamine, diethylenetriamine, triethylenetetramine and 1, 4-phenylenediamine has been studied by Vuković *et al.* [163]. A direct coupling of ethylenediamine (EDA) with carboxylic groups was used to introduce amino groups via amide formation using O-(7-azabenzotriazol-1-yl)-N,N,N',-tetramethyluronium hexafluoro phosphate (N-HATU), and a study was done on the effect of pH, contact time, temperature and initial metal ion concentration on the sorption of Cd^{2+} ions onto pristine CNTs (raw-CNT), carboxylic-functionalized CNTs (o-CNT) and ethylenediamine-functionalized CNTs (e-CNT). The results showed that the adsorption of Cd^{2+} ions by o-CNT and e-CNT was strongly dependent on the pH of the solution and, moreover, the time-dependent sorption of Cd^{2+} onto raw-CNT, o-CNT and e-CNT was described by a pseudo-second-order kinetic model. Their equilibrium experimental data also agreed well with the Langmuir isotherm model. The thermodynamic parameters were deduced for the adsorption of Cd^{2+} ions on raw-CNT, o-CNT and e-CNT, and the results showed that the adsorption process was spontaneous and endothermic.

7.4.2 Adsorption of Cr(VI)

A comparative study by Pillay *et al.* [154] on the adsorption of Cr(VI) low level concentration (parts per billion) on functionalized CNTs, unfunctionalized CNTs and activated carbon has revealed that the unfunctionalized CNTs showed a good removal capability when compared with the functionalized CNTs, but both the functionalized CNTs and unfunctionalized CNTs showed a better adsorption capability than activated carbon. However, Xu *et al.* [164] indicated that functionalized CNTs with abundant oxygen-containing functional groups have a significant potential for the removal of chromate from aqueous solution. In their study, they used carboxylic-functionalized and unfunctionalized CNTs to study the adsorption capacity toward anionic chromate CrO_4^{2-} , which is a typical toxic heavy metal ion in wastewater. Interestingly, the oxygen-containing functional groups on CNTs showed excellent absorption ability compared with nonfunctionalized CNTs. This is due to the interaction between oxygen-containing functional groups on CNTs with CrO_4^{2-} . The removal of chromium ions from aqueous solution using a combination of iron oxide and carbon nanotubes as an adsorbent has been studied by Gupta *et al.* [165]. Combining iron oxide with carbon nanotubes produces a magnetic

adsorbent. The result shows that the adsorption of Cr(III) on the composites in the batch mode is strongly dependent on contact time, agitation speed and pH, while in the fixed-bed mode it depends on flow rate and the bed thickness.

7.4.3 Adsorption of Cu(II)

The removal of Cu(II) ions from aqueous solution has been studied using chitosan/poly (vinyl) alcohol membranes modified with amino-functionalized CNTs [166] and pristine and acid-functionalized carbon nanotubes (CNTs) [167]. Yao *et al.* [168] reported in a study of the adsorption equilibrium of Cu(II) from aqueous solution, that the carboxylic functional groups on CNTs play an important role in the adsorption of Cu(II). Furthermore, they concluded that the adsorption of Cu(II) is due to the fact that carboxylic functional groups on CNTs provide not only a more hydrophilic surface structure, but also increase the ion-exchange capacity of CNTs due to the presence of many oxygen-containing functional groups on the surface of the CNTs, which leads to a significant increase in the absorption of Cu(II) onto CNTs surface. Sheng *et al.* [169] investigated the effect of the presence of humic acid (HA) and fulvic acid (FA) on the adsorption of Cu(II) on multiwalled carbon nanotubes (CNTs). According to their results, the adsorption of Cu(II) ion on CNTs is strongly dependent on the pH of the aqueous solution and, interestingly, it is independent of the ionic strength. Furthermore, they reported that the presence of the HA/FA has a positive effect on the adsorption of Cu(II) and a negative effect was observed when the pH > 7.5. However, with either the absence or the presence of HA/FA in the solution, the adsorption isotherms were better described by the Freundlich model than by the Langmuir model.

7.4.4 Adsorption of Ni(II)

Yang *et al.* [170] have studied the adsorption of Ni(II) on oxidized multiwalled carbon nanotubes (CNTs). In their study they investigated the influence of contact time, pH of the solution and, more importantly, the effect of the presence of foreign ions, polyacrylic acid (PAA), in the adsorption process. The adsorption of Ni(II) on oxidized CNTs has been found to be most efficient when the pH is between 2 and 9, ~99% is adsorbed, and the adsorption was found to increase with an increase of the pH, and reached equilibrium in 2 hours time. The presence of PAA during the adsorption revealed interesting phenomena; there was a positive effect on Ni(II) adsorption when pH < 8, however, when the pH > 8 a negative effect

was observed. Furthermore, the adsorption of Ni(II) was also affected by the addition sequences of PAA/Ni(II).

Carbon nanotubes (CNTs)/iron oxide magnetic composites have been used for the adsorptions of Ni(II) and Sr(II) from aqueous solution as a function of pH and ionic strength [171]. The adsorption process of the two metal ions on the magnetic composites is strongly dependent on the pH and ionic strength of the aqueous solution. The comparative study has indicated that the adsorption capacity of the magnetic composites is found to be much higher than that of MWCNTs and iron oxides.

Kandah *et al.* [172] synthesized multiwalled carbon nanotubes (CNTs) by CVD, and the CNTs were oxidized with concentrated nitric acid, and used them as an adsorbent for the adsorption of Ni(II). In their study they used two adsorbents: pristine and acid-functionalized CNTs. According to their findings, the adsorption capacity for nickel ions from aqueous solutions increased significantly onto the surface of the acid CNTs as compared to that on the pristine CNTs, and both Langmuir and Freundlich isotherm models were well fitted to the experimental data.

Triphenyl-phosphine-functionalized (Tpp-CNTs) and purified multiwalled carbon nanotubes have been used in the study of the adsorption of nickel ions from aqueous solutions [173]. In both cases, the adsorption capacity increased with an increase of the pH of the solution and the adsorption equilibrium for purifying MWCNTs and Tpp-MWCNTs was reached in 40 and 30 min, respectively. The experimental data of both adsorbents were well described with both Freundlich and Langmuir isotherms and also were well fitted to the pseudo-second-order model.

7.4.5 Adsorption of Pb(II)

Carbon nanotubes (CNTs) have shown exceptional adsorption capability and high adsorption efficiency for lead removal from water [174]. Wang *et al.* [175] have indicated that acid-modified CNTs have good adsorption capability for Pb(II) removal. It also was reported that the surface area of modified CNTs was slightly increased as compared to pristine CNTs. In a study by Yu *et al.* [176] on the adsorption of lead(II) from aqueous solution, O₂-plasma-oxidized multiwalled carbon nanotubes (po-CNTs) were used as an adsorbent. The plasma-assisted oxygenation process was intended to introduce oxygen functional groups on the surface of CNTs. As a result, the adsorption capacity of MWCNTs for Pb(II) increased and the removal of Pb(II) by po-CNTs was fast. Furthermore, their experimental data were well fitted to the Langmuir isotherm model and the adsorption kinetics well described by the pseudo-second-order model. The effect of pH on adsorption

was also investigated. More interestingly, a study on an X-ray photoelectron spectroscopy analysis has shown that the adsorption mechanism is mainly due to the chemical interaction between Pb(II) and the surface functional groups of po-CNTs. A study by Wang *et al.* [177] on the adsorption of Pb(II) by carboxylic-functionalized CNTs and unfunctionalized CNTs showed a chemical interaction between Pb(II), and they claimed that the oxygen-containing functional groups on the surfaces of CNTs played an important role in Pb(II) adsorption by forming complexes and accounted for about 75% of Pb(II) removal. However, the contribution of physical adsorption, which largely depends on the surface area, open-ended and defect sites, has only accounted for just over 24% of all the Pb(II) adsorption process. This study indicated that electrostatic attraction is another probable adsorption mechanism, but not the main one. MnO_2 -coated carbon nanotubes (MnO_2/CNTs) have also been used to remove Pb(II) from aqueous solution [178]. Interestingly, the adsorption of Pb(II) on MnO_2/CNTs decreases with the decrease of pH, and compared with pristine CNTs, the adsorption of Pb(II) on MnO_2/CNTs shows significant improvement.

7.4.6 Adsorption of Zn(II)

A comparative study between single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) on the adsorption of Zn(II) was conducted [179]. Both carbon nanotubes were purified by sodium hypochlorite solutions and used as sorbents to study the kinetics and equilibrium of Zn(II) sorption from aqueous solution. In this study, the adsorption of Zn(II) onto CNTs increased with a rise in temperature, and the thermodynamic analysis indicated that the sorption of Zn(II) onto CNTs is an endothermic and spontaneous process.

The effect of degree of oxygen functionalization of CNTs on the adsorption of Zn(II) and Cd(II) has been studied in detail by Cho *et al.* [180]. According to their results, surface oxygen-functionalized groups on CNTs generally enhance the sorption of both Zn(II) and Cd(II) from aqueous solution; however, preferentially the increasing surface oxidation has more of an effect on the sorption of Cd(II) than on the sorption of Zn(II).

7.5 Competitive Adsorption

It is important to understand the competitive adsorption nature of metal ions in aqueous solution and wastewater treatment because the metal ions usually exist together in industrial effluents and polluted water systems.

Salam *et al.* [181] have investigated the competition among four metal ions (Cu(II), Pb(II), Cd(II) and Zn(II)) in binding of the active sites on the surface of MWCNTs. In their study, they found that the binding order as Cu(II) > Zn(II) > Pb(II) > Cd(II). These results indicated that the preferential adsorption is mainly due to the size of the ions, Pb(II) > Cd(II) > Zn(II) > Cu(II) (1.33, 0.97 > 0.74 > 0.72, in Å° respectively), rather than the electronegativity (Pauling) Pb(II) > Cu(II) > Cd(II) > Zn(II) (2.33, 1.90, 1.69, and 1.65, respectively); Pb(II) and Cd(II) showed lower adsorption than Cu(II) and Zn(II); Cu(II) and Zn(II) ions have smaller ionic radius and this makes the ions easier to penetrate through the boundary layer and adsorb on the MWCNTs surface. Furthermore, a study by Gao *et al.* [182] have found a similar order on the adsorption of nickel, copper, zinc and cadmium from aqueous solutions on acid-functionalized carbon nanotubes oxidized for binary system; the order was Cu(II) > Ni(II) > Cd(II) > Zn(II), while for the ternary and quaternary, the order was Cu(II) > Cd(II) > Zn(II) > Ni(II). Kosa *et al.* [183] have also investigated the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions by MWCNTs functionalized with 8-hydroxyquinoline, and the preferential adsorption order was Cu(II) > Pb(II) $\approx$ Zn(II) > Cd(II). Salam *et al.* [184] studied the removal of copper, zinc, cadmium and nickel ions from aqueous solution by CNTs/chitosan nanocomposite. Their results indicated that most of the metal ions from solution were removed successfully. Furthermore, the competition among the target metal ions for the binding of the active sites of the nanocomposite was in the order of Cu(II) > Cd(II) $\approx$ Zn(II) > Ni(II). They further claimed that this competition order among the metal ions was responsible for the higher removal of the copper ions, and a similar phenomenon was reported in other studies [156, 185–188]. The adsorption of heavy metal ions on CNTs from aqueous solution at specific pH, $\sim$ 9, has been investigated by Stafiej *et al.* [153] and the affinity order of the metal ions towards the CNTs was Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II). However, in a study by Ruparelia *et al.* [189] the adsorption of metal ions on CNTs followed the order of Pb(II) > Ni(II) > Zn(II) > Cd(II). Rao *et al.* [146] have also reported the comparative adsorption of metal ions on CNTs which followed the order of Pb(II) > Ni(II) > Zn(II) > Cu(II) > Cd(II). The individual and competitive adsorption capacities of Pb(II), Cu(II) and Cd(II) metal ions were studied by Li *et al.* [190] using acid-functionalized CNTs as a function of solution pH, ionic strength and the amount of CNTs. The authors claimed that the affinity order of the three metal ions by acid-functionalized CNTs was found to be Pb(II) > Cu(II) > Cd(II), and the competitive adsorption capacities of the three metal ions increase with the increasing pH

and amount of CNTs, and decrease with the increasing ionic strength of the solution.

The removal of divalent heavy metal ions (Cu(II), Zn(II), Pb(II), Cd(II), Co(II)) from aqueous solutions using CNTs sheets have been studied by Tofighy *et al.* [191]. In their study, they functionalized CNT sheets with concentrated nitric acid at room temperature. The experimental result showed that the kinetics of adsorption did vary with initial concentration of heavy metal ions and the preference of adsorption onto the oxidized CNT sheets was in the order of Pb(II) > Cd(II) > Co(II) > Zn(II) > Cu(II). Interestingly, contrary to Salam *et al.* [181], a study by Gao *et al.* [156] revealed that the order of heavy metal ions removal from aqueous solutions by CNTs did not depend on the ionic radius of metal ions, but rather depended on the surface properties of CNTs.

Vuković *et al.* [192] used pristine, acid-functionalized, ethylenediamine, diethylenetriamine and triethylenetetramine-functionalized multi-walled carbon nanotubes as adsorbent in order to study the individual and competitive adsorption characteristics of Pb(II) and Cd(II) ions. In their study, they investigated the influence of acid functionalization, pH of the solution, contact time, initial metal ion concentration and temperature on the adsorption of either functionalized or pristine CNTs. Their results confirmed that the adsorption of Pb(II) and Cd(II) on CNTs strongly depends on the pH of the solution. Moreover, they found that the Pb(II) adsorption was well fitted to the pseudo-second-order kinetic model and adsorption by Langmuir isotherm. The competitive adsorption studies showed that the metal order affinity with respect to the diethylenetriamine- and ethylenediamine-functionalized CNTs was found to be Pb(II) > Cd(II), and the adsorption of Pb(II) on appropriate nanotubes was spontaneous and endothermic.

In a study by Pyrzyn *et al.* [193], the advantages and limitations of heavy metals (Co(II) and Cu(II)) sorption onto three different carbon materials; carbon-encapsulated magnetic nanoparticles, carbon nanotubes and activated carbon, were investigated. Moreover, they studied the effect of grain size, crystallinity and active surface area of the carbon sorbent. According to their results, carbon-encapsulated magnetic nanoparticles and carbon nanotubes showed higher sorption efficiency towards Co(II) and Cu(II) metal ions as compared to activated carbons. The differences in metal uptake yields resulted primarily from surface charge densities and overall degree of graphitization. The effect of the particle size was also the most pronounced in the case of adsorption at high ionic strengths. Studies by Rao *et al.* [146] and Vuković *et al.* [163], indicated that the metal ion adsorption capacity of oxidized CNTs does not directly correlate with their

specific surface area, pore specific volume and mean pore diameter, but rather strongly depends on their total surface acidity. Furthermore, they indicated that the higher total surface acidity, including carboxylic, lactones and phenols on the surface sites of CNTs increases the metal ion adsorption capacity of CNTs. As a result, they concluded that the adsorption of Cd(II) onto oxidized CNTs is a chemisorption process rather than a physisorption process. Moreover, acidic oxygen-containing CNTs behave as ion-exchange sites for the retention of Cd(II) cations, giving rise to the formation of metal ligand surface complexes.

7.6 Summary and Conclusion

Effluents from industries and mining activities are mainly responsible for heavy metal ion contamination of natural water systems. Unlike organic contaminants, heavy metals are not biodegradable and their half life in living organisms is long. Most of them are either toxic or carcinogenic. Therefore, nowadays heavy metal pollution has drawn much attention and has become one of the most serious environmental problems. Although there are many methods to remove heavy metal ions from natural water systems and industrial effluents, the physical and chemical adsorption methods have been recognized as effective and economically viable systems. In many cases, adsorption is a reversible process and adsorbent can be regenerated by a suitable desorption process. The use of carbon nanotubes as an adsorbent has become the most promising substitute for activated carbon and other adsorbents. This is mainly because the production cost of carbon nanotubes is less than that of activated carbon and the synthesis and the chemistry of CNTs is well developed.

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Application of Carbon Nanotube-Polymer Composites and Carbon Nanotube-Semiconductor Hybrids in Water Treatment

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Abstract

Nanotechnology has initiated a massive revolution in water research with carbon nanotubes (CNTs) and their derivatives proving to be potential tools for environmental clean-up. Carbon nanotubes possess a set of unique physical and chemical properties which has enabled their vast application in various fields including water treatment research. This chapter gives a comprehensive review of the recent trends in the use of CNT-polymer composites and CNT-based nanocomposites for the adsorption of textile dyes from aqueous medium. Moreover, the use of CNT modified semiconductor photocatalysts for the degradation of dyes is discussed in this chapter. Adsorption and photocatalytic degradation mechanisms are also discussed herein.

Keywords: Photocatalysts, carbon nanotubes, adsorption, semiconductor, nanotechnology

8.1 Introduction

Water pollution is a global environmental concern that presents serious challenges to various industrial sectors. This problem is hard felt in the developing countries where water treatment tools and methods are still in their infancy or are not easily accessible due to financial constraints.

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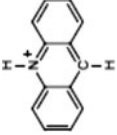
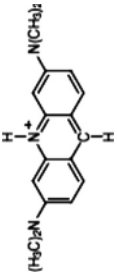
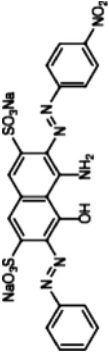
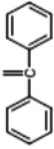
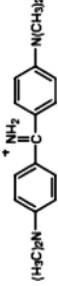
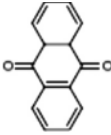
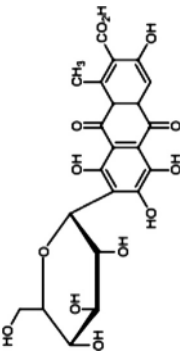
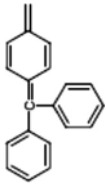
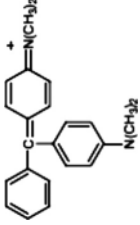
Consequently, a worldwide estimation of 1 billion people lack access to clean water supplies, while about 2.6 billion people have no access to basic sanitation. This exposes people to a lot of undesirable health effects. This problem is more pronounced in the less developed parts of Asia, Central and South America and Africa [1]. Industrialization is one of the most crucial indicators of development in a country but it comes with a massive challenge, that of pollution (water and air pollution). It is estimated that about 20% of industrial pollution emanates from textile dying and treatment processes [2].

Textile wastewater is ranked as one of the top pollutants among all industrial effluents in terms of the volume of effluent discharged and the chemical composition of the effluent. The increasing demand for cotton fabrics and brightly colored fabrics has led to the increasing complexity of the chemical composition of the textile effluent [3]. Large volumes of water are used at various processing stages such as desizing, scouring, bleaching, dyeing, printing and finishing. Consequently, an estimated 200–400 L of water are used per kilogram of finished product [4, 5]. It is estimated that about 7×10^5 tons of dyes are utilized worldwide on a yearly basis. However, inefficiencies in the dying processes result in more than 10% of the dye stuff being released directly into the wastewater [6]. Textile effluents contain loads of raw materials and reagents such as synthetic dyes, pigments, biocides, oils, heavy metals, salts, nutrients and other organic compounds. Therefore, high values of chemical oxygen demand (COD), temperature, color, changeable pH, suspended solids, and organic chlorine compounds are characteristic of textile effluent [5, 7, 8].

8.2 Classification of Dyes

There are several thousands of different commercially available dyes which may be classified according to color, source, chemical structure and their application during processing. However, classification according to chemical structure and application during processing is prominently used in the textile industry [9]. According to chemical structure, dyes can be categorized into several classes such as nitro dyes, azo dyes, anthraquinone dyes, phthalocyanine dyes, triphendioxazine dyes, xanthene dyes, aryl methane dyes, thiazine dyes, quinine-amine dyes, acridine dyes, etc. Notably, azo dyes are the most extensively exploited dyes constituting over 60% of all dye stuff utilized in the textile industry [10–14]. Table 8.1 gives a summary of the classification of dyes according to chemical structure. Moreover, the different types of azo dyes are presented in Table 8.2.

Table 8.1 Classification of dyes according to chemical structure [10].

Class	Structure	Representative dye	Structure
Acridine		Acridine O	
Azo		Amido B	
Diarylmethane		Auramine O	
Anthraquinone		Carmine	
Triarylmethane		Malachite green	

(continued)

Table 8.1 (cont.)

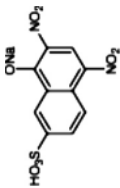
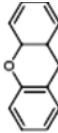
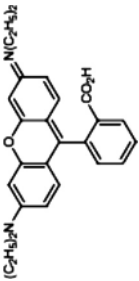
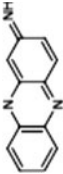
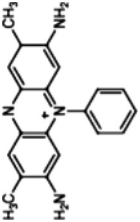
Class	Structure	Representative dye	Structure
Nitro		Naphthol	
Xanthene		Rhodamine B	
Quinone-imine		Safranin O	

Table 8.2 Classification of azo dyes [10].

Class	Representative dye	Structure
Monoazo	Orange II	
Diazo	Congo Red	
Triazo	Direct Blue 71	

Similarly, dyes can be categorized according to their application during processing into groups such as reactive dyes, disperse dyes, direct dyes, sulphur dyes, cationic (basic) dyes, acid dyes and solvent dyes. The classification of dyes according to their application during processing is summarized in Table 8.3.

8.2.1 Effects of Dyes in the Aquatic Medium

The textile industry utilizes large volumes of water as well as dye stuffs, resulting in large volumes of effluent being discharged. This effluent may find its way into the aquatic environment where it impacts negatively both on the aquatic flora and fauna. Notably, some of the textile processing stages have significant inefficiencies which result in considerable amounts of dye stuff being released into wastewater [15]. Consequently, color is the most obvious indication of dye pollution. This lowers the aesthetic merit of the water due to their bright and strong colors; dye color can be detected with the naked eye even at low parts per million levels [16, 17]. Furthermore, the presence of color in water adversely affects its transparency, which reduces light penetration through the water. Poor light penetration lowers the rate of photosynthesis, which provides nutrients for the biotic environment in the aquatic medium [2, 13, 18]. Moreover, gas solubility is often hampered by the presence of dyes in water which interrupts aquatic life. It is worth noting that color is not the only problem

Table 8.3 Classification of dyes based on application during processing [9].

Class	Principal substrates	Method of application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather	Applied from basic to neutral dyebaths	Azo, anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Azoic compounds and composition	Cotton, rayon, cellulose acetate and polyester	Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triaryl methane, azo, azine, xanthene, acridine, oxazine and anthraquinone.
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, oxazine and stilbene
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine dispersion often applied by high temperature/pressure or low pressure carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro and benzofuranone
Mordant	Wool, leather, anodized aluminium	Applied in conjunction with chromium salts	Azo and anthraquinone

Class	Principal substrates	Method of application	Chemical types
Oxidation bases	Hair, fur and cotton	Aromatic amines and phenols on the substrate	Aniline black and indeterminate structures
Reactive	Cotton, wool, silk and nylon	Reactive site on dye reacts with functional group on fiber to bind covalently under influence of temperature and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan and oxazine
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulphide and reoxidized to insoluble sulphur-containing products on fiber	Indeterminate structures
Vat	Cotton, rayon and wool	Water insoluble dyes solubilized by reducing with sodium hydrogen sulphide, then exhausted on fiber and reoxidized	Anthraquinone and indigoids

associated with dyes; azo dyes may be partially degraded under anaerobic conditions to yield aromatic amines which are considered carcinogenic and mutagenic [2, 19, 20]. Additionally, dyes are synthesized such that they are very stable towards sweat, soap and sunlight, which means that when they are released into the environment they undergo accumulation and present a serious environmental concern [13].

In addition to the large volumes of dyes, textile effluents contain dissolved solids, which when discharged can lead to high levels of total dissolved solids (TDS) of ground and surface water. This bears harmful effects to vegetation and hinders the utilization of such water for agricultural exploits. Moreover, textile effluent contains heavy loads of toxic metals which are undesirable to the biotic environment. Residual chlorine is also a common pollutant; it results in the consumption of dissolved oxygen and adversely affects aquatic life. Additionally, the residual chlorine may react with some aromatic compounds to yield toxic chlorinated aromatics. There are other non-biodegradable organics which may be found in the textile effluent which may cause an increase in COD of the effluent [19, 21].

Textile effluent is not only undesirable due to its negative effects on the environment, but it may also compromise the day-to-day operations of the industry. For example, in some countries, not only the quality of the effluent discharged is regulated, but also the volume of portable water consumed is kept in check. This is usually done to cater for shortages of portable water and ensure that the available water is shared among the different sectors of the country. However, large volumes of water are required for textile processing, which means recycling the water could be the only recommended alternative to solve this problem [20, 22]. Therefore efficient treatment of the water for reuse is necessary to ensure continuous operations of the industry. It is on that note that a lot of research has gone into finding alternative, efficient and economically viable treatment technologies for textile effluent treatment. This initiative will actually save the environment and ensure adequate supply of water for textile processing.

8.3 Conventional Treatment Technologies for Textile Effluent

This section gives a review of the different treatment technologies exploited for textile effluent remediation with the focus on dye pollution. The merits and drawbacks of these technologies are highlighted. Moreover, the exploitation of carbon nanotube-based adsorbents for textile effluent treatment is

singled out and discussed in more detail, highlighting recent research innovations. Although a lot of research has been done to develop various treatment tools, there is no single technology that has been found to treat dye pollution efficiently. Consequently, these technologies need to be exploited in conjunction with others to realize better results. There are three broad categories of textile effluent treatment tools, namely, biological methods, physical or physio-chemical methods and chemical methods.

8.3.1 Biological Methods

Biological techniques involve the exploitation of living or dead organisms such as bacteria, fungi and algae for decolorizing the textile effluent and are one of the most economical processes [23]. However, dyes are synthesized such that they are stable towards biological attack, making it difficult to achieve good decolorization with some classes of dyes. Moreover, the toxicity of these dyes renders biological treatment ineffective. This toxicity problem could be solved through the use of dead microbial biomass instead of living organisms [21, 23]. Biological treatment can either be carried out under aerobic or anaerobic conditions; however, the former is more favorable than the latter. Under aerobic conditions color removal is achieved through the enzyme catalyzed incorporation of oxygen into the aromatic rings of the dyes followed by ring fission, thereby destroying the chromophore [11]. Some dyes are better degraded under anaerobic conditions than aerobic conditions. The incomplete mineralization and generation of colorless aromatic compounds, which are usually toxic and carcinogenic, has been reported as another shortfall of biological methods for dye pollution treatment [24].

8.3.2 Physical/Physiochemical Methods

This category of treatment technologies includes processes such as the membrane processes, coagulation-flocculation, adsorption, ion exchange and electrocoagulation. Membrane filtration is one of the most important textile effluent treatment tools due to its ability to clarify, concentrate and continuously separate dye from effluent [24]. The most prominent membrane processes are reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). Each of these membrane processes has its own merits in terms of solute retention, pressure utilized and the quality of the treated water. Reverse osmosis membranes are capable of attaining more than 90% retention for most types of ionic compounds. Moreover, RO

allows the elimination of all mineral salts, hydrolyzed dyes and chemical auxiliaries [25]. Nanofiltration membranes are employed for the removal of low molecular weight organics, divalent ions, large monovalent ions, hydrolyzed dyes and dyeing auxiliaries. On the contrary, UF membranes are used to remove macromolecules and particles, but dye removal is usually ineffective. Consequently these membranes are often used as pretreatment tools for reverse osmosis and nanofiltration. Microfiltration membranes are employed for the treatment of effluent containing pigment dyes and also as a pretreatment tool for reverse osmosis and nanofiltration [24, 25]. Membrane fouling is one of the major setbacks of membrane processes, which results in membrane losing its efficiency. In processes such as reverse osmosis and nanofiltration, the use of high pressure is also another problem which reflects negatively on the operational costs of the treatment. In addition, the generation of highly concentrated sludge poses further treatment and disposal challenges [12].

Coagulation-flocculation is a typical physiochemical process that is employed for treatment of textile effluent. This process does not cater for soluble dyestuffs; it can only remove insoluble dyestuffs. However, the loads of coagulants utilized and the highly concentrated sludge generated during the process pose serious post-treatment and disposal challenges [13, 26]. Electrocoagulation is another physiochemical technique that has been exploited for treatment of textile effluent and is more favorable than chemical coagulation. Moreover, electrocoagulation has also been employed as a recovery tool for valuable chemicals from wastewater [27]. Its main advantages over chemical coagulation include the *in situ* delivery of coagulants, minimized generation of secondary pollution and the use of compact equipment [12, 23, 27]. Basically electrocoagulation entails the application of an electric current to produce metal ions in solution, usually Al^{2+} or Fe^{3+} , which then react with the OH^- ions formed at the anode during hydrogen evolution. This results in the formation of insoluble metal hydroxides, which then sorb the pollutants out of the solution [12, 28]. Sludge generation is minimized but not completely eliminated in this method, which means treatment and disposal challenges still prevail. Furthermore, the use of electric current could prove to be a costly operation in terms of the energy to drive the process.

Ion exchange is a well-documented effluent treatment technology; however, it is not widely exploited for textile effluent treatment since it can only accommodate a narrow spectrum of dyes, usually ionic dyes. The major merits of this technology include its ability to remove soluble dyes, recovery of solvents after use and the maintained efficiency after regeneration [13, 24]. The selectivity of this process in terms of the type of dyes it can remove and the cost associated with it are some of its negative features.

8.3.2.1 Adsorption Processes

This is one of the most exploited treatment technologies due to its efficiency in the removal of the stable pollutants which are not removed by other methods. Adsorption has been a very attractive process due to the development of low-cost adsorbents, high efficiency, wide range of adsorbents, high stability towards the sorbate and easy recovery and reusability of the adsorbent [29, 30]. Adsorption is a surface process whereby the dyes adhere onto the surface of the adsorbent resulting in the decolorization of the wastewater [31]. Depending on the adsorbent and adsorbate targeted, adsorption may occur via physical forces or through the formation of weak chemical bonds. The success of the adsorption process is dependent on various factors such as the dye/sorbate interaction, dye concentration, availability of competing species, contact time, pH, temperature, surface area and surface charges of the adsorbent [24]. Although adsorption has a lot of positives, it is also susceptible to some drawbacks like any other process. Generation of highly concentrated sludge poses serious disposal challenges. In addition, the recovery of the adsorbent after use is often challenging and inefficient, especially nanomaterials. This results in the generation of secondary pollution.

Activated carbon (AC) is the most popular adsorbent for textile wastewater treatment for the removal of cationic, mordant and acid dyes. Moreover, AC shows affinity for disperse dyes, direct dyes, vat dyes, pigment and reactive dyes [24]. The remarkable performance of AC emanates from its high surface area, pore volume and porosity. Furthermore, the adsorption capacity of AC depends on the method of activation and the source material [32]. Activated carbon is expensive in nature and high regeneration costs are some of its drawbacks.

A lot of work has been done to develop new and low cost adsorbents to replace activated carbon. These include zeolites, clay, sawdust, agricultural waste such as corn cob, barley husk, wheat straw, linseed cake, eucalyptus bark, the giant duck weed, rice hulls, silica gel peat, wood chips, fly ash and coal mixture, etc. [3, 33]. These adsorbents have shown potential as future adsorbents for dye effluent treatment. The discovery of carbon nanotubes (CNTs) initiated a massive research revolution with these nanomaterials showing good potential as future adsorbents for dyes. Carbon nanotubes boast unique physical and chemical properties and their flexibility towards various surface modifications make these materials versatile in textile effluent treatment [34]. Carbon nanotubes' absorption properties are attributed to their highly porous and hollow structures, large specific surface area, light mass density and strong interaction between carbon and hydrogen molecules [30].

In order to harness the unique properties of CNTs, several studies have embarked on developing CNT-based adsorbents for adsorption of dyes. These materials hold the future as textile effluent treatment tools. The CNT-based composite adsorbents exploit the benefits of the CNTs and the other materials making up the composite. The next section discusses some of the CNT-based adsorbents that have been developed and evaluated for the removal of dyes.

8.3.2.1.1 Carbon Nanotube-Based Adsorbents for Dye Removal

Yu *et al.* [30] develop a novel adsorbent based on inserting multiwalled carbon nanotubes (MWCNTs) into the cavities of diatomite and immobilized on the cell walls of flexible polyurethane foams (PUFs) to form the foam-like CNT-based adsorbent. This adsorbent was evaluated for the removal of soluble organic dyes: ethidium bromide, acridine orange, methylene blue, eosin B and eosin Y, from contaminated water. The adsorbent showed good adsorption capacity for the cationic dyes (acridine orange, methylene blue and ethidium bromide) compared to the anionic dyes (eosin Y and eosin B). It was proposed that adsorption of the dyes was influenced by the molecular geometry and surface polarities of the dyes. Hence the cationic dyes were better adsorbed due to the π - π electron-donor (MWCNTs)/acceptor (cationic dyes) interaction, while the π - π electrons/negative-charge (anionic dyes) repulsions were responsible for the poor adsorption of the anionic dyes. Moreover, better adsorption was achieved for acridine orange than methylene blue due to its planar structure promoting better interaction with the hexagonal structure of MWCNTs. The adsorbent was also found to be recyclable through washing with ethanol and it showed insignificant loss of adsorption capacity after reuse [30]. The incorporation of the MWCNTs significantly improved dye adsorption properties. Furthermore, restricting the MWCNTs inside the cavities of diatomite (Figure 8.1) minimizes free floating nanomaterials in the water which pose further treatment challenges. The PUFs provide further support of the MWCNT/diatomite nanocomposite, improving its ease of recyclability and minimizing further leaching of the nanomaterials into the water since their fate in the environment is not fully comprehended yet.

In another work, chitosan hydrogel beads impregnated with MWCNTs (CS/MWCNTs) were fabricated and the adsorbent was evaluated for the removal of Congo red in aqueous solutions. The composite showed improved adsorption capacity compared to pure chitosan, which was attributed to the addition of the MWCNTs. Most importantly, a maximum MWCNTs loading of 0.01% was found to be more efficient for enhancing adsorption. This was attributed to the fact that MWCNTs can block some

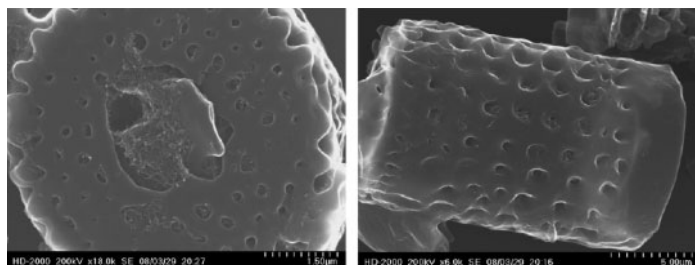


Figure 8.1 SEM images of MWCNTs loaded on cavities of diatomite [30].

of the adsorption sites of chitosan and it becomes more severe at increased MWCNT concentration. Adsorption was found to be pH sensitive with the maximum adsorption realized at pH 4. The low percentage loading of MWCNTs required for maximum enhancement makes the CS/MWCNT nanocomposites quite economical for large-scale application [29]. Similarly, chitosan hydrogel core-shell beads impregnated with MWCNTs were prepared using different dispersing solutions (chitosan (CS) solution, sodium dodecyl sulphate (SDS) solution, CS solution containing cetyltrimethylammonium bromide (CTAB), and SDS solution for gelation with CTAB-containing CS solution). These composites were investigated for the adsorption of Congo red in aqueous medium. A morphological variation as well as a variation in terms of the adsorption capacity was observed with varying MWCNTs dispersing solutions. This meant that not only the percentage of MWCNT loading is crucial but also how the MWCNTs are dispersed during formation of the hydrogels composites [35].

In a similar innovation, a biosorbent of calcium alginate/multiwalled carbon nanotubes (CA/MWCNTs) composite fiber was developed for the removal of ionic dyes: methylene blue and methylene orange. Addition of MWCNTs into the composite improved the adsorption of the dyes compared to sodium alginate fibers, with the adsorption of MO increasing to about three times to that of CA fibers. Adsorption of methylene blue was further enhanced in the composite compared to CA. This means that the addition of MWCNTs into the composite improved the versatility of the composite to accommodate both the ionic and cationic dyes [36]. Furthermore, the CA/MWCNTs fiber composite was found to be pH dependent for the removal of the dyes, as observed by Yu *et al.* [29].

Zeng and coworkers [37] developed a composite based on polyaniline (PANI) filled with MWCNTs (MWCNT/PANI) and studied its adsorption properties for the removal of malachite green. The MWCNT/PANI composite exhibited much higher adsorption capacity than neat PANI.

This improvement in adsorption property of the composite was linked to the much larger surface area of MWCNT/PANI compared to neat PANI, which means more available adsorption sites for malachite green, resulting in the rapid adsorption and high malachite green removal from solution. Furthermore, the high adsorption capacity for malachite green was attributed to the strong π - π^* interaction existing in the MWCNT/PANI composites. These interactions are beneficial for effective charge between the MWCNTs and PANI, which greatly improves the adsorption of malachite green onto the PANI surfaces [37].

As earlier highlighted, the introduction of the nanomaterials into the environment could pose serious challenges since their fate in the environment is not yet fully understood. Moreover, their small sizes make it difficult to separate them from the treated water; therefore, immobilizing these nanomaterials on polymers not only improves the adsorption capacity of the polymer for the dye but also ensures remarkable reduction of freely suspended nanomaterials in the water.

In an attempt to fabricate an adsorbent material with improved adsorption properties for dye removal and which could be separated easily from the treated water, Yan and coworkers [38] prepared a magnetic guar gum (GG)-grafted multiwalled carbon nanotube (GG-MWCNTs- Fe_3O_4) polymer nanocomposite for adsorption of neutral red and methylene blue from aqueous medium. The composite displayed improved adsorption capacity compared to MWCNTs- Fe_3O_4 and MWCNTs. This was ascribed to the synergetic effect of the MWCNTs and GG. The MWCNTs improved the surface area and adsorption properties of the composite and GG improved the dispersion of the GG-MWCNT- Fe_3O_4 in the dye solution due to its hydrophilic nature. This is important because it permitted diffusion of the dye molecules onto the surface of the MWCNTs and improved dye removal. Incorporation of the magnetic nanoparticles allowed the nanocomposite to be separated from the treated solution using a magnetic field [38]. Magnetic separation of adsorbent from treated water is illustrated in Figure 8.2.

The fabrication of magnetic carbon nanotube-based polymer composites was also investigated by Chang and coworkers [39] using magnetic soluble starch-functionalized multiwalled carbon nanotubes for the removal of methylene blue and methylene orange as model dyes. The composite displayed superior adsorption capacity for both dyes compared to the magnetic MWCNTs. The improved adsorption performance of the magnetic soluble starch-functionalized MWCNTs could be attributed to the good adsorption properties of the MWCNTs and the hydrophilic property

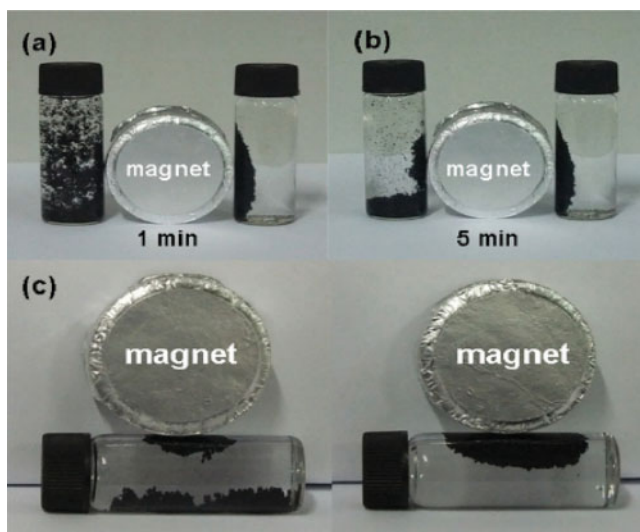


Figure 8.2 Magnetic response of M-MWCNTs and physical mixtures of MWCNTs and Fe_3O_4 to an external magnetic field in different directions; left: physical mixture of MWCNTs and Fe_3O_4 , right: M-MWCNTs [33].

of soluble starch. This improved the dispersion of composite in the aqueous solution and facilitated the diffusion of dye molecules to the surface of MWCNTs. The composite exhibited supermagnetic properties which allowed separation from solution using a magnetic field [39].

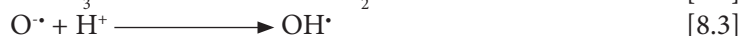
In a similar innovation, Zhu and coworkers [40] had earlier prepared magnetic $\gamma\text{-Fe}_2\text{O}_3$ and multiwalled carbon nanotubes wrapped in chitosan (m-CS/ $\gamma\text{-Fe}_2\text{O}_3$ /MWCNTs) and studied its adsorption properties for methylene orange from aqueous solution. The incorporation of the MWCNTs into the composite significantly increased the adsorption of methylene orange compared to m-CS/ $\gamma\text{-Fe}_2\text{O}_3$. The adsorption of methylene orange in the presence of other competing species was investigated and it was observed that in the presence of other competing species, the adsorption of methylene orange decreases considerably with the increasing concentration of the competing ions [40].

Konicki and coworkers [41] prepared magnetic multiwalled carbon nanotubes- Fe_3C nanocomposite and studied its adsorption capacity for the anionic azo dye direct red (DR43) from aqueous solution. The MWCNT- Fe_3C nanocomposite showed good adsorption capacity as compared to previously evaluated adsorbents for the same dye (rice husk, orange peel, TiO_2 , *Rhizophora apiculata* bark, cationized sawdust, *Uncaria gambir*).

This makes the MWCN-Fe₃C a future adsorbent for DR23 from aqueous medium. Adsorption was found to be dependent on the initial dye concentration, pH and temperature. The nanocomposite could easily be separated from the solution by an external magnetic field [41]. Similar results have been reported where magnetite loaded MWCNTs (M-MWCNTs) were used as adsorbents for methylene blue. The initial dye concentration played an important role during adsorption, where it provided driving force to overcome the mass transfer resistance of the dye between the aqueous and solid phases. Moreover, infrared spectroscopy was used to probe the adsorption mechanism of methylene blue onto the M-MWCNTs, and it was suggested that electrostatic attraction and π - π stacking interactions between MWCNTs and methylene blue were responsible for the adsorption of methylene blue. Stability studies indicated that the M-MWCNT nanocomposite was very stable especially at pH values lower than 4 [33]. Gong and coworkers [42] and Qu and coworkers [43] exploited multiwalled carbon nanotube modified with iron oxide nanoparticles for the removal of methylene blue, neutral red, brilliant cresyl blue and methylene blue and neutral red, respectively. The results obtained were consistent with the results previously reported in the literature [33, 41].

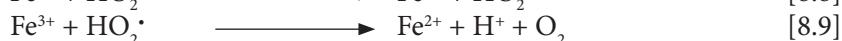
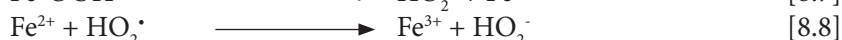
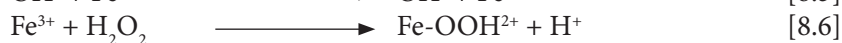
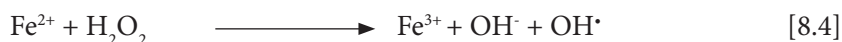
8.3.3 Chemical Methods

Chemical oxidation is the most popular method for color removal by chemical means, owing to its simplicity of application [24]. Conventional oxidizing agents for decolorization of textile effluent include chemical species such as ozone, hydrogen peroxide, hypochlorite (NaOCl), chlorine, chlorine dioxide, etc. However, due to the complexity and stability of most dyestuff, conventional oxidation processes fail to achieve satisfactory results for decolorization of textile effluent. Moreover, these dyestuffs may be refractory towards these oxidizing agents, causing further decline in performance [44]. Ozone is a powerful oxidizing agent due to its high oxidation potential as compared to hydrogen peroxide and chlorine. Ozone has been found to be efficient in decolorizing some dyestuffs and is also capable of converting biorefractory dyes in wastewater into biodegradable species which can be treated with biological process [16]. Oxidation of dye species by ozone is thought to proceed in two ways: firstly, in a basic medium, ozone is unstable and is decomposes to form the hydroxyl radical and other radical species. The formation of the hydroxyl radical proceeds as illustrated in Equations 8.1–8.3. In the second route, ozone may react directly with the dye species, under acidic conditions. This is because under acidic conditions, ozone is very stable [12, 17].



Oxidation of dyestuff depends largely on the rate of mass transfer of ozone from the gas phase to the liquid phase. This driving force for the mass transfer is sensitive to the water quality parameters and operating conditions [16]. The fact that ozone is applied in its gaseous form eliminates its contribution to the large effluent volumes. However, the short half-life (20 minutes) of ozone makes it very unstable and it needs to be applied continuously, which impacts negatively on the operational cost. The half-life of ozone is further reduced in the presence of dyes and its stability is compromised by salts, pH and temperature [24].

Fenton's reagent ($\text{H}_2\text{O}_2\text{-Fe}^{2+}$), which is basically a mixture of hydrogen peroxide and iron salts, is another powerful oxidizing agent effective for decolorizing both soluble and insoluble dyes [45]. The hydroxyl radical has been proposed as the main oxidizing species. The reactions taking place during the Fenton process are presented in Equations 8.4–8.10.



Fenton's reagent has received a lot of attention as a dye effluent decolorization technique due to low price, low toxicity of its reagents and the simplicity of the application [46].

The inability of conventional oxidizing agents to effectively treat textile effluent necessitated the improvement or search for better technologies. Complete mineralization of the dyes is a crucial point during oxidation. Consequently, advanced oxidation processes (AOPs) were developed for decolorization of textile effluent. These processes have the potential to completely mineralize organic dyes into harmless products like carbon dioxide and water [15]. The essence of AOPs entails the *in situ* formation of a hydroxyl radical which is nonselective and an extremely powerful oxidizing agent. This is followed by the attack of the organic dye, breaking it into smaller molecules [12]. In addition to the hydroxyl radical, other oxygen-based oxidizers such as ozone, atomic oxygen, hydrogen peroxide,

and perhydroxyl radicals are also generated *in situ* and aid in the degradation of the targeted pollutants. The main advantage of AOPs over the other technologies is their ability to prevent concentrated sludge generation which would otherwise create further treatment and discharge challenges [6]. The nonselective nature of the generated hydroxyl radical make AOPs versatile treatment tools for a wide range of organic dyes [19].

Although oxidation processes such as ozonation and Fenton's reagent have shown the potential to degrade organic dyes, their performance could further be enhanced by combining them with other oxidizing agents or ultra-violet (UV) light and electron beam irradiation. This gives rise to more effective oxidation tools than ozonation and Fenton's reagent alone. Oxidation tools such as photo-Fenton $\text{H}_2\text{O}_2/\text{UV}/\text{Fe}^{2+}$, ozone/ultrasonics, $\text{O}_3/\text{TiO}_2/\text{electron beam irradiation}$, ozone/UV, ozone/UV/ H_2O_2 , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2$ and ozone/ $\text{TiO}_2/\text{H}_2\text{O}_2$ have been evaluated for dye degradation. The combination of these processes shows improved results compared to the individual oxidizing agents [17, 44]. Typically, the enhanced ozonation of dyes in the presence of UV light has been attributed to the decomposition of ozone by UV light, which yields additional hydroxyl radicals which are responsible for decolorizing the contaminated water [17]. Therefore, the improved performance of the combined processes can be attributed to the synergetic effect of the various components. Semiconductor photocatalysis is another important and fast emerging AOP due to its potential as a dye effluent treatment tool. This technology is favorable over the other AOPs due to the lack of limitations in mass transfer, ease of application at ambient conditions and complete degradation of a wide variety of organic pollutants [47].

8.3.3.1 Principles of Semiconductor Photocatalysis

Semiconductor photocatalysis is an energy-driven process which is initiated by absorption of energy equal or above the band gap energy of the semiconductor. This is basically an activation step where the absorbed energy initiates the excitation of electrons from the valence band (VB) to the conduction band (CB) of the semiconductor. The excited electron leaves a positive hole in the valence band and creates a negative (electron) conduction band [48, 49, 50]. The excitation and formation of the electron hole pair is depicted in Equation 8.11.



The excitation of the electron into the conduction band is a reversible process, which means that the conduction band electron can recombine with

the valence band hole, thereby releasing the absorbed energy. Alternatively the electron may be trapped in surface states of slightly lower energy than the conduction band. In another scenario, the electron-hole pair may undergo redox reaction with electron acceptors and donors trapped on the surface of the semiconductor [51, 52]. In the aqueous medium the valence band hole will react with adsorbed hydroxide ions (OH^-) or water to form the extremely powerful, nonselective, oxidizing hydroxyl radical ($\text{OH}^\bullet$). Similarly, the conduction band electron may reduce any adsorbed oxygen (O_2) to form the superoxide radical ($\text{O}_2^{\bullet-}$), another oxidizing species [53]. The hydroxyl and superoxide radicals are responsible for the degradation of the organic dyes into carbon dioxide and water or other smaller, colorless molecules. The formation of these oxidizing species is summarized in Equations 8.12–8.18.



The effectiveness of the photocatalytic degradation of the dyes depends on the effective generation of the hydroxyl radicals and prevention of the electron-hole recombination. Electron-hole recombination is undesirable because it consumes the reacting species for the formation of the hydroxyl radical, which in turn impacts negatively on the photocatalytic activity of the semiconductor. Since semiconductor photocatalysis is a surface process, the electron donor and acceptor has to be confined on the surface of the semiconductor. This is to ensure effective separation of the electron-hole pairs and improve the photocatalytic degradation of the pollutants [51, 54, 55]. The degradation process depends strongly on the good interaction of the dyes and the photocatalyst and strong interaction between the semiconductor and the electron acceptor. Several approaches have been proposed for controlling the interfacial electron transfer at the semiconductor-electrolyte interface. Strategies such as electrostatic incorporation of electron acceptors at the semiconductors surface, modifying the semiconductor surface with electron acceptors and immobilizing semiconductor photocatalysts in redox-functionalized polymers have been proposed [51, 56].

There are numerous semiconductors that have been developed and evaluated for photocatalytic degradation of various organic pollutants including dyes both under UV and visible light irradiation. These include titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten oxide (WO_3), copper oxide (Cu_2O , CuO), iron oxide (Fe_2O_3), tin oxide (SnO_2), cadmium sulphide (CdS), zirconium oxide (ZrO_2), vanadium oxide (V_2O_5), cadmium selenide (CdSe), zinc sulphide (ZnS), etc. Among the different semiconductors, nanotitanium dioxide has shown good photocatalytic activity resulting in numerous researches around the use of this semiconductor for the degradation of organic pollutants. It is now regarded as a benchmark for semiconductor photocatalysis. Titanium dioxide is an attractive photocatalyst due to its high photoactivity, non-toxicity, biological and chemical stability, resistance towards photocorrosion and easy accessibility in terms of cost. Moreover, since it is also versatile in terms of application, it has seen use in a number of applications such as water splitting, air purification, deodorization, self-cleaning surfaces and bacterial inactivation [57–59].

However, TiO_2 has two major drawbacks: it has a large band gap (3.2 eV, anatase and 3.0 eV, rutile) which only allows activation by UV light. This renders the use of sunlight as a source of energy ineffective since UV light accounts for about 5% of the solar spectrum compared to visible light, which constitutes about 40%. The use of artificial sources of UV light consumes a lot of energy and leads to escalating treatment costs [60]. The second problem with TiO_2 is the high recombination rate of the electron-hole pairs which form the hydroxyl and superoxide radicals responsible for the photocatalytic degradation of the organic pollutants. This lowers the efficiency of the photocatalysis process remarkably [61, 62].

Consequently, extensive work has been done to improve charge separation in TiO_2 and also extend its photoresponse into the visible light region, which would enable the use of sunlight as a source of energy and curb the operational costs of the photocatalysis process. Some of the proposed strategies include doping TiO_2 with non-metals [63–66], transition metals [67–69], noble metals [70–72], rare earth metals [73–76], other semiconductors [60, 77, 78], and through dye sensitization [79]. Furthermore, hybridization of titanium and carbon nanotube has yielded nanocomposites with improved photocatalytic activity towards organic pollutants' degradation both under UV and visible light irradiation [55, 80, 81]. Notably, several other carbon nanotube-based photocatalysts have been fabricated and evaluated for the photocatalytic degradation of organic dyes. The carbon nanotubes have been found to have positive effects on the overall performance of the photocatalyst [82, 83].

8.3.3.2 Carbon Nanotube-Based Photocatalysts

Due to their unique properties, carbon nanotubes have been found to be excellent and versatile additions in the nanocomposite photocatalysts. Properties such as large surface area, high chemical and thermal stability, good mechanical properties and good electrical conductivity are extensively exploited in carbon nanotube/semiconductor photocatalysis [84, 85]. The roles played by carbon nanotubes in the various carbon nanotube-based photocatalysts include acting as support for the semiconductor nanoparticles. Carbon nanotubes also act as adsorbents for the dye molecules onto the surface of the semiconductor. This is crucial for photocatalytic decomposition of the dyes. Moreover, carbon nanotubes act as a photogenerated electron transfer station which is enabled by the extended, delocalized π -electron system of carbon nanotubes. This feature makes carbon nanotubes efficient for managing charge transfer and charge transport. Charge separation is important for enhancing the photocatalytic activity of the semiconductor. Furthermore, carbon nanotubes may also act as visible light sensitizers during photocatalysis under visible light irradiation [84]. The large surface area of carbon nanotubes improves the surface area of the nanocomposite, which is essential for high photocatalytic activity [86].

In the next sections, fabricated carbon nanotube/semiconductor photocatalyst are highlighted and briefly discussed in terms of their photocatalytic activity, role played by the carbon nanotubes and the overall mechanisms involved during photocatalytic degradation of dyes in aqueous medium. Both photocatalysis under UV and visible light irradiation are considered.

8.3.3.2.1 Dye Degradation Using Titanium Dioxide/Carbon Nanotube (CNT/TiO₂)-Based Photocatalyst under UV Irradiation

Li and coworkers prepared a CNT/TiO₂ nanocomposite via a microemulsion method and its photocatalytic degradation of methylene blue (MB) was investigated under UV light irradiation. Notably, the photocatalytic activity of the prepared nanocomposite was higher than that of pure TiO₂, P25, and a CNT/TiO₂ nanocomposite prepared by sol-gel method. The enhanced performance of the prepared nanocomposite was attributed to the incorporation of the CNTs and the method of preparation, which ensured production of well-dispersed TiO₂ nanoparticles on the surfaces of the CNTs. Kuo and coworkers [87] documented similar results for the photodegradation of C.I. Reactive Red 2 (RR2) under UV irradiation, using the CNT/TiO₂ nanocomposite. The CNTs improved the surface area of the nanocomposite and the amount of hydroxyl groups on the surface of the composite which harvested the positive holes in the valence band of

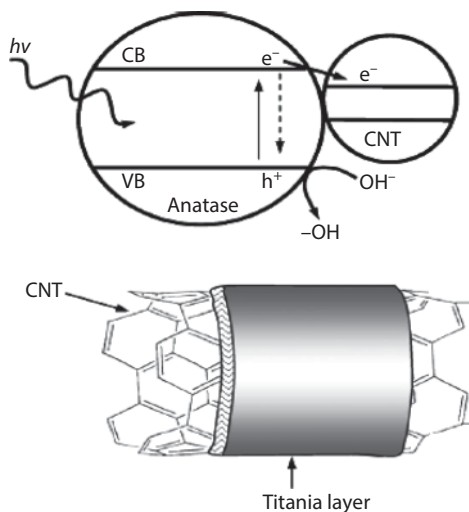


Figure 8.3 Scheme showing the photocatalysis enhancement of CNTs from the addition of a uniform TiO_2 layer [88].

TiO_2 . This is important because it reduces the electron-hole recombination which normally lowers the photocatalytic performance of TiO_2 . It was further proposed that the photodegradation of the MB may proceed as illustrated in Figure 8.3.

Basically, it was observed that the carbon nanotube's main contribution on the improved photocatalytic performance of the nanocomposite is charge separation. After illumination the electrons are scavenged by the CNTs due to their excellent electrical conductivity, which then allows efficient charge separation. This resulted in the improvement of the photocatalytic activity of the nanocomposite. This claim was further backed up with photoluminescence studies [88]. A similar photocatalytic degradation mechanism for methylene orange (MO) using a MWCNT/ TiO_2 nanocomposite was proposed (Figure 8.4), and the incorporation of the CNTs was found to play a key role in the improvement of the performance of the prepared nanocomposite [89].

Similarly, Zhou and coworkers [90] prepared a nanocomposite of TiO_2 and single-walled carbon nanotubes (SWCNTs) through a solvothermal procedure. The SWCNT/ TiO_2 nanocomposite was exploited for the photocatalytic degradation of Rhodamine B and nitrobenzene under UV irradiation. Higher photocatalytic activity was realized for the nanocomposite compared to the commercial photocatalyst, P25. This phenomenon was attributed to the large surface area, smaller crystalline size and the strong

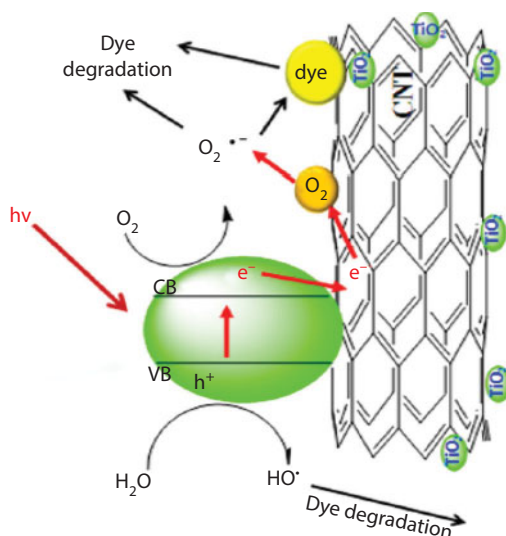


Figure 8.4 Proposed mechanism for degradation of MO by CNT/TiO₂ [89].

interface between the SWCNTs and TiO₂. The strong interface between the SWCNTs and TiO₂ enabled the easy and efficient movement of electrons from the semiconductor into the CNT skeleton, thereby facilitating charge separation. Moreover, it was demonstrated that the nanocomposite was very stable and could be recycled several times without significantly losing its efficiency. In a similar approach, a composite consisting of thin MWCNTs and TiO₂ was prepared via “Click” chemistry which sought to improve the MWCNT/TiO₂ interface and improve charge injection, which in turn improves the photocatalytic performance of the nanocomposite [91]. The mechanism for the enhancement of the photocatalytic activity of the nanocomposites had been reported elsewhere [90, 92].

It was further revealed that when fabricating the CNT/TiO₂ nanocomposites, the positive effect of CNTs can be realized maximally by ensuring complete dispersion of the CNTs in solution, which would then allow uniform coverage of their surfaces with the TiO₂ nanoparticles during synthesis. A nanocomposite of TiO₂ supported on hydrophilically surface-modified MWCNTs showed improved photocatalytic activity compared to unmodified MWCNT/TiO₂ nanocomposite for the degradation of MO. This was linked to the good dispersion of the MWCNTs due to their hydrophilic surfaces. Moreover, the hydrophilic nature of the MWCNTs allowed uniform and intimate interaction with the TiO₂ nanoparticles, which resulted in dense heterojunctions through the formation of Ti-O-C bonds [93].

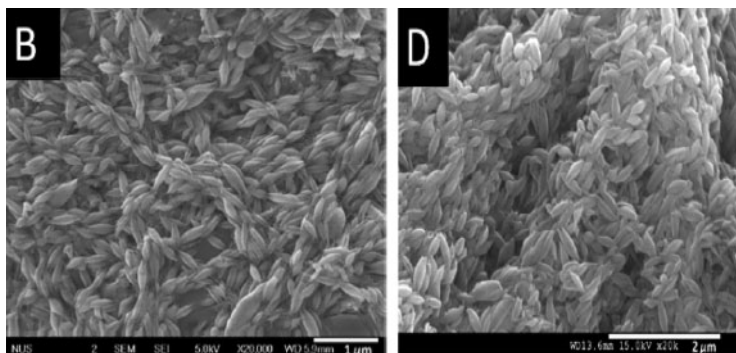


Figure 8.5 SEM images (B) rice grain-shaped $\text{TiO}_2/\text{MWCNT}$ nanocomposite and (D) pure rice grain-shaped TiO_2 nanoparticles [94].

Different synthetic routes for the CNT/TiO_2 nanocomposites have been found to yield some unique morphology but still maintained the improved photocatalytic activity over pure TiO_2 and P25. However, there had not been any established link between the morphology and the enhanced photocatalytic activity. Peining and coworkers [94] prepared rice grain-shaped $\text{MWCNT}/\text{TiO}_2$ nanocomposites (Figure 8.5) by electrospinning method and evaluated the nanocomposite for the degradation of Alizarin Red. The improved photocatalytic performance over pure TiO_2 and P25 was linked to efficient charge separation by the MWCNTs and the large surface area, pore size and pore volume of the nanocomposite.

Similarly, flower-like TiO_2 nanoparticles were deposited uniformly on the surface of CNTs via a hydrothermal synthesis method. The novel photocatalyst displayed superior performance for the degradation of rhodamine B compared to pure TiO_2 . Figure 8.6 shows the field emission scanning electron microscopy (FE-SEM) images of the pure flower-like TiO_2 nanoparticles and their composite with CNTs. The improved photocatalytic performance was linked to the enhanced light absorption due to incorporation of the CNTs and also charge separation by the CNTs [95].

Degussa P25 is the most popular TiO_2 photocatalyst which is commercially available. It is approximately 80% anatase and 20% rutile and has been used for the degradation of various organic pollutants. However, the high recombination rate of the photogenerated electron-hole pairs lowers its efficiency remarkably. A physical mixture of CNTs and P25 was used as a photocatalyst for the degradation of the azo dyes: Procion Red MX-5B, Procion Yellow HE4R and Procion Red HE3B. For comparison, a mixture of activated carbon (AC) and P25 was also evaluated for the degradation of the same dyes. Enhanced photocatalytic activity was observed for both

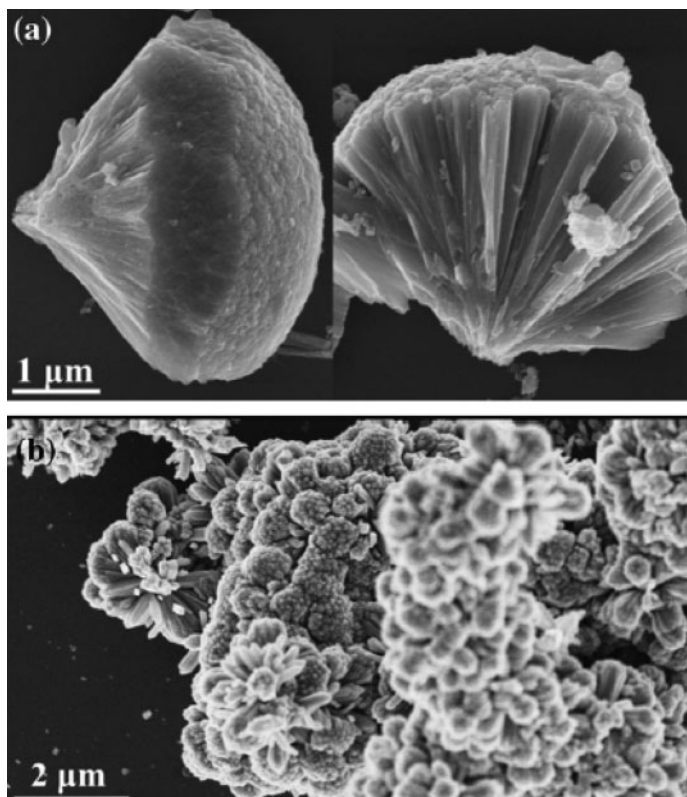


Figure 8.6 FE-SEM images of (a) pure TiO_2 and (b) CNT/ TiO_2 nanocomposite [95].

mixtures compared to P25. The CNT/P25 mixture displayed superior photocatalytic activity over the AC/P25 mixture. It was proposed that even in the physical mixture the CNTs and P25 can be in contact with each other through binding and adsorption, thereby benefiting from the charge separation effect of the CNTs [96].

Carbon nanotube/titanium dioxide nanocomposites have potential as photocatalysts for dye degradation. A composite catalyst of platinum-doped titania (Pt-TiO_2) combined with MWCNTs was fabricated through the sol-gel method. Its photocatalytic degradation of MB was studied. The composite catalyst showed improved photocatalytic activity, which was attributed to absorption of the photo-induced electrons by the MWCNTs and the electron trap effect of the Pt metal nanoparticles. The proposed photocatalytic degradation mechanism is illustrated in Figure 8.7.

It was inferred that the MWCNTs act as an electron sensitizer and donator in the nanocomposite, injecting electrons into the conduction

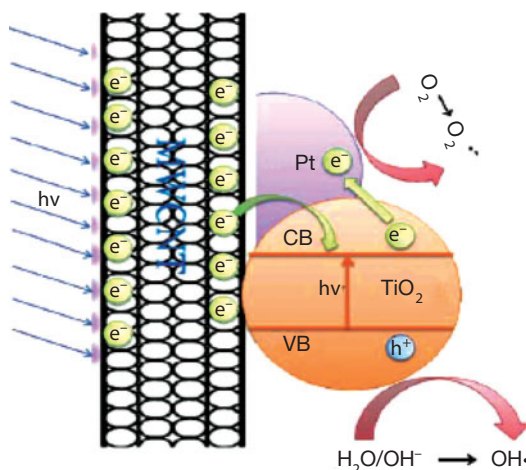


Figure 8.7 Proposed mechanism for the enhanced performance of Pt/MWCNT/TiO₂ [97].

band of TiO₂, thereby increasing the number of electrons on the semiconductor surface. This is important for the formation of the superoxide radical which oxidizes the dye. The Pt metal nanoparticles on TiO₂ ensured electron scavenging, which allowed efficient charge separation and improved the photocatalytic activity of the nanocomposite [97]. In a similar innovation, a composite catalyst consisting of titania and silver nanoparticles loaded on carbon nanotubes was prepared via photoreduction. In order to evaluate its photocatalytic properties, reactive brilliant red X-3B was used as a model dye. Improved photocatalytic activity was realized for the composite catalyst, which was linked to the loading of silver nanoparticles. It was proposed that loading the silver nanoparticles on CNT/TiO₂ composite improved electronic conductivity of the composite, which ensured efficient charge separation and improved photocatalytic activity [98].

In another work, Kan and coworkers [99] prepared a photocatalyst based on iron-doped carbon nanotube and titanium dioxide nanoparticles (Fe-CNT/TiO₂) through a modified sol-gel method. Photocatalytic property of the nanocomposite was studied using rhodamine B as a model dye in an aerated solution system. The prepared nanocomposite was found to benefit from the synergetic effect of its components for the improved performance. Figure 8.8 shows the proposed electron transfer and photodegradation mechanism.

The improved photocatalytic performance of the nanocomposite was attributed to the CNTs acting as electron transfer station between the

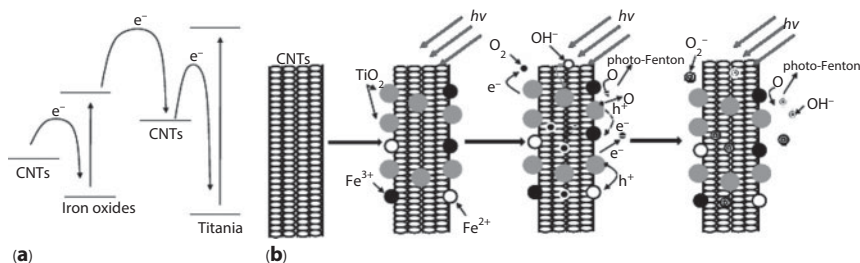


Figure 8.8 (a) Possible electron transfer process and (b) schematic of the photodegradation reaction by Fe-CNTs/TiO₂ [99].

adsorbed rhodamine B and titanium dioxide. The iron particles had the ability to cause the photo-Fenton reaction which produces more hydroxyl radicals for the degradation of the dye. Furthermore, the photocatalytic activity of the nanocomposite was further enhanced by the iron particles acting as electron sinks, thereby improving charge separation. Additionally, the strong interaction between TiO₂ and iron particles ensured efficient electron transfer. Aeration of the photocatalysis reactor accelerated the rate of dye degradation due to enhanced photo-Fenton reaction and provision of more oxygen for the formation of the superoxide radicals. These are important oxidizing species for dye degradation [99].

Jeon and coworkers [100] fabricated a composite consisting of poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAA)/titanium dioxide (TiO₂) via electrospinning method. Carbon nanotubes were used as additives in the composite to improve its photoelectronic properties. The PVA/PAA hydrogels acted as supports for the TiO₂ and CNTs to enable easier recovery and handling of the photocatalyst. Separation of the nanomaterials from the treated water is always a challenge due to their smaller size, and yet their release into the environment is undesirable since their fate is not yet fully understood. Coomassie brilliant blue R-250 (CBB) was used as a model dye in order to investigate the photocatalytic property of the prepared composite. Higher photocatalytic activity was recorded for the composite, which was linked to the synergetic effect of its components. A good interaction between the CNTs and TiO₂ was deemed key for improved performance [100].

8.3.3.2.1.1 Dye Degradation Using other Carbon Nanotube/Semiconductor Photocatalysts under UV Irradiation

Zinc oxide (ZnO) is another important semiconductor that is exploited in photocatalytic degradation of organic pollutants. Zinc oxide nanoparticles have a higher quantum efficiency than TiO₂, however, they photocorrode under acidic conditions in aqueous medium [56]. However, ZnO displays

high sensitivity to UV light and its preparation is usually cost effective. In an attempt to bolster its photocatalytic activity, ZnO nanoparticles were coated on MWCNTs and the resultant nanocomposite was employed for the photocatalytic degradation of MB under UV irradiation. The photo-reactor was constantly bubbled with oxygen to ensure adequate electron acceptors. Higher photocatalytic activity was recorded for MWCNT/ZnO nanocomposite compared to pure ZnO nanoparticles, MWCNTs and the mechanical mixture of ZnO and MWCNTs. This phenomenon was attributed to the incorporation of the MWCNTs which act as photogenerated electron acceptor. The MWCNTs promoted interfacial electron-transfer processes from the attached ZnO nanoparticles to the MWCNT skeleton [101]. Byrappa and coworkers [102] compared the photocatalytic activity of hydrothermally prepared ZnO/CNT and TiO_2/CNT nanocomposites to pure ZnO, TiO_2 , activated carbon (AC)/ZnO and AC/ TiO_2 . Photocatalytic degradation of indigo carmine both under UV and visible light irradiation was investigated. The CNT-based nanocomposites exhibited higher degradation efficiency than activated carbon-based nanocomposites, TiO_2 and ZnO. The enhancement effects of the MWCNTs were superior to those of AC; hence the better photocatalytic performance of the MWCNT-based composites [102].

Enhanced photocatalytic activity has been realized for the MWCNT/ZnO nanocomposites. Consequently, a large-scale synthesis technique was proposed for MWCNT/ZnO nanocomposites. This method is a simple reflux method in ethylene glycol with the aid of polyvinylpyrrolidone. The prepared nanocomposites were evaluated for the degradation of MB under UV irradiation. Superior performance was observed for the nanocomposites as compared to ZnO and P25. The proposed photodegradation mechanism is illustrated in Figure 8.9.

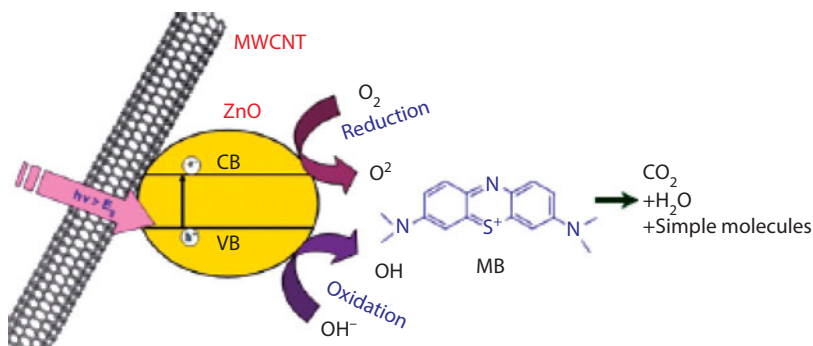


Figure 8.9 Photodegradation mechanism of MB using MWCNT/ZnO [103].

This mechanism is consistent with previously proposed degradation routes of dyes over ZnO/CNTs nanocomposites [101, 102]. The CNTs acted as photosensitizers as well as electron traps, preventing electro-hole recombination. Furthermore, the nanocomposites were stable and could be recycled several times without significant loss of their efficiency [103]. Similar results have been reported for the degradation of MB on MWCNT/ZnO nanocomposites prepared via a sol-gel method [104].

In another innovation, cadmium sulphide (CdS) and silver sulphide (Ag_2S) quantum dots were decorated on poly(amidoamine)-modified CNTs. The composite photocatalysts showed higher photocatalytic activity than CdS, Ag_2S , poly(amidoamine)-functionalized MWCNTs and P25, for the degradation of MO under UV irradiation. The improved photocatalytic performance of the composite catalyst was attributed to charge transfer processes through the interface of the functionalized MWCNTs and the quantum dots. This sufficiently lowers the electron-hole pairs' recombination rate. Consequently, formation of the oxidizing species is enhanced and so is the photocatalytic activity [105].

Tungsten trioxide (WO_3) is another semiconductor that has been exploited for the treatment of organic pollution. It has a narrower band gap than TiO_2 which allows it to absorb strongly in near UV and visible region [106]. In an attempt to improve the photocatalytic activity of WO_3 , it was coated on MWCNTs and the composite was exploited for the degradation of rhodamine B under UV irradiation. Improved photocatalytic activity was realized for the MWCNT/ WO_3 nanocomposite compared to pure WO_3 , P25 and a mixture of CNTs and WO_3 . This suggested a positive effect of the MWCNTs on the photocatalytic performance and further revealed that strong interaction between the MWCNTs and WO_3 is key for improved performance of the composite [106].

8.3.3.2.2 Dye Degradation Using Carbon Nanotube-Based Photocatalysts under Visible Light Irradiation

The phenomenal potential of semiconductor photocatalysis as an environmental clean-up tool has brought a research revolution whereby various photocatalysts are being fabricated and the existing ones are being improved to achieve acceptable performance. One major quest has been that of fabricating or modifying the currently known semiconductors, such as TiO_2 and ZnO, in order to make them absorb efficiently in the visible light region and improve their photocatalytic activity. This would enable the use of sunlight, which is abundant in most parts of the world, as a source of energy instead of the currently exploited UV sources. Carbon nanotube-based semiconductors have exhibited improved visible

light absorption and photocatalytic activity. Therefore, this section highlights the recent innovations around CNT-based photocatalysts for dye degradation.

8.3.3.2.2.1 Dye Degradation Using Titanium Dioxide/Carbon Nanotube (CNT/ TiO_2)-Based Photocatalysts under Visible Light Irradiation

Cong and coworkers [107] prepared a nanocomposite consisting of carbon-doped titanium dioxide coated on MWCNTs through the oxidation of titanium carbide (TiC). The resultant nanocomposite was exploited for the degradation of MB under visible light irradiation. Improved absorption of visible light and photodegradation performance was recorded for the prepared nanocomposite in comparison with P25, TiO_2 nanofibers, mixture of TiO_2 nanofibers and MWCNTs and a mixture of MWCNTs and P25. The improved photocatalytic activity of the nanocomposite was attributed to the synergetic effects of the carbon doping, MWCNTs and TiO_2 . Hence the photodegradation mechanism illustrated in Figure 8.10 was put forward to explain this phenomenon.

It was inferred that the incorporation of the MWCNTs in the nanocomposite improved its adsorption of MB onto the photocatalyst surface due to their large surface area, hollow and layered structures. The MWCNTs also acted as an electron transfer station, capturing the electrons from the conduction band of TiO_2 , thereby minimizing electron-hole recombination

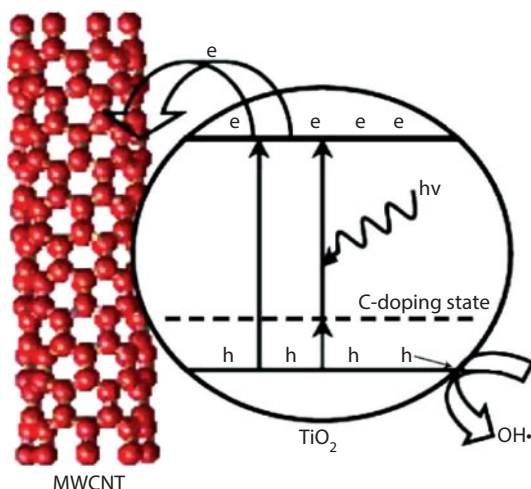


Figure 8.10 Proposed mechanism of synergistic enhancement of visible light photocatalytic activity in carbon-doped TiO_2 coating on MWCNTs [107].

and improving the photocatalytic activity of the nanocomposite. X-ray photoelectron spectroscopy (XPS) results confirmed the formation of Ti-O-C bonds, which resulted in the improvement of the MWCNT/TiO₂ interface and favored transmission of the photogenerated electron between TiO₂ and MWCNTs. The formation of Ti-C and Ti-O-C was also reported for TiO₂/grapheme nanocomposites and resulted in improved photocatalytic activity of the nanocomposite for MO degradation [108]. Furthermore, the carbon doping introduced mid band gap states close to the valence band of TiO₂. This allowed electrons to be excited by visible light into these mid-band-gap states, and hence the improved visible light absorption and photocatalytic activity. In a similar study, Vijayan and coworkers [109] documented similar results for the degradation of acetaldehyde using titania coupled with MWCNTs. Most importantly, two possible photodegradation mechanisms were put forward with one similar to that proposed by Cong and coworkers (Figure 8.11, Mech. I). In the other mechanism (Figure 8.11, Mech. II), the CNTs may act as visible light sensitizers, transferring electrons into the mid band gap states (Ti-C or Ti-O-C trapping sites). The positively charged CNTs skeleton draws electrons from the valence band of TiO₂, which then oxidizes water or hydroxyl groups to form the extremely powerful and non-selective hydroxyl radicals that degrade the pollutants [109].

The second mechanism (Mech. II) was also proposed for the photodegradation of MB using solvothermal prepared TiO₂/MWCNTs nanocomposites [110].

One of the methods of improving the visible light activity of TiO₂ involves doping it with non-metals such as N, P, S, C, B, F, Br and I. It is on that note that a nanocomposite consisting of P-doped TiO₂ supported on MWCNTs was fabricated and evaluated for the degradation of MO under visible and UV light irradiation. The MWCNT/P-TiO₂ nanocomposites showed improved photocatalytic activity as compared to P-TiO₂ and P25. The prepared nanocomposite exploited the properties of the P-TiO₂ and

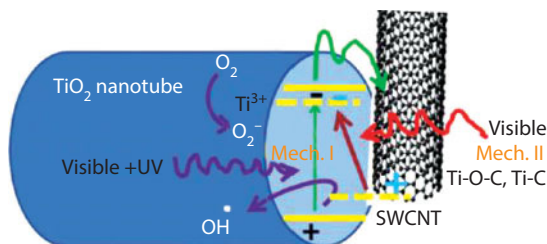


Figure 8.11 Photodegradation mechanism of acetaldehyde using titania nanotube/MWCNTs nanocomposite [109].

the MWCNTs, hence the improved photocatalytic activity. The generation of the Ti-O-P bonds introduced surface states in the nanocomposite which allowed efficient absorption in the UV and visible region. Furthermore, the MWCNTs acted as charge barriers, separating the electron-hole pairs and improving photocatalytic performance [111]. In a similar approach, palladium and nitrogen co-doped titanium dioxide was decorated on multiwalled carbon nanotubes to form a nanocomposite catalyst that is responsive under visible light irradiation. The MWCNT/N, Pd-TiO₂ nanocomposite was tested for the degradation of eosin yellow under visible and simulated solar light. A synergetic effect of the MWCNTs, N, Pd and TiO₂ was proposed as the possible explanation for the improved photocatalytic activity of the nanocomposite compared to pure TiO₂. Figure 8.12 illustrates the proposed photodegradation mechanism. A similar mechanism has been proposed elsewhere [97].

It was inferred that the MWCNTs acted as visible light sensitizers, while the incorporation of N enhanced visible light absorption by the nanocomposite. The Pd nanoparticles acted as electron sinks, further minimizing electron-hole recombination and improving the photocatalytic performance of the nanocomposite [112].

Titanium dioxide/carbon nanotube nanocomposites have been found to degrade a variety of dyes both under UV and visible light irradiation. In order to enhance the performance of the CNT/TiO₂ nanocomposite, palladium nanoparticles were loaded on MWCNTs prior to the incorporation

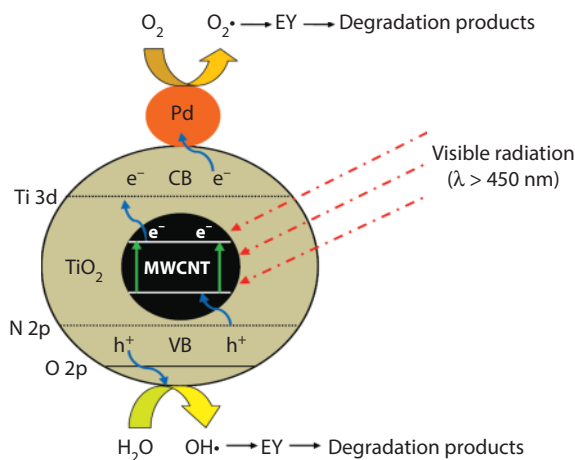


Figure 8.12 Photodegradation mechanism for eosin yellow using MWCNT/N, Pd-TiO₂ [112].

of TiO_2 onto their surface. This approach aimed at improving the CNT/ TiO_2 interface which is crucial for efficient electron transfer. Improved photocatalytic degradation of methyl orange was observed under visible light irradiation using the Pd-MWCNT/ TiO_2 nanocomposite. Its performance was superior to MWCNTs, P25 and Pd-MWCNTs. The proposed photocatalytic degradation mechanism in terms of the improved electron transfer is illustrated in Figure 8.13.

Basically, it was speculated that MO was excited by visible light and injected electrons into the conduction band of TiO_2 , which could then migrate into the MWCNTs skeleton which has a higher work function than TiO_2 . The electrons on the MWCNTs skeleton may react with adsorbed oxygen to form the superoxide radical or they are scavenged by the Pd nanoparticles due to their higher work function. The electrons on the Pd nanoparticles will react with adsorbed oxygen to form the superoxide radical and eventually the hydroxyl radical, which is extremely oxidizing [113]. Therefore, the Pd nanoparticles acted as electron transfer channel, thereby enhancing the visible light catalytic degradation of MO.

In a similar innovation, Wang and coworkers fabricated novel photocatalysts based on CNTs, graphene (GP) and gold-doped graphene (AuGP)-modified TiO_2 . Basically, TiO_2 was supported on CNTs and the entire CNT/ TiO_2 composite surface was coated with GP or AuGP through a hydrothermal method, as illustrated in Figure 8.14. The rationale of this photocatalyst design was to develop a photocatalyst with two-channel electron conduction paths and improve the photocatalytic performance of the composite.

It was observed that the prepared photocatalysts (CNT- TiO_2 /GP and CNT- TiO_2 /AuGP) had superior photocatalytic activity as compared to P25 for the degradation of MB under visible light irradiation. This suggested that the incorporation of CNTs, GP and Au improved charge separation

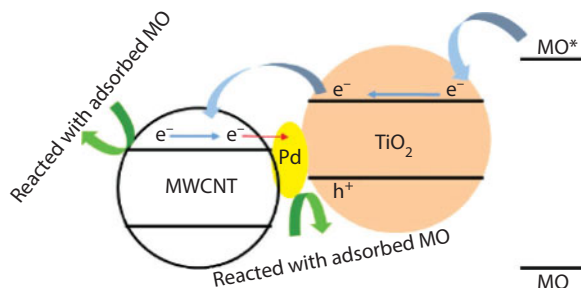


Figure 8.13 Proposed electron transfer process and degradation of MO on Pd-MWCNT/ TiO_2 under visible light irradiation [113].

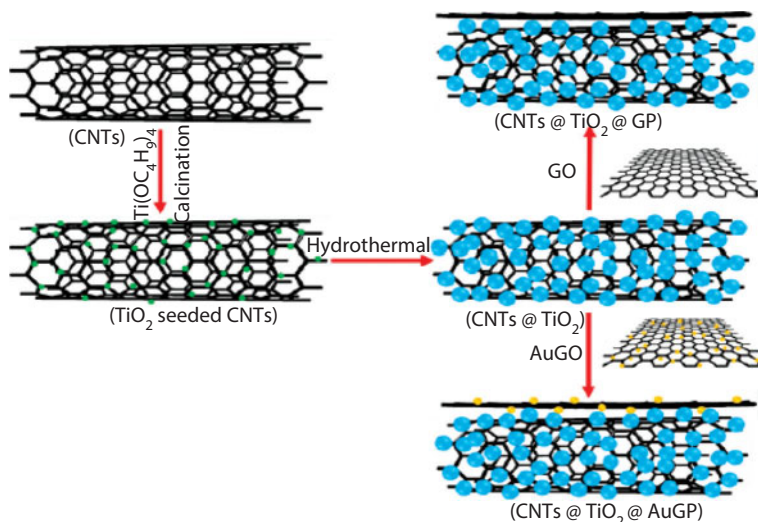


Figure 8.14 Schematic illustration of the preparation of the photocatalysts (CNT/ TiO_2 , CNT- TiO_2/GP and CNT- TiO_2/AuGP) [114].

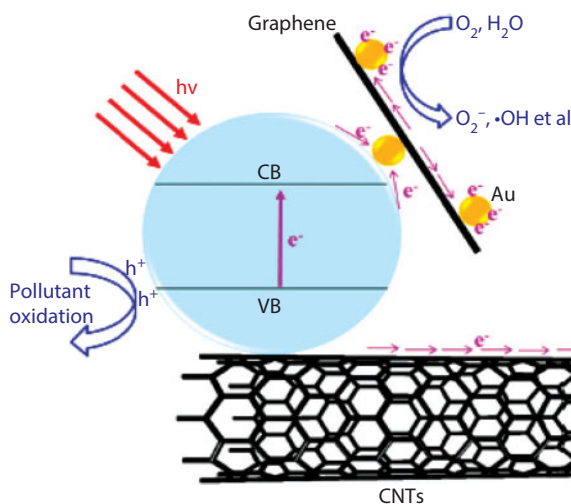


Figure 8.15 Proposed photocatalytic degradation mechanism of MB over CNT- TiO_2/AuGP [114].

in the semiconductor and also improved visible light absorption. The proposed photodegradation mechanism is presented in Figure 8.15.

According to the proposed two-channel electron conduction design of the nanocomposites, the TiO_2 nanoparticles were strongly bound on the

surface of the CNTs, which allowed injection of electrons from the inner side of TiO_2 nanoparticles into the CNTs skeleton. This lowered the recombination rate of the photogenerated species. In the case of GP-coated CNT- TiO_2 surfaces, the good electronic conductivity of GP played a key role in charge separation on the outer part of TiO_2 nanoparticles. Similarly, the Au nanoparticles on GP acted as electron sinks and the adsorbed electrons on Au were quickly transferred into the GP structure. This ensured efficient charge separation and formation of more hydroxyl radicals for dye degradation [114].

8.3.3.2.2.2 Dye Degradation Using other Carbon Nanotube/Semiconductor Photocatalysts under Visible Light Irradiation

Yan and coworkers [115] prepared a visible light responsive photocatalyst based on silver nanoparticles supported on MWCNTs. Rhodamine B was used as a model dye to investigate the photocatalytic properties of the nanocomposite. The observed photocatalytic activity was linked to the synergetic effect of the MWCNTs and Ag nanoparticles. The MWCNTs served as adsorbents for rhodamine B and as electron transmission channels. Silver nanoparticles served as electron traps, trapping electrons on the surface of the MWCNTs skeleton. Based on the recorded results, self-sensitization was proposed as the degradation mechanism, as illustrated in Figure 8.16.

It was inferred that rhodamine B is excited by the visible light and injects electrons into the MWCNT skeleton, which has a strong affinity for electrons. The MWCNTs skeleton transports the electrons freely with no resistance (ballistic effect). These electrons are trapped by the Ag nanoparticles on the surface, where they accumulate and react with oxygen adsorbed to form the superoxide radical and, eventually, the hydroxyl radical. These are important oxidizing species for dye degradation [115].

In another innovation, tungsten oxide (WO_3) nanoparticles were decorated on MWCNT and the nanocomposite was employed for the

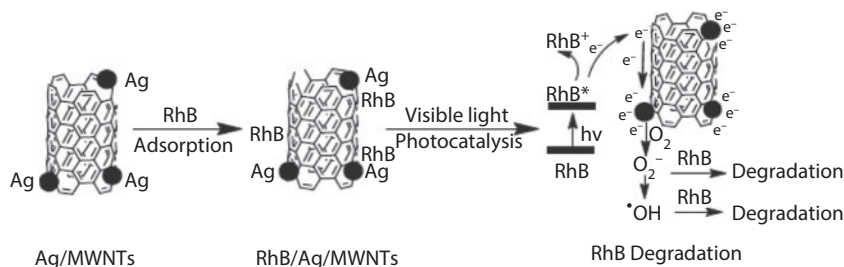


Figure 8.16 Proposed photodegradation mechanism of Ag-MWCNTs [115].

degradation of rhodamine B under solar light irradiation. The rationale behind this innovation emanates from the fact that WO_3 has interesting properties such as the small band gap (2.4–2.8 eV), relatively high oxidation power, high stability and is relatively non-toxic [116]. However, WO_3 displays poor photocatalytic activity due to the high recombination rate of the electron-hole pairs. Loading WO_3 on MWCNTs sought to improve its photocatalytic activity. Superior photocatalytic activity was observed for the MWCNT/ WO_3 nanocomposite compared to pure WO_3 . This was linked to the adsorption ability and electron transportation as a result of the strong interaction between CNTs and WO_3 . Furthermore, the MWCNTs were found to act as dispersing agents for WO_3 nanoparticles, minimizing agglomeration during degradation experiments. This provided a large surface area for photocatalysis. The degradation mechanism is illustrated in Figure 8.17. A similar photocatalytic degradation mechanism was put forward by Tian and coworkers [117] in a recent work on the use of MWCNT/ WO_3 nanocomposite prepared via a solvothermal route for the degradation of MB under visible light irradiation.

According to the proposed degradation route, WO_3 is excited by visible light, promoting electrons into the conduction band and leaving positive holes in the valence band which can react with water or hydroxyl groups to form the oxidizing hydroxyl radical. The conduction band electron is drawn by the MWCNTs skeleton due to the strong interaction between WO_3 and MWCNTs, where it reacts with adsorbed oxygen to form the superoxide

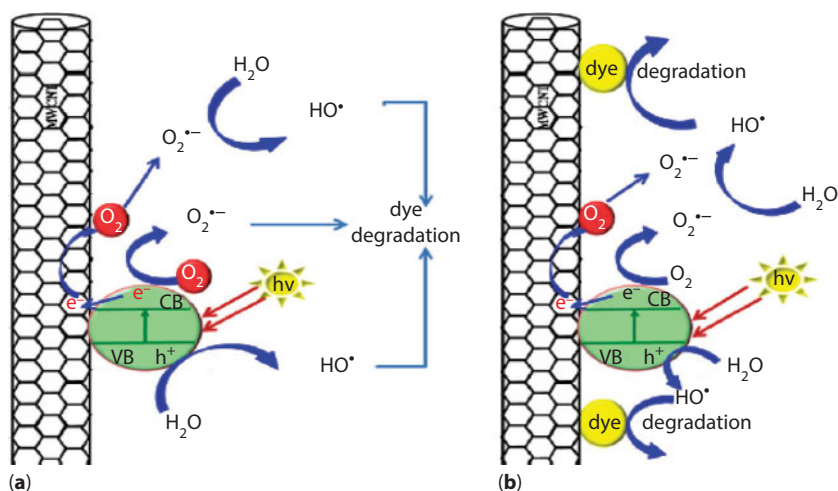


Figure 8.17 Photocatalytic degradation mechanism of MWCNT/ WO_3 [118].

radical which is also oxidizing. Moreover, the MWCNTs transferred the dye molecule from solution onto the surface of the photocatalyst [117, 118].

In order to harness the combined properties of CdSe nanoparticles and the carbonaceous nanomaterials (MWCNTs and graphene), nanocomposites based on CdSe loaded on each of the two carbonaceous nanomaterials were fabricated. The MWCNT/CdSe and CdSe/graphene nanocomposites were evaluated for the degradation of MB under visible light irradiation. Both nanocomposites displayed improved visible light activity, which was attributed to synergetic effect of the carbonaceous nanomaterials and CdSe nanoparticles. The inferred degradation mechanism is illustrated in Figure 8.18.

According to the proposed mechanism, the MWCNTs and graphene could be excited by visible light and inject electrons into the conduction band of CdSe. Similarly, CdSe can also absorb visible light and excite electrons from the valence band into the conduction band. This increased the electron density and redox reactions leading to the formation of the superoxide radicals, which are an oxidizing species. Moreover, the valence band hole reacted with water or hydroxide ions to yield the hydroxyl radical, which is a powerful oxidizing agent for organic dye degradation [119].

Samadi and coworkers [120] fabricated zinc oxide (ZnO)-nanofibers-doped MWCNTs by electrospinning method. The MWCNT/ZnO nanofibers composite showed improved photocatalytic activity as compared to pure ZnO nanofibers, both under visible and UV light irradiation, for the degradation of MB. This improvement was linked to the MWCNTs acting

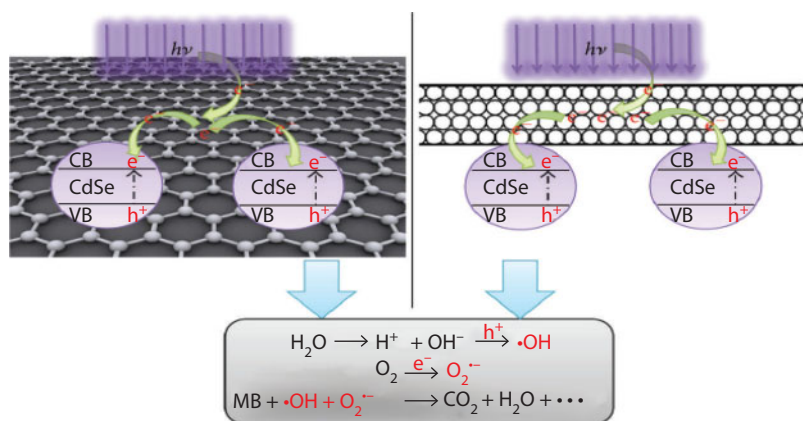


Figure 8.18 Degradation mechanism of MWCNT/CdSe and graphene/CdSe for MB under visible light irradiation [119].

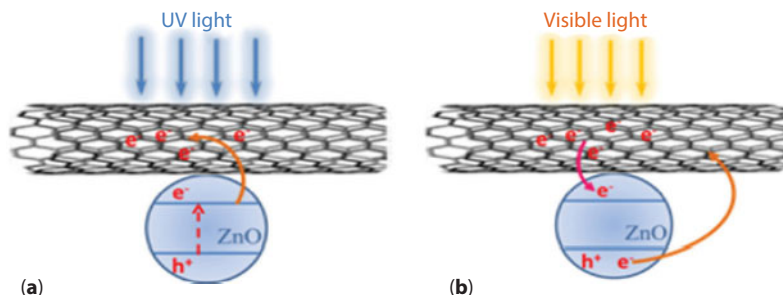


Figure 8.19 Degradation mechanism of MB on MWCNT/ZnO (a) under UV light and (b) under visible light irradiation [120].

as visible light sensitizers and the synergetic effect of MWCNTs and ZnO. Furthermore, a degradation mechanism was put forward as illustrated in Figure 8.19.

Under visible light irradiation, the MWCNTs served as visible light sensitizers, absorbing visible light and injecting electrons into the conduction band of ZnO. The electrons may react with adsorbed oxygen to form the oxidizing superoxide radical. On the other hand, the positively charged MWCNT skeleton would attract electrons from the valence band of ZnO, leaving a positive hole which reacted with water to form the hydroxyl radical which is primarily responsible for degradation of the dye. Under UV irradiation, the MWCNTs acted as electron sink, preventing electron-hole recombination [120]. In a similar innovation, zinc ferrite/multiwalled carbon nanotube ($\text{ZnFe}_2\text{O}_4/\text{MWCNTs}$) nanocomposite was prepared by a hydrothermal method. The nanocomposite was investigated for degradation of MB under visible light irradiation. Improved results were recorded for the MWCNT/ ZnFe_2O_4 nanocomposite compared to pure ZnFe_2O_4 , which could be linked to efficient charge separation by the MWCNTs. Furthermore, addition of hydrogen peroxide further improved the photocatalytic activity since it scavenges electrons to form oxidizing hydroxyl radicals [121].

8.4 Conclusion

Efficient treatment of textile effluent is an important goal not only due to environmental concerns but also to allow recycling of water and ensure adequate water supply for day-to-day operations. The use of nanotechnology-based innovations holds the future for efficient treatment

of dye pollution. Carbon nanotubes have proved to be versatile nanomaterials for dye removal. In carbon nanotube-based adsorbents, addition of carbon nanotubes resulted in great improvement of the adsorption properties of the resultant nanocomposite. This improvement could be attributed to the large surface area of carbon nanotubes, highly porous and hollow structure, light mass density and the strong interactions between carbon and hydrogen molecules. The use of polymer nanocomposites is very attractive since the polymer minimizes leaching of the nanomaterials into the treated water, which would otherwise pose serious post-treatment challenges. Furthermore, the fabrication of magnetic carbon nanotube-based nanocomposite adsorbents tackles the challenge of separating the adsorbent from the treated water. In this case, separation is easily achieved using an external magnetic field.

In addition to CNT-based adsorbents, numerous CNT-based semiconductor photocatalysts have been prepared and show potential for degradation of various dyes under visible and UV light irradiation. These photocatalysts exploit the unique properties of carbon nanotubes such as large surface area, high chemical and thermal stability, good mechanical properties and good electrical conductivity. Carbon nanotubes act as support for the semiconductor and also as adsorbents for the dye molecules onto the surface of the semiconductor, for degradation to take place. Moreover, during photocatalysis, carbon nanotubes serve as photogenerated electron transfer station, which ensures efficient charge separation. This improves the photocatalytic activity of the nanocomposite. Under visible light irradiation, carbon nanotubes serve as visible light sensitizers, which improve the visible light absorption property of the nanocomposite. The large surface area of CNTs is also important for high photocatalytic activity. Notably, in order to exploit the unique properties of carbon nanotubes, there has to be a strong interface between the carbon nanotube and the semiconductor to ensure efficient conduction of electrons.

Although nanomaterials promise to solve the problem of dye pollution, their intense utilization needs to be carefully monitored because their environmental behavior is still a subject of research and discussion. Therefore, efficient recovery and disposal after the treatment process needs to be considered to minimize secondary pollution.

Acknowledgements

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Advances in Nanotechnologies for Point-of-Use and Point-of-Entry Water Purification

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Abstract

Nanotechnology for water purification purposes has been an area of intensive research in the past two decades. This chapter reviews recent advances of nanotechnology (nanostructured materials) in small-scale water purification systems, i.e., point-of-use (POU) systems and point-of-entry (POE) devices. The POU system is the treatment process aimed at treating only water intended for direct consumption (drinking and cooking), typically at a single tap or limited number of taps. Point-of-entry (POE) treatment devices are those usually installed to treat all water entering a single home, business, school, or facility. The POU- and POE-based nanomaterials reviewed are new water purification technologies for removal of high priority pollutants such as microbial and heavy metals. These are (i) absorptive nanopolymers (i.e., cyclodextrin-based nanocomposite polymers), (ii) nanomembrane-based filters and (iii) other filters based on clay and antimicrobial nanofibers. Emphasis is placed on the various nanostructures (not the pollutants) that have been developed, focusing on their physicochemical properties and their impact in water purification globally.

Keywords: Nanotechnology, point-of-use (POU), point-of-entry (POE), nanomaterials, drinking water purification, absorptive nanopolymers, nanomembrane filters, ceramic-based nanofilters, nanofibers

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9.1 Introduction

Approximately 1 billion people in the world, mostly in developing countries, are without potable water and a further 2.6 billion people have no access to adequate sanitation [1]. Also, recent information obtained from the Water Project website reveals that more than 1 in 8 people in the world do not have access to safe drinking water; 1 out of every 5 deaths under the age of 5 worldwide is due to a water-related disease and nearly 80% of illnesses in developing countries are linked to poor water and sanitation conditions [2]. In addition to the socio-economic and environmental impact of poor water shortages [3], the physical, mental and financial wellbeing of people, particularly of susceptible groups such as children, the elderly and poor, are relatively linked to the availability of safe drinking water [4].

Clearly, the world is facing formidable challenges in meeting the rising demand for clean water. The available supplies of pure water are decreasing due to mismanagement, population growth, pollution and more strict health regulations [5]. It cannot be disputed that drinking water contamination has reached unavoidable levels in terms of the population size and economy affected. Evidently, without quality drinking water, all scientific efforts become but only ideas without any substantial practical improvement in human development [6]. The problems related to safe quality drinking water cannot be alleviated with one solution. Methods involving advanced techniques at the nanoscale still have to be probed and smart solutions with high performance must be developed.

The presence of hazardous pollutants in water remains a serious threat for water-supplying companies and municipalities. Organic, inorganic (especially heavy metals) and microbial pollutants are almost always present in water distribution networks. The presence of these contaminants in drinking water poses a major risk to human health and development in general [6]. Some of the common pollutants found in many aquatic environments are given in Table 9.1.

It must be appreciated that water treatment techniques for alleviation of these contaminants have been studied and many of them have been successful to some level, albeit involving high costs. As mentioned earlier, no one method has been found to manage all these pollutant [6]. Most of the conventional water purification methods employed have their limitations. Widely used disinfectants include chlorine, chloramine, ozone and UV light [14]. These disinfectants are able to destroy many bacteria but each one of them has its own drawbacks. For example, chlorine dissolves in water to form hypochlorous acid, which in turn reacts with natural organic matter (NOM) to form numerous disinfection by-products (DBPs), including

Table 9.1 Some common pollutants found in water systems.

Organic [7, 8]	Inorganic [6, 9]	Microbial [10–13]
Polychlorinated biphenyls	Arsenic	<i>Cryptosporidium</i>
Polyaromatic hydrocarbons	Lead	<i>Escherichia coli</i>
Dioxins	Mercury	<i>Salmonella vibrio</i>
Natural organic matter	Hydrogen sulphide	Helicobacter
Endocrine disrupting compounds	Chromium Cadmium Fluoride	Campylobacter

trihalomethanes, chlorinated biphenyls and other halogenated hydrocarbons, which are toxic [14]. Table 9.2 gives a summary of the pros and cons of some of the currently used technologies for the removal of inorganic and microbial contaminants in water [6].

The importance of POU and POE water purification systems cannot be over emphasized. While the purification of water by municipal water treatment plants is a viable process, the presence of contaminants at the final destination cannot be avoided. This is because the purified water has to be transported to the final destination, i.e., to taps at residential areas and public entities, which happens through underground pipelines. During this transportation, the water is likely to be contaminated by small traces of contaminants which could be toxic even at low concentrations (e.g., parts per billion or parts per trillion concentrations). Besides this possible contamination in pipelines, current water purification technologies are unable to remove some of the contaminants at such low levels. Many of the contaminants found in treated water are prone to bioaccumulation and become deadly after a while. This is a serious challenge that many water treatment plants face.

In addition, the quality of drinking water varies from country to country. For example, tap water produced in India can be very dangerous to someone visiting from another country such as South Africa or America. It is advisable that one carries their own bottled water or water filter to purify the tap water before drinking it or using it for cooking, when visiting such places.

Consequently, the number of research articles and patents involving the development of nanomaterials for POU/POE water purification has

Table 9.2 Review of conventional technologies utilized for drinking water purification [6].

	Reverse Osmosis	Granular Activated Carbon	UV-based Filtration	Electro-Dialysis	Distillation
Technology Description	• Flow of water across semi-permeable membrane on application of pressure	• Adsorption of contaminants on porous surface	• Works on the generation of free radicals from UV lamps	• Charge separation on application of electric field	• Reduced pressure evaporation of water followed by condensation
Pros	• Removes TDS, heavy metals, fluoride, pesticides, micro-organisms	• Removes VOCs, pesticides, excess chlorine, color, odor • High throughput	• Broad-range microorganism removal • High filtration capacity	• High TDS removal efficiency (~90%)	• Removes a broad range of contaminants • Reusable • Cost not proportional to TDS
Cons	• low recovery • brine disposal • High maintenance (membrane change in ~3 years) • Pretreatment	• Does not remove: Microbial contamination, TDS, Nitrates, Fluorides, Hardness	• Effectively degrades only micro-organisms • High costs	• Proportional increase in cost with TDS • Doesn't remove: pesticides, microorganisms	• High initial investment • Regular maintenance • Volatile organics are not removed

increased significantly since the role of nanotechnology was realized in the early 90s. This is manifested by the number of emerging products available in the market worldwide, e.g., ceramic water purifiers, the Lifesaver Bottle, the Lifestraw, the Aquaduct bicycle, PÜR®, etc. [15–17]. This chapter interrogates the types of nanomaterials that have been developed for this purpose and the extent to which they have been used commercially (if at all). Focus will be on the chemistry of the nanomaterials and a review of their efficiency to remove microbial and heavy metals from water. In particular, a recent picture of the current state of research outputs on absorptive nanopolymers (i.e., cyclodextrin-based nanocomposite polymers), nanomembrane-based filtration systems and other filters based on clay and antimicrobial nanofibers will be presented.

9.2 Nanotechnology-Enabled POU/POE Systems for Drinking Water Treatment

The role of nanotechnology in water purification has presented itself as a viable option to solve challenges relating to drinking water quality. Nanotechnology or nanomaterials technology has been defined in many ways. Most definitions revolve around the study and control of materials at length scales below 100 nm [18, 19].

The definition of nanomaterials is broad. However, nanomaterials are generally categorized as materials that have structured components with at least one dimension less than 100 nm. Nanomaterials can be created by “top down” techniques, producing very small structures from larger pieces of material; for example, by etching to create circuits on the surface of a silicon microchip. They may also be constructed by “bottom up” techniques, atom by atom or molecule by molecule. This can be done by self-assembly, in which the atoms or molecules arrange themselves into a structure due to their natural properties. Crystals grown for the semiconductor industry provide an example of self-assembly. Another approach is to use tools to move each atom or molecule individually. Although this ‘positional assembly’ offers greater control over construction, it is currently very laborious and not suitable for industrial applications [20, 21].

The advantages of nanomaterials can be observed from their size and surface effect properties. Quantum size effects result in unique mechanical, electronic, photonic, and magnetic properties of nanoscale materials. The chemical reactivity of nanoscale materials is greatly different from the macroscopic form (e.g., the color of bulk gold is yellow yet gold

nanoparticles are black). As the size of materials decreases, the ratio of surface atoms increases. Due to the high surface-to-volume ratio associated with nanometer-sized materials, a tremendous change in chemical properties is also achievable [20, 21]. In the case where the nanomaterials are used to purify water through adsorption, this leads to the availability of higher numbers of atoms/molecules on the surface for adsorption of contaminants. Accordingly, the surface energy available with each adsorbent particle also increases significantly. Consequently, this provides many advantages to drinking water purification [6]:

1. Effective contaminant removal even at low concentrations.
2. Less waste generated post-treatment as less quantity of nanomaterial will be required vis-à-vis its bulk form. This happens since more adsorbent atoms/molecules are present per unit mass of the adsorbent and thus are actively utilized for adsorption.
3. Novel reactions can be accomplished at the nanoscale due to an increase in the number of surface atoms (i.e., surface energy), which is not possible with the analogous bulk material. An example of one such process is the use of noble metal nanoparticles for the degradation of pesticides which cannot be done by noble metals in their bulk form.

The large scale use of nanotechnology-derived water purification systems remains a challenge because of the costs involved in the synthesis and fabrication of the nanomaterials. As a result many of the nanomaterials become restricted for use in low-scale POU and POE systems as filters. Many of the materials are usually synthesized as nanoparticles and can either be ceramic or polymeric. The most feasible nanotechnology-enabled water filtration technologies on a larger scale are the membrane technologies (nanofiltration and reverse osmosis membranes). Membranes are remarkable materials which form part of our daily lives. Their long history and use in biological systems has been extensively studied throughout the scientific field. The preparation of synthetic membranes is, however, a more recent invention which has received a great audience due to its applications [22].

Membranes, based on their composition and conditions of fabrication, have shown different types of morphologies. However, most membranes of practical use are mainly of asymmetric structure [23, 24]. Separation in membrane processes takes place as a result of differences in the transport rates of different species through the membrane structure, which is

usually polymeric or ceramic [23]. The versatility of membrane filtration has permitted its introduction to many processes with suitable feed stream properties. Although membrane separation does not provide the ultimate solution to water treatment, it can be economically connected to conventional treatment technologies by modifying and improving certain properties [23–25].

The sections that follow present a closer look at the nanomaterials of interest, i.e., absorptive nanocomposite materials (mainly cyclodextrins), nanostructured membranes, and other materials such as polymer clay nanocomposite materials and ion-imprinted polymers and nanofibers.

9.3 Absorptive Nanocomposites Polymers Based on Cyclodextrins

9.3.1 Background

The removal of pollutant molecules from water by nanostructured materials can either be by adsorption, e.g., attachment of molecules onto the surface of activated carbon, or by absorption, e.g., encapsulation of molecules into the cavities of cyclodextrin (CD) or zeolites through a host-guest inclusion mechanism [26–28]. It is the microstructure and chemical nature of the materials that largely determines whether it will adsorb molecules onto its surface or absorb them into its cavities. For adsorption to take place the materials must have a high surface area of active sites (usually micropores) that provide binding sites for other molecules (usually organic) to attach to them. For absorption to take place the materials must have hydrophobic cavities that will trap hydrophobic molecules (the contaminants) [27].

Pure CD polymers and activated carbon have been shown to be efficient in removing organic pollutants but not inorganic (heavy metal) and biological pollutants. In order to remove inorganic and biological contaminants, a combination of materials is used in many POU and POE filters [15–17]. These are usually packed in columns in separate layers such as the LifeStraw and the Lifesaver Bottle which contain several layers of ceramic, activated carbon and silver nanoparticles for removal of pollutants. The birth of nanotechnology has brought forth advanced systems that are more viable for use as POU and POE water purification systems. The ability to use chemistry to prepare advanced mixed matrix and nanocomposite materials has shown that these new materials are smarter in many ways. For example, advanced nanocomposites or mixed matrix material

can remove all undesired pollutants at once, they can be recycled numerous times, and large quantities are often not necessary because of their high adsorption/absorption efficiencies.

9.3.2 Synthesis and Properties of Cyclodextrin-Based Polymers

Cyclodextrin-based nanoporous polymers, also called nanosponges, were first reported for use in drinking water purification by Li and Ma in 1999 [26, 27]. These nanosponges were shown to be effective in removing various organic pollutants in water including odor-causing molecules such as geosmin and 2-methylisoborneol from water at parts per trillion levels [26, 27, 29, 30].

Three common types of cyclodextrins (α -CD, β -CD and γ -CDs), referred to as the first generation or parent CDs, are known. These possess six, seven and eight glucose units, respectively, with α -(1, 4)-linkages forming a ring (Figures 9.1 and 9.2). The β -CD is the most accessible,

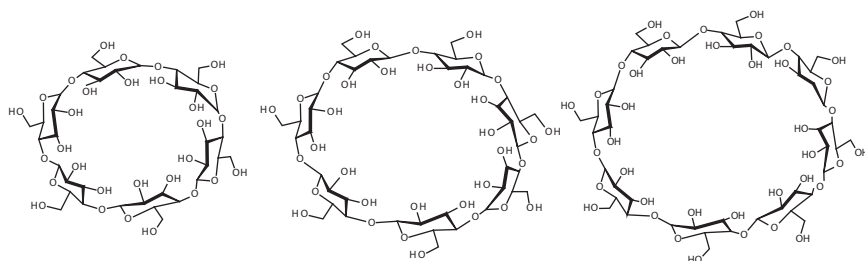


Figure 9.1 Structures of α -, β - and γ -CDs showing 6, 7 and 8 glucopyranose units respectively.

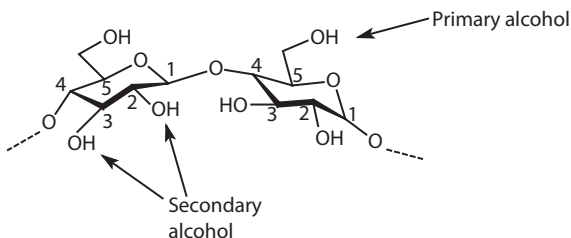


Figure 9.2 Illustration of α -(1, 4)-linkages and the primary and secondary alcohols of a CD molecule.

lowest in cost and generally the most useful. It has been extensively used in many studies [26–30]. Higher molecular weight CDs have been isolated and synthesized, although their use in industry is not as common [28, 31].

A unique characteristic feature of CDs is that they possess toroidal shapes that form well-defined cylindrical cone-shaped cavities of about 8 Å deep and 5–10 Å in diameter, depending on the number of oligomers [28, 32]. The cone is formed by the carbon skeleton of the glucose units and the glycosidic oxygen atoms that are in between them. The primary hydroxyl (OH) groups of the glucose units are located at the narrow end (also called primary face) of the cone and the secondary OH groups are at the wider secondary end (Figure 9.3).

The different types of CDs possess different characteristic features. The main properties and dimensions of α -, β - and γ -CDs are summarized in Table 9.3 [33].

As indicated in Table 9.3, the β -CD is the least soluble in water when compared with α -CD and γ -CD. Recent studies have explained this unusual solubility of β -CD in water by analyzing trajectories generated in molecular dynamics (MD) computer simulations and pulse-field-gradient spin-echo nuclear magnetic resonance (PGSE NMR) experiments [34]. The investigation revealed that the twisting motion of the macrocyclic ring and the tilting motion of the individual glucose monomer units with respect to the normal plane of the CD rings essentially influenced the internal flexibility of CDs. The analyses indicated that β -CD has the most restricted motion in solution [34]. This property renders the β -CDs a first priority if water insoluble CD polymers are to be synthesized.

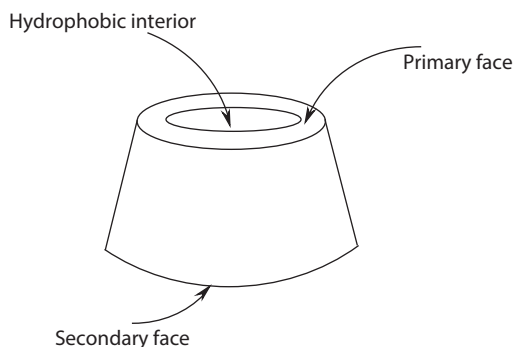


Figure 9.3 Illustration of the conical-shaped cyclodextrin molecule.

Table 9.3 A summary of the physical properties of cyclodextrins [33].

Property	α -cyclodextrin	β -cyclodextrin	γ -cyclodextrin
Number of glucose units (n)	6	7	8
MW (g/mol)	972	1135	1297
Water solubility at 25°C (g/100 mL)	14.5	1.85	23.2
Specific rotation	150 $\pm$ 0.5	162 $\pm$ 0.5	177.4 $\pm$ 0.5
Internal Diameter (Å)	4.9	6.2	7.9
External diameter (Å)	14.6	15.4	17.5
Cone height (Å)	7.9	7.9	7.9
Cavity volume (Å ³)	174	262	427

The major reasons for the preparation of CD derivatives are generally the following:

- modification of solubility,
- modification of complexation abilities (stability constant, guest selectivity); and
- introduction of groups with specific functions (catalytic).

CDs are generally soluble in water and in most organic solvents. This property is attributed to the presence of primary and secondary hydroxyl groups that are on the outside of the CDs. The cavity of the CD ring consists of a ring of C-H groups and a ring of glycosidic oxygen atoms. This renders the cavity of the CD rings less polar than the outside. Another important feature is that, although CDs have a hydrophilic surface, they contain hydrophobic cavities that enable the inclusion of the hydrophobic guest molecules into these cavities.

Since the parent CDs are soluble in water and some organic solvents (e.g., DMF and DMSO) they cannot be used directly in the absorption of pollutants from water. Their shortcoming is that they easily release the absorbed organic molecules back into the water when they dissolve, thus making recovery of the pollutants a problem. As a result, CD polymers that are insoluble in water and possess enhanced affinity for organic contaminants in water have been synthesized to solve this problem [26, 27, 35]. The design of these CD polymers is based on either the reactivity of

the hydroxyl groups or the ability to form host-guest complexes through hydrophobic forces [31, 32]. The mode in which these CD polymers can quench organic contaminants from drinking water is discussed later.

To bind the CD units together, the hydroxyl (OH) groups on the CDs are treated with bifunctional diisocyanate monomers to obtain highly crosslinked nanoporous polymers. Simple monomers that link the CD monomers include hexamethylene diisocyanate (HMDI) and toluene-2, 6-diisocyanate (TDI). Other studies have suggested more complex methods for the synthesis of these polymers. These involve the pre-modification (e.g., monofunctionalization of OH groups) of the CDs to yield polymers with diverse properties. These polymers can be prepared in the form of granular solids, powders or films by varying the ratios of the reacting species as well as the temperature [26].

The relatively nonpolar cavity in comparison to the polar exterior enables CDs to form inclusion compounds with hydrophobic guest molecules in aqueous solution (Figure 9.4). The interaction between the CD and the organic guest is purely hydrophobic; no covalent bonds are broken or formed during the formation of inclusion complexes [31, 32]. The main driving force of the complex formation is the displacement of enthalpy-rich

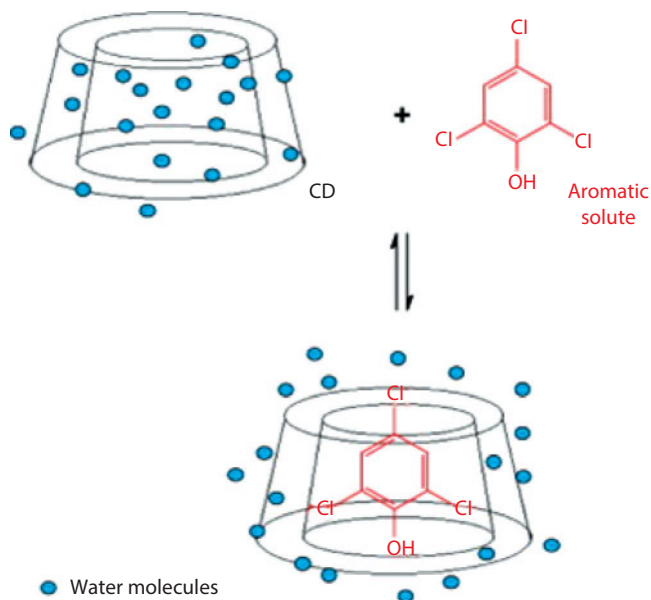


Figure 9.4 Formation of an inclusion “host-guest” complex between a CD and a pollutant in water.

water molecules from the CD cavity by more hydrophobic guest molecules in the solution to acquire a nonpolar-nonpolar association, and decrease of the CD ring strain resulting in a more stable lower energy state. However, the ability to form hydrophobic interactions represents only one of the requirements. Another important requirement is that the guest molecule must be able to fit into the cavity of the CD (i.e., geometric compatibility) [32, 36, 39].

In addition to hydrophobic interactions and geometric compatibility, many other factors generally play a role during inclusion complex formation. These include polarity of the guest molecule, the solvent and molecular weight of the guest. However, according to Martin Del Valle [31], the equilibrium to form the inclusion complex is driven by four energetically favorable interactions. These are:

1. The displacement of polar water molecules from the nonpolar CD cavity. This is a very rapid process and often occurs within minutes.
2. The increased number of hydrogen bonds formed as the displaced water returns to the larger pool.
3. A reduction of the repulsive interactions between the hydrophobic guest and the aqueous environment.
4. An increase in the hydrophobic interaction as the guest enters the nonpolar cyclodextrin cavity. This equilibrium may take longer to attain and upon entering the CD cavity, the guest molecule makes conformational adjustments in order to take maximal advantage of the weak van der Waals forces that exist.

Most frequently the complex formed is in a 1:1 ratio, where one CD molecule includes one organic guest molecule [32, 39–41]. The general thermodynamic equation can be represented as:



Where: S – organic pollutant (guest)
 CD – cyclodextrin polymer (host)
 S·CD – inclusion complex

The thermodynamic equation for equilibrium reaction constants may be used to define the K value of the inclusion complexes. Generally, the formed inclusion complexes can be isolated as stable crystalline complexes and the equilibrium is established between dissociated and associated

species upon dissolving these complexes. This is expressed by a complex stability constant K_a , which can be calculated from the equilibrium equation as follows:

$$K_{1:1} = \frac{[S \cdot CD]}{[S][CD]}$$

The parameter $[S]$ is the molar concentration of the guest, $[CD]$ and $[S \cdot CD]$ are the concentration of the cyclodextrins and inclusion complex, respectively. The K value is defined in a similar way with nanoporous polymers during polymer inclusion. The equilibrium formed involves a solid-liquid interface between the solid polymers and liquid water sample. However, in such a case, the solid species are designated as unity and the equilibrium can be simplified [26].

It is also possible to form inclusion complexes where the guest molecules are significantly larger than the CD cavity. This is done in such a way that only certain groups or side chains penetrate into the CD cavity. A 2:1 complex (CD : guest) may be formed when the guest is too large (long) to find complete accommodation in one cavity and having its other end also susceptible to complex formation [39, 40]. Other ratios including 1:2, 2:2, or even more complicated associations have been reported [32]. Be that as it may, no universal method exists for the formation of CD inclusion complexes. The methods used in this research are designed by taking into consideration the objectives of their final use and the nature of pollutants.

9.3.3 Application of CD-Based Nanocomposite Polymers in the Removal of Heavy Metals and Microbials from Water

As can be seen, CD polymers are suitable for absorbing organics due to their hydrophobic nature. However unlike activated carbon, CDs can be functionalized and polymerized with other nanomaterials that can enhance the absorption capacity or make them multifunctional by making them absorb and adsorb the various contaminants that can be found in water. As a result smart “advanced” composite materials can be obtained. However, it takes advanced technologies to characterize and study such materials.

Salipira *et al.* polymerized multi-walled carbon nanotubes (MWCNTs) with β -CDs to improve the stability of the CD polymers. This system was tested for the removal of trichloroethylene (TCE) from water and was found to be effective even after recycling it more than 20 times [42, 43]. Recently, Lukhele *et al.* improved this system by dispersing silver nanoparticles onto the MWCNTs and polymerizing with the β -CDs. Figure 9.5

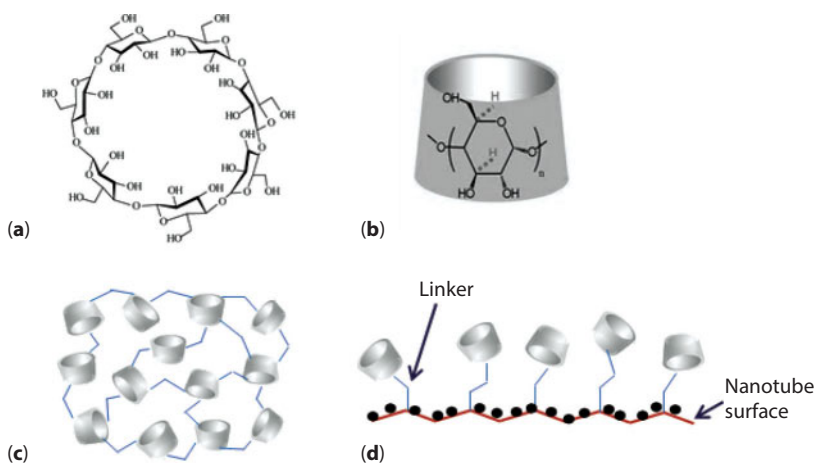


Figure 9.5 (a) The molecular structure of β -CD, (b) a 2-D image showing the bucket structure of the β -CD, (c) the formation of β -CDs polymer using a linker, and (d) the formation of a hybrid system of Ag/N-CNT/ β -CD polymer nanocomposite using a linker.

shows a schematic representation of beta-CD, β -CD polymer, and a visualization of the nanocomposite matrix. The resulting composite material was shown to effectively destroy bacteria (*E. coli*) in water [44].

Mamba *et al.* synthesized oxidized MWCNT-CD polymers and explored the possibility of using them for the remediation of heavy metals in the aquatic environment. The performance of the polymer was matched against pristine and oxidized MWCNTs. The polymer was found to perform better at lower concentration (10 mg L^{-1}) with adsorption capacities of 68.0 and 3.89 mg L^{-1} for lead and cobalt respectively [45]. Arkas *et al.* synthesized organic/inorganic hybrid filters based on dendritic and cyclodextrin “nanosponges” for the removal of organic pollutants from water. It was observed that polycyclic aromatic hydrocarbons (PAHs) could be removed very efficiently (more than 95%), and final concentrations of several ppb (ng/L) are easily obtained. Representatives of the pollutant group of trihalogen methanes (THMs), monoaromatic hydrocarbons (BTX), and pesticides (simazine) could also be removed (>80%), although the filters were saturated considerably faster in these cases [46].

Mhlanga *et al.* recently reported the synthesis of a three component water purification system containing β -CD and Ag nanoparticles dispersed on nitrogen-doped carbon nanotubes (N-CNTs). This polymer nanocomposites system was prepared under microwave irradiation in an industrial microwave for the first time. Polymerization of the N-CNTs with β -CD using hexamethylene diisocyanate as a linker could be achieved within

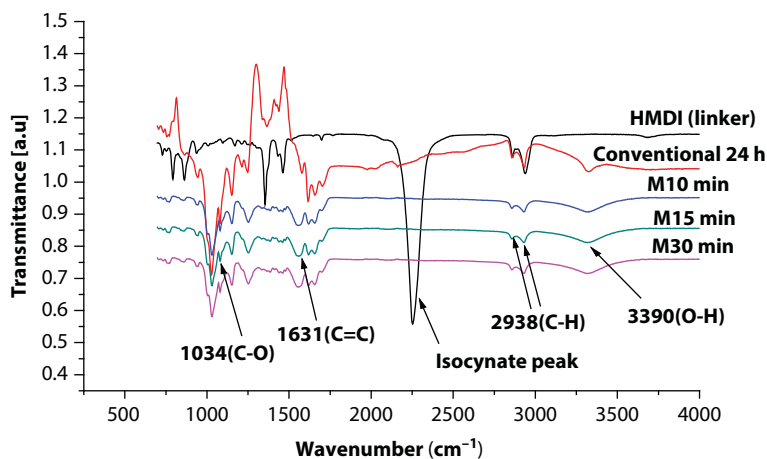


Figure 9.6 FTIR spectra of the polymer nanocomposites prepared using conventional polymerization and microwaved-induced polymerization showing the absence of the isocyanate peak. The absence of the peak suggests complete polymerization.

5 min of microwave irradiation time while stirring in a nitrogen atmosphere. The same reaction typically takes between 16–24 h under refluxing in a round bottom flask, as confirmed by infrared (IR) spectroscopy (Figure 9.6) [47].

The components of the polymer matrix were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure 9.7). The TEM revealed that the Ag nanoparticles were uniformly attached onto the surface of the N-CNTs. The nanoparticles had diameters ranging between 3–5 nm. A majority of the N-CNTs had outer diameters ranging between 30–40 nm.

Another recent study prepared cyclodextrin-ionic liquid complexes for the removal of organic and inorganic contaminants from water. Ionic liquids (ILs) have demonstrated the ability to extract heavy metal ions from water. The study demonstrated a technique that is capable of removing organic and inorganic species from water simultaneously. The CD moiety in the polymer retained its traditional role of absorbing organic contaminants; the IL component will perform the role of extracting the heavy metals present in water. The CD-IL polymers were effective at the removal of organic and inorganic pollutants from water. The β -CD-IL polymer showed high absorption efficiency for both organic (80% with respect to PNP) and inorganic (100% with respect to Cr^{6+}) pollutants. The CD-IL polymers showed very little affinity for cadmium, suggesting that the CD-IL polymers were not suitable for the absorption of Cd^{2+} from an aqueous media.

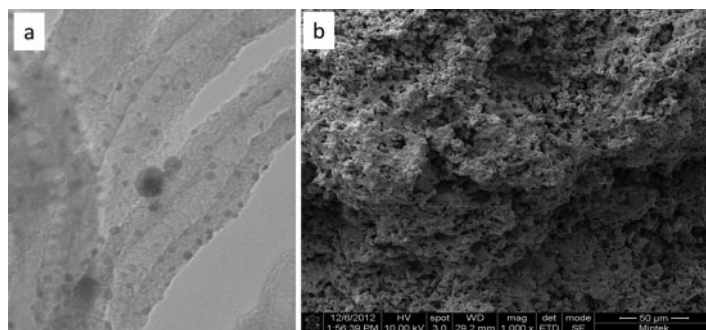


Figure 9.7 (a) A TEM image showing nanoparticles of Ag dispersed on N-CNTs, and (b) an SEM image of a Ag/N-CNT/ β -CD nanocomposite polymer matrix synthesized under microwave irradiation.

It was found that the absorption efficiency of the CD-IL polymers was generally retarded when a synthetic mixture of organic and inorganic pollutants was analyzed. This therefore revealed that the organics and inorganics compete for complexing sites of the CD-IL polymers [48].

A comprehensive survey shows that the CD-based composites nanomaterial has not been used in commercial POU filters available to the public. The major challenge holding back the commercialization of the materials is that while the CDs themselves are not toxic and biodegradable, the carbon nanotubes are still undergoing tests to ascertain their toxicity. The materials have, however, been shown to be suitable for use as POU or POE filtration materials.

9.4 Nanotechnology-Based Membrane Filtration

9.4.1 Background

Membrane filtration technologies present a promising opportunity and effective solution for delivering adequate supplies of high water quality suitable to meet human, environmental and industrial needs. Membrane technology was introduced in water treatment in the 1950s for the purpose of desalination of seawater, brackish water and groundwater [49]. Today membrane technology is one of the most supreme water treatment technologies to provide safe and sustainable drinking water. As technological advancements are made in the area of membrane synthesis, operating costs will continue to decline. Certainly, all the pressure-driven membranes (microfiltration [MF], ultrafiltration [UF], nanofiltration

[NF], and reverse osmosis [RO]) would be easily integrated into filtration systems/devices such as filters for improved water treatment for domestic use, and nanotechnology application would be in the forefront of this development.

Essentially, a membrane will allow the passage of water molecules while impermeably preventing the passage of other species such as salts (ionic species), suspended solids, e.g., microorganisms and dissolved solids, through selective separation [50, 51]. Whether species will pass through a membrane or a membrane film depends mainly on the properties of the membrane and the characteristics of the particular species. These properties will include among others porosity, permeability efficiency, hydrophilicity, surface area and roughness. The demand for membrane application in many aspects of the overall water cycle, production of drinking water and processing of water, industrial process and wastewater treatment, municipal sewage treatment and treatment of groundwater, is escalating daily. Many researchers have now started investigations into modifying the conventional techniques or devising new methodologies for membrane fabrication employing nanotechnology processes.

9.4.2 Procedures for Membrane Fabrication

Synthetic membranes have been increasingly applied in separation processes since the first integrally asymmetric flat sheet membrane of cellulose acetate was fabricated [52, 53]. The asymmetric membranes made from synthetic polymers, copolymers or blends by a phase inversion method have been the most promising and dominating in the membrane market. However, research into the development of new membrane techniques is still a major challenge and the basic understanding of mechanistic phenomena involved in membrane formation is still lacking. This is due to the difficulties encountered during the production processes.

Several methods for fabricating membranes for water purification exist. These include among others (i) the phase inversion method, (ii) the dip-coating process and (iii) the interfacial polymerization method. Diverse preparation methods, many modification techniques and a diverse range of polymers have been summarized in several reports [50, 52]. Many synthetic polymers such as cellulose acetate, polysulphone (PSf), polyethersulphone (PES), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and polyolefin have been frequently used as membrane materials. However, the use of PSf and PES as membrane backbones has been investigated widely [54, 55]. The methods have been used to make several membrane types including mixed matrix membranes, composite membranes,

etc. The objective of this section is not to discuss these processes but to explore the use of nanomaterials as functional additives during the preparation of membrane and/or membrane filters. However, most of these are either still prepared at laboratory scale or are in the development phase of commercialization.

9.4.3 Mixed Matrix Membranes

Mixed matrix membranes (MMMs) are an interesting form of membranes which are made up of polymeric membranes embedded with functional particles (e.g., nanomaterials). Mixed matrix membranes were initially developed for gas separation processes in which different types of polymers and rigid filler materials such as zeolites were used [56, 57]. The selectivity of the adsorption of ionic species is achieved as a combination of the permeation rates of the substance through the polymer and the filler material. Initially, molecular sieves were incorporated by dispersing zeolites in rubber polymers to prepare MMMs [58]. Zeolites were recently dispersed in glassy polymers added in a membrane [59]. Owing to their structures, numerous types of functional particles can be embedded in the polymeric matrix to tailor the structure of the membrane to specifically fit the desired application in water treatment. Recently, polysulfone/cyclodextrin-based MMMs were synthesized using the phase inversion method. The preparation and characterization of PSf/ β -CDPU membranes have been previously reported [60]. The authors focused on the general chemistry, morphology, thermal properties, and membrane efficiency in cadmium removal (*ca* 70%) from water, as well as the mechanical strength of membranes.

9.4.4 Composite Membranes and Nanomembranes

Composite membranes are a newly developed membrane type which exhibit superior properties, e.g., mechanical strength (provided by the porous support) and membrane separation efficiency (provided by the casting layer). The functionalization of hydrophilic membranes via the crosslinked structure significantly reduces membrane swellability to achieve high selectivity [61]. These types of membranes can form organic–inorganic hybrids which enhance thermal, chemical and mechanical properties and have great removal efficiencies. Okumuş *et al.* [62] demonstrated an increase in the polyacrylonitrile-based zeolite-filled membranes flux with a decrease in membrane selectivity. Composite membranes, therefore, provide combined advantages of superior separation efficiency of the rigid adsorptive

inorganic materials and perfect membrane forming property of organic materials.

On the other hand, nanomembranes are commonly manufactured using organic polymer-based nanocomposite materials having a thickness of less than 100 nm and are used as filters for the separation of liquids and gases at a molecular level [63]. These materials are a mixture of organic polymers and a net of silica nanoparticles. The passage of molecules through nanomembranes depends on the size of the holes in the net. Nanomembranes have found applications in seawater desalination, water purification, and in the removal of pollutants from exhaust gases. The method usually used in nanomembrane preparation is layer-by-layer assembly. This method provides precise control over the composition of the membrane and further enables the addition of a variety of components to the membrane. Nanoparticles and nanotubes (carbon) could be used to tailor the optical, mechanical, and electronic properties of the membrane.

Nanotechnology is increasingly gaining popularity in the water purification arena. Examples of materials commonly used in water treatment are nanomaterials (e.g., zeolites, titanium dioxide, dendrimers, etc.), nanoparticles (e.g., Ag, Fe nanoparticles), etc. These could include NF and UF membrane modules, media filters comprising nanofibers, carbon nanotubes (CNTs), and metal nanoparticles and many other products that are produced from nanotechnology development. In addition, nanotechnology is being used to improve conventional ceramic and polymeric water treatment membrane material through different ways. Many nanomaterials such as zeolitic and catalytic nanoparticle-coated ceramic membrane, aligned nanotube membrane and hybrid inorganic nanocomposite membranes have been used [64]. The nanomaterials used, though not exhaustive, are discussed in the subsequent sections.

9.4.5 Nanomaterials in Membrane Fabrication

The strong interest in preparing new nanomembranes composed of shaped carbon nanomaterials and nanosized inorganic materials is mainly due to their enhanced properties, such as high selectivity, higher hydrophilicity and enhanced fouling resistance. It is of noteworthy importance, however, that very limited reports have focused on the use of catalytic nanomaterial to develop new nanotechnology-enabled membranes particularly for water treatment or for use as filters. Furthermore, nanoparticles such as Al_2O_3 , Ag_2O , SiO_2 , and zeolites have high surface areas and could be used as adsorbents/membrane functional materials. However, because of the fine pores on their surfaces, not all the water can easily reach the active

surfaces as they are easily plugged. This small size of nanomaterials creates a major challenge since these fine particles cannot just be added to drinking water (but must be incorporated into a filtration medium). This technique allows for contaminants to readily interact with the active medium. In this form, these nanomaterials could be used for the development of filters by employing the physicochemical properties of nanomaterials for targeting specific contaminants from water.

As highlighted earlier, inorganic oxide nanoparticles such as ZrO_2 , SiO_2 and TiO_2 are one type of nanomaterials that have been given considerable attention. These have been blended with PSf membranes because of their incredible ability to improve membrane properties such as permeability, selectivity, thermal resistance and flux decline design [65]. Further, it has been reported that the PSf/ ZrO_2 membranes increase the permeability of membranes but decrease the rejection of dextran [66]. The addition of SiO_2 nanoparticles to PSf membranes also increases the permeability and reduces the fouling by oil and greatly enlarges the membrane pore sizes. This enlargement is caused by the agglomerated silica nanoparticles and can be prevented by the addition of PVA [67]. Polyaniline nanoparticles when incorporated to PSf membranes yielded improved membrane permeability and lower fluxes for BSA solution [68].

In a recent study, ZnO nanoparticles (with sizes between 21 and 23 nm) were incorporated into UF PSf membranes using the phase inversion method and using 1-methyl-2-pyrrolidinone as a solvent for an even dispersion of ZnO nanoparticles [69]. The mean pore sizes of the composite membrane were larger compared to the mean size of pure PSf membrane. Hence, the permeability of the composite membrane was higher, while the fouling by oleic acid was lower compared to a pure PSf membrane. The thermal stability of the bare membrane significantly improved with the addition of ZnO nanoparticles. Alumina nanoparticles were used in the modification of a polyamide membrane via the *in-situ* interfacial polymerization [70]. The addition of Al_2O_3 into nanocomposite membrane yielded improved flux permeates and increased salt rejection. In addition, the membrane also showed an enhanced hydrophilicity. The PVDF- Fe_3O_4 UF membranes were prepared in a parallel magnetic field by using various dosages of Fe_3O_4 nanoparticles; the result showed that when the amount of Fe_3O_4 added into the membrane was below 65 wt% there were no changes observed in the flux or the fouling-resistance ability of a PVDF- Fe_3O_4 ultrafiltration membrane [71].

TiO_2 nanoparticles have been incorporated to either PSf or PVDF membranes through the phase inversion and spinning processes for the removal of humic acid and bacteria from water and fouling reduction

[72]. Luo *et al.* [88] fabricated Ti nanoparticles/PES membranes by self-assembly through the coordination of sulfone and ether or hydrogen bonding, as shown in Figure 9.8. In another study, SiO_2 and TiO_2 nanoparticles were added to polyester through silica coating at 80°C to degrade ammonia, nitrates, PAHs, etc., from water [73]. Ni/Fe bimetallic nanoparticles-incorporated cellulose acetate membranes were used to remove trichloroethylene [74]. A two-step sol-gel technique was used to make Ag- TiO_2 /HAP/ Al_2O_3 MF membranes at 500°C [75]. The membranes exhibited high removal efficiencies for humic acid ($>88\%$). The Ag nanoparticles and ZnO nanoparticles incorporated into PSf membrane were prepared for reducing fouling by oleic acid, biofouling resistance and virus removal [76].

Recently, polysulfone-cyclodextrin composite NF membranes were prepared using different types of casting solvents such as N-Methyl-2-Pyrrolidone (NMP), DMSO, DMAC, and DMF [77]. It was reported that the hydrophobicity of the solvent does indeed affect the performance of the membrane, as it can be determined by water permeability. The result showed that the change of membrane morphology depends on the demixing behavior of the polymer and solvent volatility combined with

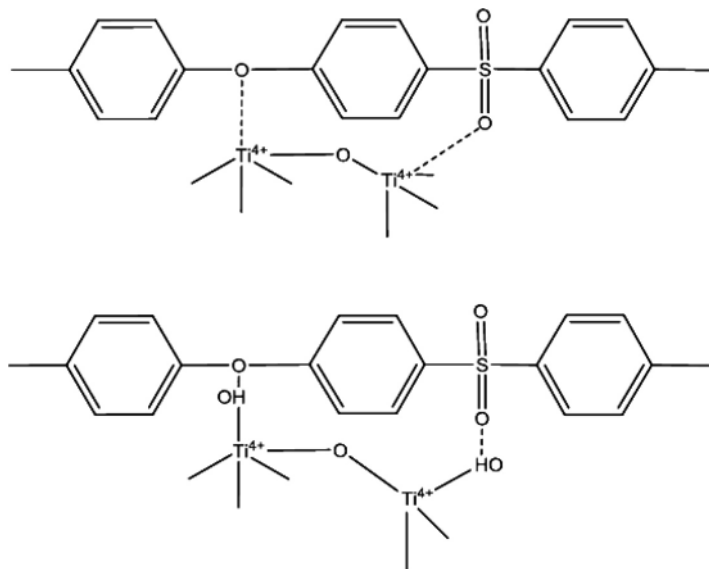


Figure 9.8 Self-assembly of Ti nanoparticles to PES membranes by coordination of sulfone and ether or hydrogen bonding [85].

polymer-solvent interactions, and it can be controlled by changing the casting solvent [77].

The method of coating and crosslinking was used to prepare N,O-carboxymethyl chitosan (NOCC)/PSf membranes. The study demonstrated the importance of varying the NOCC concentration on the rejection and the flux [78]. The PVA/PVC composite membranes were prepared by the dip-coating method. The membrane was coated with PVA solution two times to determine its effects on the morphology, structure and performance of hollow fiber nanofiltration membranes (HFNF). The results revealed that the permeability of HFNF membranes decreases with coating time, while the rejection increased with coating time [67, 79].

Sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) was coated on the top layer of UF membranes by the dip-coating method under different reaction conditions including the polymer concentration, solvent used in the coating solution, drying temperature, and the polymer molecular weight in a nanofiltration process [80]. The membrane permeation rate increased on increasing the molecular weight of glycol ethers used as the solvent, without sacrificing separation. Polyaniline nanofibers were prepared by a novel interfacial polymerization technique using a trichloroethane as organic media [81]. Ammonium peroxydisulphate was used as an oxidizing agent dissolved in aqueous media. The result showed that interfacial polymerization offers the fibrillar type of morphology having 200-nm-sized fibers and conductivity of the polymer was found to be ~ 0.1 S/cm. Commercially available ceramic membranes made from alumina, zirconia and titania were coated via the layer-by-layer technique with iron oxide nanoparticles (4–6 nm diameter) for the removal of trihalomethanes (90%) and halogenic acetic acids (85%) [82, 83]. The influence of filler concentration on the compaction and filtration properties of mechanically robust Zirfon®-composite ultrafiltration membranes was investigated by Aerts *et al.* [84].

Polypyrrole-coated Ag composites were synthesized using interfacial polymerization method and the controlling reactive condition was achieved through an immiscible organic/inorganic biphasic system in the presence of polyvinylpyrrolidone [67]. Nanostructured poly(α -naphthylamine-co-Aniline) membranes were prepared by interfacial polymerization method using ammonium persulphate in the presence of methane sulphonic acid [78]. Poly(α -naphthylamine), polyaniline and copolymer nanostructures were synthesized by tuning the preparation in a two-phase medium. The results obtained showed that the conductivity and solubility properties of nanostructure copolymers are higher than copolymers prepared by conventional methods [78, 79].

9.4.6 Application of CNTs in Membrane Production

Carbon nanotubes are widely known as superior adsorbents for removing many kinds of organic and inorganic pollutants as well as volatile organic compounds from air and aqueous solutions [85]. They are suitable for a wide range of applications related to water treatment such as environmental adsorbents, high-flux membranes, depth filters, antimicrobial agents, and environmental sensors [86]. The unique mechanical properties, low density, high aspect ratio and high in-axis strength of CNTs make them potential filling materials in polymer composites. The CNTs are known to improve the strength and stiffness of polymers, as well as add multifunctionality to polymer-based composite systems.

The addition of CNTs to polymeric membranes for water treatment has been suggested as a possible strategy to reduce membrane damage and fouling. Previous studies have shown that CNTs blended with PSf MF membranes have a higher flux and rejection rates [50, 64, 87]. These studies have also established that CNTs blended membranes have increased hydrophilicity compared to pure PSf membranes. It is suggested that the use of doped and/or functionalized CNTs in the membrane will improve the performance of the composite membranes. It is also possible that this will increase permeability and the hydrophobicity of the membrane and reduce fouling resistance in water treatment. Addition of these modified CNT materials will improve dispersibility and reduce agglomeration. For example, the structure between the sulfonic groups of PES and -COOH of MWCNTs is enhanced by hydrogen bonding interactions (Figure 9.9).

9.4.7 Nanotechnology-Based Membranes for POU/POE Use

A comprehensive book chapter aimed at discussing membrane-based POU and POE treatment technologies currently used was published recently [89]. It describes the advantages and limitations of employing the conventional RO process for POU and POE applications and includes the different types and configurations of reverse osmosis, installation, operation and maintenance, testing of RO, etc. While water treatment plants have been using NF and UF membranes for filtration, RO filters are the type mostly used for household water treatment method for the direct consumption of water (for drinking and cooking purposes). Clearly, most POU/POE techniques available are not those made from nanotechnology and are based on RO processes [89]. Numerous methods based on treating brackish water, seawater, wastewater and industrial waste are well-documented [90–94].

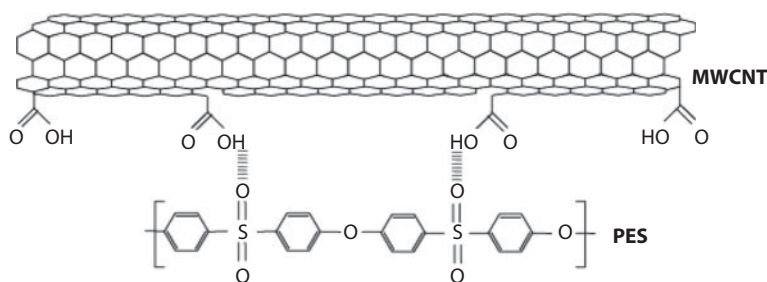


Figure 9.9 The structure of hydrogen bonding interactions between the sulfonic groups of PES and carboxylic groups of functionalized MWCNTs [50].

This present work demonstrates that a few POU and POE devices/techniques exist where nanotechnology processes are applied in water treatment. Most such techniques are still at a laboratory scale status or in the development phase in their readiness to enter the market. Nanomaterials such as CNTs, nanoparticles and dendrimers are contributing towards the development of water filtration technologies which are efficient and cost-effective. Nanostructured filters and nanoreactive membranes enhance purification of water contaminated by organic solutes, and inorganic anions are envisaged to be effective [95]. Particularly, the development of dendritic polymers provides opportunities to refine effective filtration processes for purification of water contaminated by different organic solutes and inorganic anions [95].

A UF system developed by TriSep Corporation called SpiraSep consists of spiral-wound layers of fiberglass sheets creating a permeable surface of pores in the nanorange [96]. NanoH₂O, Inc., is manufacturing a new generation of thin-film membranes by enhancing the currently used polymer-based membranes with nanostructured material that allows additional control of membrane properties [97]. This will result in a wide array of membranes with enhanced properties including improved permeability and high salt or organics rejection, as well as enhanced fouling resistance [97]. DTU Nanotech at the Technical University of Denmark has embarked on a project aimed at up-scaling nanotechnology-based membranes [98].

Durapore membrane filters are already on the market. These membranes provide high flow and throughput rates and excellent chemical compatibility [99]. Nanofibrous membrane (PA6 membrane) combines extraordinary structural and morphological properties with small pores with uniform size distribution, excellent filtration performance, high permeability and good mechanical properties. These nanofibrous membranes

can be used for a large number of applications ranging from filter media, separation membranes to biomedical products [100]. A mini-review that is dedicated to the use of nanotechnology for membranes, filters and sieves was recently published [101]. This review highlights the impact that this development has in the area of membrane separation by filtering and sieving, where exciting developments fail to impress.

9.4.8 Removal of Heavy Metals, Organometallics, Metalloids Using Nanomembranes

Pollution of water by heavy metals such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), lead (Pb), selenium (Se) and zinc (Zn) is a serious problem in many countries like South Africa. Most of these metals are present in wastewaters of mining industries. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. These metals are dangerous because they tend to bioaccumulate. Thus no matter how low the concentration, they still pose serious health problems. The various materials and methods used to fabricate the membranes and their efficiencies can be observed in a number of studies [102–117]. A number of important points can be drawn from these studies:

- Membranes can effectively be used for the removal of heavy metals from various water sources including wastewater. Depending on the materials used, efficiencies of up to 100% can be removed [104].
- There is an increase in research towards the incorporation of other nanomaterials/nanoparticles (e.g., TiO_2 , SiO_2 , CNTs, cyclodextrin) into membranes. Addition of the nanomaterials improves the antifouling properties of the membranes and sometimes the mechanical strength [103, 105–115].
- Many of the new membranes have been tested at a lab scale. A few studies have shown that the membranes are effective at large scale [104, 113].
- Electrospinning and phase inversion methods are the most widely used technologies for the preparation of nanostructured membranes.
- Most of the studies have shown that the pH of the solution treated is crucial because it affects the adsorption capacity of membranes.

9.5 Ceramic-Based Filters and Nanofibers

9.5.1 Polymer-Clay Nanocomposites in Heavy Metal Removal from Water

Polymeric composites are materials where the bulk of the polymer used is filled with synthetic or natural inorganic compounds in order to improve its chemical and physical properties or to reduce cost by acting as a diluent for the polymer [118–120]. If the filler is in the nanometer range the composite is called a nanocomposite. Polymer-clay nanocomposites are a new class of composites and they possess unique properties which are typically not shared by their more conventional microscopic counterparts [2].

A large number of nanomaterials have been used as fillers in nanocomposites preparation but clay (hydrous layer silicates) and layered silicates have been most widely used [121–123]. Clay-based nanocomposites have received considerable scientific and technological attention due to the fact that clay is environmentally friendly, is abundantly available in nature, and there is wide knowledge available on clay-intercalation chemistry [124].

9.5.2 Polymer-Clay Nanocomposite Formation

Understanding the process by which polymer-clay nanocomposites are formed is important. Any physical mixture of a polymer and clay does not essentially form a nanocomposite with improved properties. Immiscibility leads to poor physical attraction between the polymer and the clay particles, and that consequently leads to relatively poor mechanical properties. Generally, clays are hydrophilic, and this means that it is necessary to select a hydrophilic polymer to avoid immiscibility when preparing nanocomposites [125, 126]. However, hydrophilic polymers are not compatible with all composite-fabrication procedures. Fortunately, the clay can be modified accordingly to enhance compatibility. In many cases, a surfactant is used and the resulting modified clay is called organoclay. Many compounds have been used to modify clay. For example, dimethyl-sulphoxide, methanol and octadecylamine can be used. The “popular” Cloisite® organoclays are prepared by modifying montmorillonite clay with salts of dimethyl dehydrogenated tallow quaternary ammonium [125].

The concept of modifying the clay basically takes advantage of the exchangeable ions in the gallery of the clay. The general structure of a 2:1 dioctahedral smectite clay is shown in Figure 9.10 [125].

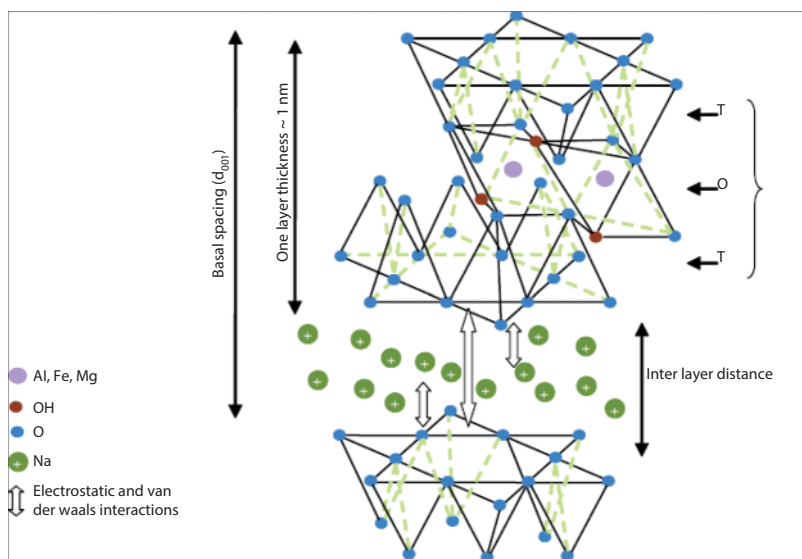


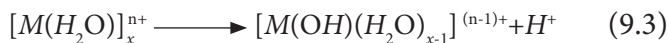
Figure 9.10 The structure of a 2:1 smectite clay [125].

In the 2:1 smectite structure, the clay possesses Li, Na, Rb, and Cs ions sandwiched between two layers. These ions can be replaced with surfactants under appropriate conditions to form an organoclay. The replacement of the exchange cations in the cavities of the layered clay structure by alkylammonium surfactants can compatibilize the surface chemistry of the clay and a hydrophobic polymer matrix. When natural montmorillonite is used, the dispersion of the clay in the polyvinyl chloride (PVC) matrix is typically poor, and when organically-modified montmorillonite is used an improved dispersion is observed [115, 127]. Consequently, organic modification of the clay is crucial as it affects the nanocomposite properties. The type of surfactant, the chain length and the packing density may also play an important role in determining the suitability of the surfactant to modify the clay [128]. Replacing the exchangeable ions in the cavity of the clay not only serves to alter the hydrophilic or polarity properties of the clay, but also widens the inter-gallery spacing to allow unhindered intercalation of the polymer chains in the clay. By definition, intercalation is the insertion of polymer chains between two galleries of clay. This enlarges the inter-gallery spacing of the clay [128].

The expansion of the gallery spacing by the organic modifier allows proper formation of a nanocomposite during fabrication. Three strategies are mainly employed in the preparation of nanocomposites: *in-situ*

polymerization [129], melt-blending method, and solution-blending method [127, 130].

Polymer-clay nanocomposites have been used for heavy-metal adsorption because of their suitable clay properties such as specific surface area, chemical and mechanical stability, layered structure, high cation-exchange capacity (CEC), etc. In addition, clays can be regarded as possessing both Brönsted and Lewis types of acidity [119], and this acidity makes them suitable for the adsorption of heavy metals. The Brönsted acidity arises from two situations, firstly through the formation of H^+ ions on the surface, resulting from the dissociation of water molecules of hydrated exchangeable metal cations on the surface, as follows:



Secondly, it can be as a result of a net negative charge on the surface due to the substitution of Si^{4+} by Al^{3+} in some of the tetrahedral positions, and the resultant charge is counter-balanced by H_3O^+ cations. On the other hand, Lewis acidity can emanate from three scenarios: (1) through dehydroxylation of some Brönsted acid sites; (2) exposed Al^{3+} ions at the edges; and (3) Al^{3+} arising from the breaking of Si-O-Al bonds. The resulting negative net charge is counter-balanced by exchangeable cations like K^+ , Ca^{2+} , Mg^{2+} , etc., adsorbed between the unit layers and around the edges, making it possible for clay to remove heavy metals from water through ion-exchange, chemisorption, or physisorption [119].

Mahlangu *et al.* have recently designed, constructed and evaluated a simplified cost-effective POU biosand filter (BSFZ) for removal of chemical contaminants from water [131]. The biosand filter was modified with the addition of zeolites (clinoptilolite). The zeolites formed the largest part of the filter media which was comprised of four layers. The complete filter had six zones which played a role during the filtration process. Filtration was done for 3 h to mimic water filtration in private homes. The filtered water was collected in a vessel for 1 h after which the samples were taken for analysis. Results indicated removal of up to 80% calcium, 89% magnesium, 99% iron, 56% arsenic, 54% fluorides, 96% turbidity, 37% nitrates and 41% total organic carbon. Higher turbidity ($r = 0.024$) and chlorophyll *a* ($r = -0.566$) concentrations resulted in a decrease in the flow rate of the filter which was between 1.74 l/h and 19.20 l/h. Higher chlorophyll *a* concentrations resulted in higher turbidity ($r = 0.609$). The filter was cost-effective (<US\$20.00), and easy to construct, operate and maintain [131].

The efficiency of the BSF was compared with a ceramic candle filter (CCF) and bucket filter (BF). The filters were evaluated for their efficiency

in removal of calcium, magnesium, iron and arsenic, nitrates, phosphates, fluorides, total organic carbon and turbidity, by determining levels of these contaminants in water before and after filtration through the filters. All the filters showed similar efficiencies in the removal of metals (average 40% – 50%) by the filters ($p \geq 0.05$), as the same removal mechanisms (straining, ammonification, fixation and adsorption) were believed to be taking place in all of the filters [132].

The Fe_3O_4 -coated polypyrrole (PPy) magnetic nanocomposite was prepared via *in-situ* polymerization of pyrrole monomer for the removal of highly toxic Cr(VI) [133]. Up to 100% adsorption was found with 200 mg/L Cr(VI) aqueous solution at pH 2. Adsorption of Cr(VI) on the surface of the adsorbent was confirmed by the ATR-FTIR and X-ray photoelectron spectroscopy (XPS). The XPS studies also suggested that ion exchange and reduction on the surface of the nanocomposite may be the possible mechanism for Cr(VI) removal by the PPy/ Fe_3O_4 nanocomposite. Adsorption results showed that Cr(VI) removal efficiency by the nanocomposite decreased with an increase in pH [133].

9.5.3 Application of Nanofibers in Drinking Water Purification

The word nanofiber has been broadly used to refer to a fiber with a diameter less than 1 micron. Polymeric nanofibers are rapidly finding their place in nanomaterials technology. They are an exciting new class of material used for several value-added applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, and energy storage.

Nanostructured materials such as nanofibers and nanobiocides for use in POU nanofiltration processes are currently being developed and have been shown to be viable in water treatment, i.e., for chemical decontamination, desalination, filtration and sanitation. Nanofibers have enormous potential for application in water filtration and sanitation [134]. The tiny pores present in nonwoven mats of electrospun nanofibers renders these materials excellent filtration properties, and due to the variety of polymers that can be used to fabricate nanofibers, and the versatility of being able to add functional molecules and chemical groups to the nanofibers, make nanofibers applicable to sanitation and purification of water [134].

Electrospinning is the most popular method applied to prepare nonwoven nanofibers made of organic polymers, ceramics and polymer/ceramic composites. It has been extensively explored as a simple and versatile method for drawing fibers from polymer solutions (or melts). The electrospinning process involves a polymeric fluid being extruded from the orifice

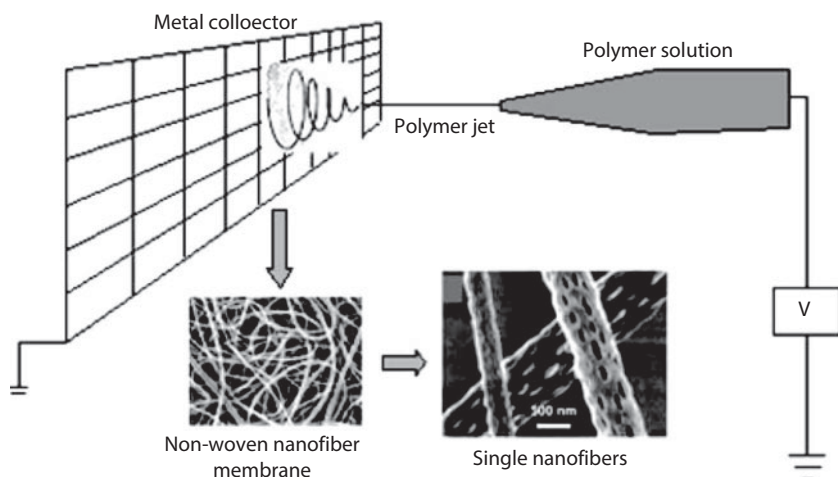


Figure 9.11 Schematic diagram showing polymer nanofibers prepared by electrospinning [135].

of a needle or pipette to form a small droplet in the presence of an electric field. When the electric field is sufficiently strong, charges build up on the surface of the droplet and overcome the surface tension. A charged jet of fluid is ejected from the tip of the Taylor cone. The jet is then accelerated toward a grounded collector (Figure 9.11) [135]. The discharged polymer solution jet undergoes a rapid whipping process through which the solvent is evaporated; the liquid jet is stretched to many times its original length to produce continuous, ultrathin fibers of the polymer. In the continuous feeding mode (through the use of a syringe pump), a mat of ultrathin fibers can be obtained within a relatively short period of time.

Biopolymers such as cellulose and chitin and their derivatives are polymers that are abundant, renewable, biocompatible and biodegradable. These factors make them ideal choices as sustainable feedstock for materials and products for use in the fields of filtration, adsorption and preconcentration of heavy metal pollutants. However, a major challenge faces the application of these biopolymers due to their insolubility in most common solvents [136]. The biosorption process utilizing inexpensive biomass to sequester toxic heavy metals is particularly useful for the removal of these contaminants from industrial effluents [137]. Chitin and chitosan have been used for the adsorption or the binding of heavy metals and dyes. Chitosan is a polycation polymer effective in coagulation and flocculation dewatering of activated sludge, and hence is used in wastewater treatment.

The functionalized cellulose and chitosan nanofibers showed enhanced removal of trace metals in natural water polluted with heavy metals. The grafted functional groups of oxolane-2, 5-dione and furan-2, 5-dione have charged sites onto which the divalent metal cations are exchanged. Undetectable metal ions are adsorbed in these materials and when eluted with suitable acids like dilute nitric acid can be measured and their levels in the natural water determined. The desorption of the adsorbed metal ions regenerates the nanofibers allowing for continuous use up to five cycles [137].

Initial testing of electrospun nanofiber filters in water filtration applications was done by Bjorge *et al.* [138]. The nanofibers were examined for three different applications. Firstly, the use of the membrane (functionalized or non-functionalized) for the removal of pathogens was investigated. Secondly, the electrospun flat-sheet membranes were applied for wastewater treatment in a laboratory-scale submerged membrane bioreactor (MBR). In addition to these applications, physical properties such as clean water permeability (CWP) and strength were also examined. The tests showed that the electrospun membranes can effectively be used for water filtration applications. The Ag-functionalized nanofibers were found to be effective in removing pathogens in water [138].

Recently, Professor Eugene Cloete's research group fabricated antimicrobial and biofouling-resistant nanofibers with silver nanoparticles and immobilized enzymes for application in water filtration. The nanofibers of poly(vinyl alcohol) (PVA) and poly(acrylonitrile) (PAN) nanofibers were synthesized by electrospinning. Both PVA and PAN nanofibers containing silver nanoparticles had excellent antimicrobial activity, with PVA nanofibers killing between 91% and 99% of bacteria in a contaminated water sample and PAN nanofibers killing 100%. The nanofibers were packed into a sachet called the "nano tea bag" and received overwhelming media publicity as a high-tech, low-cost, disposable water filter that fits into the neck of a water bottle and delivers clean water as one drinks from it [139].

9.6 Challenges and Opportunities

9.6.1 Challenges

A comprehensive survey shows that CD-based composite nanomaterials have not been used in commercial filters that are available to the public. The major challenge holding back the commercialization of the materials is that while the CDs themselves are not toxic and biodegradable, the CNTs

are still undergoing rigorous tests to ascertain their toxicity. However, studies have shown that when CNTs are embedded in a matrix such as a polymer, then they are not toxic and can be used for the purification of drinking water [140].

Nanotechnology use in membrane processes brings about several important challenges in water treatment systems and their use in POE/POU filters has generally been slow. The fundamental objective of new generation membranes is to produce membranes with enhanced separation performances, high selectivities, enhanced fouling resistance, improved mechanical stability, etc. However, it is important to note that each membrane process discussed in this chapter offers unique performance properties and each has unique drawbacks that must be overcome before they can be deemed commercially viable. As highlighted earlier, nanotechnology-enabled membrane filters for POE and POU that are near commercialization, inexpensive and manufactured using conventional fabrication procedures are infrequent at this stage. However, catalytic nanoparticles and zeolitic membranes promise improved performance and selectivities. These novel membranes are still not commercialized particularly due to high capital costs. Furthermore, nanomembranes for desalination and purification of heavily contaminated wastewaters are still in their infancy.

Currently, CNT- and nanomaterial-based membranes demonstrate significant changes in membrane efficiency in the lab due to improved structural properties. However, CNTs are expensive to synthesize and purify and have not yet been formed in large membrane surfaces for cost effectiveness. Although CNT membranes with a high level of dispersion have been made, it is still a serious challenge to keep them aligned in the polymer matrix. This property further hinders scale-up possibilities of CNT-embedded membrane materials. Carbon nanotube membranes and Ag-incorporated membranes still need to undergo a sound risk assessment process to ensure that CNTs are not released into our water during treatment procedures. However, the use of Ag as antimicrobial agent is widely known as it is used daily in cosmetic products. Nanoparticles such as TiO_2 which are very effective in membrane modification are, however, inexpensive and can be scheduled for commercialization since these membranes will be cost-effective.

It is clear that there are still many other technical problems to be overcome before nanomembrane filters can enter the market. The anonymous environmental risks are currently preventing scientists and consumers from fully benefiting from the use of nanotechnology in membrane production and their use in POU/POE devices. Analyses are underway to determine the problem associated with the use of these processes in water

treatment. Therefore, the serious challenge is to tailor-make commercially viable nanotechnology membranes with specific applications in water treatment.

Among the properties that make clay a suitable heavy-metal adsorbent is the specific high surface area. However, this property is suppressed by embedding the clay particles in a polymer despite the fact that surface area is an important parameter in adsorption technology. Furthermore, embedding the clay particles in a polymer can slow down the adsorption process because the adsorption active sites are concealed or enveloped by the polymer. This can be dominant in composites prepared by the melt-blending method which use hydrophobic polymers. Consequently, there are long equilibration periods in adsorption experiments using composites, compared to when the filler is used independently. One of the most-reported drawbacks in composites is weight increase. Weight increase tends to favor the settling of the composites in water, hence vigorous mechanical stirring would be required. Finally, depending on the polymer used in preparing the composite, erosion of support in desorption studies can be a serious problem. Desorption of the adsorbate from an adsorbent usually occurs under harsh conditions.

9.6.2 Opportunities

The CD-based nanocomposites polymers have been shown to be suitable for use as POU or POE filtration materials. With the rise of greener chemical strategies towards the synthesis of these materials, such as synthesis under microwaves, it is expected that some of the toxic chemicals used in the synthesis process will be eliminated. Synthesis of the materials under microwaves allows for good reproducibility and production of multiple batches of the materials within a short time.

Composites prepared by the melt-blending method can be molded into strips of different sizes and shapes. This makes it relatively easy to recover the composites after heavy-metal capture in water. This is crucial because to obtain clean water the used adsorbent should be successfully removed from the water. The size of the strip affords better handling and cleaning of the composites, compared to powder adsorbents like activated carbon and clay. Additionally, embedding the adsorbents like clay in a polymer reduces the risk of sludge formation.

On the other hand, the ability to modify the surface and structure of membranes using various chemical strategies and orchestrating them into filters provides opportunities for the development of nanomembranes. Membranes generally consume less energy and are suitable for large-scale

use and can easily be integrated into existing plants. Other materials such as graphene sheets are now being exploited for the removal of heavy metals [141].

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Part 4

NANOMATERIALS

Mesoporous Materials as Potential Absorbents for Water Purification

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Abstract

Mesoporous materials were reported first in the early 1990s. These materials contain well-defined pore sizes, which make them ideally suitable for tailor-made absorbents. Here we briefly describe the synthesis of mesoporous materials.

Keywords: Mesoporous materials, SBA-15, MCM-41

10.1 Introduction

Environmental pollution is a growing problem that needs to be controlled. A range of toxic and noxious organic and inorganic chemicals pollute the environment through discharge, where they cause serious air, soil and water contamination. Heavy metals, in particular, exert a deleterious effect on the flora and fauna of lakes and streams and must therefore be removed from wastewater. Heavy metals find their way into the wastewater originating from chemical manufacturing, painting and coating, mining, extractive metallurgy, nuclear and other industries. Once in the environment, these metals can be considered persistent, bioaccumulative and hazardous. Indeed the increasing level of toxic metals in the environment represents a serious threat to human health, and the detection of heavy metal ions in water samples has received considerable attention in recent years.

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Materials science has always been an important research area. In the last couple of years, the design of materials with particle sizes, shapes and/or pores of nanometric scale has resulted in a number of important breakthroughs. Recent advances in new materials research have had a direct effect on developments in catalysis, biochemistry, environmental chemistry and analytical chemistry. One of the most important advances in materials science was the discovery of the well-ordered mesoporous silica materials of the M41S family. These materials contain well-ordered pores with uniform size and a high volume and surface area. This family of materials has expanded rapidly in the years following the discovery. It is possible, by varying the reaction conditions, to obtain materials with different pore diameters, structures, surface areas, particle sizes and shapes. Subsequent chemical modification of these materials with organic groups allows hybrid mesoporous materials, which are potentially useful in those processes where the specific and selective physisorption of different kinds of compounds is required, to be obtained.

10.2 Generalized Synthesis of Mesoporous Materials

The discovery of M41S and other related ordered mesoporous solids in the 1990s signaled a breakthrough in the engineering of mesoporous materials. Much has been achieved in terms of developing a variety of new mesoporous solids using templating techniques similar to that used in the synthesis of M41S. Depending on the synthesis conditions (for example, the type of surfactant, the silica source or the synthesis temperature), mesoporous materials can be synthesized through a cooperative self-assembly pathway [1–3], the liquid crystal templating method [4] or the nanocasting method, which uses already formed ordered mesoporous materials as hard templates [5, 6]. First ordered mesoporous materials were prepared from ionic surfactants like quaternary ammonium ions and based on the electrostatic interaction between the positively charged head groups of the surfactant and the negatively charged inorganic species, resulted into inorganic-organic mesostructure.

It is possible to synthesize ordered mesoporous molecular sieves (OMMs) using surfactants as templates. A template is a structure-directing agent – (simple molecule or ion) – around which a framework is built. For the past few years, short-chain quaternary ammonium salts, typically hexadecyltrimethylammonium, were used as templates for the synthesis of a large number of zeolites. The cation exchange between a layered silicate, Kanemite (which has the nominal composition of $\text{NaHSi}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and quaternary ammonium ions resulted in

quaternary ammonium-silicate composites. The hydrothermal reaction of soluble silicates, surfactant and mineralizer under basic conditions resulted in the precipitation of silica-surfactant mesostructured materials. The mesoporous molecular sieves are obtained after calcination [7]. The removal of the surfactant from the synthesised silica-surfactant mesostructured material yields a mesoporous silica. Calcination is the most popular way of removing the surfactant, but solvent extraction has also been used [8]. Quaternary ammonium surfactants with different alkyl chain lengths yield controlled pore sizes, which is one of the most important features of such materials [9]. Therefore, the surfactant self-assembly is particularly essential for the formation of highly-ordered mesostructures. On the basis of current knowledge about surfactant self-assembly, mesoporous materials can be rationally designed and synthesis controlled.

Long chain alkyl groups, mostly the hexadecyl group, are frequently employed in the synthesis of MCM-41. The hydrophobic alkyl chain of the template ions will aggregate together in aqueous solution forming micelles. Micelles have a hydrophobic core containing the large alkyl chains and a hydrophilic surface due to the ionic character of the ammonium head groups. Spherical micelles are favoured energetically because the surface energy is minimised most efficiently and this conformation allows the largest number of micelles formed in a given amount of template. Increasing the amount of template in aqueous solution, different micelle geometries are evolved and the spherical micelle gradually transform into long tubes, often termed rod-like micelles. A further increase in template concentration, the rod-like micelles aggregates into a hexagonal liquid crystalline structure which resembles that of MCM-41 (Figure 10. 1) [14]. With a further increase in concentration of the template, the hexagonal crystalline phase transform into a cubic liquid crystal phase and then into a lamellar liquid crystalline phase [10 & 11]. The cubic phase resembles the structure of MCM-48 while the lamellar phase is structurally analogous to MCM-50 (which is an unstable material consisting of platelets of amorphous silica). By varying the synthetic conditions, such as the chemical composition (surfactant/silica ratio), and the surfactant molecular structures and their concentrations, silica-surfactant materials with variable mesostructures can be obtained, particularly lamellar, hexagonal and cubic mesostructures [7]. Other surfactants, like alkylamines [8, 10] and poly(oxy-ethylene) [11], have been used to control the mesostructure of these materials. A triblock copolymer (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene

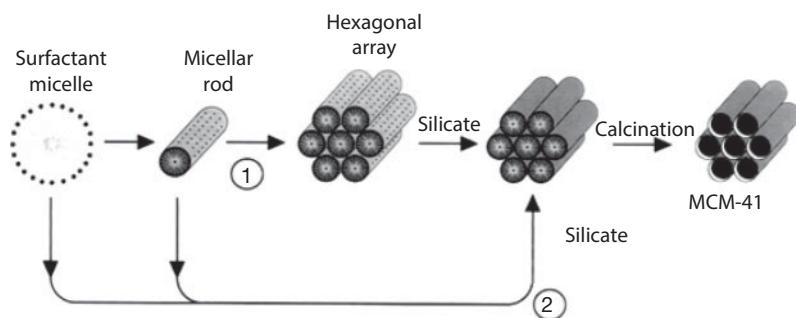


Figure 10.1 Diagrammatic representation of the formation of MCM-41 [14].

oxide) (PEO–PPO–PEO or P123) was also used as a template to produce mesoporous silicas with enlarged pore sizes of up to several tens of nanometers [12, 13].

The second most important 2D hexagonal mesostructured silica is the SBA-15 molecular sieve, which was first reported by Zhao *et al.* in 1993 [12]. Among the mesoporous silicas, SBA-15 has been extensively studied due its outstanding properties as compared to its MCM-41 counterpart. In addition results suggest that SBA-15 has a highly ordered 2D hexagonal mesostructure (space group $p6mm$) with a highly uniform pore size distribution. The SBA-15 materials prepared from P123 at 40–100°C (hydrothermal treatment) have uniform pores ranging from ~6.5 to 10 nm. The pore wall thickness is calculated to be between 3.1 and 6.4 nm, which is much thicker than MCM-41 and results in higher thermal and hydrothermal stability; it is stable for at least 48 h in boiling water [13]. Another characteristic of SBA-15 materials is their unique dual pore system: cylindrical mesopores are arranged hexagonally and micropores within the walls provide connectivity between the larger pores [15–18].

The textural characteristics of SBA-15 materials can be easily changed by using the same experimental approaches used for MCM-41 (change in surfactant structure, synthesis temperature, adding swelling agents, etc.). Often, when an increase in the mesopore diameter and pore volume is required, heat treatment during the synthesis or aging stages of SBA-15 preparation is more effective than the addition of 1, 3, 5- trimethylbenzene [19, 20]. Varying the experimental conditions during SBA-15 synthesis is a simple and efficient way to control the textural properties for different applications. Also, SBA-15 silica displays significantly higher stability under various conditions (steaming, high temperature) as compared to MCM-41 silica, making it a frequent choice for the synthesis of various advanced materials.

10.2.1 Mechanism of Formation of SBA-15

The general idea of using block copolymers as templates is based on the fact that amphiphilic block copolymers self-assemble in certain solvents to give robust, very regular superstructures that feature structural motifs on the nanometer scale (lyotropic liquid-crystalline phases). Typically, the constituting entities are spherical or cylindrical micelles or lamellar sheets with a characteristic cross-section of 5–100 nm. The block copolymer self-assembly technique is probably the best examined mode of self-organization and is governed by the microphase separation. This in turn is dictated by the mutual incompatibility of the different blocks, one being soluble and the other being insoluble in the solvent (“amphiphilic” polymers). In principle, block copolymers self-assemble in a variety of solvents, but particularly in water, alcohols or THF, which enables a certain width of chemistry for inorganic framework generation.

The mechanism is most likely via a $S^o H^+ X^- I^+$ double-layer hydrogen bonding interaction. Here I^+ are inorganic silicate precursor cations, and X^- are counter-anions. It is the cooperative interaction between inorganic and organic species on a molecular scale that leads to the assembly of 2D or 3D ordered arrangements. Silicate polyanions can interact with cationic surfactant molecules through Coulombic forces. The polymerization of silicate species at the interface changes the charge density of inorganic layers, and this in turn changes the arrangement of surfactants. The matching of charge density at the surfactant/inorganic interface governs the assembly process [21]. The two main pathways that seem to be effective in the synthesis of ordered mesostructures are cooperative self-assembly and “true” liquid-crystal templating. The most popular is the cooperative formation mechanism, which was first proposed by Stucky and coworkers and is represented in Figure 10.2.

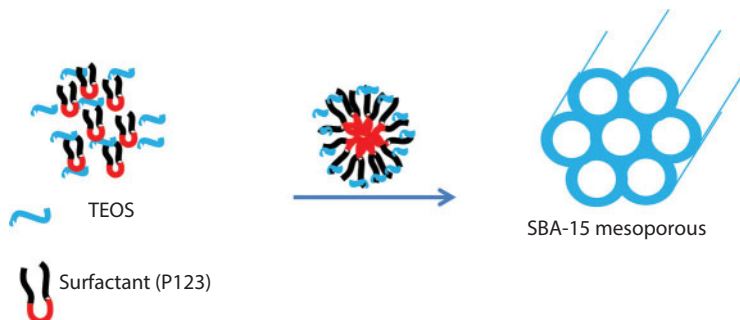


Figure 10.2 Diagrammatic representation of the formation of SBA-15.

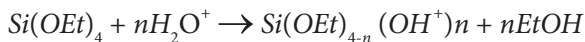
10.3 Common Method of Synthesizing Silicate Mesoporous Molecular Sieves

10.3.1 Hydrothermal Method

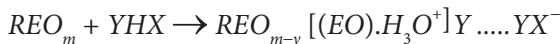
Mesoporous silicates are generally prepared under “hydrothermal” conditions, which involve the typical sol-gel process. The general procedure includes several steps: first, a homogeneous solution is obtained by dissolving the surfactant(s) in a solvent. Water is the most common solvent and medium. Silicate precursors are then added into the solution and they undergo hydrolysis catalyzed by an acid or base, which transforms them into a sol of silicate oligomers. As a result of the interaction between oligomers and surfactant micelles, cooperative assembly and aggregation gives rise to precipitation from a gel. During this step, microphase separation and continuous condensation of silicate oligomers occur [22]. The formation of mesoporous silicates is rapid, taking only 3–5 min in cationic surfactant solutions, and this is reflected by the precipitation. The process takes 30 min for non-ionic surfactants. Hydrothermal treatment is one of the most efficient methods to improve the mesoscopic regularity of products [22]. During hydrothermal treatment, the mesostructures undergo reorganisation, growth, and crystallisation. The treatment temperature is low (between 80 and 150 °C). For most synthesis, a range of 80–100 °C is used.

10.3.2 Fundamental Principles that Govern the Design and Synthesis of Mesoporous Silica

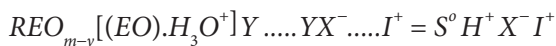
1. Amphiphilic block copolymers self-assemble as lyotropic liquid crystalline phases.
2. Alkoxy silane species are hydrolyzed.



3. EO moieties of the surfactant in strong acid media associates with hydronium ions and halides ions.



Organic-inorganic self-assembly is as a result of a combination of weak noncovalent bonds such as H bonds, van der Waals forces and electrovalent bonds between the surfactants and inorganic species.



10.3.3 Pore Size Control of Mesoporous Materials

There are several methods that can be employed to adjust the pore sizes of mesoporous silica materials. Some of these are: the selection of surfactant, hydrothermal treatment, and the use of organic swelling agents.

1. **Surfactants:** The pore size of mesoporous silica materials mainly depends on the length of the hydrophobic groups of the surfactants. Cationic quaternary surfactants with longer alkyl chains can yield larger pore sizes. However, when the alkyl chains are longer than C_{22} , they tend to be insoluble in water, which leads to the formation of disordered products. For triblock co-polymer such as PEO-PPO-PEO, the pore sizes are enlarged with increasing molecular weight of the hydrophobic blocks rather than that of the copolymers. Therefore, increasing the chain length produces materials with bigger pores.
2. **Hydrothermal treatment:** Changing the hydrothermal temperatures of mesoporous materials can change their pore sizes [23]. During hydrothermal treatment at higher temperatures, the PEO blocks become hydrophobic and retract from the silicate walls. The hydrolysis and cross-linkage of organic species continue and the large surfactant micelle results in the large pore sizes characteristic of SBA-15 materials, thin pore walls and low amount of micropores [22]. Therefore, the micropore size of mesoporous materials can be adjusted by increasing the hydrothermal temperatures for several hours or even days.
3. **Use of organic swelling agents:** Pore size enlargement of mesoporous materials can be achieved by the use of organic swelling agents, more especially large organic hydrocarbons such as 1, 3,5-substituted benzenes such as. trimethyl benzene (TMB), long chains alkyls, long chains amine etc. The hydrophobic organic species can dissolved inside the hydrophobic regions of the surfactant micelles, thereby expanding the micelle.

10.3.4 Organic Group Functionalization of Mesoporous Silicates

Since the discovery of ordered mesoporous materials, a lot of research has been devoted to the surface functionalization in order to realize their

potential in various applications [24–27]. Chemical functionalization of the inorganic framework of mesoporous materials, for example, through the covalent coupling of organic or organometallic moieties, is a promising approach to tailor pore surface properties such as hydrophilicity/hydrophobicity and polarity, as well as catalytic, optical and electronic activity [24]. The chemical transformation of the surface chemistry of mesoporous materials is of direct interest in such applications as adsorption, catalysis, chromatography, controlled drug delivery or gas and liquid separation membranes. Ordered mesoporous materials possess large pore diameters that can accommodate a variety of large molecules. In addition, they offer a high density of surface silanol groups on the pore walls making them more attractive for the introduction of functional groups with a high coverage. Organic group functionalized mesoporous silicas take advantage of the large surface areas, high stability and confined mesopores in the inorganic solids. The organic functionalization of these solids permits the tuning of surface properties like hydrophilicity/hydrophobicity, how they bind to guest molecules, surface reactivity and other bulk properties including mechanical or optical characteristics [25, 26]. Various kinds of surface modifications have been performed to provide new functions e.g., the introduction of amino groups onto the mesopores structure of these materials has enabled the use amino-functionalised mesoporous materials as solid-base catalysts and adsorbents for a variety of applications.

Incorporation of organic moieties onto mesoporous silicas can be achieved through two ways: grafting and co-condensation [25]. The post-synthetic grafting process has been widely employed to anchor various organic groups onto the surface or pore channels of mesoporous silicates, including organometallic species, amine and thiol groups, and epoxides. Mesoporous silicates contain high concentrations of surface silanol (Si-OH) groups that can act as anchors for organo-functionalization [24]. Surface modification with organic groups is most commonly carried out by silylation. Silylation occurs on free ($\equiv \text{Si-OH}$) and geminal silanol ($\equiv \text{Si}(\text{OH})_2$) groups. In this process, the silica is reacted with an appropriate organosilanes in a suitable solvent, typically toluene at reflux. This mode of functionalisation has an advantage in that the mesostructure of the starting silica phase is usually retained and allows an effective inclusion of densely populated or high concentration of covalently bound organic functional groups [24]. Therefore maintaining a large number of silanol groups for high surface coverage of functional groups after calcination is very important. The amount of grafted

functional groups is the key factor in achieving the high adsorption capacity of these mesoporous silicas. Despite the fact that this method is widely used, it is faced with a number of disadvantages: the functionalisation is accompanied by a reduction in the porosity of the hybrid material which depends on the size of the organic species and the degree of occupation [27]. If the organosilanes react preferentially at the pore openings during the initial stages of the grafting process, further diffusion of molecules into the centre of pores may be impaired, which can lead to a lower degree of functionalisation. In some cases, this can also lead to pore blocking [27], as well as difficulties in controlling the loadings and active sites.

An alternative method is the co-condensation, or one pot syntheses, approach in which tetraalkoxysilanes $(RO)_4Si$ and trialkoxyorganosilanes $(RO)_3Si-R'$ (where R is Et or Me and R' is a nonhydrolyzable ligand) co-assemble with amphiphilic ligands. The co-condensation method is often preferred to the post-grafting method because it minimizes processing steps and provides a more uniform distribution of organic functionalities. In addition, pore blocking is not an issue in the one-pot synthesis method since the organic functionalities are integral components of the silica matrix. Also, the organic units are more homogeneously distributed than in the materials synthesized using the grafting process. Incorporating two or more functional groups in a one-pot synthesis is also possible, although the location of the functional groups is not as tightly controlled as in the grafting processes described earlier; the functional groups are randomly distributed in the product [28]. However, the co-condensation method does have a number of disadvantages as well. In general, the degree of the mesoscopic order of the products decreases with increasing concentration of $(RO)_3Si-R'$ in the reaction mixture, which ultimately leads to totally disordered products. Furthermore, the proportion of terminal organic groups that are incorporated into the pore-wall network is generally lower than what would correspond to the starting concentration of the reaction mixture [27]. Moreover, an increase in loading of the incorporated organic groups can lead to a reduction in the pore diameter, pore volume and specific surface areas. Another disadvantage associated with the co-condensation method is that considerable care must be taken to preserve the organic functionality during the surfactant removal step.

The central idea should be that during preparation protocols, care should be taken when enabling the functional sites to react or chelate with active molecules to gain rich functionalities. Figure 10.3 represents a

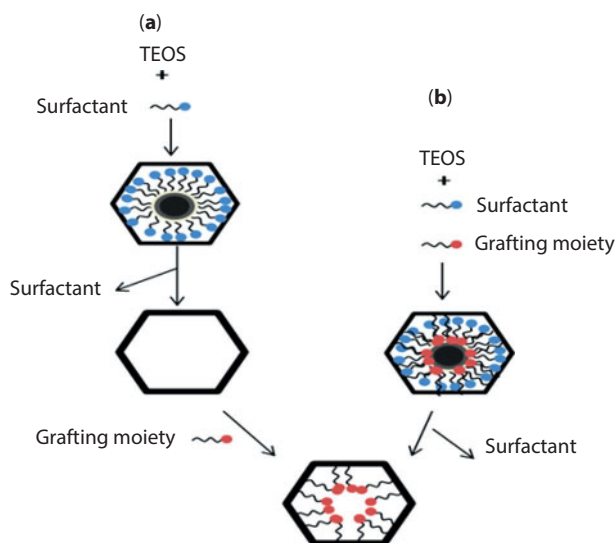


Figure 10.3 Functionalization of mesopore walls by (a) post-synthesis grafting and (b) direct condensation methods.

schematic diagram of the two methods discussed above, namely grafting and co-condensation.

10.4 Adsorption of Heavy Metals

In this application, the materials are generally required to exhibit specific binding sites for heavy metal ions. However, mesoporous silicas do not have such surface properties. An efficient approach has been developed so that functional groups can be chemically immobilized onto the surfaces of mesopores. The functionalized hybrid materials show great adsorption capacity and specificity for metal ions. Feng *et al.* first reported the preparation of MCM-41 functionalized with mercaptopropyl, which is extremely efficient in removing mercury cations (Hg^{2+}) and other heavy metal ions [29, 30]. Mercier and Pinnavaia also developed an effective adsorbent for Hg^{2+} based on thiol-functionalized mesoporous silica [31–33].

Bois *et al.* reported the syntheses of mesoporous silicas functionalized with 3-aminopropyl ($\text{H}_2\text{N}(\text{CH}_2)_3$), [6-amino-4-azahexyl ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3$), 9-amino-4, 7-diazanonyl ($\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2$

$\text{NH}(\text{CH}_2)_3$), and 3-mercaptopropyl ($\text{HS}(\text{CH}_2)_3$) groups by using dodecylamine as SDA via a direct co-condensation method. Functionalized mesoporous silicas were used as adsorbents for removing heavy metal ions from aqueous solutions. Adsorbents synthesized with 6-amino-4-azahexyl and 9-amino-4, 7-diazanonyl showed high loading capacities for Cu^{2+} , Ni^{2+} , Co^{2+} and the anion Cr(VI) . The sample synthesized with a mercaptopropyl functional group had a high loading capacity for Cd^{2+} [34].

Indeed, literature data clearly show that well-prepared mesoporous materials show excellent metal absorption capabilities as compared to their amorphous homologues, which can be attributed to their higher surface areas. Other important advantages are their good accessibility to active centers, which increases selectivity, and higher mass transport rates inside the porous structure [34]. These types of characteristics are of particular use when mesoporous materials are used in analytical applications such as solid-phase extraction, etc. The maximum absorption of these materials as well as absorbent regeneration are important when it comes to determining the reusability of the prepared materials. Even though the costs of some hybrid mesoporous materials can be higher than their amorphous counterparts, most of them have been shown to be relatively inexpensive due to their regeneration capabilities. These materials typically maintain their high metal-absorbing capacity after multiple repeated uses. The general strategy involves shifting the complexation equilibrium in the opposite direction from metal uptake. For amine-functionalized mesoporous silica materials, for example, simple metal-decomplexation can be affected by washing with an acid. This acid wash would liberate the metal ion from the amine, and recycle the amine functionality for further uptake studies.

In addition to the above mentioned examples, mesoporous silica materials have been prepared with more than one single ligand in order to extend the absorption ability to a wide range of heavy metals. The simplest of such bi-functionalizations which involve the grafting of different organosilanes, either simultaneous or successively, have been studied most extensively. For example, Burke *et al.* [35] have shown that aminopropyl and mercaptopropyl bi-functionalized mesoporous silica spheres with large pores are able to simultaneously extract a diverse range of both hard and soft metal ions from aqueous solutions.

It is generally considered to be unlikely that two neighboring coordination sites on an organic chain could work cooperatively to absorb metal ions. Thus, the positioning of two organic sites with controlled spacing and orientation has been a challenging theme as a strong, stable and selective absorption is expected for multiple coordination sites. To obtain highly selective sorbents, it is therefore necessary to utilize surface

imprinting methodologies. A simple surface ion-imprinting method for template-selective recognition sites on ordered mesoporous materials was proposed by Dai *et al.* [36]. In essence, they coated the mesopore surface with complexes of the ligands and the target metal ion, e.g., complexes of aminopropyltrimethoxysilane (APTS) with copper $[\text{Cu}(\text{APTS})_2]^{2+}$ instead of the free ligand. Subsequent removal of the metal ion leaves the ligand in a conformation that is likely to recognize these metal ions in subsequent absorption studies. This technique has been shown to be successful in creating selective recognition sites on mesoporous sorbents and allowing precise control of the stereochemistry of the absorption site. The simplicity of this technique has led to a variety of new sorbents whose properties can be optimized for many metal ions provided that they form stable coordination complexes with a suitable ligand [37, 38].

Due to the good absorption capacity of hybrid mesoporous silica particles, these materials have been widely studied during the last couple of years for the absorption of heavy metals. Some excellent reviews on the application for the removal of toxic pollutants from contaminated waters were recently published by Walcarius and Mercier [34], Yoshitake [39] and Sierra and Pérez-Quintanilla [40]. These works have demonstrated the great interest in preparing hybrid mesoporous materials that are able to complex toxic heavy metals and have opened the door to new analytical strategies for heavy metal detection.

10.5 Conclusions

The goal of this chapter is focused on the synthesis of mesoporous materials. Generally, mesoporous materials are prepared via the self-aggregation of surfactants, followed by polymerization of the silicate material around these aggregates. Following removal of the template, mesoporous materials result.

Mesoporous materials could be grafted with a number of functional groups. These could be tailored for the exact absorption of heavy metals. Various techniques for the preparation of selective mesoporous silicas are described, with the imprinting of specific ligand environments probably being the most advanced.

The methodology of absorption has been briefly described. Several promising applications were also described. However, despite the enormous promise that periodic mesoporous materials show in the field of absorption of metal ions, relatively little research has been published on the use of these materials for metal removal from wastewater.

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Removal of Fluoride from Potable Water Using Smart Nanomaterial as Adsorbent

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Abstract

Fluoride contamination in drinking water has been recognized as one of the major problems worldwide, imposing a serious threat to human health. Nanotechnology has emerged as a promising technology in the past decade in various fields. Likewise, the use of nanoparticles as sorbents for water treatment has also gained wide attention in recent years. Among several treatment technologies applied for fluoride removal, the adsorption process has been widely explored and offers satisfactory results, especially with nanomaterials like carbon nanotubes, carbon nanotubes as a support to deposit Al_2O_3 , nanoscale aluminium oxide as sorbent, granular form of Fe-Al-Ce, hydrous aluminum oxide embedded with Fe_3O_4 nanoparticle, etc., and their adsorption capacities under various conditions (pH, initial fluoride concentration, temperature, contact time, adsorbent surface charge, etc.). It is evident from a survey of the literature that various nanoadsorbents have shown very good potential for the removal of fluoride. Therefore, this article gives an overview of the use of nanomaterials in water purification with illustrative examples of nanomaterials, whose properties are of great interest in the detection and removal of key contaminants like fluoride from drinking water.

Keywords: Removal, fluoride, smart nanomaterial, adsorbent

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11.1 Introduction

Fluoride belongs to the halogen group of minerals and is a natural constituent of the environment. Fluorides are mainly found in groundwater when derived by the solvent action of water on the rocks and the soil of the earth's crust [1]. Fluoride ingestion is useful for bone and tooth development at certain amounts, but excessive ingestion causes a disease known as fluorosis. The disease fluorosis is caused by an element known as fluorine, the 13th most abundant element available in the earth's crust. While the World Health Organization (WHO) standards [2] permit only 1.5 mg/l as a safe limit of fluoride in drinking water for human consumption, people in several districts of Rajasthan are consuming water with fluoride concentrations of up to 24 mg/l. Elevated fluoride concentrations in the groundwater occur in various parts of the world [3–13].

As a result it is highly reactive and has a strong affinity to combine with other elements to produce compounds known as fluoride [14]. Fluorosis continues to be an endemic problem. More and more areas are regularly being discovered that are affected by fluorosis in different parts of the country [15]. Children in the age group of 0 to 12 years are most prone to fluorosis, as their body tissues are in formative/growth stage during this period. Expectant mothers also need to be protected, as there is growing concern about the effects of fluoride on the fetus. Fluorosis, which is considered to be a problem related to teeth, has only now turned out to be a serious health hazard [16]. It seriously affects bones and problems like joint pain, muscular pain, etc., are its well-known manifestations. It not only affects the body of a person but also renders them socially and culturally crippled. In spite of the progressive spread of the disease, so far no established data exists to determine the extent of disease, no specialized water testing facilities are available and even doctors do not have the specific orientation to correlate the disease with specific symptoms [17]. In these areas, the response of the people is reactive rather than proactive.

11.1.1 International Status

The following countries have been identified for the problem of fluorosis: Pakistan, Bangladesh, Argentina, United States of America, Morocco, the Middle East, Japan, South African, New Zealand, Thailand, etc. [18]. A particularly striking finding is the broad belt extending from northern Africa across the Middle East to Pakistan, Uzbekistan and Kazakhstan, where the risk of encountering fluoride-contaminated groundwater is high.

11.1.2 Fluorosis in India

The problem of fluorosis has reached alarming proportions, affecting at least 17 states of India:

- 50–100% districts are affected: Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat, and Rajasthan
- 30–50% districts are affected: Bihar, Haryana, Karnataka, Maharashtra, Madhya Pradesh, Punjab, Orissa, and West Bengal
- < 30% districts are affected: J & K, Delhi, and Kerala

11.1.3 Fluorosis in Rajasthan [19]

Fluorides in the drinking water of Rajasthan have been found to originate from indigenous rocks, which extend from Delhi to Gujarat. The geological distribution of rocks in Rajasthan reveals that fluorite ores occupy large areas of eastern and southeast parts of this state, in constricted synclinal bands in the central region of Aravalisynchrionium. Secondly, around the mica mines, groundwater is rich in fluorides and Rajasthan is a rich source of mica.

All the 32 districts have been declared as fluorosis prone areas. The worst affected districts are Nagpur, Jaipur, Sikar, Jodhpur, Barmer, Ajmer, Sirohi, Jhunjhunu, Churu, Bikaner and Ganganagar.

11.1.4 Sources of Fluoride in the Environment [20–22]

Usually the surface water is not contaminated with high fluoride, whereas groundwater may be contaminated with high fluoride because the usual source of fluoride is fluoride-rich rocks. When water percolates through rocks it leaches out the fluoride from these rocks. Geology is also a key factor in fluoride contamination of groundwater. In particular, high concentrations of fluoride often occur in magmatic rocks. In addition, the release of calcium from rocks plays an important role since fluoride can be precipitated in the form of calcium fluoride. Climatic conditions also need to be taken into account, as salts (including fluoride) are readily enriched in shallow aquifers in an arid climate. Soil pH is likewise important because, as an anion, fluoride is released under alkaline conditions. For simulation, eight geochemical situations involving different combinations of the above-mentioned factors were defined and separately modeled.

The rocks rich in fluoride are:

- Fluorspar: CaF_2 (sedimentary rocks, limestones, sandstones)
- Cryolite: Na_3AlF_6 (igneous, granite)
- Fluorapatite: $\text{Ca}_3(\text{PO})_2\text{Ca}(\text{FCl})_2$.

11.1.5 Human Exposure to Sources of Fluoride

11.1.5.1 Water [23, 24]

Although there are several sources of fluoride intake, it is roughly estimated that 60% of the total intake is through drinking water. This is the most available form of fluoride and hence the most toxic.

11.1.5.2 Food

The fluoride of food items depends upon the fluoride content of the soil and water used for irrigation, therefore the fluoride content of the food items may vary from place to place.

11.1.5.3 Drugs

Prolonged use of certain drugs has been associated with the chronic adverse effects of fluoride, e.g., sodium fluoride for treatment of osteoporosis [25]. Niflumic acid is used for the treatment of rheumatoid arthritis and fluoride mouth rinse (Proflo) is used to render the teeth stronger.

11.1.5.4 Air

The use of fluorides in industry leads to occupational exposure, e.g., inorganic fluoride compounds are used in the production of aluminum [26–28]. Fluorides are also released during the manufacture and the use of phosphate fertilizers.

11.1.5.5 Cosmetics viz Toothpastes and Mouth Rinses

Highly significant associations were found between estimated fluoride ingestion from toothpaste and fluorosis [29–32]. The fluoride content arising from the raw material used for the manufacturing of paste, viz calcium carbonate, talc and chalk, have high fluoride arising as a contaminant from raw materials; it can be as high as 800–1000 mg/l. In the fluoridated brands, there is a deliberate addition of fluoride, which may range from 1000–4000 mg/l.

11.1.5.6 *Other [32–40]*

1. Inorganic fluoride compounds are used in the production of aluminum and used in phosphate fertilizers.
2. Apart from the available drinking water supply, bottled mineral water may also be a source of excessive fluoride ingestion. It is therefore concluded that a sanitary regulatory system for the control of the level of fluoride in marketed bottled mineral waters is necessary.

11.1.5.7 *Chemobiokinetics and Metabolism [42]*

Ingested fluoride is rapidly absorbed through the gastrointestinal tract and lungs. Peaks are reached after 30 min in the blood. The rapid excretion takes place through the renal system over a period of 4 to 6 h. In children less than three years of age, only about 50% of the total absorbed amount is excreted, but in adults and children over 3 years old about 90% is excreted. Approximately 90% of the fluoride retained in the body is deposited in the skeleton and teeth [43]. The biological half-life of bound fluoride is several years. Fluoride also passes through the placenta and also appears in low concentrations in saliva, sweat, and milk [44].

11.2 Technologies for Defluoridation

Various commonly used processes available for defluoridation are given below.

11.2.1 **Nalgonda Process [45]**

The Nalgonda technique was developed by the National Environment Engineering Research Institute (NEERI), Nagpur. This technique involves addition of alum (aluminium sulphate), lime and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration and disinfection. It is a cumbersome technique not suitable for use by less-educated populations. The process can be used only for water having a fluoride content of less than 10 mg/l and turbidity less than 1500 mg/l. There is a high residual aluminum content in output drinking water. It is reported that the residual aluminum ranges from 2.01 to 6.86 mg/l. It is relevant to note that aluminum is a neurotoxin and concentration as low as 0.08 mg/l of aluminum in drinking water is reported to have caused Alzheimer's disease. The ISO 10500 for drinking water sets an absolute maximum limit of 0.2 mg/l

for aluminum, which is well below the minimum reported in the output water generated by this technique. Also, the taste of the output water is generally not acceptable.

11.2.2 Activated Alumina Process [46–49]

Activated alumina is an aluminium oxide and it is highly porous and exhibits high surface area. The crystal structure of alumina contains cation lattice discontinuities giving rise to localized areas of positive charge. This makes alumina attract various anionic species. Alumina has high preference for fluoride compared to other anionic species, and hence is an attractive adsorbent. In the activated alumina process, alumina is treated with HCl to make it acidic; this acidic alumina contacted with fluoride ions displaces the chloride ions and gets attached with the alumina. After that, to regenerate the adsorbent a dilute solution of sodium hydroxide is mixed with the adsorbent to get a basic alumina. Further treatment with acid regenerates the acidic alumina. Reactivation of filter material is cumbersome and it can be done only with the help of trained persons, generally not available in most of our villages. This process also results in high residual aluminum in output water ranging from 0.16 to 0.45 mg/l.

11.2.3 KRASS Process [50–53]

In the KRASS process, the fluoride-contaminated water is passed through a bed of specially designed filter media to get defluoridated water. This process differs from the known processes in its simplicity, cost effectiveness and only traces of residual aluminum in outlet water. There is no limit on fluoride concentration in input water. Temperature, pH, alkalinity and total dissolved solids (TDS) of input water do not affect this process. It is a practical approach, especially for our rural population. The importance of the process is that it is a defluoridation process which is easy to use by illiterate villagers, requires minimal involvement of technical personnel, is harmless and is cost-effective. In the process, once the filters are laid the only expenditure is in terms of recharging with alum. The large-scale field installation of KRASS process plants is underway.

11.2.4 Adsorption Process

Due to its cost and simplicity of design and operation, adsorption is a widely used method and its results are quite satisfactory. With the help of nanomaterials, fluoride can be easily removed from water. This review

is based on the potential of nanomaterials for the removal of fluoride from water and wastewater. Most of the adsorbents for removing fluoride reported in literature are micron-sized particles. In recent years, nanomaterials have attracted much interest and have been widely used as sorbents due to properties such as high surface-to-volume ratio and short diffusion route. Because of comparatively large surface areas, it is likely that nanosized adsorbents with strong affinity towards fluoride can be a useful tool in enhancing the adsorption capacity in treatment of drinking water. However, due to their small particle size, the isolation of nanosized adsorbents from matrices is difficult for practical application. Magnetic nanosized adsorbents overcome the shortcomings of nonmagnetic nanomaterials and are very promising for application in the field of preconcentration and the removal of pollutants from environmental samples.

11.2.4.1 *Nanomaterials*

In the past decade, nanotechnology has emerged as a promising technology in various fields. Likewise, the use of nanoparticles as sorbents for water treatment has also gained wide attention in recent years. Activated alumina is an effective adsorbent for removing fluoride from drinking water. The fluoride adsorption is strongly dependent on pH and other competing anionic elements. Increasing the pH significantly reduced fluoride adsorption, especially for high-fluoride surface loading conditions [54]. Ionic strength did not impact fluoride adsorption. The impact of major anions on fluoride adsorption followed the order of $\text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{Cl}^-$. A speciation-based model well described fluoride adsorption in a broad pH range (pH 5–10.5).

Carbon nanotubes (CNTs) have attracted huge interest since their discovery. Their small sizes, large surface area, high mechanical strength and remarkable electrical conductivities make them potential materials for a wide range of promising applications. Carbon nanotubes were used as support to deposit Al_2O_3 [55] and the possibility of $\text{Al}_2\text{O}_3/\text{CNTs}$ for removing fluoride from drinking water was explored. The adsorption isotherms showed that the best fluoride adsorption on $\text{Al}_2\text{O}_3/\text{CNTs}$ occurred in the pH range of 5.0–9.0. The adsorption capacity for $\text{Al}_2\text{O}_3/\text{CNTs}$ was about 13.5 times higher than that of AC-300 carbon, and four times higher than that of $\gamma\text{-Al}_2\text{O}_3$ at equilibrium fluoride concentration of 12 mg/l. The mass of fluoride adsorption for $\text{Al}_2\text{O}_3/\text{CNTs}$ at pH 6.0 reached 28.7 mg/g at equilibrium concentration of 50 mg/l. Aligned carbon nanotubes (ACNTs) were prepared by catalytic decomposition of xylene using ferrocene as catalyst, and their performance was evaluated for fluoride removal from water [56].

Both the surface and inner cavities of ACNTs were found to be readily accessible for fluoride sorption. A broad pH range of 3–9 was found optimum for fluoride removal. The highest adsorption capacity of ACNTs occurred at pH 7.0 and reached 4.5 mg/g at equilibrium fluoride concentration of 15 mg/l. The CNTs were modified with alumina; the prepared sorbent was applied for defluoridation from water and the effects of calcination temperature, alumina loading and pH on fluoride removal capacity was investigated [57]. The optimum calcination temperature for preparing the adsorbents was observed to be 450°C and the highest adsorption capacity was exhibited to take place at alumina loading of 30%. High adsorption capacity for fluoride removal was obtained for $\text{Al}_2\text{O}_3/\text{CNTs}$ at 25°C in the pH range 6.0–9.0. Fluoride sorption was found to occur by ligand exchange when the surface was positively charged and through ion exchange mechanism when the surface was neutral.

Nanosized inorganic oxides have been reported to be excellent reagents in various separation technologies through selective adsorption. They are known to exhibit remarkable adsorption properties due to their enhanced surface area and large interface volume depending on the chemistry of the constituent atoms. The preparation of a variety of nanosized inorganic oxides through thermolysis of a polymeric-based aqueous precursor solution of the desired inorganic ions was standardized [58]. The obtained Fe_3O_4 , Al_2O_3 and ZrO_2 nanosized oxide powders were incorporated in the matrix of activated charcoal through adsorption and used as the adsorbing bed for the removal of trace amounts of fluoride and various other pollutants. The charcoal embedded fine powders of the inorganic oxides have been able to remove fluoride/arsenate and arsenate ions from industrial wastewater up to 0.01–0.02 mg/l levels.

Defluoridation experiments employed nanoscale aluminium oxide hydroxide as sorbent, taking into account the advantage of the higher surface area of nanoparticles as compared to the traditional micron-sized materials [59]. The maximum Langmuir defluoridation capacity of nano-Al-OOH was found to be 3259 mg/kg. The adsorption of fluoride onto nano-Al-OOH was strongly pH dependent. The fluoride adsorption increased with the rise in pH, reaching a maximum of 96.7% at pH 6.8, and then decreased with further increase in pH. The pH of the sorbent was reported as *ca* 7.8, which was responsible for the sorption of fluoride at acidic pH, and low efficiency in alkaline medium was explained by the repulsion between the negatively charged surface and fluoride. The XPS analysis of the sorbent indicated that the adsorption of fluoride at low pH could be explained by a two-step protonation/ligand exchange reaction mechanism and exhibited participation of surface OH group in fluoride

removal. Adsorption of fluoride at an initial pH > 7.8 was attributed to van der Waals forces and not by anion exchange, which was evident from the decrease in final pH. At pH 7.8, nano-Al-OOH was said to function as a cation exchanger, as it adsorbed the sodium ions present in solution, releasing protons which were then responsible for the resulting decrease in final pH. Only the presence of sulphate and phosphate significantly affected fluoride uptake by nano-Al-OOH. Desorption studies showed that the fluoride could easily be desorbed at pH 13.

To enhance the defluoridation of water, mesoporous alumina was modified by coating copper oxide [60]. The copper oxide-coated alumina (COCA) was synthesized by impregnating alumina with copper sulphate solution followed by calcination at 450°C in the presence of air. It was observed that coating copper oxide improves the adsorption capacity of unmodified alumina from 2.232 to 7.770 mg/g. Various adsorption isotherm and kinetic parameters were computed using batch adsorption studies to determine the adsorption capacity and to understand the mechanism of adsorption. The results revealed that the adsorption follows Langmuir isotherm and pseudo-second-order kinetic models. The adsorption capacity obtained from Langmuir isotherm plots were 3.155 mg/g. Assessment of the water quality before and after treatment with COCA also confirmed that there is no leaching of copper and other parameters were also within permissible limits of Indian drinking water standards, indicating that the COCA can be used for treatment of fluoride-contaminated drinking water. The effect of coexisting anions such as sulphate, nitrate, carbonate, bicarbonate and chloride, which compete in the adsorption process; the adsorption studies were carried out in the presence of 100–1000 mg/l of these anions. The initial concentration of fluoride was maintained at 10 mg/l and initial pH of the solution was 5.2. The effect of these anions on fluoride removal is observed. It was observed that at up to 1000 mg/l of Cl⁻, and the fluoride removal efficiency remained above 80% for most of the concentrations of these anions. However, in the presence of HCO₃⁻ / CO₃²⁻ above 200 mg/l the fluoride removal efficiency drops down to about 70% and further decreases with increasing concentrations of these anions, which may be due to competition for the adsorption sites and also to the increase in pH of the solution. The adsorption isotherm data was best explained by the Langmuir model and the adsorption capacity obtained from Langmuir isotherms was 7.220 mg/g, which is three times higher than unmodified alumina. The adsorption kinetics followed the pseudo-second-order model. The results of pH studies reveal that the COCA can be used for defluoridation of water in broad pH range (between 4 and 9). The assessment of water quality after treatment confirms that there is no leaching of metals, namely aluminium

or copper. Moreover, other physicochemical water quality parameters of treated water were within the prescribed limits, indicating that COCA can be used for defluoridation of drinking water.

A novel hydrous-manganese-oxide-coated alumina (HMOCA) material was prepared through a redox process. The manganese oxides were amorphous and manganese existed mainly in the +4 oxidation state. Batch and column experiments were carried out to investigate the adsorption potential of the adsorbent. Fluoride adsorption onto HMOCA followed the pseudo-second-order equation well, with a correlation coefficient greater than 0.99. Both external and intraparticle diffusion contributed to the rate of transfer and removal. The adsorption of fluoride was thought to take place mainly by ion exchange. Optimum removal of fluoride occurred in a pH range of 4.0–6.0. The maximum adsorption capacity calculated from the Langmuir model was 7.09 mg/g. The presence of HCO_3^- , SO_4^{2-} and PO_4^{3-} had negative effects on the fluoride adsorption. The adsorbed fluoride can be released by alkali solution. The individual effects of coexisting ions, including HCO_3^- , SO_4^{2-} , PO_4^{3-} , SiO_3^{2-} , Fe^{2+} and humic acid usually present in groundwater samples have been investigated in a batch reactor. The initial concentration of the fluoride was maintained as 5 mg/l. The initial pH and temperature of the solution was maintained at 7.7 and 30.72°C, respectively. Variation in pH after the sorption process was not monitored. However, the presence of 10 mg/l humic acid has resulted in a 50% reduction in fluoride removal efficiency. This may be attributed to the blocking of active MnO_2 sites by the bigger humic acid molecule. The occurrence of HCO_3^- up to 200 mg/l has shown negligible reduction in fluoride uptake. The presence of silicate and iron has not shown any interpretable trends for the concentration range studied. More detailed studies are needed to assess the effects of various coexisting ions on fluoride removal by MOCA. Column studies were performed and 669 bed volumes were treated with the effluent fluoride under 1.0 mg/l at an influent F^- concentration of 5.0 mg/l and flow rate of 2.39 $\text{m}^3/(\text{m}^2 \text{ h})$ (empty bed contact time = 7.5 min) [61].

Hydrous manganese oxide was coated on the surface of AA to enhance fluoride removal potential. HMOCA can reduce fluoride concentration from 6.0 mg/l to 0.45 mg/l, while the removal efficiency was 45% for the virgin AA at the same condition. No secondary pollution was induced by organic or Mn^{2+} release. Adsorption kinetics followed the pseudo-second-order equation well. Adsorption isotherms can be well described by Langmuir equilibrium model. The maximum adsorption capacity was calculated to be 7.09 mg/g at pH 5.2 ± 0.05 . Adsorption of fluoride was thought to take place mainly by ion-exchange. The optimum removal ranked from

pH 4.0 to 6.0. A column study indicated the practicality of HMOCA for fluoride removal from groundwater. The adsorption rate of MOCA was found to be very rapid compared to that of AA, which was used as the base material for MOCA preparation. The adsorption of fluoride onto MOCA and AA followed Langmuir isotherm model. The MOCA loading capacity was found to be around 2.65 times that of AA. The pH conditions of the initial solution influenced the fluoride removal by MOCA. The optimum fluoride removal was observed between pH ranges of 4–7. Among the competing ions, HCO_3^- , SO_4^{2-} and PO_4^{3-} have shown no significant effect on fluoride removal by MOCA over the range of concentrations studied. Fluoride sorption onto MOCA followed second-order kinetics with a correlation coefficient greater than 0.98.

With synthetic wastewater, competitive adsorption characteristics of fluoride and phosphate on calcined Mg–Al– CO_3 layered double hydroxides (CLDH) were investigated [62]. It was found that the optimal pH is around 6 and it took 24 h to attain equilibrium when fluoride and phosphate were simultaneous added.

The potential of CaO nanoparticles for fluoride removal was investigated [63]. Particles of CaO were synthesized by the sol–gel method in the study. The percentage removal of fluoride decreased from 98.0% to 89.0% with initial concentration (100 mg/l) for 298–353 K, although the fluoride adsorption at a given temperature increased with time. The main cause of decreased removal at higher temperature was attributed to the escaping tendency of the molecules from interface at higher temperature, which diminished the extent of adsorption. The Langmuir maximum sorption capacity for fluoride removal was 163.3 mg/g. Fluoride adsorption onto CaO nanoparticles was explained by the fact that CaO was converted into $\text{Ca}(\text{OH})_2$ in water, and adsorption of fluoride occurred by surface chemical reaction, where hydroxide ions of calcium hydroxide were rapidly replaced by fluoride ions with the formation of CaF_2 . Fluoride adsorption was found to be almost constant in the pH range of 2–8. A progressive decrease in fluoride uptake above pH 8 was attributed to electrostatic repulsion of fluoride to the negatively charged surface and the competition for active sites by an excessive amount of hydroxyl ions. Competitive anions such as sulphate and nitrate did not affect the adsorption of fluoride by CaO nanoparticles.

The advantage of the granular form of Fe–Al–Ce adsorbent was utilized; it was used in acrylic–styrene copolymer latex as a binder for Fe–Al–Ce and spray-coated onto sand in a fluidized bed. The introduction of latex was found to increase the stability of the coated layer. The granules had a spherical shape and high stability with a size of about 2–3 mm and coating

thickness up to 200 μm to 0.20 μm [64]. The coating amount was from 3% to 36%. Granule stability was found to decrease and adsorption capacity increased with an increase in coating amount. The results of FTIR analysis indicated that the latex could react with active hydroxyl on the Fe–Al–Ce adsorbent, which led to a decrease of the adsorption capacity. With increasing coating amount, adsorption capacity increased while the stability of the granules decreased. For an acceptable adsorption capacity and stability, the coating amount of 27.5% is suggested. Using the coated granules as adsorbent, the fluoride adsorption capacity was 2.22 mg/g (coated granules) at pH 7 and initial fluoride concentration of 0.001 M. 300 bed volumes can be treated with the effluent fluoride below 1 mg/l for an influent fluoride concentration of 5.5 mg/l, pH of 5.8, and SV of 5 h^{-1} . For optimal stability and adsorption capacity, a coating amount of 27.5% was suggested. Coated granules with a coating amount of 27.5% had a fluoride adsorption capacity of 2.22 mg/g (coated granules) at pH 7.0 and initial fluoride concentration of 0.001 M. With an influent fluoride concentration of 5.5 mg/l, and pH 5.8, the effluent fluoride was below 1 mg/l until 300 bed volumes were treated, and reached 1.5 mg/l at 500 bed volumes, showing that the coated granules could be used in a packed bed for defluoridation from drinking water, and especially in a rapid recycle and coupled process of adsorption and regeneration, due to the simple preparation, cheap cost and high stability of the coated granules.

By co-precipitation method, Mn–Ce oxide adsorbents with high sorption capacity for fluoride removal have been prepared [65]. Different methods like Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis have confirmed that the hydroxyl groups on the adsorbent surface were involved in the sorption of fluoride. The formation of solid solution by Mn species entering CeO_2 lattices was also indicated.

Taking into consideration the advantages of the magnetic separation process and the potential of activated alumina for defluoridation, two effective types of super paramagnetic [66] nanoscale adsorbents of barite/ $\text{SiO}_2/\text{Fe}_3\text{O}_4$ were synthesized via three sequential steps: chemical precipitation of Fe_3O_4 , coating of SiO_2 on Fe_3O_4 using acidifying method, and further coating of barite $[\text{Al}(\text{OH})_3]$ on $\text{SiO}_2/\text{Fe}_3\text{O}_4$ adopting sol–gel (MASG) or homogeneous precipitation (MAHP) methods for the elimination of fluoride from aqueous solution; the adsorption potential of the prepared sorbents was compared with that of commercial activated alumina (CA). The Langmuir isotherm well described the equilibrium of fluoride adsorption on CA, MASG, and MAHP. The result revealed that the adsorption capacity of CA could effectively be enhanced when the initial pH value was 3.5, which was the approximate pKa value of the dissociation constant of

hydrofluoric acid. The MASG was found to be the most effective adsorbent, of which the adsorption capacity was reported as 38 g/kg, and it competed with CA even at a higher pH value such as 6.0 versus 3.5. The removal of fluoride ions from the solution in which MASG and MAHP were suspended was attributed to the functional groups on MASG and MAHP surface which adsorbed fluoride ions.

The advantages of $\text{Al}(\text{OH})_3$ and magnetic nanoparticles were used to fabricate nanosized adsorbents with high surface area, high affinity towards fluoride and good magnetic separability, to develop a new kind of magnetic fluoride adsorbent [67]. This nanosized adsorbent was prepared using hydrous aluminium oxide embedded with Fe_3O_4 nanoparticle ($\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ NPs), and was applied to remove excessive fluoride from aqueous solution. The $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ NPs exhibited strong adsorption of fluoride when the pH was between 5.0 and 7.0, which was ascribed to the electrostatic attraction between the positively charged $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ surface and fluoride. The adsorption capacity calculated by Langmuir model was 88.48 mg/g at pH 6.5. Fluoride removal in the presence of anion increased in the order of $\text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{Br}^- \approx \text{NO}_3^- \approx \text{Cl}^-$. Fluoride adsorption was driven by both electrostatic attraction and surface complexation, which was confirmed by XPS data and experimental results. Drinking water contains many ions such as sulfate, phosphate, chloride, bromide and nitrate. They will consequently compete with fluoride anions for the adsorption sites on the magnetic adsorbents surface. The effect of anion on the adsorption of fluoride was studied in batch mode with the concentration of each anion at 50 mg/l. The results found that the adsorption capacity of $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ (2:5) NPs decreased slightly when competing anions were present. Generally, multivalent anions are adsorbed more readily than monovalent anions. Fluoride removal in the presence of anion increased in the order of $< < \text{Br}^- \approx \text{Cl}^-$. It closely correlated with the Z/r (charge/radius) values of the anions which vary in the order of $(3/3.40) > (2/2.40) > \text{Cl}^- (1/1.81) > \text{Br}^- (1/1.95) > 1/2.81$. All of the results indicated that the $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ NPs possessed specific affinity toward fluoride, making it a highly suitable adsorbent for fluoride-contaminated water treatment.

Polypyrrole (PPy)/ Fe_3O_4 magnetic nanocomposites as novel adsorbents were prepared via *in-situ* polymerization of pyrrole (Py) monomer using FeCl_3 oxidant in aqueous medium in which Fe_3O_4 nanoparticles were suspended [68]. The magnetic adsorption process provides a cost effective and environmentally benign water treatment process. Consequently, a novel nanocomposite with magnetic property combining both polypyrrole and Fe_3O_4 was prepared, characterized and applied in the removal of fluoride as a model contaminant in water. The material was effective in water

defluoridation. The fluoride uptake was very rapid and depended on the initial concentration, temperature, adsorbent dose and pH. The adsorption kinetics were described by the pseudo-second-order kinetic model. The adsorption process was endothermic in nature and proceeded by ion exchange mechanism. Adsorption of fluoride in the presence of other anions such as chloride, nitrate, sulphate and phosphate was not remarkably affected. Up to 97% of the adsorbed fluoride on the PPy/Fe₃O₄ nanocomposites was desorbed at pH 12.

Amorphous iron- and aluminum-mixed hydroxides have been used for the removal of fluoride from aqueous solutions. Mixed Fe/Al samples were prepared at room temperature by co-precipitating Fe and Al mixed salt solutions at pH 7.5. The compositions (Fe:Al molar ratio) of the oxides were varied as 1:0, 3:1, 2:1, 1:1 and 0:1. The XRD studies indicated the amorphous nature of the samples and Al(III) incorporation on Fe(III) hydroxides. The XRD pattern of Fe:Al hydroxides indicated the amorphous nature of the materials and it was confirmed by X-ray diffraction patterns. Two broad peaks with d-values in the range of 2.54–2.57 and 1.47–1.48 corresponding to two-line ferrihydrate were observed in all the samples except for pure aluminum hydroxide. The 3:1, 2:1 and 1:1 samples have almost identical XRD patterns to that of pure ferrihydrate (1:0). No additional peaks corresponding to aluminum hydroxide were observed due to the amorphous nature of the Fe/Al samples. The pure Al sample showed four major XRD peaks for gibbsite phase with corresponding d-values of 4.82, 3.73, 2.99, 2.61, 2.34, 2.17, 2.04 and 1.93 Å. All the samples have shown high specific surface area values; surface area increased with the decrease of molar ratio. The sample with molar ratio 1 has shown markedly high specific surface area of 268. Batch adsorption studies for fluoride removal on these materials showed that the adsorption capacities of the materials were highly influenced by solution pH, temperature and initial fluoride concentration. The rate of adsorption was fast and equilibrium was attained within 2 h. The adsorption followed first-order kinetics with intraparticle diffusion as the rate determining step for all the samples. All samples exhibited very high Langmuir adsorption capacities; the sample with molar ratio 1 has shown maximum adsorption capacity of 91.7 mg/g. The thermodynamic parameters were determined to study the feasibility of the adsorption process. The increase of Al content in Fe(OH)₃ matrix slightly increased the surface area and pH ZPC values. The fluoride adsorption on these materials is encouraging; the equilibrium time data for all samples followed first-order kinetics and was governed by intraparticle diffusion model. The optimum pH range for fluoride adsorption was found to be 4–5 for the samples 1:0, 3:1 and 2:1, whereas it was in the range of 4–7.5 for 1:1

and 0:1. The thermodynamic studies demonstrate that the fluoride adsorption on these materials is thermodynamically favorable, spontaneous and exothermic in nature.

The adsorbent retained the original adsorption capacity after one complete adsorption–desorption cycle, confirming the reusability of the nanocomposite for fluoride removal. The synthesis of nanoparticles of MgO [69] by self-propagated combustion of the magnesium nitrate were trapped in cellulose fibers to increase the adsorption capacity of MgO for fluoride removal. Characterization studies revealed that the synthesized nanomagnesia was crystalline with high phase purity, and the particle size varied in the range of 3–7 nm. With the help of various spectroscopic, microscopic and macroscopic studies, the mechanism of fluoride uptake by nanomagnesia was attributed to fluoride removal through isomorphic substitution of hydroxyl groups by fluoride in brucite lattice. This reaction was found to be possible since both the F^- and OH^- ions are isoelectronic in nature and of similar size and comparable ionic radii. Langmuir maximum sorption capacity for fluoride removal was reported as 267.82 mg/g. Fluoride adsorption by nanomagnesia was less sensitive to pH variations. Only a slight decrease in fluoride adsorption was observed at higher pH, which was attributed to the competition from the negatively charged OH^- ions. Phosphate was the greatest competitor for fluoride followed by bicarbonate and nitrate.

A bioinorganic composite, namely nano-hydroxyapatite/chitosan (n-HApC) composite, which could be employed for technology development was prepared and studied for its defluoridation efficiency. It has been observed that there was a slight enhancement in the defluoridation capacity (DC) of n-HApC composite (1560 mg/F/kg) than nano-hydroxyapatite (n-HAp) which has a DC of 1296 mg/F/kg. The fluoride sorption was explained with Freundlich and Langmuir isotherms. The sorption process was found to be controlled by pseudo-second-order and pore diffusion models. Field studies were carried out with the fluoride containing water sample collected from a fluoride-endemic area in order to test the suitability of the sorbents at field conditions [70]. The n-HApC composite possessed higher DC than n-HAp. The DC of n-HApC composite was influenced by the pH of the medium and decreased in the presence of bicarbonate ions.

The surface acquired positive charge at lower pH values and hence the fluoride sorption at this pH level was mainly due to electrostatic attraction between the positive surface and negatively charged fluoride ions, and chemisorption dominated. As the pH increased slowly, the surface acquired negative charges; physisorption dominated, hence DC decreased.

In addition, ion exchange mechanism was also involved as the $-OH$ group present in n-HApC composite is considered as the charge carrier and gets exchanged with fluoride. The slight enhancement in DC of n-HApC composite over n-HAp may be due to biosorption by chitosan, adsorption by physical forces and fluoride ion entrapped in fibrillar capillaries and spaces of polysaccharide network of the chitosan moiety. The sorption of fluoride on n-HApC composite followed Langmuir isotherm and was spontaneous and endothermic in nature. The rate of sorption followed pseudo-second-order kinetic model and occurred through pore diffusion. Field trial studies indicated n-HApC composite could be used as an effective defluorinating agent. This bioinorganic nanocomposite throws more light on the development of defluorination technology as it is efficient, cost effective, indigenous and biocompatible.

Removal of fluoride from drinking water by cellulose@hydroxyapatite nanocomposites was studied. Cellulose@hydroxyapatite nanocomposites were prepared in NaOH/thiourea/urea/H₂O solution via *in situ* hybridization [71].

Magnesia (MgO) is a well-known adsorbent showing extremely high defluorination capacity (DC). In order to overcome the limitations of MgO for field applications, an attempt has been made to modify magnesia with abundant biomaterial chitosan to form magnesia/chitosan (MgOC) [72] composite in a usable form, and its merits over conventional magnesia and raw chitosan is established. Removal of fluoride from aqueous solution with MgO and MgOC composite was studied with batch equilibrium experiments. At equilibrium, MgOC composite has a DC of 4440 mg per i.e./F/kg while for magnesia it is only 2175 mg/F/kg. The physicochemical properties of the synthesized MgOC composite were analyzed with FTIR and SEM with EDAX studies. The specific surface area of MgOC composite was found to be 45.5143 m²/g. The FTIR spectrum is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band and can obtain structure, bond information, and study of strength and fraction of hydrogen bonding. The band at 3700 cm⁻¹ corresponds to $-OH$ stretching vibration. Although there is a possibility of overlapping between $-NH_2$ and $-OH$ stretching vibrations, the band 3437 cm⁻¹ corresponds to $-OH$ and $-NH_2$ stretching vibrations. The bands at 2929 and 1430 cm⁻¹ correspond to aliphatic stretching vibrations of $-CH$ and $-NH$ bending vibrations of chitosan, respectively. The slight broadening of $-OH$ stretching vibration band at 3437 cm⁻¹ in the fluoride-sorbed MgOC composite when compared with MgOC composite corresponds to the formation of $O-H \cdots F$ bond, which confirms the existence of hydrogen bonding.

The fluoride-contaminated drinking water may contain several other anions which may compete with the sorption of fluoride. The DC of MgOC composite was experimentally verified in the presence of other common anions like Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- , and was investigated with varying initial concentrations of these ions ranging from 100 to 500 mg/l by keeping 10 mg/l as initial fluoride concentration at 303 K. There is a slight increase in the DC of MgOC composite in the presence of Cl^- , SO_4^{2-} , NO_3^- ions, but the DC decreases in the presence of HCO_3^- ions. This is due to the competition of bicarbonate ions with fluoride ions in the sorption process. Parallel interference of bicarbonate ions on the C has been cited earlier by using montmorillonite on its adsorbent for fluoride removal. A novel adsorbent, namely MgOC composite, was prepared to remove fluoride from drinking water which possesses an appreciable higher DC than magnesia. The DC of both the sorbents is not influenced by pH of the medium. The DC of MgOC composite was not affected in the presence of co-anions except bicarbonate ion. The sorption process follows Freundlich isotherm. The thermodynamic parameter values indicate that the fluoride removal process is spontaneous and endothermic in nature. The kinetics of MgOC composite follows pseudo-second-order particle and intraparticle diffusion models. The results of field trial indicate that both the sorbents can be effectively used to remove fluoride from water. However, the treated water was found to be alkaline in nature when both the sorbents were used as the defluoridating medium.

The adsorbent was synthesized by calcining magnesia (MgO) with pullulan, an extracellular water-soluble microbial polysaccharide, and characterized using FTIR, SEM, XRD and BET. The results showed that the surface area and the adsorption micropore of the calcined MgO/pullulan composite [73] were increased from 7.5888 m^2/g and 13.91507 nm for pure MgO to 32.8992 m^2/g and 29.11552 nm, respectively. The FTIR analysis showed that hydrogen bonds were formed in the adsorption of fluorides on to the calcined MgO/pullulan composite. At 30°C and pH 7.0, the adsorption capacity was determined as 4537 mg/kg using the initial concentration of 10 mmol/l fluoride solution. The adsorption capacity of calcined MgO/pullulan composite remained stable in the range pH 2–10. The adsorption isotherms fitted well to the Langmuir isotherm model. The adsorption kinetics of fluoride onto the calcined MgO/pullulan composite closely followed the Lagergren's pseudo-second-order rate mode, which indicates that the chemical adsorption, rather than mass transfer, is the rate-determining step. The effect of initial concentration on the uptake of fluoride by MgO and cMgOP was studied with initial fluoride concentrations ranging from 10 to 30 mg/l, all other parameters were held constant. The results showed that the defluoridation capacity of both sorbents increased with increasing

initial fluoride concentration. This may be due to the fact that a higher concentration gradient was formed in the presence of more fluoride ions. An increased availability of fluoride ions in solution at the solid–solution interface also enhances adsorption performance as cMgOP clearly exhibits higher defluoridation capacity than MgO; further investigations were limited to cMgOP only. The defluoridation capacity of cMgOP showed only a small variation in the pH range 2–10. The presence of Cl^- , SO_4^{2-} and NO_3^- led to negligible change in defluoridation capacity, however the presence of HCO_3^- decreased the defluoridation capacity significantly. The sorption of fluoride on cMgOP followed Langmuir isotherm and was spontaneous and endothermic in nature. The rate of sorption closely followed the pseudo-second-order kinetic model and can be characterized by the particle diffusion model. The mechanism of fluoride removal by cMgOP involves both electrostatic attraction and hydrogen bonding. With the high F^- removal efficiency, the ability to be shaped into any desired form and excellent penetrability for water, cMgOP has a good potential to be used as an effective adsorbent in water treatment for defluoridation.

Magnetite nanoparticles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} and synthesis of a new sorbent consisting of 3-aminopropyl triethoxysilane (APTES)-coated magnetic nanoparticles functionalized with a zirconium (IV) porphyrin complex $\text{Zr}(\text{TCCP})\text{Cl}_2$ [TCCP: tetrakis(4-carboxyphenyl) porphyrin]. The Fe_3O_4 nanoparticles were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} in an ammonia solution; for introducing the reactive groups onto the particles' surface, nanoparticles were modified by APTES. These modified nanoparticles were functionalized with Zr (III) metalloporphyrins. The sorbents showed a good efficiency in fluoride extraction and a high selectivity toward the target anion. The effects of pH, contact time, nanosorbent dosage and foreign ions on the extraction efficiency were studied [74, 75]. Under optimal conditions for a fluoride concentration of 10 mg l^{-1} (contact time: 20 min; pH: 5.5 and nanosorbents dosage: 100 mg) the percentage of the extracted fluoride ions was $92.0 \pm 1.7\%$. The advantages of this product are the ease of separation by an external magnetic field, possibility of simple recovery after washing with a basic aqueous solution and its reuse for up to five cycles. The sorption of fluoride on a novel zirconium-modified-Na-attapulgite (Zr-A) adsorbent was studied. The fluoride adsorption capacity of the Zr-A adsorbent was higher in comparison with attapulgite, which was due to the changes of the surface charge of the adsorbent and the generation of abundant hydroxyl ions. The Zr-A adsorbent exhibited good adsorbity for fluoride over a wide pH range of 3.70–7.50. Adsorption of fluoride reached the equilibrium in 110 min for different initial fluoride concentration [76].

11.3 Conclusions

Nowadays we are facing a problem of fluorosis. Different types of techniques and methods have been used for the removal of fluoride from water like the Nalgonda process, activated alumina process, electrodialysis, reverse osmosis, KRASS process, adsorption process, etc. The adsorption process is the best method for defluoridation, but for this process selection of good adsorbent is a big challenge for us. Among these cost-effective methods, today's nanomaterials are the first choice. Nanoadsorbents have attracted considerable attention in recent years in fluoride removal, and these materials have shown higher fluoride uptake capacity. So, future research should be concentrated on evaluating the efficacy of adsorbents in terms of cost and feasibility for removal of fluoride. It would be worthwhile to study the suitability of different chemicals to regenerate the spent adsorbents.

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Chemical Nanosensors for Monitoring Environmental Pollution

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Abstract

Due to the enhancement in industrial development and population, the natural atmospheric environment has become polluted and is rapidly deteriorating. Presently, environmental monitoring is needed in order to protect the public and the environment from toxic contaminants and pathogens that can be released into a variety of media including air, soil, and water. Thus, the need for monitoring and proper control of such pollutants is essential to prevent environmental disasters. Nanomaterials-based chemical sensors are the solution for the prevention of these environmental disasters. This chapter will provide a brief review on current research status of chemical sensors based on various new types of nanostructured materials such as nanoparticles (NPs) nanotubes (NTs), nanorods (NRs), nanobelts (NBs), and nanowires (NWs). In this chapter, the focus for the application of chemical nanosensor will be placed on gas sensors that have been developed for environmental monitoring, along with their sensing principles. These nanomaterials-based chemical sensor devices have a number of salient characteristics, including high sensitivity, excellent selectivity, fast response and recovery.

Keywords: Environmental pollution, chemical sensor, nanostructure, response time, sensitivity, gas sensor

12.1 Introduction

The first decade of the 21st century of high technology and advanced industry has produced an incredible rise in the standard of living of human

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beings. However, this has led to serious environmental pollution, which is caused by industry, automobiles, home and agricultural activities, such as heavy metal ions (Hg^{2+} , Cd^{2+} , As^{3+} , Pb^{2+} , Cr^{3+} , etc.), various toxic gases (SO_2 , NO_x , CO , HCl , etc.), volatile organic compounds (VOCs), formaldehyde (HCHO), fluorocarbon, organophosphorus (OP) and compounds (pesticides and insecticides); these can directly or indirectly effect the ecosystem resulting in global environmental issues, such as acid rain, the greenhouse effect, sick house syndrome, and ozone depletion, which greatly threaten environmental security and human health.

Environmental pollution can be classified mainly into three categories: atmospheric, water, and soil pollution. It has been observed that out of the three different types of pollution, air pollution and water pollution are majorly disastrous because they spread very rapidly and directly impact living beings. Thus there is an urgent need for rapid, reliable and accurate development of sensors for monitoring and controlling these pollutants.

With the advancement of nanotechnology, different sensors based on nanostructures are being widely used for many applications such as critical care, safety, industrial hygiene, process controls, product quality controls, human comfort controls, emissions monitoring, automotive industry, clinical diagnostics, home safety alarms, and, more recently, homeland security (Table 12.1).

Basically, this chapter describes the fundamental knowledge about sensors, various sensor devices fabricated by research made on gas sensors that contain nanomaterials, and the main quality parameters of these sensing devices. The main goal of this chapter is to make the reader aware of the application of chemical sensors based on nanostructured materials for environmental monitoring of harmful gases present in the environment. We start with the definition of chemical sensors, typical parameters of chemical sensors, then different types of nanostructures used for chemical sensing, detailed studies of each nanostructure, and metal oxides. Next we move on to discuss carbon nanotubes which are widely used and even functionalized with other compounds to increase their selectivity to particular analytes. We finally conclude our discussion with the conducting polymer-based gas sensor.

12.1.1 Chemical Sensors

A chemical sensor usually contains two basic components connected in a series: a chemical (molecular) recognition system (receptor) and a physicochemical transducer. A scheme of a typical chemical sensor system arrangement is outlined in Figure 12.1.

Table 12.1 Application of sensors.

Application	Examples of detected chemical compounds and classes
Automotive	O ₂ , H ₂ , CO, NO _x , HCs.
Indoor air quality (IAQ)	CO, CH ₄ , humidity, CO ₂ , VOCs such as benzene, methylene chloride
Food	Bacterial, biologicals, chemicals, fungal toxins, humidity, pH, CO ₂
Medical	O ₂ , glucose, urea, CO ₂ , pH, Na ⁺ , K ⁺ , Ca ²⁺ , Cl ₂ , biomolecules, H ₂ S
Agriculture	NH ₃ , amines, humidity, CO ₂ , pesticides, herbicides
Infectious disease	ketones, anesthesia gases such as nitrous oxide and xenon
Water treatment	pH, Cl ₂ , CO ₂ , O ₂ , O ₃ , H ₂ S, CH ₄ , NH ₃
Environmental	SO _x , CO ₂ , NO _x , HCs, NH ₃ , H ₂ S, pH, heavy metal ions such as Cd ²⁺ , Zn ²⁺ , Hg ²⁺ , Cr ³⁺
Petrochemical	ethylene, propylene, butadiene, benzene, toluene, xylenes, carbon monoxide, hydrogen, Methane, ethane, propane and butanes etc
Military agents	explosives, propellants, chlorine, HCl, NO, phosgene, sulphur mustard, nitrogen mustard, HCN
Aerospace	H ₂ , O ₂ , CO ₂ , humidity
Chemical laboratory	H ₂ , NH ₃ , methane, CO, benzene
Home safety	LPG, smoke, power overloading.

In the majority of chemical sensors, the receptor interacts with analyte molecules. As a result, its physical properties are changed in such a way that the attached transducer can gain an electrical signal. In some cases, one and the same physical object acts as receptor and as transducer. This is the case, e.g., in metallic oxide semiconductor gas sensors which change their electrical conductivity in contact with some gases. Conductivity change itself is a measurable electrical signal. In mass sensitive sensors, however,

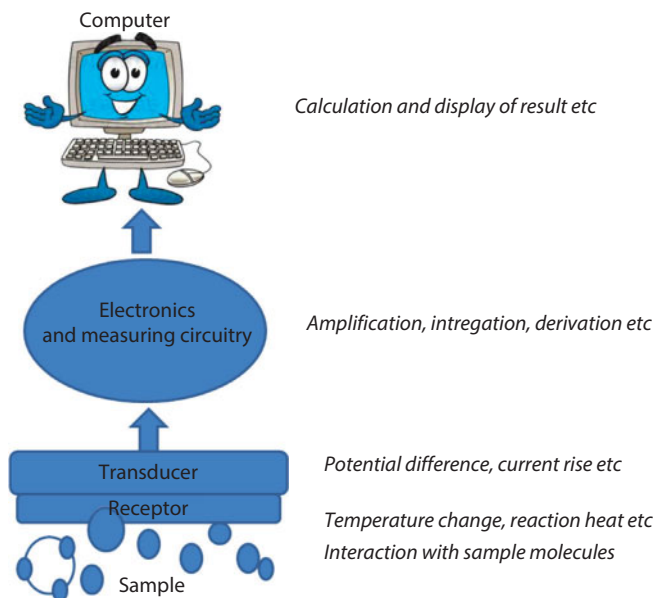


Figure 12.1 Scheme of a typical chemical sensor system.

receptor and transducer are represented by different physical objects. A piezoelectric quartz crystal acts as transducer. The receptor is formed by a sensitive layer at the crystal surface. The latter is capable of absorbing gas molecules. The resulting mass change can be measured as a frequency change in an electrical oscillator circuit.

There are different definitions of chemical sensors.

- IUPAC, (1991) [1]: “A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal.”
- Wolfbeis, (1990) [2]: “Chemical sensors are small-sized devices comprising a recognition element, a transduction element, and a signal processor capable of continuously and reversibly reporting a chemical concentration.”
- Francia *et al.* (2009) [3]: “A chemical nanosensor is an electronic device, consisting of a transducer and a sensitive element whose operation relies on at least one of the physical and chemical properties characteristic of the nanostate.”

The most important aspects in the investigation of a variety of sensors are the three S's, i.e., sensitivity, selectivity, and stability. Chemical sensors should possess the following important characteristics:

- Transform chemical quantities into electrical signals,
- Respond rapidly,
- Maintain their activity over a long time period,
- Be small,
- Be cheap,
- Be *specific*, i.e., they should respond exclusively to one analyte, or at least be *selective* to a group of analytes,
- Have *low detection limit*, or a *high sensitivity*.

12.1.2 Typical Parameters of Chemical Nanosensors

The following list contains static as well as dynamic parameters which can be used to characterize the performance of chemical sensors.

1. *Sensitivity*: change in the measurement signal per concentration unit of the analyte.
2. *Drift*: slow changes in the signal of a sensor maintained in a solution of constant composition and temperature.
3. *Detection limit*: the lowest concentration of the analyte that can be detected and/or measured by a sensor.
4. *Dynamic range*: the range of concentrations in which the sensor sensitivity is greater than zero.
5. *Selectivity/Specificity*: an expression of whether a sensor responds *selectively* to a group of analytes or even *specifically* to a single analyte.
6. *Linearity*: the relative deviation of an experimentally determined calibration graph from an ideal straight line.
7. *Resolution*: the lowest concentration difference which can be distinguished when the composition is varied continuously.
8. *Response time*: the time for a sensor to respond from zero concentration to a step change in concentration. Usually specified as the time to rise to a definite ratio of the final value.
9. *Hysteresis*: the maximum difference in output when the value is approached with (a) an increasing and (b) a decreasing analyte concentration range. It is given as a percentage of full-scale output.

10. Long-term *stability*: the ability of the sensor to maintain its performance for a certain period of time.
11. *Life cycle*: the length of time over which the sensor will operate. The maximum storage time (*shelf life*) must be distinguished from the maximum.
12. *Operating life*: the latter can be specified either for continuous operation or for repeated on-off cycles.
13. *Reproducibility*: the closeness of replicate measurements on the same sample, using the same measuring technique, under the same conditions.
14. *Thermal and Mechanical stability*.
15. *Miniaturization*: the creation of ever-smaller scales for mechanical, optical, and electronic products and devices. Miniaturization is a continuing trend in the production of such devices.
16. *Working range*: the temperature range at which sensors work.
17. *Compatibility to pressure, temperature, explosiveness, Radioactivity, biological condition, sterilization*.

12.1.3 Chemical Sensors Based on Nanomaterial

Nowadays, chemical sensors based on various new types of nanostructured materials such as nanoparticles (NPs), nanotubes (NTs), nanorods (NRs), nanobelts (NBs), and nanowires (NWs) are used.

- Nanowires (NWs): The typical length of the NWs ranges from several tens to several hundred micrometers.
- Nanorods (NRs): The nanorods are only several micrometers long.
- Nanotubes (NTs): Nanotubes possess wire-like nanostructures but they have hollow cores.
- Nanobelts (NBs): The belt-like nanostructure has a rectangular cross section. Each NB has a uniform width along its entire length, and the typical widths of the NBs lie in the range of several tens to several hundred nanometers.

These nanostructure-based sensors are used for detection in biological, electrochemical, gas, and pH sensors. But in this chapter the focus for the application of chemical nanosensor will be on the gas sensor. The sensing

devices include individual nanostructured sensors, multi-nanostructured sensors and nanostructured film sensors. These nanosensor devices have a number of salient characteristics.

- Reduced size of the sensing parts and transducer: miniaturization of the devices,
- surface properties are important due to large surface-to-volume ratio, and
- surface-engineered nanomaterial can be used as chemical sensor for:
 - increased sensitivity,
 - improved detection limits,
 - faster instrumental responses, and
 - smaller amounts of samples.

These properties set them apart from currently available sensor technologies.

12.1.4 Nanomaterial-Based Gas Sensor

A *gas nanosensor* is a device which detects the presence of various gases within an area, usually as part of a safety system. This type of chemical sensor is used to detect a gas leak and interface with a control system so a process can be automatically shut down. A gas sensor can also sound an alarm to operators in the area where the leak is occurring, giving them the opportunity to leave the area. This type of device is important because there are many gases like CO_2 , CO , NO_2 , SO_2 , O_2 , O_3 , H_2 , Ar , N_2 , NH_3 , and H_2O , and organic vapors such as methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), isopropanol ($\text{C}_3\text{H}_8\text{O}$), benzene (C_6H_6), chlorofluorocarbons (CFCs) and some haloalkanes that can be harmful to organic life, such as humans, animals or plants. Gas sensor can be used to detect combustible, flammable and toxic gases, and oxygen depletion. This type of device is widely used in environmental monitoring, hospitals, military and household security, chemical, pharmaceutical and research laboratories, and industry; and can be found in a variety of locations such as on oil rigs, to monitor manufacturing processes, and in emerging technologies such as photovoltaics. They may also be used in firefighting.

Gas detection using semiconducting oxides has been making a considerable impact to date [4]. However, the need to operate the device at high temperatures often limits the use of this type of detection. Due to this limitation, a proposal to modify some of the structural parameters

has been undertaken: for example, orientation and crystal shape [5]. Nanostructured materials (nanomaterials) can also be used to reduce working temperatures and consume less power and are safer to operate. One of the important characteristics of nanomaterials is their high surface area/volume ratio. And this important characteristic of nanomaterials favors the adsorption of gases on the sensor and can increase the sensitivity of the device because the interaction between the analytes and the sensing part is higher. Apart from this, many studies have focused on reducing the size of the metal oxides in the form of nanoparticles and nanowires, thin films of conducting polymers, metal nanoparticles, and, more recently, carbon nanotubes have also been used for gas sensor devices. These materials change their electrical properties (e.g., conductivity or impedance) and optical properties (e.g., coefficient of molar absorptivity or refractive index), among others, when they receive the stimulus of the sensing layer after the molecular- or ion-recognition event. The mechanisms for recognizing the gases to be determined include absorption processes, particularly in metal oxides and carbon nanotubes, and specific recognition for the formation of supramolecules or covalent bonds between the sensor and the analyte, as occurs with some metal complexes.

12.1.4.1 *Sensing Mechanism*

Sensing of chemiresistor relies on the conductance change. Here, we have focused on the detection of analytes based on the conductance change with a special attention to enhance the sensitivity and improve the selectivity.

In order to employ a particular material for sensing different gases, it is essential to understand the sensing mechanism. It is well known that the conductance of n-type semiconductors (e.g., ZnO, SnO₂) increases with a reducing analyte and decreases with an oxidizing one. On the other hand, p-type semiconductors (e.g., NiO, CuO) exhibit the opposite response. Assuming the resistance is mainly due to the neck resistance and the grain-boundary resistance, a model of the neck-grain boundary control is shown in Figure 12.2. Here, it is assumed that the semiconductor-based elements are in polycrystalline form with large numbers of grain boundaries and necks. When the semiconductor material is annealed in air atmosphere, oxygen gets adsorbed on the surface and extracts the conduction electrons to form a depletion layer. As a consequence, the conductance decreases and the amount of change depends on the size. The smaller the size, the bigger is the change. Reaction of a reducing gas with the adsorbed oxygen results in its removal, thereby increasing the conductance.

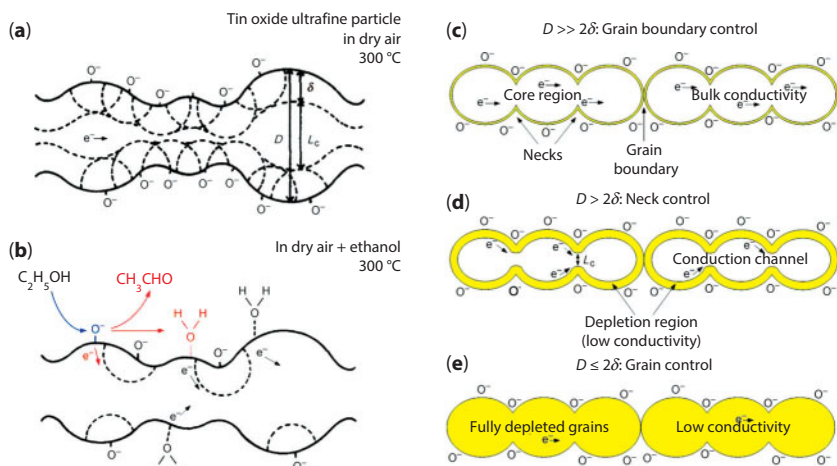


Figure 12.2 Schematic model of oxygen ionosorption on the SnO_2 surface in (a) pure dry air and (b) with ethanol [6]. The adsorbed oxygen species (a) trap electrons from SnO_2 forming ions that scatter electrons within the Debye length δ of the oxide (3 nm for SnO_2 at 250 °C) [6]. This decreases the electron concentration and mobility resulting in a reduction of the SnO_2 conductivity. The reaction between ethanol and the ionosorbed oxygen (b) decreases the concentration of these scattering centers (O^-) and releases the trapped electrons, thereby increasing the SnO_2 conductivity. The mechanism controlling the conductivity change and its magnitude depends mainly on the ratio between grain size (D) and Debye length [7]. Three different cases have been discussed in Fig. 12.2: If $D \gg \delta$ (c), $D > 2\delta$ (d), $D \leq 2\delta$ (e) [7]. (Adapted with permission from [8]; Copyright (2013) Wiley-VCH publication)

Three different cases have been discussed in Figure 12.2: (c) $D \gg \delta$, (d) $D > 2\delta$ and (e) $D \leq 2\delta$. It may be noted that the nanowire is depleted completely for $D \leq 2\delta$. When $D \gg \delta$, a small part of the semiconductor is affected by interaction with the analyte and the sensitivity to the analyte is expected to be low. For $D > 2\delta$, a conduction channel with high conductivity exists but its wideness (L_c) can be controlled by the surface concentration of oxygen ions leading to moderate sensitivities. When $D \leq 2\delta$, the whole conduction channel is depleted and changes in the surface oxygen concentration affects the whole semiconductor, resulting in high sensitivity [7]. The smaller the size, the bigger is the change.

Silicon nanowire (SiNW) sensors functionalized with peptide nucleic acid (PNA) are used for electrical detection of DNA. In this case, conductivity of Si nanowires changes when the DNA approaches/comes in contact with the nanowires (Figure 12.3). The net change in the conductance depends on the concentration of the DNA (Figure 12.4) [9].

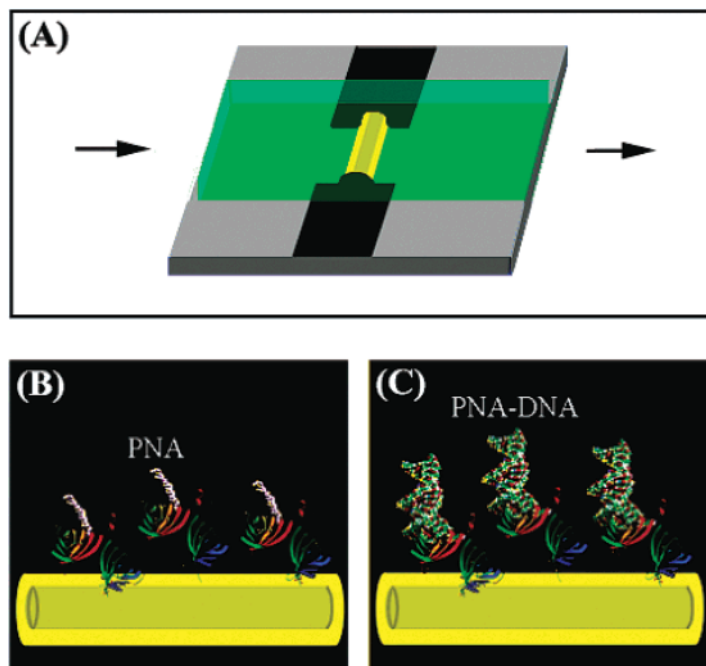


Figure 12.3 (A) Schematic of a sensor device consisting of a SiNW (yellow) and a microfluidic channel (green), where the arrows indicate the direction of sample flow. (B) The SiNW surface with PNA receptor. (C) PNA-DNA duplex formation. (Adapted with permission from [9]; Copyright (2013) American Chemical Society)

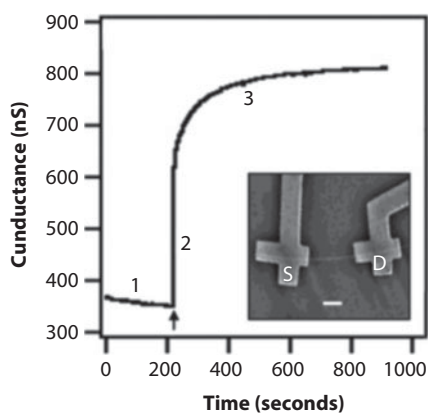


Figure 12.4 Real-time conductance response from a SiNW device functionalized with PNA receptor. The arrow marks the point in time when the 60 fM WT DNA sample was added. The inset shows a SEM image of a typical SiNW device with source (S) and a drain (D) indicated; scale bar is 1 μm. (Adapted with permission from [9]; Copyright (2013) American Chemical Society)

12.1.5 Metal Nanoparticle-Based Gas Sensors

The metal nanoparticles provide electronic conductivity, while the organic matrix furnishes the selective binding sites on which the adsorption of analyte molecules takes place. The ability to control the sensor properties by molecular design is the attractive feature of this approach. The study of metal nanoparticle-based gas sensors has been done by many scientists and researchers.

In the year 1998, a chemiresistor¹ consisting of a film of octanethiol-encapsulated gold nanoparticles deposited on interdigitated electrodes was demonstrated [10]. This chemiresistor showed a fast, reversible response towards water vapors, toluene, tetrachloroethene and 1-propanol. After the interval of 2 years, several other groups reported the tenability of the selectivity of sensor films by introducing chemical functionality into the organic ligand shell [11]. The detection of harmful gases, CO and NH₃ in the 300 ppb to 5000 ppm range by crosslinking gold and platinum nanoparticles with nonanedithiol was also shown [12].

It is also found that in most of the cases, metal nanoparticles are dispersed on the surface of a substrate to increase the area/volume ratio and favors the adsorption of gases. Metal nanoparticles change their electronic properties or the properties of the substrate when they are in contact with the analyte because the gas molecules adsorb on the metal.

Take for example the hydrogen sensor. Hydrogen, being an important source of alternative energy for transportation, residential, and industrial sectors, needs a great deal of attention in research related to its storage, transportation, and handling. One of the major problems is that hydrogen is extremely inflammable and volatile. The presence of only 2%–4% hydrogen in air can cause an explosion. Hence, the scientific community is aiming for a better hydrogen sensor for safety monitoring.

Thus Hydrogen sensor based on the Pd nanoparticles deposited on Si p-type substrate was fabricated [13]. Here the formation of nanopores of diameter 10 nm takes place on the surface of Si p-type substrate, when the substrate was submitted to an electrochemical etching with HF/ethanol/H₂O. Finally SiO₂ and PdO formation takes place when the Pd film of 4 nm was deposited and then stabilized with an annealing at 900°C for 1 hour. This process resulted in an increase in the contact surface area of the sensor, and the electrical resistance also increased because vacancies were generated in the silicon. This porous silicon–Pd sensor was used in a custom testing chamber with a four-point probe configuration. The

¹ A chemiresistor is a small, simple, sensitive, rugged microsensor with low power requirements capable of detecting chemical vapors in air, soil, or water.

conductivity of the device used increased under nitrogen and with hydrogen concentrations of 0–1.5%. Here, Pd acted as the catalyst for the dissociation of hydrogen, which transferred electrons to the silicon substrate, thus decreasing the resistance. Because the PdO formed during the annealing can be reduced at temperatures of 100°C or above, which affects detection, the device is operated at ambient temperature.

In order to detect SO₂ in acidic and basic solutions, a Pt electrode with Au nanoparticles was used on its surface (with an Ag/AgCl reference electrode). The attachment of Au nanoparticles to a cysteine-modified Pt electrode takes place by dipping this electrode into a Au colloid for 1 day. The amperometric detection was carried out in H₂SO₄ 1M, HClO₄ 0.1M, HCl 0.1 M, and NaOH 1 M, as internal electrolytes. Results were best observed in 1 M NaOH: Other gases in the system such as CO, NO, NH₃ and CO₂ did not interfere, and the linear response was between 5 and 500 ppm of SO₂ and the sensitivity was found to be $5.4 \times 10^{-10} \text{ A ppm}^{-1}$ with a detection limit of 2.6 ppm [14].

12.1.5.1 Metal Oxide Gas Sensors

Nanostructured metal oxides are found to be one of the main types of material used to fabricate gas sensors. The semiconducting nature of some of these compounds makes it possible for the electrical conductivity of the material to change when the composition of the surrounding atmosphere changes. Thus we can say that most of these devices can be classified as conductimetric nanosensors. As we have already discussed above, nanosized materials have a very favorable area/volume ratio. Thus, for the same chemical composition, the smaller the nanomaterials are, the more sensitive the sensor is.

Chemical sensors are based on nanotubes (NTs), nanorods (NRs), nanobelts (NBs), nanowires (NWs), nanoribbons (NRs), mesowires (MWs), and nanofibers (NFs) as follows [15]:

1. In general, nanotube-based sensors include metal oxide tubes such as Co₃O₄, Fe₂O₃, SnO₂, and TiO₂, and metal tubes such as Pt nanosensor.
2. MOX nanorods are ZnO, MoO₃, and tungsten oxide.
3. As for nanobelts-based sensors, the main attention has been focused on MOXs such as ZnO, SnO₂, and V₂O₅ nanosensors, especially on ZnO-NB sensors.
4. Nanowires include In₂O₃, SnO₂, ZnO, β -Ga₂O₃, etc.

Some of the different nanostructured-based chemical sensors for detecting environmental gases are listed in Table 12.2.

Table 12.2 Metal oxide-based gas sensors.

Materials	Analytes	References
Co_3O_4 (NTs)	H_2	[16]
β - Fe_2O_3 (NTs)	H_2 , $\text{C}_2\text{H}_5\text{OH}$	[17]
SnO_2 (NTs)	H_2 , CO, ethylene oxide	[18]
TiO_2 (NTs)	H_2	[19, 20]
ZnO impregnated with Pt (NTs)	$\text{C}_2\text{H}_5\text{OH}$	[21]
Pt coated single ZnO (NWs)	H	[22]
Pt coated ZnO (NRs)	H_2	[23]
ZnO (NRs)	$\text{C}_2\text{H}_5\text{OH}$, H_2S	[24]
ZnO (NWs)	$\text{C}_2\text{H}_5\text{OH}$	[25]
multiple ZnO (NRs)	H_2 , O_3	[26, 27]
Pd/multiple ZnO (NRs)	H_2 , $\text{C}_2\text{H}_5\text{OH}$	[28]
MoO_3 (NRs)	CO, $\text{C}_2\text{H}_5\text{OH}$	[4]
tungsten oxide (NRs)	$\text{C}_2\text{H}_5\text{OH}$, NH_3 , NO_2 .	[29]
SnO_2 (NBs)	O_2 , H_2	[30]
SnO_2 (NRs)	NO_2	[31]
SnO_2 nanobelt/CdS nanoparticle core/shell(NBs)	$\text{C}_2\text{H}_5\text{OH}$	[32]
SnO_2 (NRs)	H_2S	[33]
SnO_2 (NBs)	CO, NO_2 , $\text{C}_2\text{H}_5\text{OH}$.	[34]
V_2O_5 (NBs)	$\text{C}_2\text{H}_5\text{OH}$	[35]
Pd (NWs)	H_2	[36]
Pd (NWs)	H_2	[37]
Ag (MWs)	NH_3	[38]
Ag (MWs)	2,4-dinitrotoluene (2,4-DNT),	[39]
Si (NWs)	NH_3 , H_2O	[40]
Single In_2O_3 (NWs)	NO_2 , NH_3	[41]
ZnO (NWs)	NH_3	[42]
β - Ga_2O_3 (NWs)	$\text{C}_2\text{H}_5\text{OH}$	[36]

(continued)

Table 12.2 (*cont.*)

Materials	Analytes	References
V ₂ O ₅ (NFs)	organic amines	[43]
In ₂ O ₃ (NW)	NO ₂ , NH ₃ , O ₂ , CO, H ₂	[44]
SnO ₂ (NW)	O ₂ , CO, NO ₂ , C ₂ H ₅ OH	[45]
	O ₂ , CO	[44]
	CO	[46]
In-SnO ₂ (NWs)	C ₂ H ₅ OH	[47]
Sb-SnO ₂ (NWs)	C ₂ H ₅ OH	[48]
Ru-SnO ₂ (NWs)	NO ₂ , Liquid petroleum gas	[49]
ZnO (NWs)	NH ₃ , NO ₂	[50]
	C ₂ H ₅ OH	[51]
	O ₂	[52]
	O ₃	[53]
Ga-ZnO (NWs)	CO	[51]
Pd-ZnO (NWs)	H ₂	[23]
Pt-ZnO (NWs)	H ₂	[22]
	NH ₃ , NO ₂	[54]
WO ₃ (NWs)	NO ₂ , H ₂ S	[55]
TeO ₂ (NWs)	NO ₂ , H ₂ S, NH ₃	[56]
Co ₃ O ₄ (NTs)	H ₂	[16]
β-Fe ₂ O ₃ (NTs)	H ₂ , C ₂ H ₅ OH	[17]

* nanotubes (NTs); nanorods (NRs); nanobelts (NBs); nanowires (NWs); nanoribbons (NRs); Mesowires (MWs); nanofibres (NFs).

12.1.5.2 Carbon Nanotube Gas Sensors

Carbon nanotubes are known to be very interesting in the field of sensors because they are characterized by high, theoretically infinite, surface/volume ratio [57]. Today, the development of CNT-based gas sensors has attracted great interest because of their high response, sub-ppb concentration detection levels, prompt response, low operating temperature, small

power consumption, miniature size for nanodevice shrinking, functionalization for specific detection of molecules, and ability to build massive sensor arrays. Sensors have been fabricated using single-walled, multi-walled, and well-aligned CNT arrays [58].

It was found that the normalized response of the SWCNT sensor was higher than that of the MWCNT sensor [59]. Probably this is because SWCNTs contained more semiconducting tubes. In general, MWCNTs show a conducting (metallic) behavior at room temperature. However, MWCNTs could contain some semiconducting tubes among predominantly metallic ones. The higher normalized response of the SWCNT sensor may be attributed to the higher abundance of the semiconducting tube, which is responsible for the sensor response. A lot of work in the field of CNT-based gas sensors has been performed so far.

In this chapter we have tabulated some examples of pristine CNT sensor, organic polymer-functionalized CNT gas sensors, and metal nanoparticle/nanocluster-functionalized CNT gas sensors for the detection of some harmful gases (Table 12.3).

Table 12.3 CNT-based gas sensors.

Materials	Sensor configuration	Detection	References
SWNTs	ChemFET	NO_2 , NH_3	[60]
SWNTs	Chemiresistor	NO_2 , nitrotoluene	[61]
SWNTs	Chemiresistor	O_2	[62]
SWNTs	Chem FET	DMMP	[63]
MWNTs	Chemiresistor	NO_2	[64]
MWNTs	Chemiresistor	NH_3	[65]
SWNTs	Chemiresistor	SOCl_2 (thionyl chloride), DMMP (dimethyl methylphosphonate)	[66]
SWNTs	Chemiresistor	O_3	[67]
SWNTs	Chemiresistor	Methanol, Acetone	[68]
SWNTs	Chemiresistor	H_2O	[69]

(continued)

Table 12.3 (*cont.*)

PANI-SWNT	Chemiresistor	NH ₃ gas	[70]
Pd loaded SWNT		CH ₄	[71]
Carboxylated SWNTs	Chemiresistor	CO	[72]
PEI, Nafion- SWNTs	ChemFET	NO ₂ , NH ₃	[73]
PMMA-MWNTs	Chemiresistor	Dichloromethane, chloroform, acetone	[74]
PEI -SWNTs	ChemFET	NO	[75]
Polypyrrole -SWNTs	ChemFET	NO ₂	[76]
Poly(3-methylthiophene)-MWNTs	Chemiresistor	CH ₂ Cl ₂ , CHCl ₃ , CCl ₄ , CH ₄	[77]
Poly(vinyl acetate), Polyisoprene -MWNTs	Chemiresistor	Tetrahydrofuran, ethanol, cyclohexane	[78]
Polyaniline-SWNTs	Chemiresistor	NH ₃	[70]
Pd -Single SWNT	ChemFET	H ₂	[79]
Pd -SWNTs	Chemiresistor	CH ₄	[71]
Au, Pt -MWNTs	Chemiresistor	NO ₂ , NH ₃	[80]
Au -SWNTs	Chemiresistor	NO ₂	[81]
Pt, Pd- MWNTs	Chemiresistor	H ₂ , NO ₂ , H ₂ O	[82]
Pd -SWNTs	Chemiresistor	H ₂	[83]
Pd -SWNTs	Chemiresistor	H ₂	[84]

12.1.6 Conducting Polymer-Based Gas Sensor

Nowadays for the sensing application, conducting polymers such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have also been used as active layers of gas sensor. In comparison

with most of the commercially available sensors usually based on metal oxides and operated at high temperatures, the sensors made of conducting polymers have many improved characteristics. They have high sensitivities and short response time; especially those sensors that work at room temperature. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be conveniently modified by copolymerization or structural derivations. Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors.

The main problems associated with these materials are their (i) lack of selectivity and (ii) their lower stability regarding time and temperature.

Additive materials such as carbon NPs or fibers have been explored to increase the selectivity and stability of polymer-based sensors.

Hernandez *et al.* reported the synthesis, electrical characterization and ammonia gas sensing with single nanowire conducting polypyrrole [85]. Three hundred nanometers in diameter and 50- to 60- μm long polypyrrole nanowires were synthesized by chemical polymerization inside SiO_2 -coated alumina membranes. Temperature-dependent electrical resistance studies established that the chemically synthesized nanowires were more ordered compared to electrochemically synthesized nanowires. They further demonstrated that gas sensors based on single polypyrrole nanowire exhibited good sensitivity towards ammonia, and provided a reliable detection at concentration as low as approximately 40 ppm.

It has been observed that the detection limits are rather low for sensors based on conducting polymers. For redox active or acid-base active analytes, the detection limit is smaller than 1 ppm, and for inert organic analytes, that limit is about several ppm or lower. Some of the conducting polymer-based gas sensors are listed in Table 12.4.

12.2 Conclusion

This chapter presented a brief overview of atmospheric pollution and emitting sources, a definition of chemical sensors, different sensing mechanisms of sensors and different types of gas sensors. It also showed that in comparison to the conventional sensors, the chemical nanosensors are compact, robust, and inexpensive and are required as an effective alternative for environmental monitoring. Today, human beings desire to live in a comfortable environment; along with significant advances in sensor technologies for monitoring pollutants, gases have resulted in a more focused and rapid development of environmental gas sensors.

Table 12.4 Detection limit of conducting polymers and their composite-based sensors for several gases.

Sensing material	Sensor type	Detection limit	Analyte	References
² PAni/Heavy metal salts	Chemiresistor	<10 ppm	H ₂ S	[86]
PAni/FeAl	Chemiresistor	10 ppm	CO	[87]
PAni/In ₂ O ₃ ³ PPy/PET	¹ SAW Chemiresistor	<0.5 ppm <20 ppm	NO ₂	[88] [89]
PAni/SWNT	Chemiresistor	50 ppb	NH ₃	[90]
PAni/Pd	Chemiresistor	<1 ppm	C ₂ H ₅ OH	[91]
⁴ PTh copolymer	Chemiresistor	200-300 ppm	C ₆ H ₅ CH ₃	[92]

¹Surface acoustic waves; ²Polyaniline; ³Polypyrrole; ⁴Polythiophene

12.3 Challenges and Future Prospect

As with everything there are always challenges that need to be faced and the field of chemical nanosensors is no exception. Some of these are in the reduction of the cost of materials and devices, and improving the selectivity, sensitivity, stability, reproducibility and reliability of them. Another challenge that is faced is in the actual packaging of them and putting them into a product that is useful for consumers. Perhaps one of the largest challenges with chemical nanosensors is in the actual production of them.

In the future, there is no doubt that nanocrystalline metal oxides will constitute the key for the development of semiconducting gas sensors for environmental monitoring with improved gas-sensing properties. Not only in chemiresistive gas sensors, but in general, in solid-state gas sensors, nanostructured material will play a fundamental and determinant role in the gas sensors of a new generation. Nanoscience and Nanotechnology are, in fact, devoting great efforts to the development of novel materials for gas-sensor applications. Just as an example, the interest in inorganic-organic hybrid nanocomposites containing conducting polymers as the organic part and metal oxides as the inorganic part, and in nanorods, nanowires, nanotubes and nanobelts made of semiconducting metal oxides. The latter are chemically pure, structurally uniform and largely defect-free, with clean surfaces not requiring protection against oxidation. These new

classes of nanostructures offer a great potential for applications in ultra-small sensors because the conductivity of these materials changes dramatically when gas or liquid molecules attach to their surfaces.

Some of the advantages that would come from using chemical nanosensors are due to their tiny size, the fact that they require less power to run, their greater sensitivity and the fact that they have better specificity than today's sensors. All of these advantages would allow us to accomplish things that we could never imagine before, such as atomic-sized sensors flowing in our blood streams that could predict cancer and other diseases.

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Reduction of 4-Nitrophenol as a Model Reaction for Nanocatalysis

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Abstract

Noble metal nanocomposites have received a great deal of attention in the field of catalysis due to their unique properties, which are directly related to their shapes and sizes. To investigate and derive a definite conclusion about the catalytic activity of various nanocatalysts with different sizes, shapes, and even porosities, a model reaction needed to be selected. The reduction of 4-nitrophenol (4-NP) by NaBH_4 has been widely used as this model reaction, since it is easy to monitor with simple and fast analytical techniques, and there are no by-products. This reaction is also valuable in the view of green chemistry since 4-NP, one of the toxic substance in the wastewater, is converted into a commercially important substance, 4-aminophenol (4-AP). Here we present an overview of the mechanistic studies into 4-NP reduction, followed by a comprehensive overview of materials evaluated for this reaction.

Keywords: 4-nitrophenol reduction, nanocatalyst, kinetics, mechanism

13.1 Introduction

Noble metal nanocomposites have received much attention in the field of catalysis due to their high surface-to-volume ratio and their high surface energy. These properties render their surface atoms very active [1]. The reduction potential is significantly different for metal nanocomposites of varying sizes in comparison to bulk metals, since the Fermi potential of nanocomposite becomes more negative. This specific

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property allows for efficient catalysis during various electron transfer processes [2]. Interestingly, the size, shape, composition, and porosity of noble metal nanocomposites can be controlled to improve their activity. Most nanocomposites are spherical, however, recently, several authors reported protocols to synthesize different shapes. These include rods [3], polygons [4], cubes [5, 6], dendrites [7, 8], nanoboxes [9], nanocages [9, 10], rattles [11], and nanowires [12]. Nanocatalysis has been reviewed extensively [13–21].

4-NP and its derivatives are used in the production of pesticides (such as nitrofen and parathion), herbicides, insecticides [22], explosives, synthetic dyes used to darken leather [23], and pharmaceutical drugs. They are also present in agricultural irrigation effluents. This means that 4-NP and its derivatives are some of the most common organics of non-biodegradable and toxic persistent pollutants in industrial, agricultural wastewater and aquatic environments [24–30]. They are considered as one of the 65 major pollutants [31], hazardous wastes, and as priority toxic pollutants by the United States Environmental Protection Agency (US EPA) [32]. Among phenol compounds, 4-NP is produced in the highest quantities worldwide and has a higher toxicity than other mononitrophenols [32]. The presence of a nitro-group in the aromatic ring enhances stability, making chemical and biological degradation difficult in the purification of wastewater polluted with 4-NP. These pollutants are unaffected by aerobic biodegradation [33], and anaerobic degradation produces nitroso and hydroxylamine compounds which are known to be carcinogenic [34]. Due to their high toxicity, water solubility, and stability as well as their resistance to water purification methods [34], attention has been given to researching the fate of these compounds in the environment, and to develop methods to remove these compounds from surface and groundwater. These methods include direct photolysis, microwave-assisted catalytic oxidation [35], microbial degradation [34], photocatalysis [26, 27, 36–38], polymeric adsorption [39–43], the electro-Fenton method [44], electrocoagulation [45], and electrochemical treatment [46].

On the other hand, 4-Aminophenol (4-AP) is a commercially important intermediate for the manufacture of analgesic and anti-pyretic drugs such as acetanilide, paracetamol, and phenacetin [47–49]. It is also used extensively as a photographic developer, a corrosion inhibitor in paints, an anti-corrosion-lubrication agent in fuels for two-cycle engines, wood stain, imparting a rose-like color to timber, and a hair-dyeing agent [50]. Due to the usefulness of 4-AP, various methods have been reported to

synthesize it, including conventional multi-step iron-acid reduction of 4-nitrochlorobenzene or 4-NP [51], catalytic hydrogenation of 4-NP [48, 52] or nitrobenzene [47, 49, 51, 53], and an electrochemical synthesizing method [54]. However, the multi-step iron-acid reduction generates large amounts of Fe-FeO sludge, which cannot be reused and causes severe disposal problems [47]. In the case of the catalytic hydrogenation of nitrobenzene in a strong acid, the aqueous medium yields a significant amount of aniline and smaller amounts of other impurities. In addition, the use of highly corrosive mineral acids is a major drawback. Because these disadvantages restrict the production efficiency and the quality of 4-AP, it has become less economically attractive. Therefore, in order to meet the growing demand of 4-AP, more efficient and eco-friendly catalytic methods are needed. Two such methods have been proposed: 1) the hydrogenation of 4-NP in the presence of various heterogeneous metal catalysts such as Ni [52, 55, 56] and Pt [48], and 2) the reduction of 4-NP by hydrazine in ethanol-water and in the presence of a Raney nickel catalyst [57]. A 4-NP reduction by borohydride in the presence of suitable catalysts has also been an attractive alternative for many researchers, since the low toxicity of borates renders borohydride relatively environmentally friendly [58].

Since the unique properties of noble metal nanocomposites are as a direct result of their size and shape, a model reaction has to be chosen to conclusively define and evaluate their catalytic action. The degree of favorable conversion in such a reaction should be easy to monitor using simple and fast analytical techniques. The reaction should also yield no by-products. As such, the reduction of 4-NP by NaBH_4 to 4-AP represents a satisfactory model for the following reasons: 1) 4-NP reduction can be easily observed by means of a color change from yellow to colorless, and by the decrease in absorption of the 4-nitrophenolate anion at λ 400 nm (as observed by UV-Vis spectroscopy), leading directly to the rate constant; 2) this organic reaction can be catalyzed by free or immobilized nanocomposites in aqueous solution at ambient temperature [59]; 3) several isosbestic points in the spectra of the reacting mixtures demonstrate that no by-products are formed [60–63]; 4) although this reaction is thermodynamically favorable, it is not kinetically so since the reduction potential of 4-NP converted to 4-AP is 0.76 V (measured versus normal hydrogen electrode), while that of borate-borohydride ($\text{H}_3\text{BO}_3/\text{BH}_4^-$) is -1.33 V. In the absence of a catalyst [60, 61, 64–68], the reaction does not occur even in 2 days [58] however, in the presence of metal nanocatalysts, the reaction proceeds easily. Therefore, 4-NP reduction is very important

and valuable in green chemistry and from an industrial and academic point of view. The experimental illustration conducted in the authors' lab is presented in Figure 13.1.

The Pal group [66] was the first to report the model reaction of 4-NP reduction to 4-AP by sodium borohydride (NaBH_4) using Au, Ag, and Cu NPs in 2001. Since then, interest in this reaction has grown significantly among researchers. In mid-2000, the number of papers using 4-NP reduction rapidly increased (Figure 13.2b). The most popular metal nanocomposites for this reaction were Au, followed by Ag and Pd (Figure 13.2a).

This review aims to compile all available information regarding 4-NP reduction in the presence of various metal nanocomposites. It will cover the theories involved in the kinetic evaluation of 4-NP reduction, including possible mechanisms, as well as the catalytic activities of various metal nanocomposites synthesized according to different protocols.

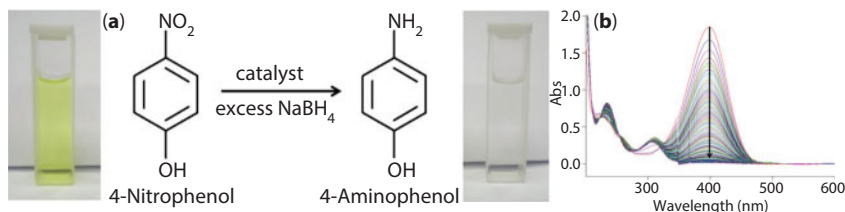


Figure 13.1 (a) The illustration of 4-NP reduction to 4-AP by excess NaBH_4 . (b) Typical UV-Vis spectrum of 4-NP reduction. The spectrum was taken every 30 seconds for 50 minutes. $[\text{NaBH}_4] = 10.0 \text{ mmol}\cdot\text{dm}^{-3}$, $[4\text{-NP}] = 0.10 \text{ mmol}\cdot\text{dm}^{-3}$ and dendrimer encapsulated Pd nanoparticle $[\text{G4-OH}(\text{Pd}_{40})] = 0.050 \text{ }\mu\text{mol}\cdot\text{dm}^{-3}$ [69].

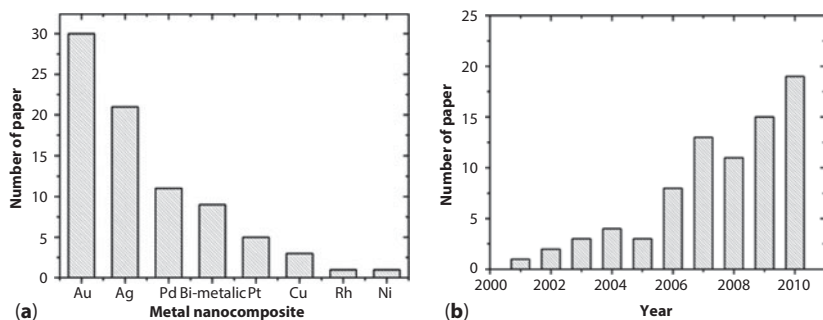
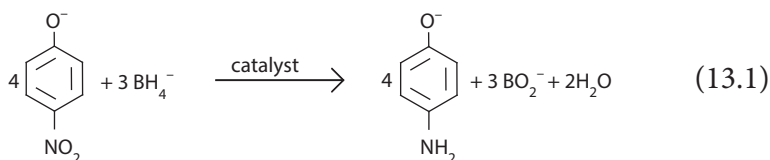


Figure 13.2 (a) Number of papers vs metal nanocomposite used in the reduction of 4-NP; (b) Number of papers vs years.

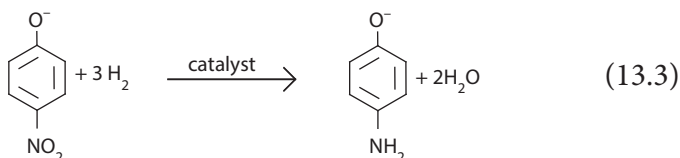
13.2 Kinetic Evaluation and Mechanism of 4-NP Reduction

13.2.1 Kinetic Evaluation

The reduction of 4-NP is carried out in the presence of a catalyst, with an excess of freshly prepared NaBH_4 as a reducing agent under alkaline conditions. Upon addition of NaBH_4 to the system, 4-NP is converted to 4-nitrophenolate ($\text{pK}_a=7.15$). The 4-NP peak moves from λ 317 nm to λ 400 nm, indicating the presence of the 4-nitrophenolate anion. This peak remains unaltered over time, which suggests that the reduction does not proceed in the absence of a catalyst, as reported by several authors [60, 61, 64–68]. A significant reduction of the peak at λ 400 nm is observed after addition of catalyst, along with the development of a peak at λ 300 nm, indicating the formation of 4-AP. Clear isosbestic points show that 4-AP is the sole product of the reaction (Figure 13.1b) [60–63]. The concentration of BH_4^- is much higher than 4-NP, so it essentially remains constant during the reaction and prevents aerial oxidation of 4-AP [68]. Additionally, the evolution of small hydrogen gas bubbles helps to stir the solution, ensuring that the catalyst particles remain homogeneously distributed. These factors contribute to favorable conditions for a smooth reaction. The total reduction reaction is summarized in Equation 13.1 [8].



The reaction can be split into two parts: the hydrogen radical production from borohydrite by electron transfer (Eq. 13.2) and the addition of protons to 4-NP while removing oxygen (Eq. 13.3). These reactions can proceed almost independently.



The conversion process can be directly read off from the corresponding graph since the ratio of the concentration $[4\text{-NP}]_t$ of 4-nitrophenolate at time t to its value $[4\text{-NP}]_0$ at $t = 0$ ($[4\text{-NP}]_t/[4\text{-NP}]_0$) is directly given by the ratio of the respective absorbance ($A_{4\text{-NP}(t)}/A_{4\text{-NP}(0)}$). Since the concentration of NaBH_4 largely exceeds the concentration of 4-NP to ensure *pseudo*-first-order reaction conditions, the reduction rate can be assumed to be independent of borohydride concentration. So, in this case, first-order kinetic with regard to the 4-nitrophenolate concentration could be applied to evaluate the catalytic rate [60–62, 70]. Therefore, the kinetic equation of the reduction could be shown as

$$-\frac{d[4\text{-NP}]}{dt} = k_{app} \cdot [4\text{-NP}] \text{ or}$$

$$\ln A_{4\text{-NP}(t)} = -k_{app} \cdot t + \ln A_{4\text{-NP}(0)} \quad (13.4)$$

where k_{app} is the apparent rate constant, $A_{4\text{-NP}(0)}$ is the initial absorbance at λ 400 nm.

According to the Equation 13.4 and from the graph in Figure 13.3b, the apparent rate constant (k_{app}) can be determined by the slope. The representative graphs obtained from the authors' lab, using $0.050 \mu\text{mol}\cdot\text{dm}^{-3}$ Pt and Pd dendrimer encapsulated nanoparticles (DENs), are presented in Figure 13.3. The induction time (t_0) was observed with Pt DENs, however, it disappeared when the oxygen was removed from the system by degassing of the solution with N_2 gas purging. The values of k_{app} obtained by the slope of the fitted line in Figure 13.3b are $2.1 \times 10^{-3} \text{ s}^{-1}$, $1.2 \times 10^{-4} \text{ s}^{-1}$, and $1.4 \times 10^{-4} \text{ s}^{-1}$ for G4-OH(Pd_{40}) without degassing, G4-OH(Pt_{40}) with degassing, and G4-OH(Pt_{40}) without

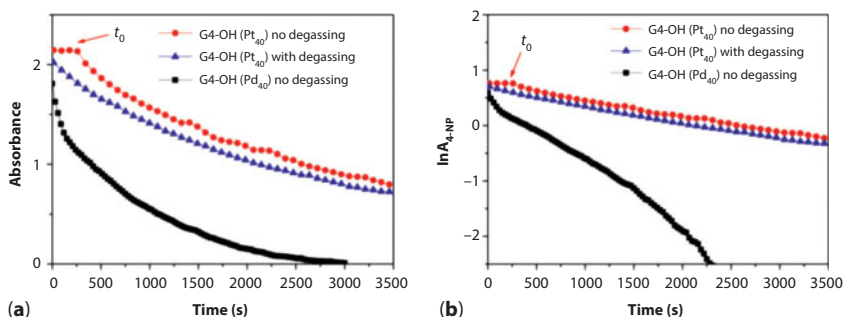


Figure 13.3 (a) Absorbance vs time graph after the background correction by subtracting the absorbance value from λ 400 nm to λ 550 nm. (b) The corresponding time-resolved kinetic trace at λ 400 nm showing apparent first-order kinetics. (Experimental conditions: $[\text{Metal DENs}] = 0.050 \mu\text{mol}\cdot\text{dm}^{-3}$, $[4\text{-NP}] = 0.1 \text{ mmol}\cdot\text{dm}^{-3}$, $[\text{NaBH}_4] = 10.0 \text{ mmol}\cdot\text{dm}^{-3}$, $T = 284 \text{ K}$, degassing time = 30 minutes [69]).

degassing, respectively. The catalytic efficiency is higher with Pd DENs than with Pt DENs in this conditions.

13.2.2 Induction Time (t_0)

An induction time t_0 , i.e., a delay, was found for the 4-NP reduction in many cases [8, 9, 61, 63–65, 67, 70–74] although some authors reported no such delay [75–78]. The induction time has been observed with various catalysts, including Pd-Ag dendrite [8], Ag NPs immobilized in core-shell microgel [64], Ag NPs immobilized onto the highly branched polymer brush [72], Pt NPs immobilized onto the spherical polyelectrolyte brush (SPB) [61], chitosan-stabilized Pd NPs [73], and Cu DENs [74]. Such delay times might be caused by an oxidized metallic surface [64, 70] or by the activation of the catalyst in the reaction system. Some authors argue that it is as a result of the dissolved oxygen in water reacting at a faster rate with borohydride than with nitrophenol [60, 61, 66, 70, 79]. In many cases, nitrogen is purged before the addition of NaBH_4 to remove the oxygen. The experimental results presented in Figure 13.3 are from authors and also support this statement [69]. No induction time was observed with Pd DEN catalysts but there was a delay with Pt DENs. However, once N_2 purging of the solution was performed for 30 minutes to remove oxygen in the system, the induction time disappeared (Figure 13.3b). Recently, Wunder *et al.* [63] stated that the induction time is related to a slow surface reconstruction of the NPs, the rate of which is directly related to the surface reaction.

13.2.3 4-NP Reduction Mechanism

Most of the papers listed in Table 13.1 reported that the reduction followed first-order kinetics with respect to the 4-nitrophenolate ion concentration, with the exception of a few cases [58, 62]. Pradhan *et al.* [62] investigated the 4-NP reduction using *in situ*-generated, still-growing microelectrode (GME) and fully grown microelectrode (FGME) Ag NPs in aqueous solution. They found that the reduction follows first-order kinetics with FGME but zero-order kinetics with GME. Saha *et al.* [58] also reported zero-order kinetics for calcium-alginate-stabilized Ag and Au NPs.

Saha *et al.* [58] proposed that the mechanism of 4-NP reduction is a six-electron transfer process. The role of metal particles in various redox reactions can be explained by their electrochemical current potential [80, 81]. In the case of 4-NP reduction, electron transfer takes place between BH_4^- and nitrophenolate through the adsorption of the reactant molecules onto

Table 13.1 Summary of nanocatalyst system for the reduction of 4-NP.

Criteria/ carrier system	Metal	Synthetic method/ stabilizing agent	Shape	Size (nm)	Catalyst dosing	4-NP rate constant* /temperature of catalysis (K)	Activation energy (kJ·mol ⁻¹)	Ref
NC/ templateless	Au	Citrate reduction/ Ammonium bis- muth citrate	Porous spongy	20 ~ 140	0.006 g catalyst	0.35 s ⁻¹ ·g ⁻¹ /288	-	[119]
NC/ -	Au-Ag	Galvanic replacement/ -	Flake	- ^b	0.006 g catalyst	10.1 s ⁻¹ ·g ⁻¹ /-	-	[126]
NC (dendrite)/ templateless	Ag	Wet chemical reduction/ Triammonium citrate (TAC)	coral	700~ 1400	0.004 g catalyst	1.30 s ⁻¹ ·g ⁻¹ /-	-	[7]
			Banana leaves	-		0.70 s ⁻¹ ·g ⁻¹ /-		
			spherical	9 ~ 25		0.09 s ⁻¹ ·g ⁻¹ /-		
NC (dendrite) /-	Pd-Ag	Galvanic replacement/ -	Flake	20	0.001 g catalyst	0.039 s ⁻¹ /rt ^c	-	[8]

NP/ biomolecule	Ag	Wet chemical reduction/ Chitosan	spherical	< 5	3.24 g·dm ⁻³ catalyst	1.5 × 10 ⁻¹ s ⁻¹ ·m ⁻² ·dm ³ /296	-	[73]
NP/ microgel	Ag	Photoemulsion polymerization Wet chemical reduction/ PNIPA-BIS-PS ^e	spherical	8.5	6.3 mg·dm ⁻³ catalyst	- /283 ~313	-	[65]
NP/ microgel	Ag	Photoemulsion polymerization Wet chemical reduction/ PNIPA-BIS-PS ^e	spherical	8.5	6 mg·dm ⁻³ catalyst	5.2 × 10 ⁻² s ⁻¹ ·m ⁻² ·dm ³ /293	-	[64]
NP/ SPB ^f	Ag	Photoemulsion polymerization UV irradiation/ PAA-PS ^g	spherical	3	-	7.81 × 10 ⁻² s ⁻¹ ·m ⁻² ·dm ³ /-	-	[104]
NP/ SHBPP ^h	Ag	Photoemulsion polymerization UV irradiation/ PEGMA-PS ⁱ	spherical	7.5	4.56 mg·dm ⁻³ catalyst	7.27 × 10 ⁻² s ⁻¹ ·m ⁻² ·dm ³ /293	62	[72]
NP/ hydrogel	Ag	Photoemulsion polymerization UV irradiation/ PVA/PEGMA-PS	spherical	35	1.98 mg catalyst	7.80 × 10 ⁻⁵ s ⁻¹ ·m ⁻² ·dm ³ /293	-	[105]

(continued)

Table 13.1 (cont.)

NP/ hydrosol	Ag	Wet chemical reduction/ Ag hydrogel	spherical	25	5.0×10^{-6} catalyst	3.78×10^{-7} $\text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{dm}^3 / -$	41	[62]
NP/ resin-bound	Ag	Wet chemical reduction/ Anion-exchange resin bead	spherical	30	1.5×10^{-3} catalyst	3.16×10^{-3} min^{-1} /303	24.08	[87]
NP/ Layer-by- layer film	Ag	Sequential electro- static deposition/ PAMAM-PSS-PAA ^k	spherical	5~ 10	-	-	-	[113]
NP/ Conducting polymer	Ag	Wet chemical reduction/ pEDOT/PSS	spherical	10~ 15	-	-	-	[121]
NP/ Magnetic oxide	Ag	Wet chemical reduction/ Fe_2O_3	spherical	5~ 10	-	$1.5 \times 10^{-2} \text{ s}^{-1}$ /308	45	[90]
NP Hollow sphere	Ag	Self-removing pro- cess & wet chemi- cal reduction PNIPAM	spherical	10	0.5 g catalyst	$0.014 \text{ s}^{-1} \cdot \text{g}^{-1}$ /rt	-	[94]

NP/ Polymer-SiO ₂	Ag	Polymerization, Wet chemical reduction/ PTMSPA ^m -SiO ₂	spherical	10	14.4 mg catalyst	$7.30 \times 10^{-3} \text{ s}^{-1}$ /303	190.9	[89]
NP/ hollowsite nanotube	Ag	Polyol process/ Halloysite nanob- utes (HNTs)	spherical	10	6.0×10^{-6} mol·dm ⁻¹	$0.087 \text{ s}^{-1}\cdot\text{g}^{-1}$ /-	-	[103]
NP/ polymer	Ag	UV irradiation/ PS/PMPS ⁿ	spherical	-	4.0×10^{-2} Mg catalyst	-	-	[135]
	Au	P[S-co-NIPAM ^o]/ PMPS						
	Pd							
NP/ Carbon sphere	Ag	Microwaving hydrothermal/ Carbon sphere, PVP	spherical	10	1.0 mg catalyst	$1.69 \text{ s}^{-1}\cdot\text{g}^{-1}$ /-	-	[101]
NP/ Carbon sphere	Ag-Au	Microwaving hydrothermal/ Carbon sphere, PVP	spherical	-	1.0 mg catalyst	$6.46 \text{ s}^{-1}\cdot\text{g}^{-1}$ /-	-	[102]
NP/ dendrimer	Au	Laser irradiation/ dendrimer	spherical	$6.0 \sim$ 16.4	0.01 mmol· dm ⁻³ Au	11.1×10^{-3} /288	-	[68]

(continued)

Table 13.1 (cont.)

NP/ bead	Au	Deposition reduc- tion/ PMMA ^p beads	spherical	6.9	8.8×10^{-2} $\mu\text{mol Au}$	$7.9 \times 10^{-3} \text{ s}^{-1}$ /295	38	[91]
NP/ Micelle	Au	Wet chemical reduction/ CTAB ^q , SDS ^r , TX-100 ^s	-	< 55	1.0×10^{-6} $\text{mol}\cdot\text{dm}^{-3}$ Metal	-	-	[66]
	Ag							
	Cu							
NP/ Micelle	Au	Atom trans- fer radical polymerization, Wet chemical reduction/ PNIPAM-b-P4VP ^t	spherical	2 ~ 4	0.20 $\text{mmol}\cdot\text{dm}^{-3}$	$1.48 \times 10^{-3} \text{ s}^{-1}$ /298	-	[75]
NP/ Micelle	Au	atom transfer radical polymerization, wet chemical reduction/ PS-b-P4VP ^u	spherical	15	0.000375 $\text{g}\cdot\text{dm}^{-3}$ catalyst	$3.15 \times 10^{-3} \text{ s}^{-1}$ /293	-	[96]

NP/ SPB ^f	Au	Photoemulsion polymerization Wet chemical reduction/ PAEMH-PS ^v	spherical	2	-	-	-	[79]
NP/ SPB ^f	Au	Atom transfer radical polymerization, Wet chemical reduction/ PDMAEMA-PS ^w	spherical	4.2	1.1 mg·cm ⁻³ Au NPs	$3.2 \times 10^{-3} \text{ s}^{-1}$ /298	-	[76]
NP/ SPB ^f	Au	Atom transfer radi- cal polymerization Wet chemical reduction/ PAEMH-PS ^v	spherical	1.3	-	0.51 s ⁻¹ ·m ² ·dm ³ /293.15	43	[92]
NP / SPB ^f	Au	Atom transfer radi- cal polymerization Wet chemical reduction/ PAEMH-PS ^v	spherical	1.5	0.00687 m ² ·dm ⁻³	$\sim 0.008 \text{ s}^{-1}$ /-	40	[63]
	Pt			2.3	0.01078 m ² ·dm ⁻³	$\sim 0.006 \text{ s}^{-1}$		

(continued)

Table 13.1 (cont.)

NP/ Hollow capsule	Au	Wet chemical reduction & layer by layer self assembly/ PAMAM-HC ^x	spherical	2.3	3g·cm ⁻³	2.0 × 10 ⁻³ s ⁻¹ /-	-	[77]
NP/ Hollow capsule	Pd	Polymerization, Wet chemical reduction/ Poly(AG-co-VP) ^y	spherical	-	1.30 μmol·dm ⁻³ metal	8.83 × 10 ⁻³ s ⁻¹ /288	-	[120]
	Au					7.36 × 10 ⁻³ s ⁻¹		
	Pt					3.58 × 10 ⁻³ s ⁻¹		
	Ag					1.23 × 10 ⁻⁴ s ⁻¹		
NP/ macro- porous	Au	Frens method [132]/ IRA-400 Anion exchange resin	spherical	17	0.2 g catalyst	-	-	[71]
NP/ macro- porous	Au	Frens method [132]/ Anion exchange resin	-	20	6 mg catalyst	1.63 × 10 ⁻⁴ s ⁻¹ /298	31.01	[70]
NP/ micro- sphere	Au	Polymerization Wet chemical reduction/ Poly(DVB-co-AA) ^z	spherical	10	1.47 × 10 ⁻⁴ mmol Au	6.0 × 10 ⁻³ s ⁻¹ /298	-	[78]

NP/ micro-sphere	Au	Distillation-precipitation polymerization/ Poly(DVB-co-AA) ^z poly(EGDMA-co-VPy) ^{z-1} poly(EGDMA-co-HEMA)-SH ^{z-2} poly(MBAAm) ^{z-3}	spherical	5.2 ~ 10.7	1.47 × 10 ⁻⁴ mmol Au	-/298	-	[98]
NP/ micro-sphere	Au	Distillation-precipitation polymerization, Stöber method/ poly(MBAAm) ^{z-3}	spherical	-	6 × 10 ⁻⁵ mmol Au	-/rt	-	[97]
NP/ hollow micro-sphere	Au	Distillation-precipitation polymerization, Stöber method/ P(EGDMA-co-MAA) ^{z-4}	spherical	28/31	6 × 10 ⁻⁵ mmol Au	-/rt	-	[99]
NP/ templateless	Au	Citrate reduction/ templateless	polygonal	100	0.0167 mmol Au NPs	12.0 × 10 ⁻³ s ⁻¹	-	[4]
			spherical	-		1.7 × 10 ⁻⁵ s ⁻¹		

(continued)

Table 13.1 (cont.)

NP/ silica support	Au	Wet chemical reduction/ Azacryptand-silica	spherical	10	8.0×10^{-4} mmol	-	-	[100]
NP/ biomolecule	Au	Wet chemical reduction/ Horse spleen apofer- ritin (HSAF)	spherical	3.6	5 ~ 150 nmol·dm ⁻³ protein	-	-	[129]
				15.4				
NP/ biomolecule	Au	Adsorption- reduction/ Chitosan-coated iron oxide	spherical	3.14	0.49 mg catalyst	1.25×10^2 s ⁻¹ /303	51.2	[93]
NP/ biomolecule	Au	Thermal treatment/ Chitosan	spherical	-	1.0 mmol·dm ⁻³ Au	-	-	[124]
	Ag				6.0 mmol·dm ⁻³ Ag			
NP/ biomolecule	Au	UV irradiation/ Calcium-alginate	spherical	5	1.2 g·dm ⁻³	0.20×10^{-5} mol·dm ⁻³ ·min	20.5	[58]
	Ag			7		1.04×10^{-5} mol·dm ⁻³ ·min	13.8	

NP/ ligand	Au	Wet chemical reduction/ azacryptand	spherical	20.9	2.88×10^{-2} mmol·dm ⁻³ Au	1.0×10^{-2} s ⁻¹ /298	-	[118]
NP/ conducting polymer	Au	Wet chemical reduction/ pEDOT/PSS	spherical	> 3	0.5 µg Au	4.39×10^{-2} s ⁻¹ /rt	-	[111]
NP/ polymer	Au	Wet chemical reduction/ Polyvinylpyrrolidone (PVP)	spherical	6.7	-	-	-	[112]
				13.8				
				22				
nanocages	Au	Galvanic replacement /-	square	50	3.8×10^9 NPs·cm ⁻³	4.72×10^{-2} s ⁻¹ /297	28.04	[9]
nanoboxes			square			1.87×10^{-2} s ⁻¹	44.25	
hollow nanoboxes			square			9.83×10^{-3} s ⁻¹	55.44	
solid NPs			spherical			3.33×10^{-3} s ⁻¹	-	

(continued)

Table 13.1 (cont.)

Nanocage	Pd	Gavanic replacement /-	Cubic hollow	57 ^{z-5}	0.2 cm ³ catalyst	1.90 × 10 ⁻² min ⁻¹ /rt	94.6	[10]
	Pt			52		3.60 × 10 ⁻³ min ⁻¹	16.2	
	Pd/Pt			53		3.50 × 10 ⁻³ min ⁻¹	20.7	
	Pt/Pd			51		1.90 × 10 ⁻² min ⁻¹	18.5	
	Pt-Pd			47		1.35 × 10 ⁻² min ⁻¹	26.2	
Nonarattles	Au	Galvanic replacement/ Ag coated Au nanorods	Rod	6 ^{z-6}	3 × 10 ¹⁰ NPs·cm ⁻³	- /rt	-	[3]
Nanorattles	Au	Template- deposition, surface-protected etching /-	rattle	3	0.1 cm ³ catalyst	- /rt	-	[11]
NP/ dendrimer	Cu	Wet chemical reduction/ PAMAM dendrimer	-	-	23.5 μmol·cm ⁻³ Cu	3.7 × 10 ⁻² s ⁻¹ / rt	-	[74]

NP/ -	Cu ₂ O	Microwave irradiation /-	spherical	10 ~ 20	10 mg catalyst	-/-	-	[127]
Nanocube/ -	Cu ₂ O	Wet chemical reduction/ Sodium polyacrylate	cube	18	5 × 10 ⁻⁶ mol·dm ⁻³	0.018 mmol s ⁻¹ m ⁻² /298	-	[6]
	Cu		spherical	14		0.026 mmol s ⁻¹ m ⁻² /298		
NP /gel	NiCo ₂ O ₄	Citrate gel method/ citrate	-	-	0.1 g catalyst	-/rt	-	[122]
NP/ Metal oxide	CuCrMoPO ₄	Wet chemical, calcinations/ triethanolamine	spherical	71	0.1 g catalyst	-/-	-	[123]
	CoCrMoPO ₄			53				
NP/ micelle	Pt-Ni	Wet chemical reduction/ CTAB micelle	-	19 ~ 20	4.0 µg	4.80 × 10 ⁻⁵ ~ 1.93 × 10 ⁻⁴ / 303	30.86	[67]
NP/ polymer	Pd-Ag	γ-irradiation/ Polyvinylpyrrolidone (PVP)	spherical	20 ~ 30	4 × 10 ⁻⁵ mmol	-	-/rt	[116]
	Pd-Cu			15				
	Pd- Ni			5 ~ 10				
	Pd-Au			-				
	Pd-Pt			2 ~ 5				

(continued)

Table 13.1 (cont.)

NP/ CSs	Ag	Microwaving/ carbon spheres (CSs)	spherical	10	1.0 mg	1.69 s ⁻¹ .g ⁻¹	-	[102]
	Ag-Au					2.74 ~ 6.46 s ⁻¹ .g ⁻¹ /rt		
NP/ micelle	Pt	Wet chemical reduction/ CTAB micelle	-	20	8.69 × 10 ⁻³ mmol.dm ⁻³	1.05 × 10 ⁻² s ⁻¹ .m ⁻² .dm ³ /303	-	[67]
NP/ dendrimer	Pt	Wet chemical reduction/ PAMAM & PPI ⁷⁻⁷ dendrimer	spherical	1.5	2.00 × 10 ⁻² mmol.dm ⁻³	6.02 × 10 ⁻² s ⁻¹ /288	-	[82]
	Pd			2.0		4.07 × 10 ⁻¹		
	Ag			7.5		1.22 × 10 ⁻³		
NP/ SPB ^f	Pt	Photoemulsion polymerization Wet chemical reduction/ PMPTTAC-PS ⁸	spherical	2.1	6.60 × 10 ⁻⁴ mmol.dm ⁻³ Pt NPs	1.1 s ⁻¹ .m ⁻² .dm ³ /303	43.7	[61]
						5.62 × 10 ⁻¹ s ⁻¹ .m ⁻² .dm ³ /288		
NP/ SPB ^f	Pt	Photoemulsion polymerization Wet chemical reduction/ PMPT TAC-PS ⁸	spherical	2.3	-	0.002 ~ 0.006 s ⁻¹	40	[63]
	Au			1.5		0.0016 ~ 0.008 s ⁻¹		

NP/ Mesoporous film	Pt	single dipping technique boehmite sols/ CTAB ⁴	spherical	4.9	-	3.2×10 ⁻² min ⁻¹ /295	-	[108]
NP/ nanowire	Pt	Atom trans- fer radical polymerization, wet chemical reduction/ PDMAEMA- PMETAI ²⁻⁹	spherical	3	3.75 × 10 ⁻³ mmol·dm ⁻³ Pt	3.1 × 10 ⁻¹ s ⁻¹ ·m ⁻² ·dm ³ /rt	-	[107]
NP/ Magnetic	Pt	Surface-initiated ring-opening polymerization/ Fe ₃ O ₄ /SiO ₂	spherical	4.8	7 mg catalyst	6.9 × 10 ⁻³ s ⁻¹ /rt	-	[106]
NC/ polystyrene	Pt	Polystyrene support /-	Cube	20	0.15 cm ³	0.037 min ⁻¹ /298	12.1	[5]
	Pt	Wet chemical reduction/ TTAB ²⁻¹⁰	-	-	0.01 cm ³	0.0057 min ⁻¹ /298	13.8	
NP	Pt	Wet chemical reduction/ glucose	Spherical	5.0	0.5 cm ³	0.50 mg ⁻¹ min ⁻¹	-	[12]
Nanowire			wire	5.7		0.31 mg ⁻¹ min ⁻¹		

(continued)

Table 13.1 (cont.)

NP/ SPB ^f	Pd	Photoemulsion polymerization Wet chemical reduction/ PMPTTAC-PS ^{z-3}	spherical	2.4	3.66×10^{-4} mmol·dm ⁻³ Pd NPs	$1.10 \text{ s}^{-1} \cdot \text{m}^{-2} \cdot \text{dm}^3$ /288	44	[60]
NP/ Microgel	Pd	Photoemulsion polymerization Wet chemical reduction/ PNIPA-BIS-PS ^e	spherical	3.8	2.15×10^{-3} mmol·dm ⁻³ Pd NPs	1.01×10^{-1} $\text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{dm}^3$ /288	44	[60]
NP/ biomolecule	Ag	Wet chemical reduction/ Chitosan	spherical	< 5	$3.24 \text{ g} \cdot \text{dm}^{-3}$ catalyst	1.5×10^{-1} $\text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{dm}^3$ /296	-	[73]
NP/ Polymer	Pd	γ -irradiation/ PVP	-	-	10 mmol·dm ⁻³ catalyst	-	-	[115]
NP/ Conducting polymer	Pd	Wet chemical reduction/ IpEDOT/PSS	spherical	1~9	$2 \text{ g} \cdot \text{dm}^{-3}$ Pd	$6.58 \times 10^{-2} \text{ s}^{-1}$ /296	-	[114]
NP/ alumina	Pd	Physical precipitation/ Al ₂ O ₃	spherical	6.0	$0.05 \text{ g} \cdot \text{dm}^{-3}$ catalyst	$9.0 \times 10^{-3} \text{ s}^{-1}$ /298	43	[88]

NP/ MCM-41	Pd	Polymerization/ MCM-41	spherical	7 ~ 15	0.65 mg catalyst	1.77×10^{-2} mol. dm ⁻³ . min ⁻¹ /-	-	[109]
NP/ polymer	Pd-Ag	γ -irradiation/ PVP	spherical	20~30	4×10^{-5} mmol catalyst	-	-	[116]
	Pd-Au			-				
	Pd-Cu			15				
	Pd-Ni			5~10				
	Pd-Pt			2~5				
	Pd			-				

*: highest value from series of results, data collected from the respective paper

^a: nanocrystal

^b: no data

^c: room temperature

^d: nanoparticle

^e: poly(Nisopropylacrylamide) cross-linked with N,N'-methylenebisacrylamide grafted on to solid polystyrene core

^f: spherical polyelectrolyte brush

^g: poly(acrylic acid) grafted onto solid polystyrene core

^h: spherical highly branched polymer brush

ⁱ: poly(ethylene glycol) methacrylate grafted on to solid polystyrene core

^j: PEGMA-PSⁱ entrapped into a poly(vinyl alcohol)

^k: Poly(amidoamine) dendrimer-poly(styrenesulfonate)-poly(acrylic acid)

^l: poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate

^m: poly[N-(3-Trimethoxy silyl)propyl]aniline

(continued)

Table 13.1 (cont.)

n:	polystyrene particles incorporating polymethylphenylsilane
o:	N-isopropyl acrylamide
p:	Poly(methyl methacrylate)
q:	cetyl trimethylammonium bromide
r:	sodium dodecyl sulfate
s:	poly(oxyethylene)isooctylphenyl ether
t:	poly(<i>N</i> -isopropylacrylamide)- <i>b</i> -poly(4-vinyl pyridine)
u:	polystyrene-block-poly(4-vinyl pyridine)
v:	polyaminoethyl methacrylate hydrochloride grafted on to solid polystyrene core
w:	Poly(2-(dimethylamino)ethyl methacrylate) grafted on to solid polystyrene core
x:	Poly(amidoamine) based hollow capsule
y:	Poly(alginate acid-co-4-vinylpyridine)
z:	Poly(divinylbenzene-co-acrylic acid)
z ₁ :	poly(ethylene glycol dimethacrylate-co-4-vinylpyridine)
z ₂ :	mercapto modified poly(ethyleneglycoldimethacrylate-co-2-hydroxyethyl methacrylate)
z ₃ :	poly(<i>N,N'</i> -methylenebisacrylamide)
z ₄ :	poly(ethyleneglycoldimethacrylate-co-methacrylic acid)
z ₅ :	cavity size
z ₆ :	Ag shell thickness
z ₇ :	Poly(amidoamine) & polypropylene imine dendrimer
z ₈ :	poly(2-methylpropenoyloxyethyl) trimethylammonium chloride grafted onto a solid polystyrene core
z ₉ :	poly(<i>N,N</i> -dimethylaminoethylmethacrylate)- poly[[2-(methacryloyloxy)ethyl] trimethylammoniumiodide]
z ₁₀ :	trimethyltetradecylammonium bromide

the catalyst surface. The molecule then diffuses to the active site to form a surface complex that reacts to form the adsorbed product. This product then undergoes a final desorption. A similar mechanism was proposed by Panigrahi *et al.* [70]: the positive charge (R^+) of the resin matrix invites the negatively charged nitrophenolate and borohydride ions to adsorb, which in turn facilitates the electron transfer from BH_4^- to nitrophenolate ion using the Au nanoparticle surface. As soon as $NaBH_4$ is added, the metal particles start the catalytic reduction by relaying electrons from the donor BH_4^- to the acceptor nitrophenolate ion immediately after the adsorption of both onto the catalyst surface. Excess $NaBH_4$ increases the pH of the reaction medium, thereby retarding the degradation of the borohydride ions. Obviously, the reduction of oxygen proceeds much faster than that of the nitrophenols—the reduction of 4-NP only starts once all the oxygen in the system has been consumed. This prevents the aerial oxidation of the 4-AP product.

Esumi *et al.* [82] investigated the catalytic activity of dendrimer-stabilized Au, Ag and Pd NPs in the reduction of 4-NP. They concluded that the reaction is diffusion controlled. Khalavka *et al.* [3] proposed the Eley-Rideal mechanism: only one reactant, in this case hydrogen, needs to be adsorbed onto the surface of their Au nanorattles. However, several authors recently suggested that the kinetics of 4-NP reduction can be modeled on the Langmuir-Hinshelwood mechanism: both reactants need to be adsorbed on the surface of the nanocatalyst prior to the reaction [58, 63, 83, 84]. Saha *et al.* [58] demonstrated that 4-NP reduction took place on the surface of the NPs by systematically studying the reaction kinetics. They varied the initial concentrations of borohydride, 4-NP, and the calcium-alginate-stabilized Ag and Au NPs. Zhang *et al.* [83] investigated the mechanism by analyzing the catalytic activity of Ag NPs supported on TiO_2 . They concluded that a surface hydrogen species is transferred to the Ag NPs by borohydride before reacting with 4-NP to yield 4-AP. Most recently, Wunder *et al.* [63, 84] provided an intensive kinetic evaluation and successfully applied the Langmuir-Hinshelwood mechanism (Figure 13.4) using Pt and Au NPs immobilized onto the spherical polyelectrolyte brush (SPB). They varied the concentration of 4-NP and $NaBH_4$, the catalyst dosing, and the temperature. The authors exploited the quantitative explanation of the kinetic data, especially the mutual dependence of k_{app} on the concentration of 4-NP and $NaBH_4$, using the classical Langmuir isotherm. According to the Langmuir-Hinshelwood model, k_{app} is strictly proportional to the total surface area (S) and can thus be defined as

$$-\frac{d[4-NP]}{dt} = k_{app} \cdot [4-NP] = k_1 \cdot S \cdot [4-NP] \quad (13.5)$$

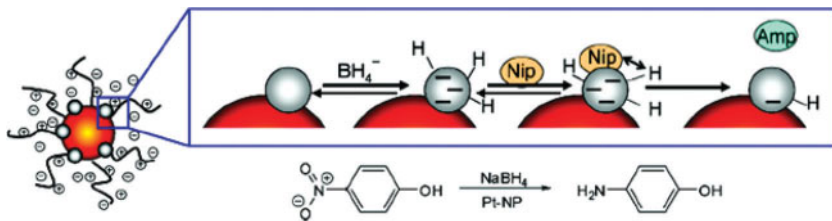


Figure 13.4 Langmuir-Hinshelwood mechanism for the reduction of 4-NP by NaBH_4 in the presence of metallic NPs bound to spherical polyelectrolyte brush (SPB) particles [63] (reprinted from ref [63], copyright 2010, with permission from American Chemical Society).

where k_{app} is the apparent rate constant, $[4\text{-NP}]$ is the concentration of 4-NP at a given time t , S is the surface area of the metal nanocomposites normalized to the unit volume of the system, and k_1 is the rate constant normalized to S . The adsorption of the reactants is modeled on the Langmuir-Freundlich isotherm:

$$\theta_i = \frac{(K_i \cdot [i])^{n_i}}{1 + \sum_{j=1}^N (K_j \cdot [i])^{n_j}} \quad (13.6)$$

Here, θ_i is the surface coverage of compound i , K_i is the adsorption equilibrium constant of the component i , and $[i]$ is the concentration of compound i in solution, n indicates the heterogeneity of the sorbent. Equation 13.5 can be re-written according to the Langmuir-Hinshelwood model:

$$-\frac{d[4\text{-NP}]}{dt} = k \cdot S \cdot \theta_{4\text{-NP}} \cdot \theta_{\text{BH}_4^-} \quad (13.7)$$

Here, $\theta_{4\text{-NP}}$ and $\theta_{\text{BH}_4^-}$ denote the surface coverage of the nanoparticles by 4-NP and borohydride, respectively, and k is the surface rate constant. They are modeled by a Langmuir isotherm:

$$\theta_{4\text{-NP}} = \frac{(K_{4\text{-NP}} \cdot [4\text{-NP}])^n}{1 + (K_{4\text{-NP}} \cdot [4\text{-NP}])^n + (K_{\text{BH}_4^-} \cdot [\text{BH}_4^-])^m} \quad (13.8a)$$

$$\theta_{\text{BH}_4^-} = \frac{(K_{\text{BH}_4^-} \cdot [\text{BH}_4^-])^m}{1 + (K_{4\text{-NP}} \cdot [4\text{-NP}])^n + (K_{\text{BH}_4^-} \cdot [\text{BH}_4^-])^m} \quad (13.8b)$$

K_{4-NP} and $K_{BH_4^-}$ are the adsorption constants of 4-NP and borohydride, and n and m are related to the heterogeneity of the sorbent [85]. Hence, Equation 13.7 can be written as follows:

$$\frac{-d[4-NP]}{dt} = \frac{k \cdot S \cdot ([k_{4-NP} \cdot [4-NP]]^n \cdot (K_{BH_4^-} \cdot [BH_4^-])^m)}{(1 + (K_{4-NP} \cdot [4-NP])^n + (K_{BH_4^-} \cdot [BH_4^-])^m)^2} = k_{app} \cdot [4-NP] \quad (13.9)$$

Thus,

$$k_{app} = \frac{k \cdot S \cdot K_{4-NP}^n \cdot [4-NP]^{n-1} \cdot (K_{BH_4^-} \cdot [BH_4^-])^m}{(1 + (K_{4-NP} \cdot [4-NP])^n + (K_{BH_4^-} \cdot [BH_4^-])^m)^2} \quad (13.10)$$

They demonstrated that the reaction is surface-controlled and can be analyzed in terms of the Langmuir-Hinshelwood mechanism. The rate-determining step is given by the reaction of the adsorbed species. The adsorption/desorption equilibrium is assumed to be much faster and is modeled on a Langmuir isotherm. From data fitting to Equation 13.10, they derived the adsorption constants of 4-NP (K_{4-NP}) and borohydride ($K_{BH_4^-}$), as well as Freundlich exponents for both Pt and Au NPs. The adsorption constant for 4-NP was 100 times higher than that of $NaBH_4$. Interestingly, the K_{4-NP} was larger in the case of Au NPs, but the kinetic constant k_{app} , which determines the reaction rate of the adsorbed molecules, is considerably smaller for Au. From this the authors concluded that Au NPs are less catalytically active than Pt particles in the reduction of 4-NP. Additionally, the dependence of the induction time, t_0 , on the various parameters, as well as the dependence of 4-NP reduction on temperature, were quantitatively analyzed and related to parameters derived from the Langmuir-Hinshelwood analysis [63, 84]. Hence, the Langmuir-Hinshelwood kinetic model, in which both reactants are adsorbed on the surface of the nanoparticles, is a fitting description of the catalytic reduction of 4-NP using metal nanocatalysts.

13.2.4 Efficiency of the Reaction

The efficiency of a reaction can be judged by the yield of the product [58]. Catalyst turnover number (TON) and turnover frequency (TOF) are two important quantities used to judge the efficiency of a catalyst. The TON is the number of reactant molecules that 1 g of catalyst can convert into products, and TOF is TON/time [86]. The percentage yield of 4-AP at the end of the reaction can be estimated spectrophotometrically by generating a calibration curve at λ_{max} 300 nm, which is the characteristic band of 4-AP.

13.3 Effect of Various Conditions

13.3.1 Concentration of the Catalyst

In the case of heterogeneous or microheterogeneous catalysis, the reaction rate generally increases linearly with the amount of catalyst [58, 60, 61, 70, 87]. The rate constant obtained from the slope of the kinetic curves has been related to catalyst dose, while keeping other parameters such as the initial concentrations of 4-NP and borohydride the same. It was observed that with an increase in catalyst amount, the rate constant increases in both cases and showed a linear relationship. This is obvious because an increase in the dose means there is an increase in the surface area. There is a strict relation between the apparent rate constant (k_{app}) and the surface area of the metal NPs. The k_{app} is certainly proportional to the total surface area (S) of the metal NPs in the system [60, 61, 64, 88], which can be expressed using Equation 13.5. To calculate the surface area of metal NPs, the bulk density of the corresponding metal, the metal contents as obtained from TGA or ICP-OES, and the size of the metal NPs as measured from TEM images were used. The experimental results from several groups [60, 61, 64, 88], including the authors (Figure 13.5) [69], indeed show a linear relationship between catalyst doses and apparent rate constants (k_{app}) up to the point where the diffusion limitation occurred.

Figure 13.5 demonstrates the influence of Pd NPs surface area changes in the reduction of 4-NP as obtained by the authors. The Pd NPs synthesized

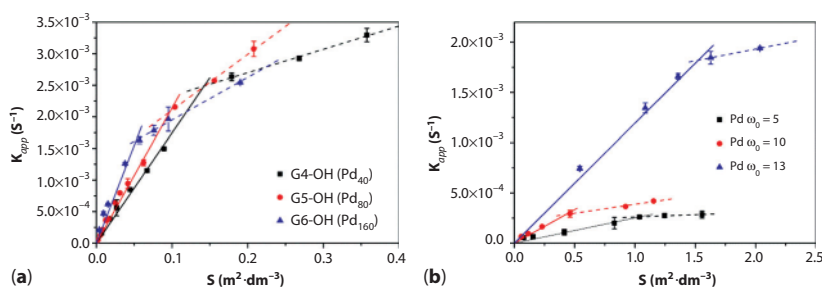


Figure 13.5 The influence of surface area changes on the reduction of 4-NP. The apparent rate constant constants (k_{app}) as a function of volume normalized surface area with (A) dendrimer-templated Pd nanoparticles, (B) Pd nanoparticles by reverse microemulsions. The solid lines indicate the intrinsic kinetic region and the curvature area with dotted lines indicate the region where diffusion limitation occurred. The surface normalized rate constant (k_l) was obtained from the slope of linear line fit indicated with solid line of each graph. Reaction conditions: $[\text{NaBH}_4] = 10.0 \text{ mmol} \cdot \text{dm}^{-3}$, $[\text{4-NP}] = 0.10 \text{ mmol} \cdot \text{dm}^{-3}$, $T = 294 \text{ K}$.

by dendrimer templates (Figure 13.5A) exhibit higher surface normalized rate constant (k_1) than those prepared using reverse microemulsions (Figure 13.5B) [69].

13.3.2 Concentration of 4-NP and NaBH_4

Investigations into the effect of 4-NP and NaBH_4 concentration on rate constants have been conducted by several groups. The results obtained by the authors are presented in Figure 13.6 [69].

The effect of the two reactants' concentration on 4-NP reduction was examined in depth by varying the concentration of either 4-NP or NaBH_4 , while keeping all other conditions constant. The trends of the graphs are similar to those of Wunder *et al.* [63]. A high concentration of 4-NP results in nearly full NP surface coverage. This slows down both the reaction with borohydride ions and the injection of electrons onto the metal surface (Figure 13.6a). The nonlinear relation of k_{app} to the borohydride concentration (Figure 13.6b), as well as the saturation at high concentrations, directly indicate that the reactants are competing for the reactive sites on the metal surface. This means that there should be an optimal concentration where the reaction rate is at a maximum.

13.3.3 Temperature and Activation Energy

The effect of temperature on 4-NP catalysis is directly related to the thermodynamic value. Several authors have investigated the activation energy (E_A) of this reaction by carrying out kinetic runs at different temperatures

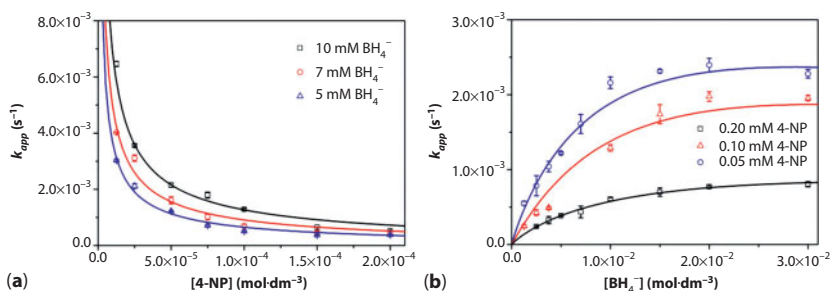


Figure 13.6 Influence of 4-NP (a) and NaBH_4 (b) concentration on the rate constant of 4-NP reduction and the fitting with Langmuir-Hinshelwood model. Experimental conditions: $[\text{G4-OH}(\text{Pd}_{40})] = 0.025 \mu\text{mol}\cdot\text{dm}^{-3}$, $T = 294 \text{ K}$ [69].

[5, 9, 10, 58, 60–63, 67, 70, 72, 87–93]. Activation energy is defined as the minimum energy required to initiate a chemical reaction. The Arrhenius activation energy term, from the Arrhenius equation given below, is an experimentally determined parameter which indicates the sensitivity of the reaction rate to temperature.

$$\ln k_{app} = \ln A - \frac{E_A}{R \cdot T} \quad (13.11)$$

where A is an Arrhenius factor, k_{app} is the apparent rate constant of the reaction at temperature T (in Kelvin), and R is the universal gas constant.

The E_A can be obtained by plotting a graph with the data series $\ln k_{app}$ vs $1/T$, which is linear in most cases. The slope corresponds to the value of $-E_A/R$. Wunder *et al.* [63] reported an E_A of 40 kJ·mol⁻¹ for the normalized rate constant of Pt NPs immobilized onto a cationic spherical polyelectrolyte brush. This was in good agreement with their previous work using the same carrier system for metal NPs, where the E_A was found to be 44 kJ·mol⁻¹ [60, 61, 92]. They demonstrated that the E_A reflects the temperature dependence of the kinetic constant k_{app} and of the two thermodynamic adsorption constants K_{4-NP} and K_{BH^+} . However, E_A values obtained for other systems were significantly different (see Table 13.1). For instance, Lu *et al.* [72] reported an E_A of 62 kJ·mol⁻¹ for Ag NPs embedded onto the highly branched polymer brush, while 24.08 kJ·mol⁻¹ was found for Ag nanoshell-coated cationic polystyrene beads [87], and 45 kJ·mol⁻¹ for silver-deposited magnetic nanoparticles [90]. With regards to Au NPs deposited on poly(methyl methacrylate), Kuroda *et al.* [91] found the E_A to be 38 kJ·mol⁻¹, while 51.2 kJ·mol⁻¹ was reported by Chang *et al.* [93] for chitosan-coated, magnetically-recoverable Au NPs. The Pal group [70] obtained an E_A value of 31.01 kJ·mol⁻¹ for Au NPs deposited onto an anion exchange resin and pointed out that the activation energy is dependent on the surface of the catalyst. Thus, smaller particles exhibit a higher activity due to an increase in the roughness of the available surface. An activation energy of 20.5 kJ·mol⁻¹ was found for calcium alginate-stabilized Au NPs and Khalavka *et al.* [3] reported the activation energy for CTAB-stabilized Au nanorods to be 38 kJ·mol⁻¹. Zeng *et al.* [9] compared the various E_A s of different shapes, namely Au nanocages (28.04 kJ·mol⁻¹), hollow Au nanoboxes (44.25 kJ·mol⁻¹), and partially hollow Au nanoboxes (55.44 kJ·mol⁻¹).

Mahmoud *et al.* [5] compared Pt nanocubes synthesized without a solid support with Pt nanocubes immobilized on polystyrene microspheres and

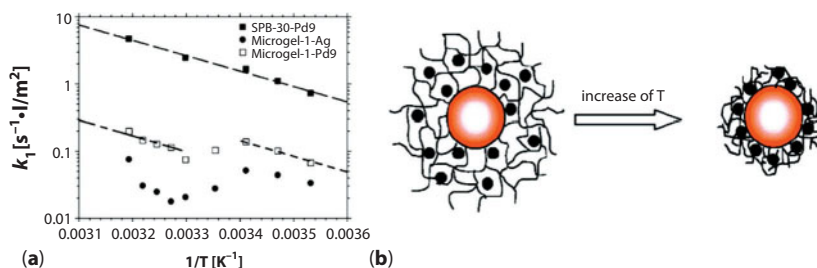


Figure 13.7 (a) Dependence of the rate constant on temperature for different systems. (b) Schematic representation of thermosensitive microgel metal composite particles [64]. (Reprinted with permission from [64]; Copyright 2006, American Chemical Society.)

obtained E_A s of 14 and 12 $\text{kJ} \cdot \text{mol}^{-1}$, respectively. Ghosh *et al.* [67] reported an E_A of 30.86 $\text{kJ} \cdot \text{mol}^{-1}$ with Pt-Ni bimetallic NPs stabilized with CTAB micelles. Mahmoud *et al.* [10] also compared the E_A values of mono- and bi-metallic nanocages. They obtained 94.6 $\text{kJ} \cdot \text{mol}^{-1}$, 16.2 $\text{kJ} \cdot \text{mol}^{-1}$, and 26.2 $\text{kJ} \cdot \text{mol}^{-1}$ for monometallic Pd nanocages, Pt nanocages, and Pd-Pt bimetallic nanocages, respectively.

Interestingly, the Ballauff group [60, 64] reported some exceptional cases that went against conventional Arrhenius-type dependence (a linear pattern). As shown in Figure 13.7a, an S-curve pattern was observed for both Ag and Pd NPs immobilized on a thermosensitive microgel carrier system, while Pd NPs immobilized on a spherical polyelectrolyte brush system presented the conventional Arrhenius-type dependence. They found that the k_{app} first decreases with an increase in temperature when approaching the volume transition. This is due to the shrinking of microgel (a thermal-responsive polymer) when heated to above its lower critical solution temperature (LCST) as shown in Figure 13.7b. Only at temperatures above the volume transition is the normal Arrhenius-type dependence of k_{app} found again. Wang *et al.* [75] also reported that the catalytic activity of micelle-stabilized Au NPs could be modulated by the thermo-responsiveness of poly(*N*-isopropylacrylamide) (PNIPAM). Below the lower critical solution temperature (LCST), the PNIPAM chains were hydrophilic and the reactants could easily diffuse through the PNIPAM corona to reach the surface of the Au NPs. Within this temperature range, the catalytic activity increased with the increase in temperature. However, above LCST, the PNIPAM chains collapsed to form a hydrophobic barrier on the Au NPs, which decelerated diffusion of the reactants. A similar tendency was observed for hollow PNIPAM-Ag nanocomposite spheres, as reported by Xie *et al.* [94].

13.4 Synthetic Methods of Metal Nanocomposites and Their 4-NP Catalysis

13.4.1 Introduction

Metal nanocomposites have been widely exploited as efficient catalysts due to their large surface-to-volume ratio and electronic properties different to those of their corresponding bulk metals [95]. Despite high catalytic efficiency and reactivity, such nanocomposites require a suitable stabilizing agent to prevent aggregation during catalysis [61]. As such, metal nanocomposites have been chemically synthesized using salt as a starting material and with reduction in the presence of a stabilizer like a heterogeneous support (solid support) [5, 11, 58, 60, 61, 64, 65, 70–72, 76–79, 87–93, 96–110], polymer [6, 94, 111–116], dendrimer [68, 74, 82, 117], ligand [118], or surfactant [12, 75]. In this review, we divided the nanocomposites into two subdivisions, based on synthetic protocols. The first is the liquid suspension of metal nanocomposites (in homogeneous media) [3, 4, 7–10, 12, 68, 70, 73, 75, 82, 94, 111–126] and the second is the solid support of the nanocomposites (on heterogeneous media) [5, 11, 58, 60, 61, 64, 65, 70–72, 76–79, 87–93, 96–110]. The application of liquid suspensions of metal nanocomposites in catalysis is limited due to the inherent difficulties involved in separating the products and recycling the catalysts. Furthermore, their large-scale application is hindered by a reduction in catalytic activity due to particle aggregation. To overcome these disadvantages, metal nanocomposite catalysts have been immobilized onto solid supports such as inorganic oxide [89, 90, 93, 100, 106, 109, 110], ion exchange resins [70, 71, 87], alumina [88, 108], titania [11], polymer microspheres [78, 91, 97–99], polystyrene [5, 72, 76, 77, 79, 92, 96, 104, 105], nanotubes [103], carbon spheres [101, 102], and biomolecule beads [58]. These supports must not take part in the catalytic mechanism, i.e., they must be inert. Mahmoud *et al.* [5] measured the E_A values of Pt nanocrystals with and without polystyrene to be nearly the same, proving that the support material was indeed inert. The recyclability of these catalysts makes the process cost-effective.

Metal nanocomposites have been characterized using the following techniques: HR TEM (High resolution transmission electron microscope), P-XRD (power X-ray diffraction), UV-Vis spectroscopy, XPS (X-ray photoelectron spectroscopy), EDS (Energy dispersive X-ray spectroscopy), SAED (selected area electron diffraction), SEM (scanning electron microscopy), cryogenic electron microscopy (cryo-TEM, an effective method to investigate the morphology *in situ*).

13.4.2 Liquid Suspensions of Metal Nanocomposites

13.4.2.1 Template Free Method [4, 7, 119, 120, 127]

Gao *et al.* [120] developed a simple method to make nanocapsules (Figure 13.8). Compared with other common methods, this method uses an aqueous solution without any organic solvent or template cores. As such, it is unnecessary to prepare any uniform spherical templates, regular amphiphilic polymers, complex dendrimers, or hyperbranched polymers beforehand, and repeated absorption and washing processes are not required. They compared the catalytic activity of noble metal NPs and found the rate to be in the series $\text{Pd} > \text{Au} > \text{Pt} > \text{Ag}$.

Rashid and Mandal [4] synthesized polygonal and spherical Au NPs by applying an *in situ* reduction technique that uses ferric ammonium citrate as the reducing agent in the absence of any surfactant or polymeric template (Figure 13.9). Polygonal Au NPs showed higher catalytic activity than spherical Au NPs by a factor of 300–1000 in the reduction of 4-NP. This is because there are more active sites present on the polygonal shape, as determined by its specific crystallographic plane [13, 128]. Hence, both the reactivity and selectivity of metal NPs can be tailored by controlling their shape. The El-Sayed group was the first to discuss the correlation between the catalytic activity of Pt NPs and the number of surface atoms.

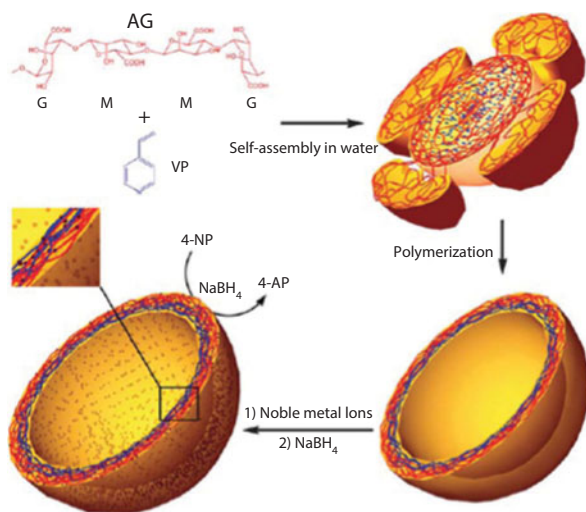


Figure 13.8 A proposed method for the formation of nanocapsules [120]. (Reprinted with permission from [120]; Copyright 2007, Royal Society of Chemistry.)

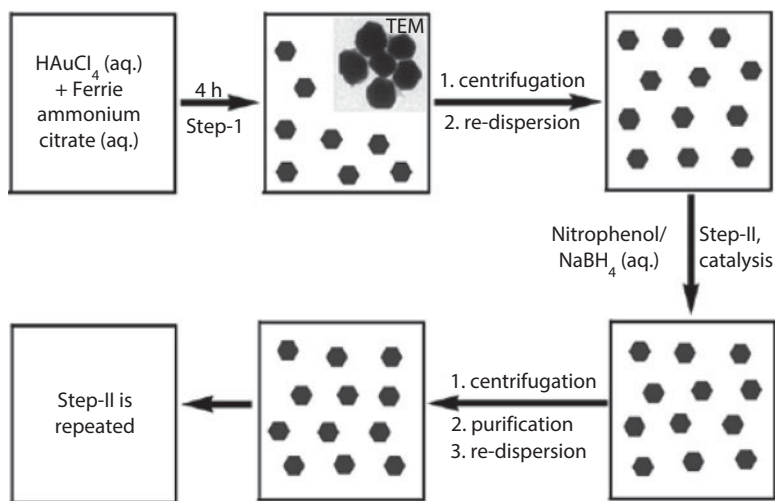


Figure 13.9 Schematic representation of the formation of polygonal GNPs, their purification, catalytic applications and reusabilities [4]. (Reprinted with permission from [4]; Copyright 2008, Wiley-VCH.)

They concluded that a large number of edge and corner atoms actually hold the key to improving their catalytic performance [13]. They suggested that metal NPs with a predominantly (111) lattice plane have sharp edges and corners, and hence the fraction of active surface sites is very high compared to spherical particles with (111) and (100) facets and with corners and edges located at the interfaces of these facets [13, 128]. It is known that anisotropic metal NPs exhibit better catalytic activities than their spherical counterparts [7, 13, 119]. Therefore, the polygonal Au NPs with (111) facets should have more sharp edges and corners and should thus be more catalytically active [13]. These polygonal gold nanoparticle (GNP) catalysts are very stable and could be reused several times in the 4-NP reduction reaction without losing much of their virgin catalytic activity, even though no solid support is used in this synthetic protocol.

Rashid *et al.* [119] synthesized spongy Au nanocrystals (NCs) using ammonium bismuth citrate as both the reducing and stabilizing agent (Figure 13.10). The rate constant observed for spongy Au nanocrystals was very close to that of Au NPs stabilized by poly(amidoamine) (PAMAM) dendrimers, but somewhat lower than that of Au NPs stabilized by poly(propyleneimine) (PPI) dendrimers [68]. Again, the Au NP rate constant is higher than that of Ag NPs but it is one order of magnitude lower than that of Pt and Pd NPs stabilized by PAMAM dendrimers [82].

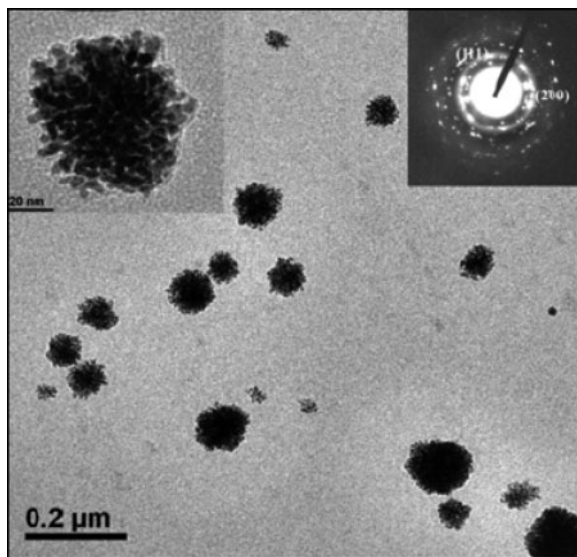


Figure 13.10 TEM image of spongy Au NCs. The left inset shows an enlarged view and the right inset is the electron diffraction pattern of a single Au NC [119]. (Reprinted with permission from [119]; Copyright 2006, American Chemical Society.)

But, Pt and Pd NPs usually have higher catalytic activities than Au NPs. According to Hayakawa *et al.* [68] and Praharaj *et al.* [71], dendrimer and resin bead supports both affect the diffusion of 4-NP to the surface of Au NPs and thus also affect the catalytic properties. They concluded that this might be the reason for the slightly lower rate constants as compared to PPI stabilized Au NPs. In their case, the spongy Au nanocrystals have no such host materials, so the pronounced catalytic activity is solely due to their unique porous nature, which also provides a large surface area ($42 \text{ m}^2\cdot\text{g}^{-1}$). This is one of the most important merits in using spongy Au NCs as catalysts or autocatalysts.

Rashid and Mandal [7] synthesized Ag dendrites with different morphologies using the wet chemical reduction of AgNO_3 by citrate salts. They also synthesized Ag NPs and compared the result with NCs (Figure 13.11). The Ag dendrites showed higher catalytic activity than Ag NPs. The rate constant is higher than that obtained for both PAMAM/PPI dendrimer stabilized Ag NPs [82] and resin bead-coated Ag NPs [87]. The reason for this is that the dendrimer or polymeric resin supports interfere with the diffusion of 4-NP onto the surface of Ag NPs. The dendritic Ag NCs are free of these hindrances, meaning their higher catalytic activities are solely attributed to the hyperbranched structure.

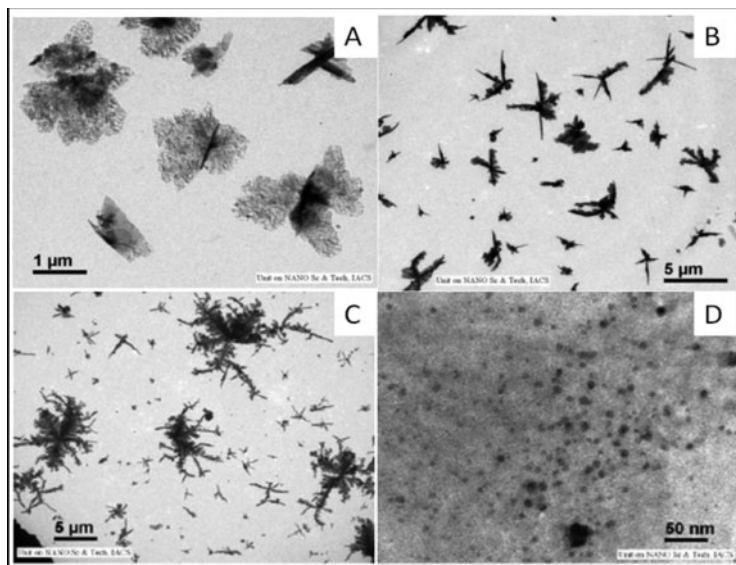


Figure 13.11 Various Ag nanocrystals. (A) Coral-like dendrite; (B) banana-leaf-like dendrite; (C) highly branched dendrite; and (D) Ag NPs [7]. (Reprinted with permission from [7]; Copyright 2007, American Chemical Society.)

Metal oxide NPs such as Cu_2O [127], NiCo_2O_4 [122] and $\text{M}^1_x\text{Cr}_{1-x}\text{Mo}_x\text{P}_{1-x}\text{O}_4$ [$\text{M}^1 = \text{Co}, \text{Cu}$] NPs [123] also have a demonstrated ability to reduce 4-NP to 4-AP. Of particular interest is a report by Ghorai *et al.* [123] that showed mixed metal oxides as being more catalytically active than their corresponding molybdates (CoMoO_4 and CuMoO_4) and phosphates (CrPO_4).

13.4.2.2 Biomolecule Stabilized NPs [129]

Research on biomolecule-inorganic NP assemblies [73, 129] is becoming popular as a result of their environmentally friendly characteristics, which are in line with the principles of “green chemistry”.

Murugadoss and Chattopadhyay [73] used chitosan, a product of the deacetylation of chitin (the second most abundant natural polymer in the world after cellulose) to stabilize Ag NPs (<5 nm). In this case the normalized rate constant was much higher than that of other Ag NPs such as 25 nm Ag hydrogel [62] and 8–10 nm Ag NPs stabilized by thermosensitive microgel [64]. They suggested that this was due to smaller Ag NPs in their system as well as the microheterogeneous working conditions. They hence concluded that reaction conditions (microheterogeneous versus

heterogeneous) and the particle size (catalyst) are crucial in catalysis involving metal NPs. Wei *et al.* [124] also employed the chitosan biomolecule to produce Au and Ag NPs and found that the Ag NPs were more catalytically active than Au NPs, and they were reusable for up to seven cycles. The Au NPs were only effective for the first cycle; they deactivated in the 2nd cycle. Another example of a stabilizing biomolecule is Horse spleen apoferritin (HSAF) [129], which was used with Au NPs for complete reduction.

13.4.2.3 Ligand-Stabilized NPs [118]

Lee *et al.* [118] employed an aqueous-phase method for the preparation of stable Au NPs (20.9 nm) by using 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8] hexacosane (azacryptand) as both reductant and stabilizer (Figure 13.12). They compared conventional citrate-reduced Au NPs with azacryptand-reduced Au NPs and found the rate to be 5 times greater for the latter. The low reduction rate of the citrate-reduced Au NPs can be attributed to the negatively charged surface of the anionic citrate stabilizer, which hindered the incorporation of the phenolate ion onto the surface of Au NPs [66]. The rate constant of the azacryptand-reduced Au NPs is also higher than that of poly(amidoamine) dendrimer-stabilized Au NPs [68] and spongy Au NPs [119]. It is, however, comparable to that of poly(propyleneimine) dendrimer-supported Au NPs, which affects the diffusion of 4-NP to the surface of catalyst particles and thus strengthens catalytic activity [68].

13.4.2.4 Polymer-Stabilized NPs [94, 111, 112]

Kumar *et al.* [111] stabilized Au NPs using polystyrene sulfonate (PSS), sodium dodecylsulfate (SDS) and polyvinylpyrrolidone (PVP) with reduction by 3,4-Ethylenedioxythiophene-polystyrenesulfonate (EDOT) in aqueous solutions. The kinetic rate decreased in the order PSS > SDS > PVP due to an increase in the hydrodynamic diameter of the Au

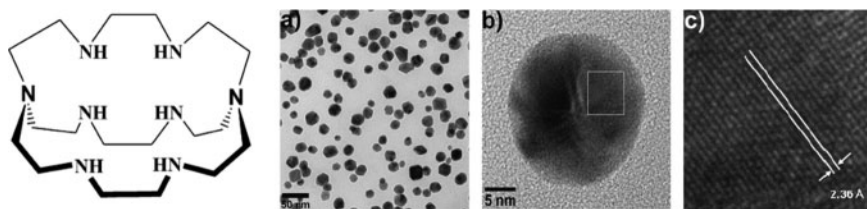


Figure 13.12 The molecular structure of azacryptand and a TEM image of azacryptand-reduced Au NPs [118]. (Reprinted with permission from [118]; Copyright 2006, Elsevier.)

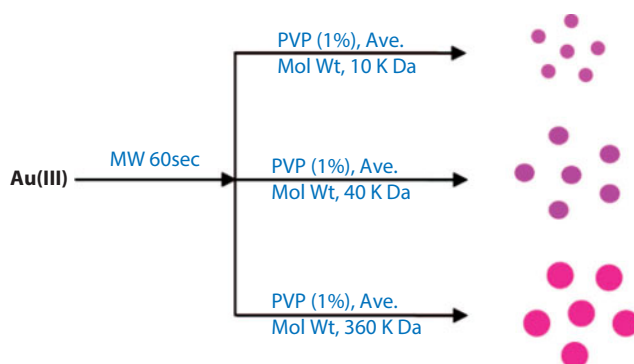


Figure 13.13 Schematic presentation for the formation of different sizes of Au NPs [112]. (Reprinted with permission from [112]; Copyright 2009, American Chemical Society.)

nanocomposites in the order PSS (26.3 nm) < SDS (45.3 nm) < PVP (219.9 nm), clearly demonstrating an increase in the aggregate size.

Kundu *et al.* [112] produced size-controlled Au NPs (6.7, 13.8, and 22 nm) by varying the molar ratio of poly(N-vinyl-2-pyrrolidone) (PVP) to Au ions and by using different molecular weights of PVP (Figure 13.13). The fastest rate of 4-NP reduction was obtained in the presence of smaller Au NPs. The suggested reason for this is as follows: Au NPs are stabilized by PVP polymers of different molecular weight, which wrap around the particle surfaces. For smaller Au NPs, the availability of fresh and renewed surfaces is greater because of the low molecular weight of the PVP; for larger particles it is lower because of the high molecular weight of the PVP. The longer chain lengths of the polymers make it difficult to remove them from the surface of larger particles. Another reason for the difference in catalytic rate might be an increase in steric hindrance for larger Au NPs as a result of BH_4^- and 4-NP [112].

Xie *et al.* [94] synthesized Ag-NPs-doped hollow poly(N-isopropylacrylamide) (PNIPAM) sphere (Figure 13.14). PNIPAM is a functional microgel and a thermal-responsive polymer that undergoes a phase transition from a hydrophilic, water-swollen state to a hydrophobic, shrinkage state when heated above its lower critical solution temperature (LCST). This microgel can be grafted onto a polystyrene support to be used as template for metal NP synthesis [60]. However, these carrier systems are often of a core-shell structure, which is usually heavy and limited in terms of tunable properties. The authors of the paper tried to use hollow PNIPAM spheres as carriers for Ag NPs without any solid support.

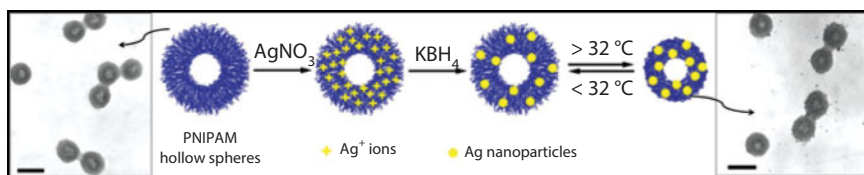


Figure 13.14 A schematic illustration of the *in situ* formation of Ag NPs in thermosensitive, hollow PNIPAM microgel networks with TEM images [94]. (Reprinted with permission from [94]; Copyright 2009, Wiley-VCH.)

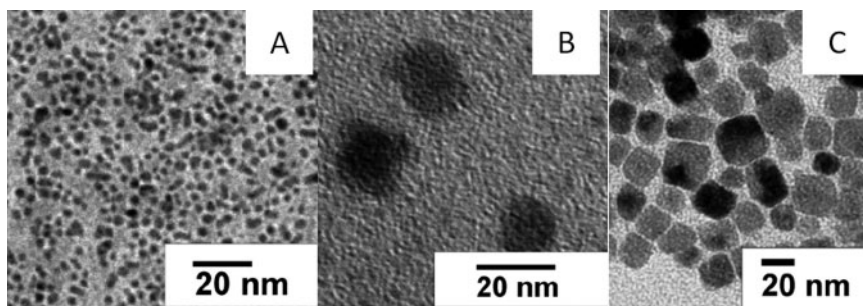


Figure 13.15 TEM images of (A) Cu NPs, (B) Cu nanocrystals and (C) Cu_2O nanocubes [6]. (Reprinted with permission from [6]; Copyright 2009, Royal Society of Chemistry.)

The hollow PNIPAM-Ag nanocomposite spheres showed a typical thermal sensitivity, as well as good and controllable catalytic activity throughout five stages of variation versus temperature. The Cu NPs (3 nm) were synthesized via the reduction of Cu ions with sodium borohydride in the presence of sodium polyacrylate. The final Cu nanocrystals had a diameter of 14 nm and were generated through the aggregation and coalescence of the primarily formed Cu NPs. The controlled aeration of the Cu NPs transformed them into Cu_2O nanocubes with an average size of 18 nm (Figure 13.15) [6].

The normalized reaction rate for Cu NPs ($0.026 \text{ mmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$) is only 1.5 times larger than that of Cu_2O nanocubes ($0.018 \text{ mmol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$). This is because of a lower concentration of Cu atoms on the surface of the Cu_2O nanocubes due to oxygen diffusion and lattice expansion. Another reason is that Cu NPs do not have the smooth surfaces associated with Cu_2O nanocubes that may offer more active catalytic sites. The normalized rates obtained for Cu NPs and Cu_2O nanocubes are comparable with that of Ag NPs (3 nm) [64, 104], Au NPs (1.25 nm) [92], Pt NPs (2.1 nm) [60], and Pd NPs (2.4 nm) [61]. These results indicate that Cu could potentially replace more expensive metals in certain catalytic applications.

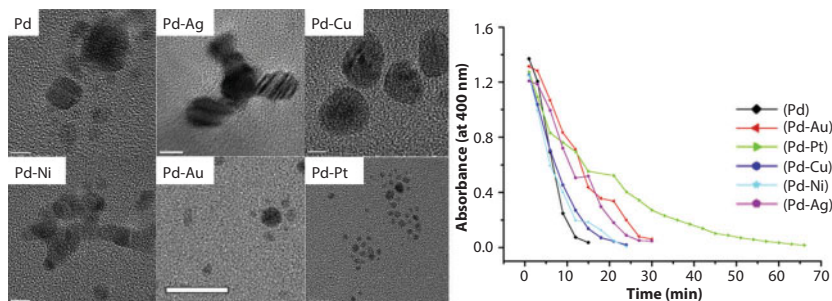


Figure 13.16 TEM images and the catalytic activities of various bimetallic Pd-M catalysts [116]. (Reprinted with permission from [116]; Copyright 2008, American Chemical Society.)

Monometallic Pd [115] and bimetallic Pd-M (M = Cu, Ni, Pt, Au, Ag) [116] NPs were synthesized using γ -irradiation with polyvinylpyrrolidone (PVP) as a stabilizing agent (Figure 13.16). The catalytic activity of Pd and Pd-M alloy NPs decreased in the order Pd > Pd-Cu $\approx$ Pd-Ni > Pd-Ag $\approx$ Pd-Au > Pd-Pt. This result is extraordinary since most of the bimetallic catalysts had an enhanced catalytic activity as compared to the monometallic catalysts reported so far [8, 67, 102, 126].

Ag NP layer-by-layer films supported on assembled polyelectrolytes/dendrimers [113] and Ag NPs (10–15 nm) and PdNPs (1–9 nm) stabilized on conduction polymers [114, 121] were also catalytically active in the reduction of 4-NP.

13.4.2.5 Dendrimer-Stabilized NPs [68, 74]

Hayakawa *et al.* [68] synthesized dendrimer-stabilized Au NPs using different generations of poly(amidoamine) (PAMAM) and polypropyleneimine (PPI) dendrimers (Figure 13.17). The average diameters of the resultant Au NPs tended to decrease with an increase in dendrimer concentration. This is due to a faster termination process when the molar ratio of [dendrimer]/[Au³⁺] increases. The rate constants of PPI dendrimers are considerably higher than that of PAMAM dendrimers, whereas the size of PPI dendrimers is considerably smaller than that of PAMAM dendrimers of the same generation. It was concluded that the diffusion of 4-NP mainly controls the rate of reduction [117] and that the rate constant is predominantly controlled by the size of the dendrimer adsorbing on the Au NPs.

Esumi *et al.* [82, 117] synthesized dendrimer-stabilized Au [117], Pt [82], Pd [82], and Ag [82] NPs using various concentrations of PAMAM and PPI dendrimers. They observed that the catalytic activity relied on both the concentration and generation of the dendrimer, as well as

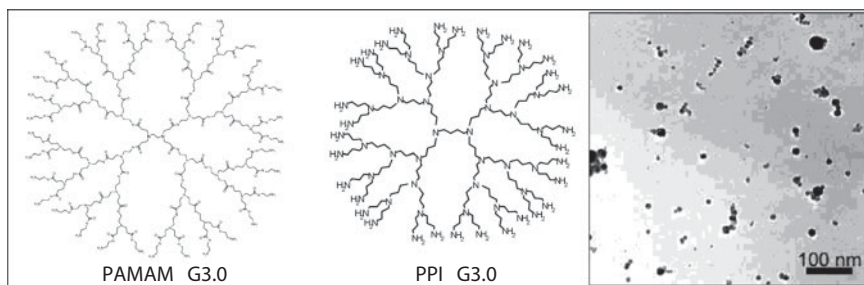


Figure 13.17 The structure of the dendrimer and dendrimer-stabilized Au nanoparticles [68]. (Reprinted with permission from [68]; Copyright 2003, American Chemical Society.)

their surface functional groups. The rate constants were significantly greater for the PPI dendrimers and decreased with an increase in dendrimer concentration. This decrease is attributed to an increase in dendrimer adsorption onto the metal nanoparticles. The authors proposed that 4-NP reduction is diffusion controlled, hence the easier diffusion of 4-NP to Au NPs stabilized by PPI dendrimers, which have smaller hydrodynamic diameters than PAMAM dendrimers. The magnitude of the rate constants for both the PPI and PAMAM dendrimers decreased in the order $\text{Pd} > \text{Pt} > \text{Ag}$. Quite a few metal nanoparticles stabilized by dendrimer template and their application in 4-NP reduction have been reported by the Crooks [74] and the authors group [69].

13.4.2.6 NPs Stabilized by Surfactants, Micelles and Microemulsions [75]

Wang *et al.* [75] investigated 4-NP reduction using micelle-supported Au NPs (2–4 nm). The block copolymer poly(*N*-isopropylacrylamide)-*b*-poly(4-vinylpyridine) (PNIPAM-*b*-P4VP) self-assembled in water to form core-corona micelles with the P4VP block as the core and the thermoresponsive PNIPAM block as the corona. The lower critical solution temperature (LCST) was about 32°C.

Qin *et al.* [12] demonstrated the synthesis of Pt NPs and Pt nanowires using a glucose surfactant as a stabilizing agent (Figure 13.18). By changing the molar ratio of the reducing agent:Pt ions, they obtained either Pt NPs (3.7 or 5.0 nm) or Pt nanowires (5.7 nm). They found the catalytic activity to increase with an increase in particle size for monodispersed Pt NPs (5.0 nm), and even more so for Pt nanowires (5.7 nm) of a similar mean size. Because of this similarity, size plays a minor role in catalytic activity. Instead, the enhanced rate of the nanowires is due to the abundance of grain boundaries.

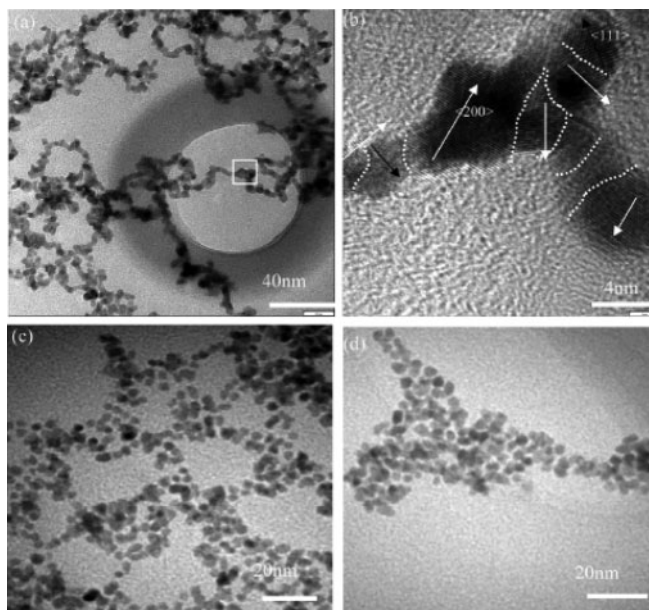


Figure 13.18 (a–b) TEM images of Pt NWs and (c–d) Pt NPs [12]. (Reprinted with permission from [12]; Copyright 2010, American Chemical Society.)

13.4.2.7 Galvanic Replacement [3, 8–10, 126]

Zeng *et al.* [9] presented the occasional case of synthesis using the titration of Ag nanocubes with chloroauric acid (HAuCl_4) in an aqueous solution under reflux to produce three different types of Au-based hollow nanostructures. These were nanocages (the most porous morphology with the thinnest walls), nanoboxes and partially hollow nanoboxes. This process is known as the galvanic replacement reaction. They compared the catalytic activity (Figure 13.19E) of these three structures with that of commercially available Au NPs (50 and 5 nm; Figure 13.19A–D). They found a relationship between catalytic activity and particle morphology. The highest catalytic activity was obtained for Au nanocages, which have a more open morphology with thinner walls. The advantage of Au nanocages lies in the intrinsic electrical connection across its entire surface and multiple holes around its corners, allowing both the outer and inner surfaces to serve as catalytic sites.

Mahmoud *et al.* [10] prepared five nanocages from Ag nanocubes by means of the galvanic replacement of Ag atoms with Pt and/or Pd atoms (Figure 13.20). Five conclusions were drawn from their comparative study: (1) Pd NCs and Pt/Pd NCs (Pd covers the cavity surfaces and forms an

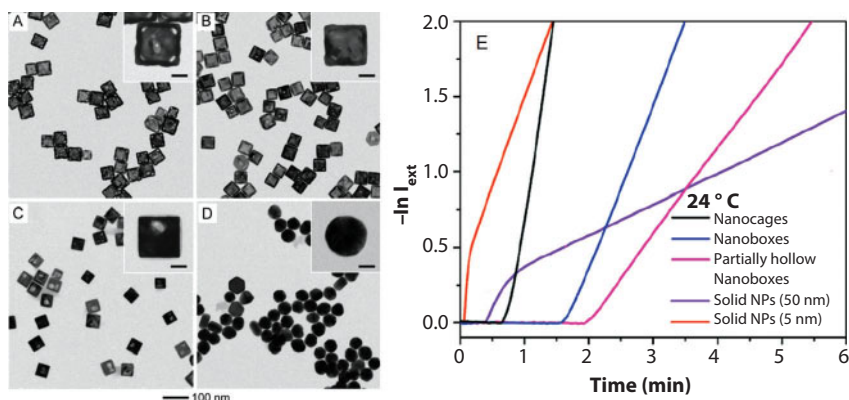


Figure 13.19 TEM images of Au-based nanocages (A), nanoboxes (B), partially hollow nanoboxes (C) and solid nanoparticles (D) with an average size of 50 nm. (E) Plots of $-\ln I_{\text{ext}}$ against time [9]. (Reprinted with permission from [9]; Copyright 2006, American Chemical Society.)

inner shell) have similar kinetic parameters. (2) Pt NCs and Pd/Pt shell-shell NCs (Pt covers the cavity surfaces) have similar kinetic parameters. (3) From (1) and (2), the catalytic reaction takes place within the confines of the cavity. (4) Pt on the nanometer scale is a better catalyst for this reaction than Pd, as observed from the metallic surface. (5) The frequency factors were the highest ever reported for this reaction, again confirming the confined nature of the cavity mechanism in hollow NPs.

Khalavka *et al.* [3] prepared rod-shaped Au nanorattles-solid Au nanorods surrounded by thin Au shells using a galvanic replacement process that started with Ag-coated Au nanorods. Figure 13.21A illustrates the growth of Au nanorattles as follows: Starting with Au nanorods (a), a layer of Ag is deposited (b). A reaction with Au ions (blue arrows) produces a shell of Ag-Au, which then transforms into a cage. The dealloying of Ag leads to either a closed (c) or porous shell (d), depending on the amount of Au that was added. Figure 13.21B shows the normalized absorption at the peak position of 4-NP as a function of time after the addition of sodium borohydride (black curve). The concentration of 4-NP decreases slowly over time, but in the presence of metal nanoparticle catalysts the reaction rate increases significantly. Au-rattles (blue) are more active than the same number of nanorods (red) by a factor of 4. This is because there is a 4-fold increase in surface area, as estimated from TEM images. Replacing the outer Au shell with a thin Pd shell further increases the catalytic activity (orange) simply because Pd is more catalytically active than Au [82].

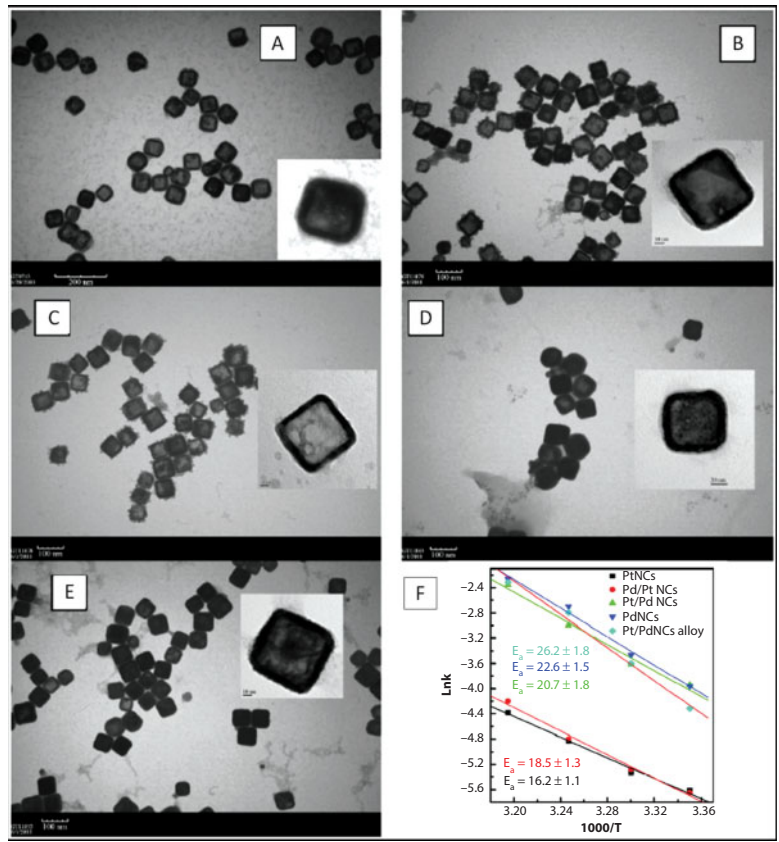


Figure 13.20 TEM images of the different nanocages. (A) PtNCs, (B) Pd/Pt shell-shell NCs, (C) PdNCs, (D) Pt/Pd shell-shell, and (E) Pt-Pd alloy NCs. (F) Arrhenius plots [10]. (Reprinted with permission from [10]; Copyright 2010, American Chemical Society.)

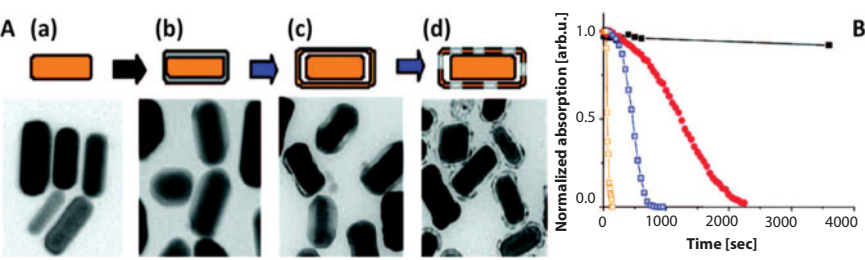


Figure 13.21 (A) Growth of Au nanorattles. (B) Normalized absorption at the peak position of p-nitrophenol as a function of time after the addition of sodium borohydride (black curve) [3]. (Reprinted with permission from [3]; Copyright 2009, American Chemical Society.)

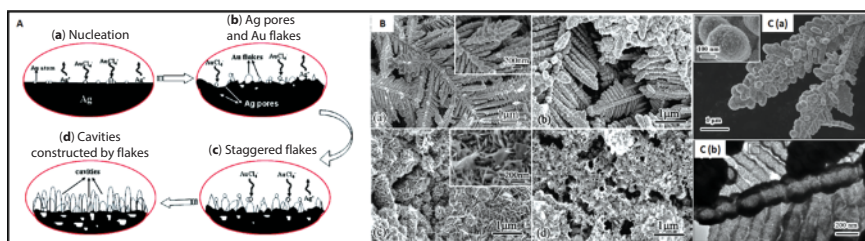


Figure 13.22 (A) The formation of bimetallic Au-Ag nanostructures [126]. (B) FESEM images showing (a) the initial Ag dendrites (at reaction time = zero) and the Ag/Au structures after GRR for (b) 4, (c) 8 and (d) 12 min. The insets are corresponding magnified views [126]. (Reprinted with permission from [126]; Copyright 2009, American Chemical Society). (C) Pd-Ag bimetallic dendrites (a) SEM image (b) TEM image [8]. (Reprinted with permission from [8]; Copyright 2010, American Chemical Society.)

Huang *et al.* synthesized Au-Ag [126] and Pd-Ag [8] bimetallic dendrites using Ag dendrite-based galvanic replacement (Figure 13.22). They obtained different morphologies, compositions, and crystal structures by varying the reaction times. The catalytic activity was higher than that of a spongy Au catalyst [119]. The activity also increased with an increase in Au for bimetallic Au-Ag dendrites and better activity was observed for Pd-Ag dendrites than for Au-Ag dendrites. Au-Ag dendrites are highly active to begin with and the presence of Pd only enhances the activity. It does so by adding a hydrogen relay mechanism to the very effective electron relay capability of the bimetallic dendrites. From an economical point of view, this bimetallic morphology is beneficial because it is a very expensive catalyst (Au) located precisely where it is needed (at the accessible surface) on top of a much less expensive substrate (Ag).

13.4.3 NPs Supported on Solid Supports

13.4.3.1 Resin-Supported NPs [70, 71, 87]

Anion-exchange resin is a polymer containing amine or quaternary ammonium groups as integral parts of the polymer lattice with an equivalent amount of anions such as chloride, hydroxyl, or sulfate [130]. Au or Ag NPs have a negative surface charge [131] so they cannot be immobilized on a cation-exchange resin bed. They can, however, be immobilized on a strongly basic anion exchanger (Figure 13.23). For these anion-exchange resin-stabilized NPs, Jana *et al.* [87] found the rate of reduction of 4-NP to be 2-fold lower with Au than with Ag. Panigrahi *et al.* [70] synthesized Au

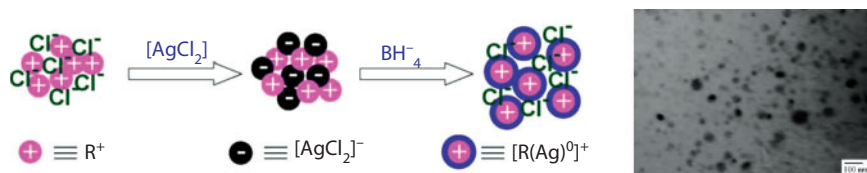


Figure 13.23 Schematic representation of the synthesis of Ag nanoshell-coated polystyrene beads with corresponding TEM images [87]. (Reprinted with permission from [87]; Copyright 2006, Elsevier.)

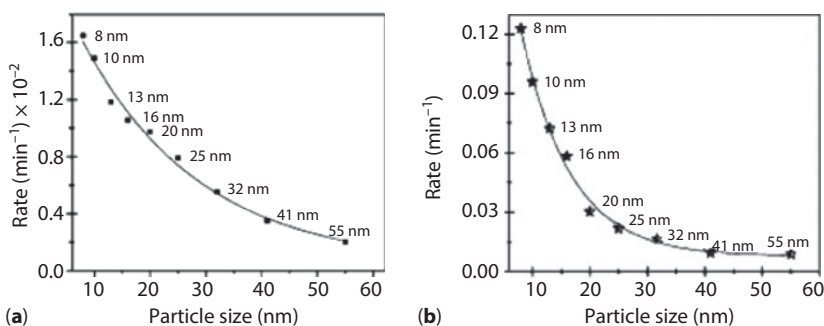


Figure 13.24 (a) The rate vs the particle size of resin-bound Au NPs (heterogeneous catalysis). (b) The rate vs the particle size of Au sol (homogeneous catalysis) [70]. (Reprinted with permission from [70]; Copyright 2007, American Chemical Society.)

NPs of various sizes (8–55 nm) using the Frens method [132] and immobilized them onto the resin beads by means of polystyrene-based commercial anion exchangers. They evaluated the kinetics of the Au NPs before and after immobilization and found a significant correlation between particle size and reduction rate (Figure 13.24). The kinetics in Figure 13.24 show that the rate increases with a decrease in particle size for both homogenous and heterogeneous Au NP catalysis. Smaller particles are more active because there are more surface atoms available for catalysis. In addition, the faster rate observed for smaller particles might be due to the larger Fermi level shift that occurs in the presence of highly electron-injecting species such as BH_4^- ions [133]. The induction time is reduced with a decrease in particle size, which indicates a decrease in activation energy and an increase in the roughness of the surface. The observed dependence of the rate on particle size is attributed to the higher reactivity of coordinatively unsaturated surface atoms on small particles, compared to the low-index surface atoms of larger particles.

13.4.3.2 Inorganic Oxide-Supported Magnetic Nanoparticles [90, 93, 100]

Chang and Chen [93] fabricated magnetically recoverable Au nanocatalysts (3.14 nm) by means of the simple adsorption–reduction of Au(III) ions on chitosan-coated iron oxide magnetic nanocarriers (Figure 13.25). As in the case of dendrimer-stabilized metal NPs, 4-NP reduction was found to be diffusion controlled due to the presence of the chitosan layer on the Au nanocatalysts [82]. In addition, the magnetically recoverable Au nanocatalysts were not deactivated or poisoned during the catalytic and separation processes, even after the 11th cycle. This points to a stable nature and good catalytic ability. Shin *et al.* [90] also synthesized magnetically removable Ag NPs deposited on Fe_2O_3 . They easily recovered the NPs from the solution using a neodymium magnet and they reused the catalyst in 21 successive reactions, which all gave 100% conversions within 3 min periods.

Zhou *et al.* [106] reported a facile approach for the production of Pt (4.8 nm), Au (6.0 nm), and Pd NPs (4.0 nm) using multicarboxylic hyper-branched polyglycerol (HPG)-grafted, SiO_2 -coated iron oxide ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) as a magnetic hybrid support (Figure 13.26). This support combines the merits of both Fe_3O_4 and HPG, namely facile magnetic separation and a favorable molecular structure with numerous functional groups. They compared $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -HPG-Pt and $\text{Fe}_3\text{O}_4/\text{SiO}_2$ - NH_2 -Pt catalysts (both had identical Pt content). A higher rate and better recyclability, even after 10 consecutive cycles, was obtained for the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -HPG-Pt catalyst. This was because the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ -HPG-Pt NPs remained uniformly distributed

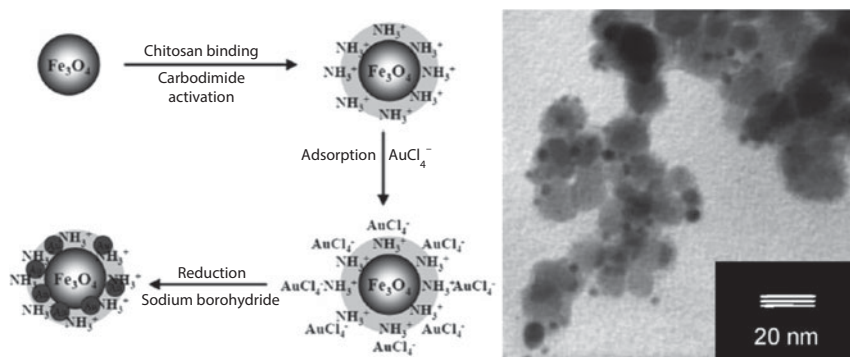


Figure 13.25 An illustration of the fabrication of magnetically recoverable Au nanocatalysts by means of the adsorption–reduction of Au(III) ions on chitosan-coated iron oxide magnetic nanocarriers and a TEM image of the Au nanocatalyst [93]. (Reprinted with permission from [93]; Copyright 2009, Elsevier.)

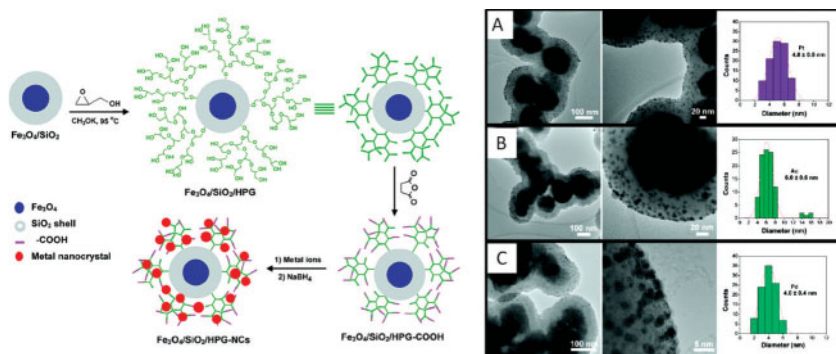


Figure 13.26 The preparation of noble metal nanocrystals (NCs) supported on hyperbranched polyglycerol-functionalized magnetic hybrids with TEM images and the size distribution of Pt (A), Au (B), and Pd (C) NPs on $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG}-\text{COOH}$ supports [106]. (Reprinted with permission from [106]; Copyright 2010, American Chemical Society.)

on the magnetic supports, even after three cycles of reduction. However, 3–10 nm $\text{Fe}_3\text{O}_4/\text{SiO}_2-\text{NH}_2$ -Pt NPs became sparsely dispersed, aggregated, and leached significantly after three cycles.

13.4.3.3 Silica Supported [89, 100]

Lee *et al.* [100] demonstrated a simple, one-step synthesis of Au NP-silica composites (10 nm) using azacrypt and as a molecular anchor between Au NPs and silica as well as reductant and stabilizer in the formation of the Au NPs (Figure 13.27). The catalytic efficiency of the Au NP-coated silica gel is higher than that of other supported catalyst systems in which citrate-stabilized Au NPs are deposited onto an alumina membrane [134] and an anion exchange resin [71] under similar experimental conditions.

Manesh *et al.* [89] produced Ag NPs (10 nm) distributed in a poly-aniline-bridged silica network (poly[N-(3-trimethoxy silyl) propyl]aniline (Ag@PTMSPA)) (Figure 13.28). The 4-NP reduction was completed within 30 min at pH 7.2, but only a 58% reduction was accomplished at pH 5. The rate of 4-NP reduction for this catalyst is much higher than that of poly(N-isopropylacrylamide)-b-poly(4-vinyl pyridine) AuNPs [75] or anion exchange resin Au NPs [70].

Yuan *et al.* [107] presented Pt NPs (3 nm) immobilized onto water-soluble organosilica hybrid nanowires with a poly(N,N-dimethyldimethylaminoethylmethacrylate) (PDMAEMA) weak polyelectrolyte shell templated from core-shell-structured cylindrical polymer brushes (Figure 13.29).

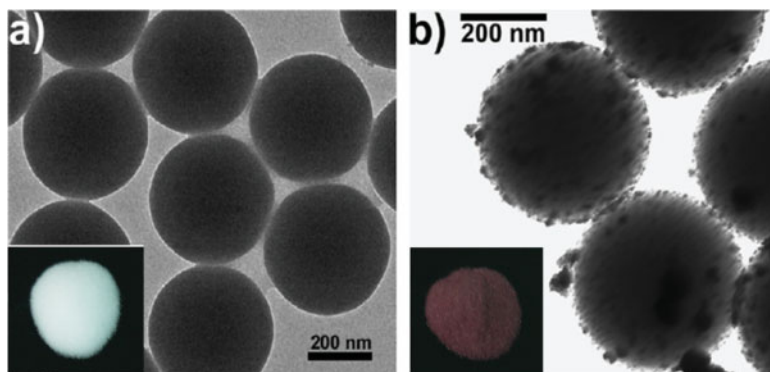


Figure 13.27 TEM images of submicrometer silica gel particles (a) and Au NP-silica gel composites (b). The insets are the corresponding photographs [100]. (Reprinted with permission from [100]; Copyright 2008, Elsevier.)

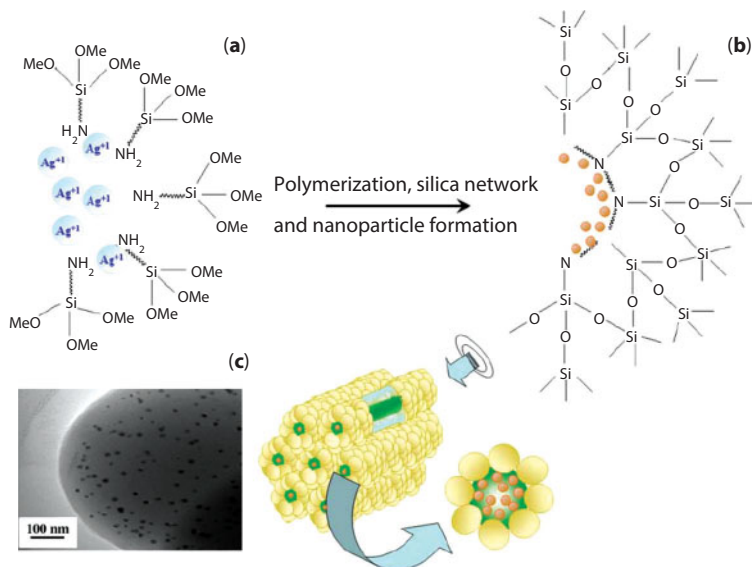


Figure 13.28 Formation of an Ag@PTMSPA composite through simultaneous reactions: (a) TMSPA and Ag⁺ ions assemble in the presence of β-NSA; (b) Ag@PTMSPA composite, silica network and poly aniline formation; (c) a portion of the PTMSPA showing a porous silica network, PANI covalently bound to the silica network and loaded Ag NPs [89]. (Reprinted with permission from [89]; Copyright 2010, Elsevier.)

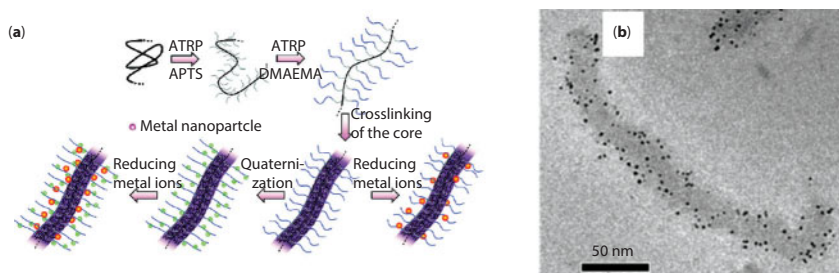


Figure 13.29 (a) Synthesis of metal nanoparticle-functionalized organosilica hybrid nanowires templated by core-shell-structured CPBs. (b) Cryo-TEM images of Pt-functionalized organosilica hybrid nanowires with a PDMAEMA shell [107]. (Reprinted with permission from [107]; Copyright 2010, American Chemical Society.)

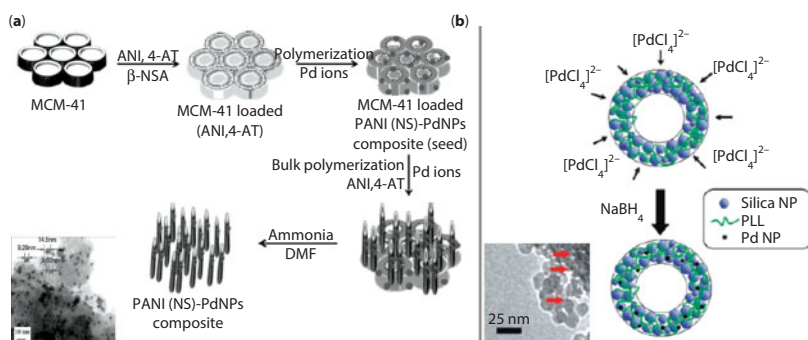


Figure 13.30 (a) Large-scale preparation of PANI(NS)-Pd NP composites through "seed"-mediated polymerization [109]. (Reprinted with permission from [109]; Copyright 2010, Wiley-VCH); (b) Methodology for the encapsulation of Pd NPs in nanoparticle-assembled microcapsules [110]. (Reprinted with permission from [110]; Copyright 2008, Royal Society of Chemistry.)

Pt NPs obtained through this method exhibited a slightly lower catalytic activity than Pt NPs immobilized on SPB [61] and a higher activity than dendrimer-stabilized Pt NPs [82].

Silica support materials were successfully applied for the large-scale preparation of Pd NPs with MCM-41 ordered mesoporous silica (Figure 13.30a) [109], and Pd NPs in a microcapsules structure [110] (Figure 13.30b). Both showed good catalytic activity with complete reduction and recyclability.

13.4.3.4 Titania Supported [11]

Kong *et al.* [11] produced porous titania hollow microspheres (permeable to chemical species) functionalized with multiple Au NPs on the

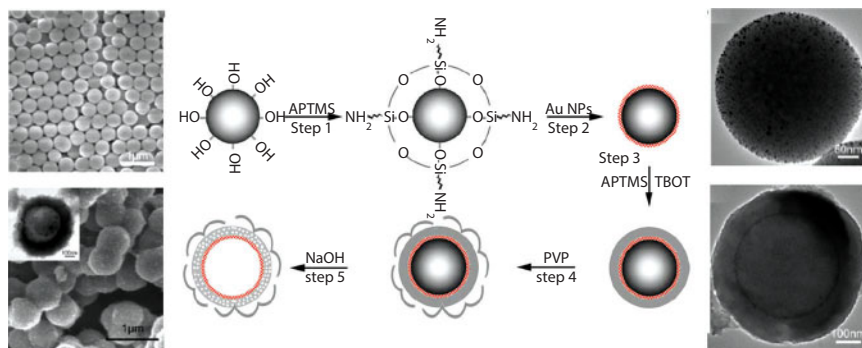


Figure 13.31 Schematic illustration of the preparation of Au@TiO₂ nanorattles based on multi-step template-deposition and surface-protected etching, with corresponding TEM images [11]. (Reprinted with permission from [11]; Copyright 2010, Elsevier.)

inside (rattle-type hollow microspheres of Au@TiO₂). The synthesis was based on multi-step template-deposition and surface-protected etching. A rattle-type hollow structure refers to a spherical shell layer and a solid core, separated by interstitial space. Figure 13.31 illustrates the procedure for creating Au@TiO₂ nanorattles. First, Au NPs are bound to the amino groups on the surface of SiO₂ microspheres modified by 3-aminopropyltrimethoxysilane (APTMS) in order to form amino functional groups (Steps 1, 2). This results in strawberry-like SiO₂@Au microspheres. Then, SiO₂@Au–TiO₂ composite microspheres are formed via the hydrolyzation of tetrabutyltitanate (TBOT) (Step 3), followed by the removal of SiO₂ cores using a NaOH solution under PVP protection (Steps 4, 5). This results in the multicore hollow Au@TiO₂ nanorattle microspheres. Initially, the catalytic activity of these nanorattles is slightly lower than that of SiO₂@Au, but they are much more durable, lasting for three successive cycles. This is because the porous TiO₂ shells can maintain the high dispersity of the Au NPs. The shells are also permeable enough to allow reactants and products access to the catalytic surfaces. In the case of the SiO₂ support surface, Au NPs gradually detach and form large aggregates, which dramatically reduce active surface areas.

13.4.3.5 Alumina Supported [88, 108]

A thick, nanocrystalline, mesoporous γ -Alumina film has been employed on glass substrates as a support material for Pt NPs [108] (Figure 13.32). Highly dispersed Pt NPs are found inside the mesopores of the nanocrystalline γ -Alumina film matrix. This catalyst presented good activity for up to 5 cycles of 4-NP reduction.

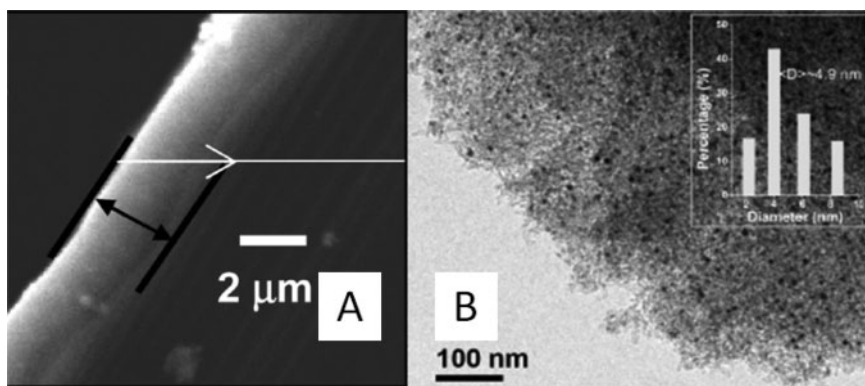


Figure 13.32 (A) A cross-section image of the film. The black double-headed arrow shows the film thickness and the white line with the arrow indicates the EDS scanning line. (B) A TEM image of Pt-incorporated mesoporous γ -Alumina film (500°C) [108]. (Reprinted with permission from [108]; Copyright 2009, American Chemical Society.)

The Pd NPs (6 nm) immobilized on alumina by Arora *et al.* [88] also showed the complete reduction of 4-NP.

13.4.3.6 Polymer Microsphere Supported [78, 91, 97–99]

Several papers reported Au NPs supported on polymer microspheres [78, 91, 97–99]. Liu *et al.* [78] found that the catalytic activity of microsphere-stabilized Au nanocolloids decreased gradually after each reaction cycle due to coagulation. However, an amount of supported catalyst could be quantitatively recycled during the recovery of the catalyst.

Liu *et al.* [98] synthesized Au NPs of various diameters in the presence of polymer microspheres using different functional groups as stabilizers. These were the carboxylic acid of poly(DVB-co-AA), the pyridyl group of poly(EGDMA-co-VPy), the mercapto group of poly(EGDMA-co-HEMA)-SH, and the amide group of poly(MBAAm) (Figure 13.33). The catalytic activity, as measured by reaction time (min), decreased gradually in the order poly(EGDMA-co-AA)@Au (96 min) > poly(EGDMA-co-VPy)@Au (132 min) > poly(EGDMA-co-HEMA)-SH@Au (215 min). All of the microsphere-supported metallic colloids had comparatively high catalytic properties and were easy to recovery. However, individual catalytic activities varied due to different interactions between the functional groups and Au NPs. Tamai *et al.* [135] also reported a dependence of catalytic activity on both metal and surface functional group.

Liu *et al.* [97] synthesized hollow polymer microspheres with movable Au cores, as described in Figure 13.34.

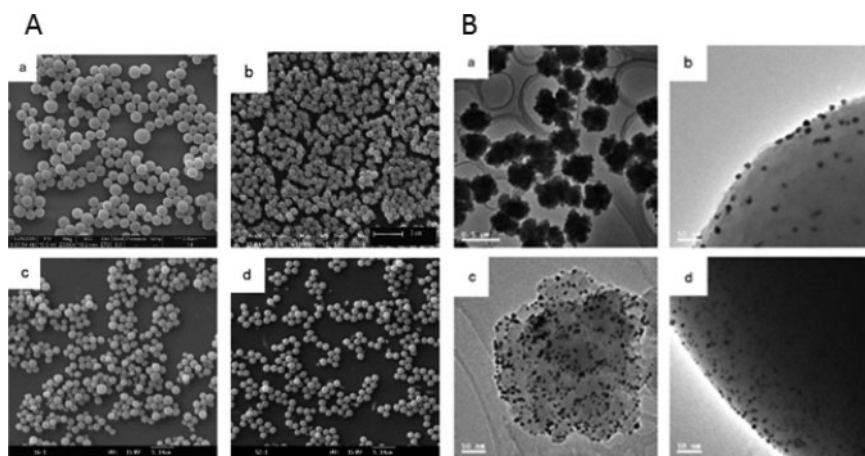


Figure 13.33 (A) SEM micrographs of the functional polymer microspheres: (a) poly(DVB-co-AA); (b) poly(MBAAm); (c) poly(EGDMA-co-VPy); (d) poly(EGDMA-co-HEMA)-SH. (B) TEM micrographs of microsphere-stabilized Au NPs. (a) A general image with poly(MBAAm)@Au as the sample; (b) poly(DVB-co-AA)@Au; (c) poly(MBAAm)@Au; (d) poly(EGDMA-co-VPy)@Au [98]. (Reprinted with permission from [98]; Copyright 2007, Elsevier.)

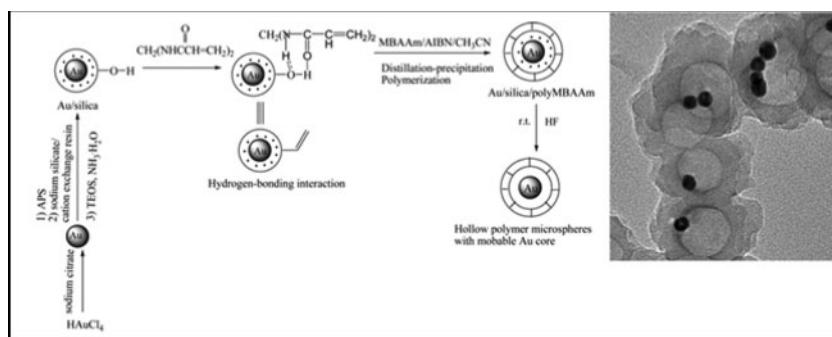


Figure 13.34 The preparation of Au/Silica/PolyMBAAm composites and the corresponding hollow polymer microspheres with Au cores and TEM micrographs of polyMBAAm hollow microspheres with movable Au cores [97]. (Reprinted with permission from [97]; Copyright 2008, American Chemical Society.)

These hollow polyMBAAm microspheres were isolated from the reaction system by simple ultracentrifugation and decantation. The heterogeneous catalyst was recovered, washed, dried, and then recycled for the reduction of 4-NP to 4-AP. The results demonstrated that the catalyst

remained highly active during the recycling, as indicated by a consistent reaction time of about 20 min.

Wang *et al.* [99] also synthesized hollow polymer microspheres with a Au nanoparticle core adsorbed onto the inner surface as a catalytic microreactor (Figure 13.35). This nanocatalyst retained high activity even after three cycles, as measured by a constant reaction time of 31 minutes. All results implied that the hollow P(EGDMA-co-MAA) microspheres with Au cores adsorbed on the inner surface and acted as an efficient and recyclable catalytic microreactor for the reduction of 4-NP to 4-AP in aqueous solution. Sodium citrate-stabilized, pure, 23 nm Au NPs performed better than the hollow microspheres (1860 s) in the first catalytic cycle. Despite this, Au NPs adsorbed on the inner surface of hollow polymer microspheres can be recycled, unlike pure Au NPs, which can hardly be recovered and aggregate severely after one catalytic cycle.

13.4.3.7 Polystyrene-Supported

13.4.3.7.1 Micelle Structure [96]

Chen *et al.* [96] reported micelle-supported Au composites (15 nm) comprised of a polystyrene core and a poly(4-vinyl pyridine)/Au shell (Figure 13.36). They were synthesized using NaBH_4 to reduce a mixture of micelle and HAuCl_4 in an acidic aqueous solution ($\text{pH} \sim 2$). The template micelle is formed by the self-assembly of block copolymer polystyrene-*block*-poly(4-vinyl pyridine).

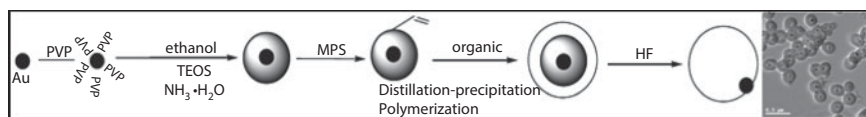


Figure 13.35 The synthesis of Au/SiO₂/polymer trilayer microspheres and corresponding hollow polymer microspheres with Au cores. The TEM image is on the right [99]. (Reprinted with permission from [99]; Copyright 2010, Springer Link.)

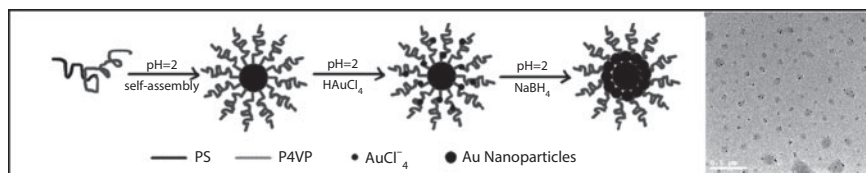


Figure 13.36 Schematic illustration of the formation of micelle-stabilized Au NPs on a polystyrene support with a TEM image [96]. (Reprinted with permission from [96]; Copyright 2008, Elsevier.)

13.4.3.7.2 Brush Structure – Spherical Polyelectrolyte Brush (SPB) [60, 61, 76, 79, 92, 104]

The Ballauff group [79] first reported spherical polyelectrolyte brushes (SPB) as a carrier system for the immobilization of Au NPs (2 nm). The method has been expanded to Ag NPs [72, 104, 105], Au NPs [76, 92], Pd NPs [60], and Pt NPs [61]. The system consists of a solid core made up of polystyrene-latex particles onto which long anionic or cationic polyelectrolyte chains are densely grafted. The advantage of the SPB system is that the surface consists of nearly monodisperse core particles that are well defined, and approximately 95% of the counter-ions are confined in the brush layer [136]. Moreover, no additional stabilizing agent, which could passivate the active sites on the surface of NPs, is needed to keep the metal particles in the truly nanoscopic range (2–5 nm). Subsequent reduction of the metal salt within these “nanoreactors” yields the corresponding metal NPs with narrow size distributions [60, 61, 76, 79, 92] (Figure 13.37).

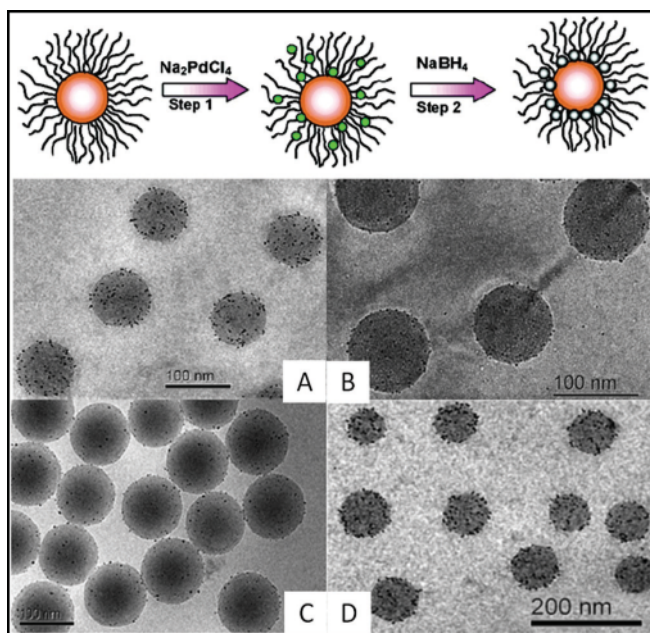


Figure 13.37 A schematic representation of the formation of Pd NPs in spherical polyelectrolyte brushes (SPB) and Cryo-TEM images of (A) Pt NPs [61]. (Reprinted with permission from [61]; Copyright 2005, American Chemical Society); (B) Au NPs [92]. (Reprinted with permission from [92]; Copyright 2007, Wiley-VCH); (C) Ag NPs [104]. (Reprinted with permission from [104]; Copyright 2007, American Chemical Society); and (D) Pd NPs [60]. (Reprinted with permission from [60]; Copyright 2007, American Chemical Society.)

The Pt NPs (2 nm) [61] immobilized on an SPB carrier system exhibit higher normalized rate constants than Pt NPs (20 nm) [67] synthesized from micellar solutions. This indicates that smaller particles exhibit considerably higher activity when the apparent rate constants are reduced to the surface of the particles. Similarly, Ag NPs (3 nm) [104] immobilized on SBP are smaller than certain others synthesized using the following carrier systems: microgel (8.5 nm) [65], PVA polymer (25 nm) [62], PVA/PS-PEGMA composite hydrogel (35 nm) [105], and PVA hydrogel (45 nm) [105]. Because of the smaller particle size and free diffusion of the reactant within the latex particles, the rate constants were higher [62, 65, 72, 104]. In the same SPB carrier system, the catalytic activity decreased in the order Pd (2.4 nm) [60] > Pt (2.1 nm) [61] > Au (1.3 nm) [92] > Ag (3 nm) [104]. This is related to a specific property of the metal and the substrates may exhibit an interaction with the surface of the particles that depends on the metal [92]. Another reason is the different kinetic barriers that exist for different metal particles [104]. The method can be modified slightly by using branched chains (“nano-tree”-type morphology) instead of linear polymer chains [72] (Figure 13.38).

Ballauff and coworkers further developed a new type of composite hydrogel in which nano-tree-type polymer brush particles are chemically entrapped in a poly(vinyl alcohol) (PVA) matrix. This reaction leads to chemical crosslinking of the nano-tree brush particles within the PVA hydrogel [105] (Figure 13.39). These Ag-hydrogel nanocomposites are the most catalytically active when compared to other Ag NPs tested under the same conditions [62, 64, 72]. This may be because Ag particles prepared in this way are smaller than those of other carrier systems. Moreover, an additional experiment showed Ag hybrid hydrogel to exhibit much higher catalytic activity than Ag NPs stabilized by a PVA polymer. This confirms that the composite hydrogel is a highly effective carrier for catalytic Ag NPs. With regards to recyclability, the catalytic activity of the PVA/PS-PEGMA/

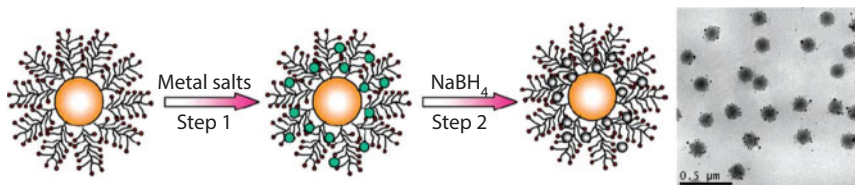


Figure 13.38 Preparation of Ag NPs using nano-tree-type branched chains and the corresponding TEM images [72]. (Reprinted with permission from [72]; Copyright 2006, Elsevier.)

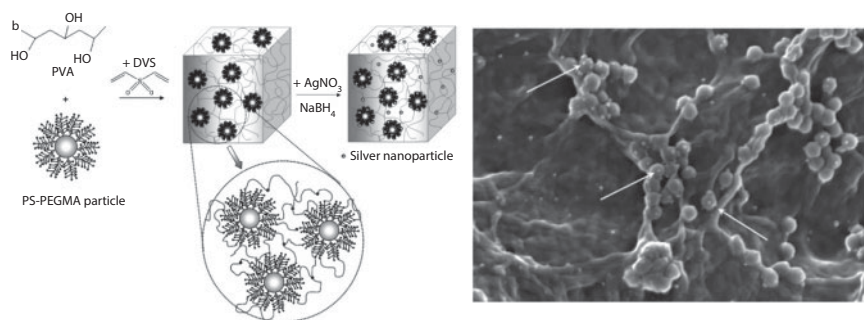


Figure 13.39 A scheme for the formation of Ag embedded composite hydrogels and FESEM images for the PS-PEGMA/Ag hybrid hydrogel [105]. (Reprinted with permission from [105]; Copyright 2007, Wiley-VCH.)

Ag hybrid hydrogel remained higher than that of PVA/Ag hybrid hydrogels throughout all three runs.

13.4.3.7.3 Core-Shell Microgels [65]

A microgel is a thermal responsive polymer with a special property: it undergoes a transition from a hydrophilic, water-swollen state to a hydrophobic, shrinkage state when heated above its lower critical solution temperature (LCST). Lu *et al.* [65] first employed this system to modulate the activity of metal NPs through a thermodynamic transition that takes place within the carrier system. They embedded Ag NPs in a polymeric network attached to a colloidal core particle. The core consists of poly(styrene) (PS) while the network consists of poly(nisopropylacrylamide) (PNIPA) crosslinked with N,N'-methylenebisacrylamide(BIS) (Figure 13.40A). The PNIPA network undergoes a perfectly reversible phase transition at about 293 K and the process of shrinking and reswelling can be repeated without degradation or coagulation of the particles (Figure 13.40C). The shrinkage of the network slows both the rate and the diffusion of the reactants within the network. This results in a nonlinear Arrhenius plot (Figure 13.40D). By measuring the dynamic light scattering (DLS) at different temperatures, it was found that the thermosensitive properties of the PNIPA network were not hindered by the incorporation of Ag particles. The Ag NPs also do not disturb the phase transition within the network. Furthermore, it was found that the crosslinking density of the shell could be tuned by varying the amount of BIS in the system [64]: An increase in BIS led to a decrease in the size of the corona and an increase in the crosslinking density of the carrier system. When the percentage of BIS was increased, the size of the Ag NPs decreased from 8.5 nm to 6.5 nm

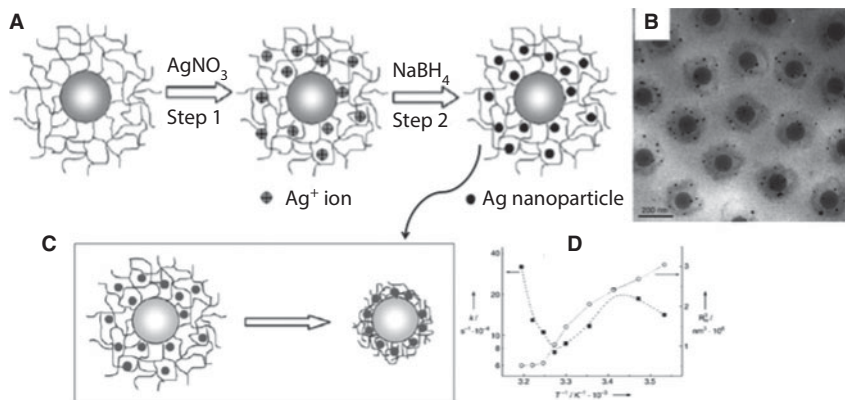


Figure 13.40 (A) The formation of Ag NPs in the PS–NIPA core–shell thermosensitive system. (B) A cryo-TEM image for the Ag NPs. (C) Phase transition of the thermosensitive system. Above LCST ($T > 293 \text{ K}$), the network shrinks and the catalytic activity of the NPs is strongly reduced. (D) An Arrhenius plot of the reaction rate k . ■: reaction rate k measured in the presence of PS-NIPA-Ag particles at different temperatures. °: volume change of the particles with a change in temperature [65]. (Reprinted with permission from [65]; Copyright 2006, Wiley-VCH.)

due to a possible limitation of Ag NP growth in the densely crosslinked network. The same amount of Ag was immobilized in every system, indicating that a greater number of smaller particles form when crosslinking is more dense. This leads to an increase in the total surface area of the Ag particles and hence a higher rate.

Mei *et al.* [60] evaluated the influence of different carrier systems by synthesizing Pd NPs using both SPB (Pd NPs 2.4 nm) and microgel (Pd NPs 3.8 nm) systems. The catalytic activities of these NPs were compared to that of other metal NPs (Figure 13.41). Two conclusions were drawn from the comparison. Firstly, the catalytic activity depends on the type of metal and not on the type of carrier system, as determined by comparing the rate constants for different metals in the same system (Pd [60] > Pt [61] > Au [92] > Ag [104]). Secondly, the catalytic activity is directly influenced by the carrier system, as determined by comparing the rate constants for the same metal in both systems. As shown in Figure 13.41, the catalytic activities obtained for the SPB system are higher than those obtained for the microgel system. The reason for this is that in the latter, metal NPs are immobilized in the crosslinked PNIIPA shell, which delays reactant molecules in reaching the catalytically active center. The SPB system, on the other hand, has an open structure that allows reactant molecules to diffuse through the latex particles and reach the metal NPs more quickly [60, 104].

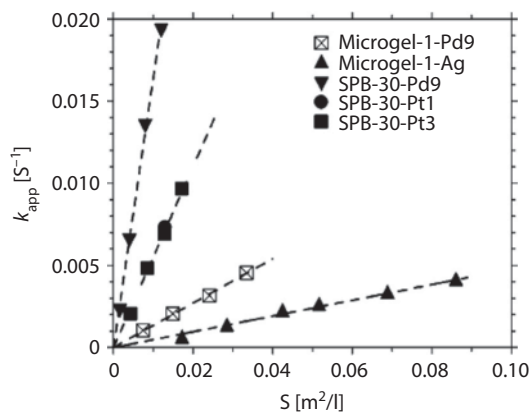


Figure 13.41 Rate constant k_{app} as the function of surface area S of metal NPs normalized to the unit volume of the system [60]. (Reprinted with permission from [60]; Copyright 2007, American Chemical Society.)

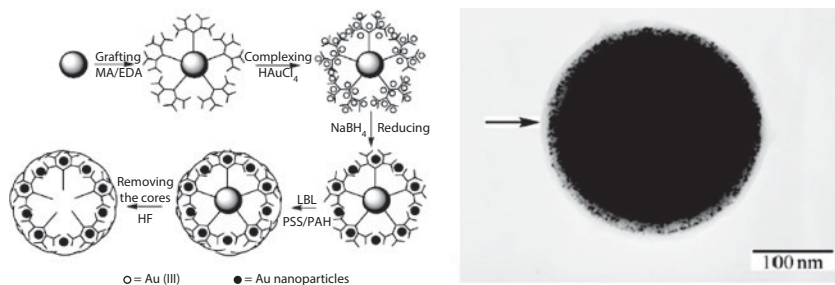


Figure 13.42 The preparation of hollow capsule-stabilized Au NPs and a TEM image of the dendrimer-modified silica spheres encapsulating Au NPs after LBL self-assembly. The arrow points to the layer of polyelectrolytes [77]. (Reprinted with permission from [77]; Copyright 2006, Elsevier.)

Moreover, there was no indication of any specific interaction between the polymer chains and the Pd NPs.

13.4.3.7.4 Hollow Capsule Structure [77, 120]

Wu *et al.* [77] synthesized hollow, capsule-stabilized Au NPs via successive dendrimer encapsulations in a layer-by-layer (LBL) self-assembly process of polyelectrolytes. Modified silica acted as a template and hydrofluoric acid was used to remove the silica core (Figure 13.42). These Au NPs (2.3 ± 0.8 nm) effectively catalyzed the reduction of 4-NP. The NPs were recovered, washed and recycled 5 times, which exceeds the performance of homogeneous catalysts such as DENs.

13.4.3.8 Carbon Sphere Supported [101, 102]

Metal NPs deposited on the outside of silica or carbon spheres are often characterized by non-uniform distribution, low density and poor long-term stability. As such, Tang *et al.* tried to embed Ag NPs (10 nm) inside porous carbon spheres (CSs) to enhance the stability, lower the toxicity and alter the electro-optical properties resulting from matrix embedding and the different collective interactions of the NPs [101]. They produced CSs doped with a high yield of highly dispersed Ag NPs. Depending on the reaction conditions, Ag NPs of various average sizes can be formed in different locations within and on the spheres (Figure 13.43).

The catalytic activity in the reduction of 4-nitrophenol (4-NP) by sodium borohydride (NaBH_4) was found to be higher than that of Ag-NP-doped hollow poly(*N*-isopropylacrylamide)spheres [94], Ag dendrites of various morphologies [7], and halloysite nanotube-supported Ag NPs [103]. This is because of the small size, high dispersion and high number density of these Ag NPs.

Tang *et al.* [102] further expanded their method to synthesize Ag-Au bimetallic NPs (Figure 13.44).

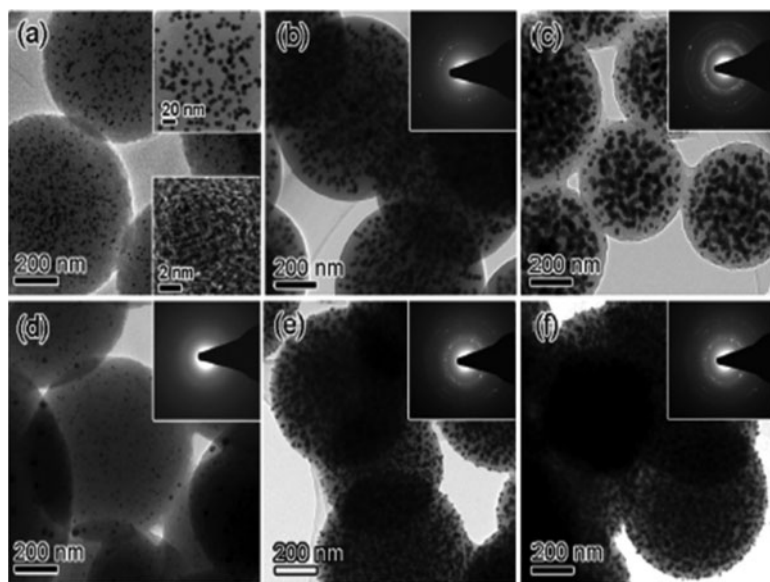


Figure 13.43 TEM images of the products obtained under various reaction conditions [101]. (Reprinted with permission from [101]; Copyright 2010, American Chemical Society.)

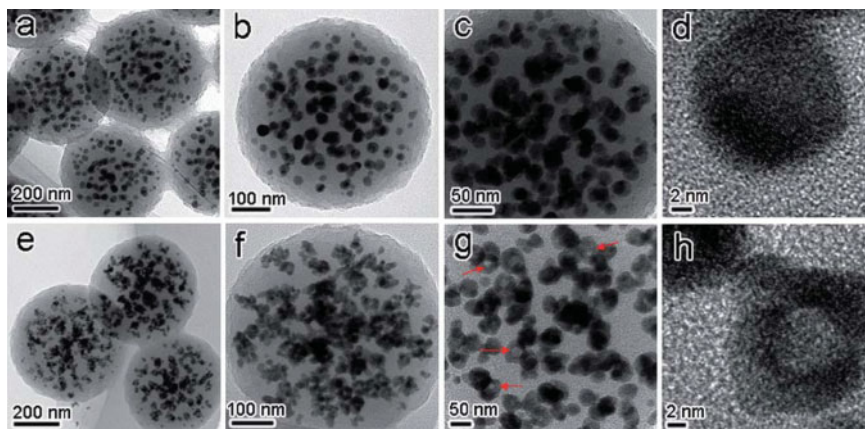


Figure 13.44 TEM images of different magnifications showing the initial Ag-C (a–d) and Ag–Au–C (e–h) composite particles. The red arrows in (g) indicate NPs with a hollow core [102]. (Reprinted with permission from [102]; Copyright 2010, Royal Society of Chemistry.)

Reduction occurred faster with the Ag–Au–C bimetallic composites than with the monometallic Ag–C, and much faster than with spongy Au nanocrystals. The rate was also above the highest value achieved for polymer-supported Au NP catalysts [91], but below that of bimetallic Ag/Au dendrites [126]. The synthesis of dendrites does, however, give a low yield at a comparatively high cost (Ag and Au are both noble metals). The yield of the Ag–Au–C composites, on the other hand, is much higher and easy to scale up for industrial production.

13.4.3.9 Nanotube Supported [103]

Liu *et al.* [103] immobilized Ag NPs (~10 nm) onto halloysite nanotubes (HNTs) via the *in situ* reduction of AgNO_3 by the polyol process (Figure 13.45). The effect of a variable concentration of NaBH_4 on the reduction of 4-NP was also investigated. It was found that the reduction rate increased and the induction time decreased with an increase in the amount of NaBH_4 .

13.4.3.10 Biomolecule Bead Supported [58]

Saha *et al.* [58] used biopolymer calcium alginate (CA) gel beads as support in the synthesis of Ag and Au NPs (<10 nm) (Figure 13.46). Alginate has a mild reducing ability and is a biocompatible, renewable, low-cost bio-resource, making it ideally suited for “green chemistry” approaches.

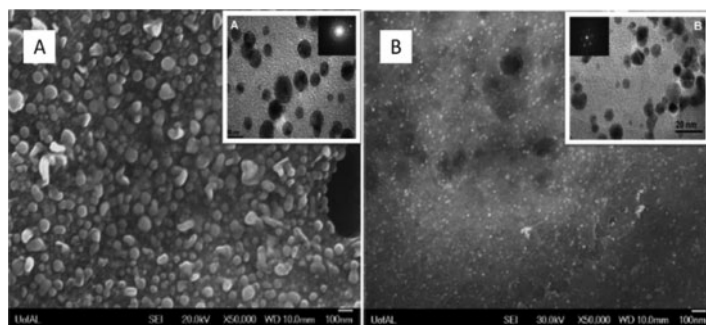


Figure 13.45 TEM images of HNTs (A) and Ag/HNTs (B) [103]. (Reprinted with permission from [103]; Copyright 2009, Elsevier.)

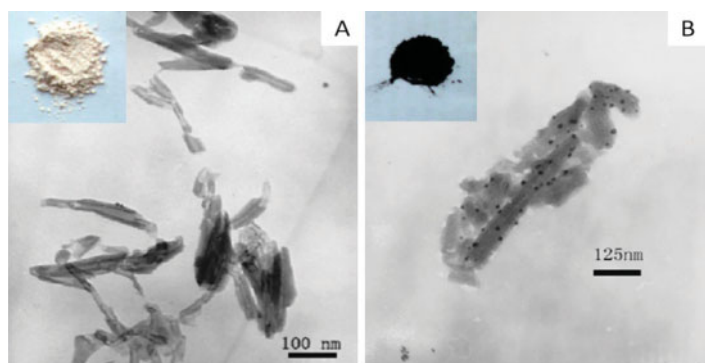


Figure 13.46 SEM images of dried (A) Ag/CA and (B) Au/CA. Inset: corresponding TEM images [58]. (Reprinted with permission from [58]; Copyright 2010, American Chemical Society.)

The catalytic activity was found to be higher for Ag/CA NPs than for Au/CA NPs. This is because only the former showed almost complete Ag surface coverage. They also found the Ag catalyst to be much more efficient than the Au catalyst in terms of TOF and recyclability. One remarkable feature was that for both catalysts, the 1st cycle followed zero-order kinetics with respect to the 4-nitrophenolate ion concentration. From the 2nd cycle onwards, reduction by the Ag/CA catalyst followed first-order-kinetics. Another interesting observation was that the rate increased up to the 3rd cycle, after which the efficiency remained almost constant. This could be an advantage in terms of different applications and cost-effectiveness. The phenomenon is due to the catalyst being more diffusible or the surface of catalyst being refreshed as the cycle goes on [137].

13.5 Conclusion

The shapes and sizes of noble metal nanocomposites are directly responsible for their unique properties. A model reaction, namely the reduction of 4-NP by NaBH_4 has been chosen to investigate the catalytic activities of various nanocatalysts of different sizes, shapes, and even porosities. The reaction is easy to monitor using simple and fast analytical techniques and there are no by-products [60–63]. 4-NP reduction is not only very important in academia and industry, but also from a “green” chemistry point of view since it converts a harmful substance (4-NP) [24–31, 33, 34] to a commercially important intermediate (4-AP) [47–49]. Most reports deal with monometallic spherical nanocomposites, but bimetallic nanocomposites [7, 8, 67, 94, 102, 115, 116, 126, 138] and nanocomposites of different morphologies (rod [3], polygonal [4], cube [5, 6], dendrite [7, 8], nanobox [9], nanocage [9, 10], rattle [11], and nanowire [12]) also have been reported.

Various synthetic protocols for nanocatalysts used in the reduction of 4-NP were presented in this review under two main categories: those synthesized on solid supports [5, 11, 58, 60, 61, 64, 65, 70–72, 76–79, 87–93, 96–110] and those synthesized in liquid suspensions [3, 4, 7–10, 12, 68, 70, 73, 75, 82, 94, 111–126]. As measured by the complete reduction of 4-NP, most of the nanocomposites proved effective catalysts. Moreover, heterogeneous nanocatalysts proved superior to liquid-suspended metal nanocomposites in terms of recyclability. A comparison of the different sizes and shapes of nanocomposites was also successfully performed using the 4-NP reduction reaction. The results confirm 4-NP reduction as a promising and efficient model reaction for evaluating the efficiency of nanocatalysts.

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Part 5

WATER TREATMENT

Doped Diamond Electrodes for Water Treatment

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Abstract

Doped diamond anodes which allow the direct production of OH radicals from water electrolysis with very high current efficiencies are especially interesting for the destruction/detection of organic pollutants in water. This has been explained by the very high overvoltage for oxygen production and many other anodic electrode processes on diamond anodes. Anodic oxidation with boron-doped nanocrystalline diamond (BDND) anodes is a new advanced oxidation process (AOP) with many advantages compared to other known chemical and photochemical AOPs. The technology of the p-type doped diamond thin films (mainly boron-doped films) has become quite mature. However the preparations of the n-type doped diamond thin films are quite difficult. We have calculated the electronic structures and the density of states (DOS) in the phosphorus-doped diamond with different phosphorus concentrations by the first principle method. The calculation results show the conductivity increases as the doped concentration increases. We have also calculated the density of states and the Mulliken population of the diamond and the co-doped diamonds with different concentrations of lithium (Li) and phosphorus (P) by the density functional theory method. The results show that the Li-P atoms can promote the split of the energy band near the Fermi level, and improve the electron conductivities, or even make the diamond from semiconductor to conductor. The Li-P co-doped diamond and nanocrystalline diamond may be used as conductive electrodes and present great potential for electrochemical water treatment, allowing the indirect oxidation of pollutants with hydroxyl radicals.

Keywords: Phosphorus-doped, Li-P co-doped, diamond electrode, AOP, impurity level, density of states, nanocrystalline diamond

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14.1 Introduction

Diamond has great potential for applications. It has a wide band gap, high breakdown voltage, high carrier mobility, high thermal conductivity and chemical inertness and so on. Diamond devices can be used in the adverse circumstances of high temperature, high pressure and strong radiation and other harsh environments. Diamond has extremely attractive prospects in industries. The intrinsic electrochemical properties of diamond are independent of the grain size (nano or micro), and are different from other commonly used sp²-bonded carbon electrodes. These properties are (1) low and stable background current over a wide potential range; (2) excellent morphological and structural stability at high temperature and current density; (3) good responsiveness for some aqueous and nonaqueous-based redox analytes without any conventional pretreatment; (4) long-term response stability; (5) optical transparency in the UV-Vis and IR regions, useful properties for spectroelectrochemical measurements [1]. Doped diamond anodes allow the direct production of OH radicals from water electrolysis with very high current efficiencies, which is especially interesting for destruction/detection of organic pollutants in water. This has been explained by the very high overvoltage for oxygen production and many other anodic electrode processes on diamond anodes.

In 1994, Gruen and coworkers reported that the “fine-grained” or nanocrystalline diamond (NCD) films were grown by Chemical Vapor Deposition (CVD) in hydrogen-poor and argon/carbon-rich conditions [2–4]. And the new material was reviewed under the label of “nanocrystalline-diamond films” in 1999 [5]. The doped NCD films may be grown by adding nitrogen or boron in growth mixture to obtain n-type or p-type semiconductor materials, respectively [6]. Boron is the most successful and widely used acceptor in diamond because it has a low charge carrier activation energy of 0.37 eV [7]; and the doping can be achieved by adding substances as diborane, trimethyl borane, and boron trioxide. At low doping levels, the diamond acts as an extrinsic semiconductor. At high doping levels the material acts as a semimetal. The success of such a doping will be largely dependent on the dopant position within the films and the nature of the bonding of the dopant atoms to the surrounding carbon atoms. Zhou *et al.* [8] have got some interesting results from the use of photochemical functionalization on BDND electrodes. The electron transfer is faster on the BDND than boron-doped diamond (BDD) because of the incorporated sp² state carbon as charge transfer mediators on BDND surface. Anodic oxidation with boron-doped nanocrystalline diamond (BDND)

anodes is a new advanced oxidation process (AOP) with many advantages compared to other known chemical and photochemical AOPs.

The present technology of the p-type doped diamond thin films (mainly boron-doped films) has become quite mature and is fully used in water treatment [9–12], medicine [13, 14] and electrochemical detection [15–17]. By incorporating the boron atoms into the diamond, the diamond thin films can obtain the shallow acceptor impurity levels near the top of its valence band, and become the p-type semiconductors. In these years, the p-type diamonds have got a lot of developments, and have had a wide range of applications in the industry [18–21]. In the last two years, the superconducting characteristics of the boron-doped diamond thin films have attracted a great deal of attention [22–24]. However the preparations of the n-type doped diamond thin films are quite difficult, the impurity levels of the n-type doped diamond films are relatively deep, and the electrical resistivity is very high [25, 26]. The n-type doped diamond thin films cannot meet the technical requirements of the devices. Thus these difficulties limit the application of the n-type doped diamond thin films.

The n-type impurity atoms are mainly lithium atoms and the sodium atoms in Group I of the Periodic Table, the nitrogen atoms and the phosphorus atoms in Group V, and the sulfur atoms and the oxygen atoms in Group VI. Seeking appropriate donors and improving the experimental technique is a long-term goal.

In order to get the appropriate donors, some people have tried using atoms such as aluminum, phosphorus and sulfur. Among these donor atoms, besides the nitrogen atoms, the phosphorus atoms and sulfur atoms have been studied most. In 1990, Koblar Jackson and his teammates theoretically studied the donor level and the crystal lattice relaxation of the phosphorus-doped diamond. And they concluded that the crystal lattice relaxation had a great impact on the stability of the phosphorus atoms in the diamond crystal lattice [27].

In 1991, experiments succeeded on the conductivity of the phosphorus-doped diamond thin films [28]. In 1997, the n-type conductance of phosphorus-doped homogeneous extension diamond thin films were prepared successfully by the microwave plasma chemistry gas phase deposition method [29]. But the impurity levels (hot activation energy) which formed in phosphorus-doped diamond were generally 0.6 eV [30, 31]. And the electronic mobility was too low to be satisfactory. Moreover, there were different measurement results about the activation energy of the phosphorus-doped diamond thin films, such as 0.43 eV [29], and 0.54 ± 0.02 eV [32].

In 1996, by theoretical calculations, Jones found that the phosphorus vacancy complexes were the deep acceptors, and would compensate any donor and make the phosphorus-doped diamond remain the insulator [33]. In 2005, the thermal ionization energy and the capture cross-section of the phosphorus donor were estimated to be 0.54 ± 0.02 eV and $(4.5 \pm 2.0) \times 10^{-17}$ cm² in the experiment which analyzed the conductivity of the phosphorus-doped diamond [32]. The electrical properties and the shapes of the phosphorus-doped diamonds, which are prepared by the organic phosphorus gas ($\text{P}(\text{C}_4\text{H}_9)_2$ and $\text{P}(\text{CH}_3)_3$) or by the inorganic phosphorus gas PH_3 , are the same in the experiment of the preparation of the phosphorus-doped diamond by the plasma-enhanced chemical vapor deposition method [34]. At the same time, in the analysis of the relationship between the mobility of the phosphorus-doped diamond's (001) surface and temperature, the largest mobility (approximately 450 cm²/Vs) lies in 260 K, and the mobility at room temperature is 350 cm²/Vs [35]. In 2006, when Takatoshi Yamada and his mates studied the field emission properties of the heavy phosphorus-doped diamond thin films, they found that the reconstruction film surface which annealed in a vacuum had a minimum threshold field value of 16 V/ μm , while the threshold field values of the thin film surface which was terminated by the oxygen or hydrogen were 28 V/ μm or 44 V/ μm [36]. In 2008, Pernot and his coworkers found that when the phosphorus atom concentrations were less than 10^{17} cm⁻³, the electron mobility was decided by the lattice scattering; when the phosphorus atom concentrations were between 10^{17} cm⁻³ and 10^{18} cm⁻³, the electron mobility was decided by both the lattice scattering and the ionized impurity atoms scattering; when the phosphorus atom concentrations were higher than 10^{18} cm⁻³, the electron mobility were decided by the neutral impurity atoms scattering [37].

Although both the experiments and theories of only the single phosphorus atoms doped diamond have greatly increased and improved, the electron conductivities of the phosphorus-doped diamond thin films remain low in experiments and cannot meet the requirements for the preparations of the devices. So some people referred to the doping experiments of the GaAs and advised that the co-doping method might be a good way. In 1995, the experiment of the preparation of the nitrogen-phosphorus co-doped diamond thin films by hot-filament chemical vapor deposition showed that adding some nitrogen atoms was advantageous to the phosphorus-doping and raise the films' growth rate, and also can get higher doping concentration: the maximum concentration of the phosphorus atoms and the nitrogen atoms were separately 3×10^{19} and 6×10^{19} atoms/cm³ [38]. In 2004,

when Li Rong-Bin and his mates prepared the boron-sulfur co-doped diamond thin films by traditional microwave plasma chemical vapor deposition, they found that adding some boron atoms could be advantageous to the sulfur doping, and made the amount of the sulfur atoms increase 1.5 times, while the activation energy of the electron conductivity was reduced from 0.52 eV to 0.39 eV [39]. In 2005, Lee and his coworkers found that the Hall coefficient of the boron-lithium co-doped diamond thin films was $-2.974 \times 10^{-2} \text{ cm}^3/\text{C}$, and its resistivity was $0.01 \sim 0.02 \text{ }\Omega\text{m}$. They also confirmed that the co-doping method could improve the stability of the lithium in the diamond thin films [40]. In 2007, Lombardi and his coworkers also studied the interstitial doping and the substitution doping of the lithium and sodium atoms. By the experiment they confirmed that the lithium atom was interstitial atom and the sodium atom was the substitution atom [41]. In 2009, according to the calculation of the first principle, Iori found that the co-doped diamond where two kinds of impurity atoms lied in the nearest neighbor has the lowest impurity formation energy [42].

It was possible to manufacture good n-type diamond devices with the phosphorus atoms as the dopant. But the reports of physical properties of the phosphorus-doped diamonds, which contained the formation mechanism of the impurity levels, the activation energy, and electron mobility, were very few. In recent years, despite many improvements and enhancements in phosphorus-doped diamond experiments, there was not enough theoretical research. We calculated the energy band structures and the density of states of phosphorus doped diamond unit cells with different doping concentrations by first principles density functional theory (DFT), and analyzed their electronic structures. These methods enable us to understand the bond properties between the impurity atoms and the carbon atoms, the situations of the electric charge distributions, and the influences after introducing the phosphorus impurity atoms. We also studied the influences of the vacancy in the phosphorus-doped diamond thin films, and found improvement on their conductivity.

In recent years, although the co-doping method has been tried a lot in experiments and theories, much progress has not been achieved. And the researches of the Li-P co-doped diamonds are very few. Therefore, in this chapter based on the first principle of the density functional theory (DFT), we also calculated the Mulliken population and the DOS of the co-doped diamonds with different concentrations of Li and P, analyzed their electronic structures, and determined the bonding properties and the charge distributions among lithium atoms, phosphorus atoms and carbon atoms and their impact on the electrical properties after doping.

14.2 Calculation Method

In this chapter, we do our calculation work with ab initio calculation quantum mechanics module Cambridge Serial Total Energy Package (CASTEP), which is based on the density functional theory in Accelrys Materials Studio software [43]. The module uses the local atom-based groups and numerical periodic boundary condition to describe the valence electrons, and the interactions between the electrons and the ions are mainly described by the Norm-Conserving Pseudopotential and the Ultrasoft Pseudopotential [44]. In order to minimize the number of plane wave basis sets, we chose the Ultrasoft Pseudopotential to describe the interactions between the electrons and the ions, and the exchange-correlation energy is described by the PBE parameterized form of the generalized gradient approximation (GGA) [45].

We first did the calculation for the phosphorus-doped diamond. In all the geometry optimization computation, the computational precision of the total energy is 1.0×10^{-5} eV atom⁻¹, and the cut-off energy value is 280.0 eV. All the super cells are permitted to relax. The stress of each atom in the diamond crystal lattice is smaller than 0.3 eV atom⁻¹, and the stress of each structural unit is smaller than 0.05 GPa, and the atomic displacement from two successive structural parameters changing is less than 1.0×10^{-4} nm, so that they maintain the real structures under the geometry optimization. The K value of the undoped diamond crystal cell is $12 \times 12 \times 12$, and the K values of doped diamond super cells, in which the atomic ratios are 1:15, 1:23, 1:31, 1:47, 1:63, 1:71, 1:95, are separately $4 \times 7 \times 7$, $2 \times 7 \times 7$, $4 \times 4 \times 7$, $2 \times 4 \times 7$, $4 \times 4 \times 4$, $2 \times 2 \times 7$, $2 \times 4 \times 4$.

Secondly, we have only computed the situation in which two kinds of impurity atoms lie in the nearest neighbor. By this way, a Li atom and a phosphorus atom are incorporated into the diamond lattice with an atom pair at a random site. The valence electron configurations of the carbon atom, the phosphorus atom and the lithium atom are respectively selected to be C: $2s^2 2p^2$, P: $3s^2 3p^3$ and Li: $1s^2 2s^1$. The cut-off energy of the plane waves is 300.0 eV. In order to study the Li-P co-doped diamond lattices of different concentrations, we have separately calculated the diamond lattices where the ratio of the lithium atom, phosphorus atom, and the carbon atoms are 1: 1: 6, 1: 1: 14, 1: 1: 30, 1: 1: 62, 1: 1: 70, 1: 1: 94, 1: 1: 142, 1: 1: 214, and the structures are shown in Figure 14.1. Their k values are set for $7 \times 7 \times 7$, $4 \times 7 \times 7$, $4 \times 4 \times 7$, $4 \times 4 \times 4$, $2 \times 2 \times 7$, $2 \times 4 \times 4$, $2 \times 2 \times 4$, $2 \times 2 \times 2$, so as to ensure the convergences of the system's energy and the structures in the plane-wave basis set.

In the Self-Consistent Field (SCF) calculation, we chose the Pulay density hybrid approach, and set the SCF to 1.0×10^{-6} eV.atom⁻¹. In the geometric

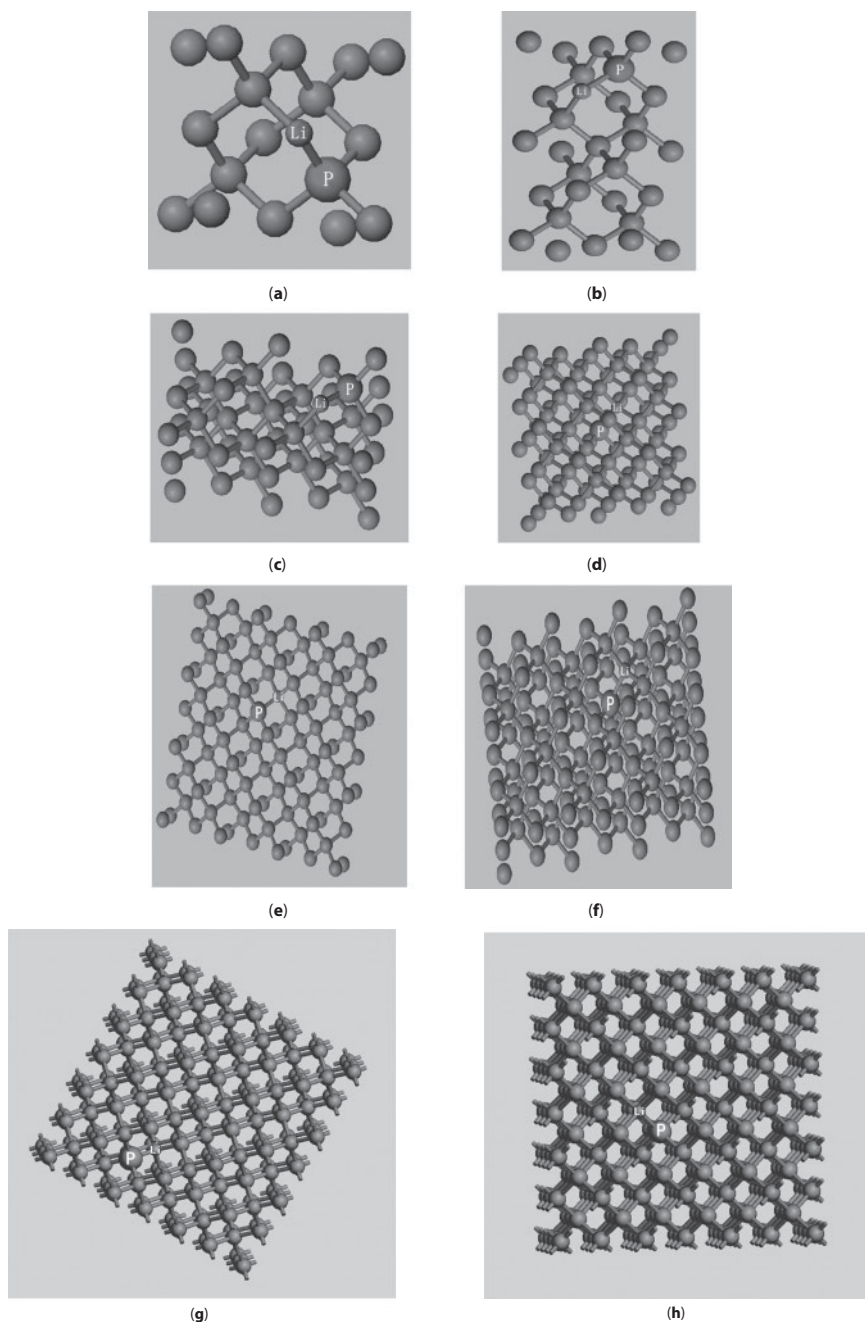


Figure 14.1 The structure of the doped diamond where the number of the Li atom is 1, P atom's number is 1 and the C atom's number is (a) 6, (b) 14, (c) 30, (d) 62, (e) 70, (f) 94, (g) 142, or (h) 214.

optimization, we chose the BFGS algorithm. The accuracy of total energy was 1.0×10^{-5} eV.atom⁻¹, the crystal force of each atom was less than 0.3 eV.nm⁻¹, the stress of each structural unit was less than 0.05 GPa, and the atomic displacement caused by the changes of the structural parameters was less than 1.0×10^{-4} nm.

14.3 Calculation Results and Discussions

14.3.1 Total Energies and Electronic Structures of Phosphorus-Doped Diamond

In order to study the phosphorus doped diamond crystal lattices with different doping concentrations, we separately calculated the diamond unit cell and several phosphorus-doped diamond super cells, in which the atomic ratios between phosphorus atoms and carbon atoms are 1:15, 1:23, 1:31, 1:47, 1:63, 1:71, 1:95. Because a phosphorus atomic radius is bigger than that of a carbon, a phosphorus atom can substitute for a carbon atom when it is introduced into the diamond crystal lattice. The phosphorus atomic radius is 110 pm, and the carbon atomic radius is 77 pm. When the phosphorus atoms are introduced into the diamond crystal cells to substitute for carbon atoms, they will cause the inflations of the diamond super cells and distort the diamond crystal lattices. Then they will have a great impact on the diamond structures, the bond types and the electric charge spatial distribution [46]. As the doped concentrations are reduced, the bond angles which come from the combination of a phosphorus atom and four nearest neighbor carbon atoms are also reduced, but they change only a little. The impurity phosphorus atoms have a great impact on the bond angles of the nearest neighbor carbon atoms, but have little influence on the bond angles of the farther carbon atoms. What's more, there is nearly no influence on the bond angles out of several atomic radius distances. In order to further understand the influences of the phosphorus atoms on the diamond crystal lattices, we analyzed the relations between the bond lengths and the phosphorus atomic concentrations. The results are shown in Table 14.1. The table describes the bond lengths and the electric charge distributions between the phosphorus atoms and the nearest carbon atoms. By the data in the table, we find that the electric charge distributions of the carbon bonds of the undoped diamond are as many as five or six times that of the doped diamonds, and the bond lengths have increased by 0.1588–0.17332 Å (10.25% ~ 11.19%). This was the same as in document [27]. Lombardi and his teammates also obtained similar results by theoretically

Table 14.1 The electric charge distributions of the phosphorus nearest neighbor atoms.

P/C	Bond	Length (Å)	Population
1:15	C 003–P 001	1.72203	0.55
1:23	C 009–P 001	1.71803	0.55
1:31	C 002–P 001	1.71607	0.60
1:47	C 036–P 001	1.71369	0.59
1:63	C 061–P 001	1.70791	0.68
1:71	C 040–P 001	1.71134	0.56
1:95	C 010–P 001	1.70751	0.69
0:8	C 001–C 002	1.54871	2.99

calculating the interactions between the hydrogen atoms and the impurity atoms in the diamond crystals. They found that the phosphorus atoms had the smallest energy in the T_d symmetrical position, all the nearest neighbor atoms of the phosphorus atoms relaxed outward and the phosphorus ions and the neutral phosphorus atoms had the same geometry structures in the T_d symmetrical position [47].

As the doping concentrations were reduced, the electric charge distributions of the bonds increased gradually, but the bond lengths were reduced gradually. This showed that the combinations of the C-P bonds would be improved as the concentration of the phosphorus atoms was reduced. Thus, when the bond lengths shortened, the integrities of the diamond crystal lattices could be improved. In the experiment of the preparations of phosphorus-doped diamond thin films by microwave enhancement plasma chemistry gas phase deposition, Koizumi found that the homogeneity extension diamond thin films got worse with increased P/C ratios [29]. Therefore, this also demonstrated the accuracy of our computational results in the experiment. When the diamond thin films were doped in low concentrations, the carrier concentrations were very low. According to the formula of the semiconductor's conductivity $\sigma = ne\mu$ (n is current carrier density), their electric conductivities were too low to meet the actual requirements.

The changes of the total energy after substituting a phosphorus atom for a carbon atom are shown in Table 14.2. The energy variations ($\Delta E = E_2 - E_1$) after substituting a phosphorus atom for a carbon atom would be reduced as the phosphorus atom concentrations increased, possibly due to the aggravation

Table 14.2 The changes of the phosphorus-doped diamond crystal lattice energy.

Numbers of total atoms	Total energy before doping (E_1 (keV))	Total energy after doping (E_2 (keV))	Changes of energy (ΔE (keV))
16	-2.47830196	-2.49776669	-0.01946473
24	-3.71745398	-3.73680229	-0.01934831
32	-4.95661760	-4.97574041	-0.01912281
48	-7.43492948	-7.45393921	-0.01900973
64	-9.91321221	-9.93204790	-0.01883569
72	-11.1523980	-11.1713091	-0.0189111
96	-14.8698961	-14.8886010	-0.0187049

of the phosphorus-doped diamond crystal lattices’ inflation and the decrease of interactions between parts of the electrons and the nucleuses. This demonstrated that when the concentration of the phosphorus atoms in the diamond crystals was higher and the inflations of the diamond crystal lattices were more serious, the SP^3 carbon bonds would be more unstable and they would be converted to the SP^2 more easily. When the diamonds have been highly doped, we may obtain the appropriate electronic conductivity, but the diamond crystal lattices will be damaged seriously. Therefore, if we want to obtain the ideal diamond thin films, we must make sure that the impurity atoms do not damage the diamond structures when they are introduced into the diamond crystal lattices by efficient experimental methods.

The valence electronic structure of a phosphorus atom is $3S^23P^3$, while the valence electronic structure of a carbon atom is $2S^22P^2$. By the limitation of the periodic arrangements of crystal lattices, the electronic orbits of the phosphorus atoms are compelled to hybridize in the SP^3 . But the residual electrons always go into the orbits of the anti-bonds of the higher energy, and form the impurity levels near the bottom of the conduction bands. Because of the covalent bonds between the phosphorus atoms and the four nearest neighbor carbon atoms, the residual valence electrons of the phosphorus atoms can become the mutual local charges of the four nearest carbon atoms.

Thus, these give the C-P bonds a small amount of ionic characteristics. Then the conductivity of the semiconductors can be improved. According to the Mulliken population analysis of the phosphorus-doped diamonds, we find that besides a delocalized electron, small parts of the phosphorus ion charges are uniformly close to the four nearest neighbor carbon

atoms, probably because the phosphorus ionic radius is bigger than the carbon ionic radius. For maintaining the stable structures, the carbon ions adsorb small parts of the phosphorus ionic charges, and develop covalent bonds of the stronger ionic characteristics. Therefore, the electrons of the phosphorus-doped diamond thin films in the impurity levels are provided by the p-orbits electrons of the phosphorus atoms. But these electrons have some ionizing energy, and are generally limited to a very small region. They cannot move freely in the diamond crystal lattices. So reducing the ionizing energy of the most outer shell electrons of the impurity atoms or their barrier heights can effectively improve the current carrier concentrations.

14.3.2 Influences of Vacancies in Phosphorus-Doped Diamond Thin Films

The above analysis obviously showed that although the high concentration of doping in the phosphorus-doped diamonds could enhance the conductivity of the thin films, it also damaged the integrities of the diamond thin films. Therefore, we thought that introducing some vacancies into the appropriate positions could enhance the impurity concentrations of the phosphorus atoms, then improve the conductivity of the thin films, and also effectively reduce the damages of the phosphorus-doped diamond thin films. We researched the 64 atom super cells of the phosphorus-doped diamond crystal lattices, and considered two different circumstances as follows: the first one is introducing a vacancy into the position of the nearest neighbor of a phosphorus atom, and the other one is introducing a vacancy into the position of several atomic distances from a phosphorus atom. Their PDOS are shown in [46]. We found that the low energy levels (approximately lower than -13 eV) were mainly occupied by the s electrons, and the high energy levels (higher than -13 eV) were mainly occupied by the p electrons. The situations are very similar to those of the diamond. The results of the Mulliken population analysis and the optimized structures gave rise to our findings. On the one hand, there were more phosphorus atomic orbits occupied by the electrons after introducing a vacancy into the phosphorus-doped diamond crystal lattice. And before introducing the vacancy, the p orbits were occupied by 2.45 electrons. Then after introducing the vacancy, the p orbits were occupied by 2.66 electrons. On the other hand, before introducing a vacancy into the phosphorus-doped diamond, the bond lengths between the phosphorus atom and the nearest neighbor carbon atoms were 1.70791 Å, the bond angles between the phosphorus atom and the nearest neighbor carbon atoms were 109.471°,

and the bond angles of the nearest neighbor carbon atoms were approximately 113.238° . After introducing a vacancy into the phosphorus-doped diamond, the bond lengths between the phosphorus atom and the nearest neighbor carbon atoms were $1.95552 \text{ \AA}$, the bond angles between the phosphorus atom and the nearest neighbor carbon atoms were 86.605° , and the bond angles of the nearest neighbor carbon atoms were approximately 108.064° . So the bond lengths were increased by $0.24761 \text{ \AA}$, and the bond angles were reduced by more than 10° . It was possible that after introducing a vacancy into the phosphorus-doped diamond, the phosphorus atom would move close to the vacancy. Then it would cause the bond lengths to increase and the bond angles to reduce. And it would limit the inflation of the phosphorus-doped diamond crystal lattices. This method could solve the question of the inflation of the phosphorus-doped diamond crystal lattices to a certain extent. The Fermi energy level moved toward the valence band and even entered it, so the n-type semiconductor became the p-type semiconductor, which did not meet our expectancies.

By the other method, when introducing a vacancy into the position of several atomic distances from a phosphorus atom, we obtained a better result [46]. The energy levels less than $\sim 15 \text{ eV}$ were occupied by the s electrons, while the energy levels higher than $\sim 15 \text{ eV}$ were occupied by the p electrons. The numbers of the energy levels which were occupied by the p electrons with this method were less than with the first method, and more than with the no vacancy method. In the computation result, the bond lengths between the phosphorus atom and the nearest neighbor carbon atoms were $1.71430 \text{ \AA}$, the bond angles between the phosphorus atom and the nearest neighbor carbon atoms were 108.894° , and the bond angles of the nearest neighbor carbon atoms were approximately 111.218° . Compared with the phosphorus-doped diamonds without a vacancy, the integrities of the crystal lattices were greatly improved, and the energy band gap became smaller due to the impurity levels near the Fermi energy level. Therefore, this method could effectively improve electron conductivity. In order to further study the influences of the vacancies on the electron conductivity by this method, we calculated the plane-wave density of states (PDOS) of the phosphorus-doped diamonds in which the concentration of the phosphorus atoms had been enhanced [46]. When the concentration of the phosphorus doping atoms was enhanced, the width of the forbidden band obviously became smaller, and the Fermi energy level moved closer to the conduction band. This indicated that the electron ionizing energy or the potential barrier of the impurity level across the conduction band was reduced. And it was possible that there were more free electrons entering the conduction band. Thus the concentration of the free current carriers

could be enhanced, and the electron conductivity of the n-type diamond thin films could be effectively improved.

14.3.3 Electron Density of States of Lithium-Phosphorus Co-doped Diamond

Secondly, we calculated the DOS of the diamond and the co-doped diamonds with different concentrations of Li and P. The total density of states (TDOS) of the diamond and the partial density of states (PDOS) of the diamond are shown in Figure 14.2. The middle point line is the Fermi level. On its left is the valence band and on its right are the energy gap and the conduction band. The energy gap is 4.138 eV and it was a little different as the value of the experimental measuring 5.4 eV. The phenomenon that the energy gap is underestimated is prevalent in the density functional calculations [48], but it does not affect our following qualitative analysis on the doped diamonds. The valence band of the diamond consists of two areas: in the high energy region (approximately -13 eV ~ 0 eV), it is mainly occupied by the C2p states, while in the low energy region (approx. -21.5 eV ~ -13 eV), it is mainly occupied by the C2s states, and the conduction band of the diamond is mainly occupied by the C2p states. From the PDOS in

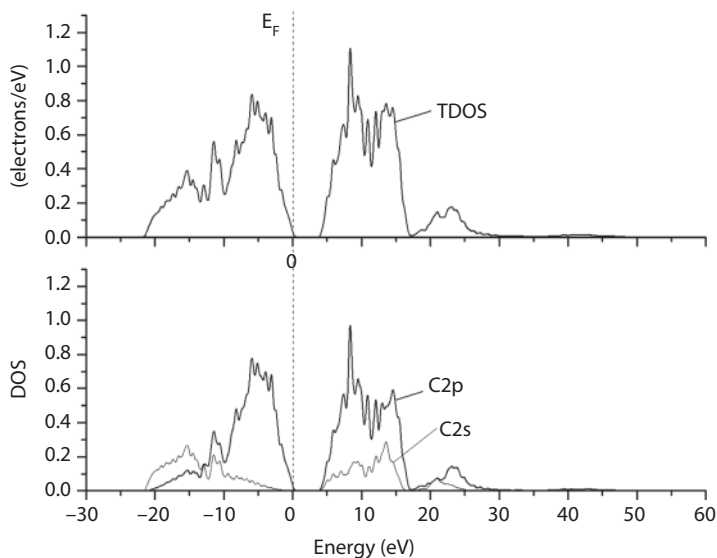


Figure 14.2 The total density of states (TDOS) and the partial density of states of the diamond. The E_F stands for the Fermi level. The C2s and C2p represent the electric charge distributions of 2s and 2p orbits.

the conduction band, we can see that the area ratio of the C2s states and C2p states is approximately 1:3. Here, although the above result has been known for long time, we will illustrate it again as to compare it with the situations of the doped diamond.

By comparing the TDOS of the Li-P co-doped diamond in Figure 14.3 with the TDOS of the diamond in Figure 14.2, we can find that the Fermi level of diamond after doping obviously moves near the bottom of the conduction band. When the doping concentration is relatively low, such as in the TDOS shown in Figure 14.3(b) and (c), the Fermi level of the Li-P co-doped diamond moves near the bottom of the conduction band, the energy gap width is almost the same as in the diamond (as shown in Figure 14.2), and the donor levels are formed in the band gap and near the bottom of the conduction band. But when the doping concentration is higher, such as in the TDOS shown in Figure 14.3(a), the energy gap of the Li-P co-doped diamond has disappeared. This is most probably caused by the impurity level broadening and an impurity band forming, which completely fill out the energy gap region. So the Li-P co-doped diamond becomes a conductor. All this illustrates that when the donor impurity atoms are incorporated into the diamond, the impurity levels will appear near the bottom of the conduction band, and the insulated diamond then will become a semiconductor which has some conductivity.

When the concentrations of the lithium atom and phosphorus atom are not too high, some impurity levels only formed near the bottom of the conduction band. But when the concentrations of the lithium atom and phosphorus atom are high enough, the impurity levels will increase, broaden and become an impurity band, or even extend to the entire energy gap. Then they will make the energy gap disappear, and the semiconductor will become a conductor. Here, the magnitude of the concentration of the lithium atom or the phosphorus atom is about 10^{21} , three orders of magnitude higher than the concentration of the phosphorus atoms in reference [34], where its concentration is about $2 \sim 3 \times 10^{18} \text{ cm}^{-3}$, and two orders of magnitude higher than the concentration of the phosphorus atoms in reference [36], where its concentration is determined to $7 \times 10^{19} \text{ cm}^{-3}$. Although some impurity atom concentrations of the calculation models in this chapter are higher than those of the experiment, the change or tendency of the doped diamond for different doping concentrations shown in this chapter are clear, so it does not affect our analysis. In addition, we also found that in the TDOS of the doped diamond whose energy gap has disappeared (as shown in Figure 14.3), the peak value of the DOS of the lithium atom's valence band lies between about $-48.5 \text{ eV} \sim -45 \text{ eV}$, while in the TDOS of the doped diamond whose energy gap has not disappeared, the peak value

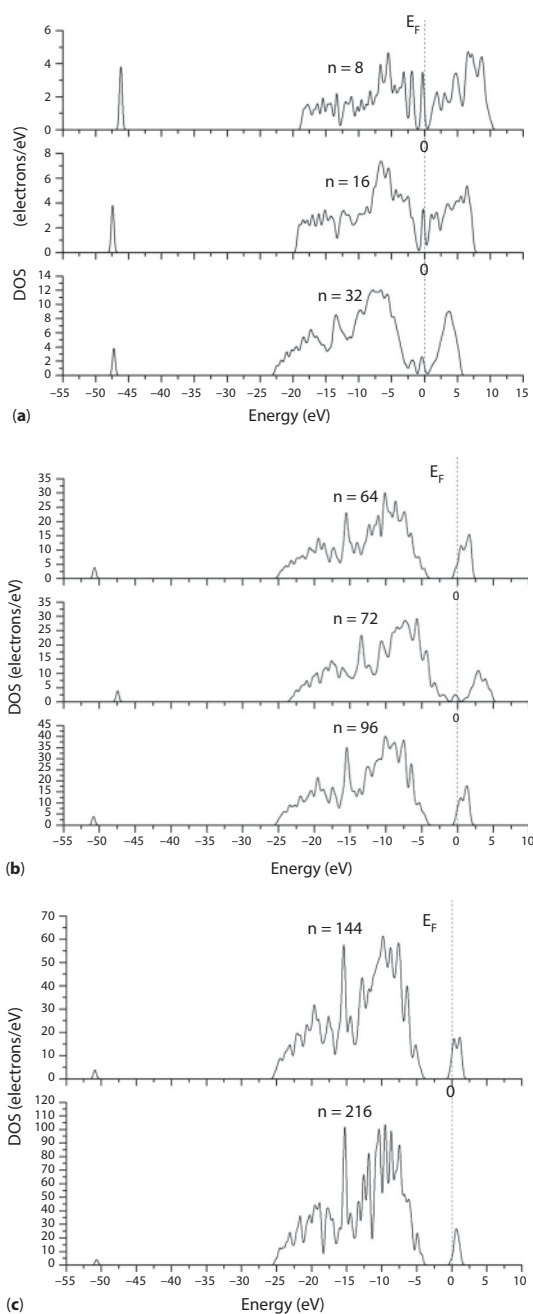


Figure 14.3 The total density of states (TDOS) of the Li-P co-doped diamond; the n is the total atomic number, and each cell has a lithium atom and a phosphorus atom (the Li-P atom-pair). The E_F stands for the Fermi level.

of the DOS of the lithium atom's valence band lies between about -51.5 eV ~ -50 eV. This indicates that when the doping concentration of the Li-P co-doped diamond is high, the DOS of the lithium atom's valence band will move toward the high energy's direction. In short, when the atomic ratio of the lithium atoms or the phosphorus atoms to the carbon atoms is less than 1:70 (or the concentration of the lithium atom or the phosphorus atom is less than $2.35 \times 10^{21} \text{ cm}^{-3}$), the Li-P co-doped diamonds are always the semiconductors, on the contrary they are the conductors.

In order to further analyze the impact of the Li-P atom-pairs co-doping on the electrical properties of the diamond, we also calculated the PDOS of the Li-P co-doped diamond in different doping concentrations (see Figures 4–11 in reference [49]). From these pictures, we can see that when the doping concentration is high (see Figures 4 and 5 in reference [49]), the 1s and 2s electrons of the lithium atom have some contributions to the conduction band near the Fermi level; and when the doping concentration is low (see Figures 6–11 in reference [49]), the s electrons of the lithium atom nearly have no contribution to the conduction band near the Fermi level. Therefore, on the one hand, we can improve the electron conductivity of the heavy phosphorus-doped diamond by incorporating some lithium atoms; on the other hand, when the lithium atoms are incorporated into the non-heavy, phosphorus-doped diamond, although the lithium atoms have almost no impact on the conductive properties of the phosphorus-doped diamond, they can effectively reduce the vacancies and defects of the doped thin films, thus maintaining the integrity of the films. In the figures, the part of the conduction band near the Fermi level mainly comes from the contributions of the carbon atom's 2p orbit, the phosphorus atom's 2p orbit, a little of the carbon atom's 2s orbit, the phosphorus atom's 2s orbit and the lithium atom's 1s and 2s orbits. With the different doping concentrations, the contributions of the carbon and phosphorus atom's 2s orbit and the lithium atom's s orbit are different. And the part of the valence band near the Fermi level mainly comes from the contributions of the carbon atom's 2p orbit and the phosphorus atom's 2p orbit. As the doping concentration increases, the area of DOS of the valence band portion will increase. Therefore, when the Li-P atom-pair is incorporated into the diamond lattice, the covalent bond near the Li-P atom-pair will be destroyed. Thus, under the interactions among the outer electrons of the lithium atom, the phosphorus atom and the carbon atoms, the energy bands of the carbon atoms and the phosphorus atom will split near Fermi level. The higher the concentration, the greater the energy band splits. And the split of the energy band near the Fermi level is propitious to improve the conductance properties of the semiconductor.

14.3.4 Orbital Charge Distribution of Li-P Atoms and Analysis of Bond Length

By the analysis of the Mulliken population, we can understand the orbital electron distributions of each atom in the Li-P co-doped diamond in detail, and then determine the bonding mechanism among the different atoms. In the first line of Table 14.3, the S (or P) stands for the s (or p) orbital charge after an atom combined with the other atom, and the "Charge" stands for the charge an atom loses after it is combined with the other atom. The orbital charge distributions of the lithium atom and the phosphorus atom in the Li-P co-doped diamond are showed in Table 14.3. In this table, both the atomic charges of the lithium atom and the phosphorus atom are positive, indicating that there is some charge transfer to the vicinity of the carbon atoms. When the total atomic number of the

Table 14.3 The orbital charge distributions of the Li and P atoms in the Li-P co-doped diamond.

Number	atom	S	P	Total	Charge (e)
8	Li	1.99	0.00	1.99	1.01
	P	1.49	2.81	4.30	0.70
16	Li	1.81	0.00	1.81	1.19
	P	1.54	2.67	4.21	0.79
32	Li	1.17	0.00	1.17	1.83
	P	1.21	2.54	3.75	1.25
64	Li	0.98	0.00	0.98	2.02
	P	1.21	2.63	3.84	1.16
72	Li	1.13	0.00	1.13	1.87
	P	1.21	2.54	3.75	1.25
96	Li	0.97	0.00	0.97	2.03
	P	1.21	2.67	3.88	1.12
144	Li	0.96	0.00	0.96	2.04
	P	1.21	2.69	3.90	1.10
216	Li	0.96	0.00	0.96	2.04
	P	1.20	2.79	3.99	1.01

cell is less than or equal to 32, the concentration of the impurity atoms is high. With a decrease in the concentration of the impurity atoms, the *s* orbital charge number of the lithium atom decreases from 1.99 to 1.17, and the charge increases from 1.01 to 1.83, which the lithium atom loses after it is combined with the other atom. This indicates that when the doping concentration is high, the higher the doping concentration of lithium atom, the less the charge contributing to the bonding of the lithium atom. While the total atomic number of the cell is more than 32, the concentration of impurity atoms is low. The *s* orbital charge number of the lithium atom and the charge which the lithium atom loses have almost no change as the doping concentration changes. This indicates that when the doping concentration is low, the charge contributing to the bonding of the lithium atom almost does not change for the different doping concentrations. As the doping concentration decreases, the *s* orbital charge of the phosphorus atom firstly increases, then decreases, and keeps an invariable value. And as the doping concentration decreases, the *p* orbital charge of the phosphorus atom firstly decreases, then increases. Therefore, the total change of the *s* and *p* orbital charge of the phosphorus atom makes the charge, which the phosphorus loses after bonding firstly increases, then decreases. From the above discussion combined with the analysis of the DOS in Section 14.3, we can find that the interactions of the outer electrons among the lithium atom, the phosphorus atom and the carbon atoms are very strong. When the doping concentration is high (or the total atomic number of the cell is less than or equal to 32), the doping concentration greatly influences the *s* orbital charge contributing to the bonding of the lithium and phosphorus atoms. When the doping concentration is low (or the total atomic number of the cell is more than 32), the doping concentration nearly does not affect the *s* orbital charge contributing to the bonding of the lithium and phosphorus atoms, which keeps an almost invariable value. Moreover, whether in the high-doping or low-doping diamond, the doping concentration also has a great influence on the *p* orbital charge contributing to the bonding of phosphorus atoms. The above results may provide some reference in doping experiments of diamond.

When the lithium atom and phosphorus atom are incorporated into the diamond, the impurity atoms can form the Li-P bond, the Li-C bonds and the P-C bonds. The bond lengths and the bond populations of the Li-P bond, the nearest neighbor Li-C bond and the nearest neighbor P-C bond are showed in Table 14.4. As the table shows, the bond populations of the Li-C atoms are all less than zero. And when the doping concentrations of the impurity atoms are low (as the total atomic number of the crystal cell is more than 64), the bond population of the Li-C atoms is

Table 14.4 The bond lengths and the bond population among the nearest neighbor Li-C atoms, Li-P atoms and the nearest neighbor P-C atoms in the Li-P co-doped diamond.

Number	bond	length (Å)	population
8	Li—C	2.31932	-0.12
	Li—P	2.55735	0.12
	P—C	1.75806	0.71
16	Li—C	2.34108	-0.04
	Li—P	2.70780	-0.03
	P—C	1.77178	0.66
32	Li—C	1.63001	-0.12
	Li—P	2.09692	-0.26
	P—C	1.74612	0.66
64	Li—C	1.63768	-0.32
	Li—P	1.97483	-0.33
	P—C	1.68708	0.59
72	Li—C	1.59965	-0.17
	Li—P	2.02061	-0.29
	P—C	1.72473	0.64
96	Li—C	1.62917	-0.32
	Li—P	1.96159	-0.31
	P—C	1.68730	0.53
144	Li—C	1.63096	-0.32
	Li—P	1.94782	-0.32
	P—C	1.68045	0.53
216	Li—C	1.63744	-0.32
	Li—P	1.94659	-0.35
	P—C	1.67908	0.29

equal to about -0.32. This indicates that the Li-C bond is the anti-bonding, and as the doping concentration decreases, the anti-bonding states reach a stable value of -0.32. With the exception of the bond population of the Li-P atoms in the crystal cell whose total atomic number is 8 is positive,

the other bond populations of the Li-P atoms are negative, and their values increase as the doping concentration increases. This indicates that the Li-P bond is also anti-bonding, but the constituents of the anti-bonding states decrease as the doping concentration increases. When the doping concentration reaches a certain value, the anti-bonding states of the Li-P atoms may be transferred into the bonding states (such as the situation of the crystal cell whose total atomic number is 8). And the bond populations of the P-C atoms are all positive, and in general their values increase as the doping concentration increases. This indicates that the P-C bond is the bonding, and at the same time the constituents of the bonding states increase as the doping concentration increases. By the bond lengths shown in Table 14.4, when the total atomic number of the crystal cell is 8 or 16, the bond length of the Li-C bond is about 2.3 Å, and the average value of the Li-P atom's bond lengths is about 2.6 Å. And when the total atomic number of the crystal cell is more than 32, the average value of the Li-C atom's bond lengths is about 1.6 Å, and the average value of the Li-P atom's bond lengths is 2.0 Å. But the bond lengths of the P-C atoms are nearly not affected by the doping concentration, and the average value of their bond lengths is about 1.7 Å. From the above analysis, the doping concentration has a great impact on the bond lengths of the Li-C bond and the Li-P bond, but has little impact on the bond length of the P-C bond.

14.4 Conclusions

With the first principle computation, we have researched the lattice expansion phenomenon of the phosphorus-doped diamond unit cells with different concentrations, the bond nature and charge distributions of the phosphorus atoms in the crystal lattices, and the influences of the vacancies on the physical properties of phosphorus-doped diamond thin films. First, the phosphorus atom only obviously affects the bond nature in its vicinity of a few atoms, and the closer the atoms, the greater the impacts. The smaller the concentrations of the phosphorus atoms, the stronger the C-P bonds and the more stable the structure. Second, introducing some vacancies into the right positions of the phosphorus-doped diamond thin films not only reduce the damages of the diamond thin films, but also effectively improve the electrical conductivity of the n-type diamond thin films.

By the first principle calculation theory of the DFT, in this chapter we also calculated the electrical properties (such as the DOS and the orbit

charge distributions and so on) of Li-P co-doped diamonds with different doping concentrations. First of all, the Li-P atoms are incorporated into the diamond; this makes the Fermi level of the Li-P co-doped diamond move into the vicinity of the bottom of the conduction band and the conductance property of the Li-P co-doped diamond thin film is greatly improved. When the concentration of the impurity atoms is low (the concentrations of the lithium atom or the phosphorus atom are less than $2.35 \times 10^{21} \text{ cm}^{-3}$), the Li-P co-doped diamond thin film presents the characteristic of the semiconductors. When the concentration of the impurity atoms is high (the concentrations of the lithium atom or the phosphorus atom are more than $2.35 \times 10^{21} \text{ cm}^{-3}$), the Li-P co-doped diamond thin film presents the characteristic of the conductors. Secondly, when the doping concentration is high, the 1s and 2s orbits of the lithium atom will have some contributions to the conduction band near the Fermi level, and also may promote the splits of the phosphorus atom's and the carbon atom's 2p orbits near the Fermi level. Thus it is helpful to improve the electron conductivity of the Li-P co-doped diamond. The orbital charge distributions of the Li-P atoms also illustrate this phenomenon in detail. Finally, incorporating the lithium atoms into the doped diamond not only improves the electron conductivity of the semiconductors, but also may reduce the vacancies and defects of the doped diamond thin films. At the same time, the doping concentration of the impurity atoms also has a great impact on the bond lengths of the Li-C atoms and the Li-P atoms. To sum up, the lithium atoms have an influence on the electron conductivity and the integrity of the diamond lattice in the Li-P co-doped diamond thin films.

Conducting diamond and nanodiamond with exceptional hardness, inertness, and stability has been proven as a versatile electrode material for a wide variety of applications. Doped-diamond and nanodiamond electrodes can play an active role in water treatment without any microstructural and morphological degradation. With favorable mass transport, nanoscale devices enhance the response of many electroanalytical sensors. Apparently, the BDND can be considered as one of the most ideal electrode materials for electroanalysis of many chemistry compounds. The n-type phosphorus-doped diamond thin films with improved electrical conductivity and the Li-P co-doped diamond and nanocrystalline diamond may be used as conductive electrodes and present great potential for electrochemical water treatment, allowing the indirect oxidation of pollutants with hydroxyl radicals to be produced directly in water.

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Multifunctional Silver, Copper and Zero Valent Iron Metallic Nanoparticles for Wastewater Treatment

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Abstract

With the advent of different nanomaterials, nanotechnology plays a key role in water treatment. Metal nanoparticles, especially silver, copper and zero valent iron nanoparticles, have the properties of microbe inactivation and heavy metal removal. In this chapter we will be focusing on the role of hybrid metallic copper, silver and iron nanoparticles in wastewater treatment due to their ability for anti-microbial activities and removal of various pollutants. In our previous studies we have treated wastewater, textile and tannery effluents using such multifunctional hybrid nanoparticles. We will also be discussing the existing multifunctional metal nanoparticle products available for wastewater treatment and new variations being made by researchers around the world.

Keywords: Silver nanoparticles, copper nanoparticles, zero-valent iron nanoparticles, multifunctional metallic nanoparticles, wastewater treatment, effluent treatment, microbe inactivation, hybrid nanoparticles

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15.1 Introduction

Water is called “the elixir of life.” Wastewater may be industrial effluents, domestic waste from households or sewage which are deleterious to the environment. Industrial effluents include tannery and textile dye effluents which are being released into precious water resources without treatment. Pesticides and fertilizers commonly used in agriculture also pose potential pollution threats. Microbes which include viruses, bacteria, fungi, etc., and heavy metals like lead, mercury, chromium, arsenic, etc., from the above-said effluents are terribly damaging to the environment on a large scale in both developing and developed countries. Most of these pollutants easily integrate with water resources which are one of the most vulnerable natural resources that can be easily and rapidly polluted. They are one of the most important causes of diseases and disorders in the world. Waterborne diseases are leading causes of mortality and morbidity in developing countries [1]. Target 10 of the UN Millennium Development goals is to reduce by half the proportion of people without sustainable access to safe drinking water by 2015 [1].

Waterborne diseases mainly arising from microbial contamination are a global problem that affect all parts of the world. Worldwide, 80% of all sickness and disease results directly or indirectly from a poor water supply and 19% of deaths are due to waterborne infections. In developing countries like India 80,000 people die per day because of poor water supply and sanitation. Around 37.7 million Indians are affected by waterborne diseases annually; 1.5 million children are estimated to die of diarrhea alone, and 73 million working days are lost due to waterborne disease each year. The resulting economic burden is estimated at \$600 million a year. The need for a clean and safe water supply is not only important for the rural villages but also in metropolitan cities where there is a lack of adequate infrastructure to purify and treat the water. Wastewater treatment and water purification are done conventionally by reverse osmosis [2, 3], ion exchange [4, 5], cyanide treatment [6], electrochemical precipitation [6], and adsorption [7–14]. Some of these methods have been pursued from time immemorial. For example, the first recorded use of the ion exchange process is present in the New Testament of the Holy Bible [15].

Metal nanoparticles are being explored for many applications, including biosensors, antimicrobial agents, labels for cells and biomolecules, antimicrobial agents and cancer therapeutics [16–21]. They have wide industrial applications in electrocatalysis, chemical sensors, catalysis and optical

devices [22–24]. Currently metal nanoparticle-based water treatment technologies are being pursued and products have come out on the market.

15.2 Metal Nanoparticles and Microbial Inactivation

15.2.1 Silver Nanoparticles

Wastewater contains a number of microorganisms leading to the rapid spread of diseases in humans and animals. Silver nanoparticles are known to possess antimicrobial properties against more than 700 microorganisms and are one of the most broad spectrum antimicrobial agents [25]. Silver nanoparticles target the microorganisms in more than three mechanisms; hence the microbes are unable to create mutations to exhibit resistance [25]. Size-dependent activity has been studied and these nanoparticles work efficiently even at low concentrations [26, 27]. Silver ion binding to bacterial DNA can inhibit a number of transport mechanisms, like succinate and phosphate uptake, and may interfere with the cellular oxidation process and respiratory mechanisms [28]. Silver nanoparticle-embedded alginate [29], polyvinyl alcohol [30], cellulose acetate [31], PLGA, PTBAM and PMMA [32] membranes have been fabricated for membrane-based separation processes. Biocidal polymers are being introduced with silver to have durable antimicrobial activity [32]. Silver nanoparticles are also being used as larvicidal and vermicidal agents. They are being evaluated to form antifouling membranes to be used in ultrafiltration processes. The silver nanoparticles inherent ability to kill microorganisms has been put to use against multidrug-resistant microbes and biofilm-forming bacterial cells. Biofilm-forming microbes are not like normal microorganisms since they form a hardened cyst which is difficult to act upon. Silver nanoparticle-based polymeric membranes prevent such biofilm formation. Such antifouling membranes are essential in wastewater treatment. Table 15.1 lists the antimicrobial activity exhibited by different nanoparticles and their composites against various infectious pathogens.

15.2.2 Copper Nanoparticles

Copper and its derivatives have been used for centuries as antibacterial and antiviral agents [63]. Copper nanoparticles exhibit antimicrobial activity against both gram-positive and gram-negative bacteria, viz *E.coli*.

Table 15.1 List of silver, copper and zero-valent iron nanoparticles, its nanocomposite exhibiting antimicrobial activity.

S.No	Nanoparticle/ Nanocomposite	Pathogen	Reference
1	Silver-coated Mn Zn ferrite	<i>Staphylococcus aureus</i> , <i>Bacillus cereus</i> , <i>Pseudomonas aeruginosa</i> , <i>Enterobacter cloacae</i> , and <i>Escherichia coli</i> .	[28]
2	Silver-embedded poly(methyl methacrylate) (PMMA) nanofibers, PTBAM	<i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	[32]
3	Ionic liquid (IL) phase in incorporating silver nanoparticles	<i>Pseudomonas aeruginosa</i>	[33]
4	Silver	<i>Klebsiella pneumoniae</i> , <i>Bacillus anthracis</i> , <i>Bacillus subtilis</i> , <i>Staphylococcus aureus</i> and <i>Acinetobacter baylyi</i> .	[34]
5	Silver-Zein Composites	<i>E. coli</i> and <i>S. aureus</i>	[35]
6	Silver-containing thermoplastic hydrogel nanofibrous	<i>Escherichia coli</i>	[36]
7	Silver-ion-exchanged titanium phosphate films	<i>Escherichia coli</i>	[37]
8	Hybrid Silver – Titanium dioxide	<i>B. subtilis</i>	[38]
9	Silver-Sodium Alginate	<i>E. coli</i> and <i>S. aureus</i>	[29]
10	Silver	Antimicrobial and other biological activity.	[39]
11	Silver Colloid	Methicillin-resistant <i>Staphylococcus aureus</i> .	[40]
12	Silver nanoparticles within third-generation dendritic poly(amidoamine) (PAMAM) grafted onto multiwalled carbon nanotubes	<i>Staphylococcus aureus</i> (<i>S. aureus</i>), <i>Escherichia coli</i> (<i>E. coli</i>), and <i>Pseudomonas aeruginosa</i> (<i>P. aeruginosa</i>).	[41]
13	Silver-poly(acrylate) clusters	<i>Staphylococcus aureus</i> , <i>Staphylococcus epidermidis</i> , <i>Pseudomonas aeruginosa</i> , and <i>Candida albicans</i> .	[42]
14	Colloidal silver	<i>E. coli</i> and <i>S. aureus</i>	[43]

Table 15.1 (cont.)

S.No	Nanoparticle/ Nanocomposite	Pathogen	Reference
15	Poly(methyl methacrylate) (PMMA) nanofiber containing silver nanoparticles	<i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	[44]
16	Silver-PAMAM dendrimer nanocomposite	<i>Staphylococcus aureus</i> , <i>Pseudomonas aeruginosa</i> , and <i>Escherichia coli</i> bacteria	[45]
17	Silver-coated engineered magnetic nanoparticles	<i>Staphylococcus aureus</i> (ATCC 19636) and <i>Staphylococcus epidermidis</i> (ATCC 35984)	[46]
18	Silver	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , <i>Bacillus anthracis</i> , and <i>Candida albicans</i>	[47]
19	Silver	<i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	[48]
20	Silver	<i>Klebsiella</i> and <i>Aspergillus</i> ; and <i>Pseudomonas</i> and <i>Fusarium</i>	[49]
21	Silver	<i>Staphylococcus aureus</i> , <i>Salmonella Typhimurium</i> , or <i>Escherichia coli</i>	[50]
22	Silver	<i>S.typhi</i> , <i>S.epidermidis</i> , <i>K.pneumoniae</i> , <i>P.aeruginosa</i> , <i>P.vulgaris</i> , <i>E.coli</i>)	[51]
23	Silver	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , <i>Salmonella typhi</i> , and <i>Candida Albicans</i>	[52]
24	Silver	<i>Staphylococcus aureus</i> ATCC25923, methicillin-sensitive <i>S. aureus</i> (MSSA), and methicillin-resistant <i>S. aureus</i>	[53]
25	Silver	<i>Staphylococcus basil-lus</i> , <i>Staphylococcus aureus</i> , and <i>Pseudomonas aeruginosa</i>	[54]
26	Silver nanoparticles stabilized by different polymers	<i>E. coli</i>	[55]
27	Zero-valent Iron	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i>	[56]
28	Iron oxide	<i>Staphylococcus aureus</i>	[57]

(continued)

Table 15.1 (cont.)

S.No	Nanoparticle/ Nanocomposite	Pathogen	Reference
29	Iron oxide	<i>Staphylococcus aureus</i> (MTCC 1144), <i>Shigella flexneri</i> (Lab isolate), <i>Bacillus licheniformis</i> (MTCC 7425), <i>Bacillus brevis</i> (MTCC7404), <i>Vibrio cholerae</i> (MTCC 3904), <i>Pseudomonas aeruginosa</i> (MTCC 1034), <i>Streptococcus aureus</i> (Labisolate), <i>Staphylococcus epidermidis</i> (MTCC 3615), <i>Bacillus subtilis</i> (MTCC 7164) and <i>E. coli</i> (MTCC 1089)	[58]
30	Zinc/iron oxide composite	<i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	[59]
31	Cu ₂ O	<i>E.coli</i>	[60]
32	Soda-lime glass containing Copper	<i>E. coli</i>	[61]
33	Copper	<i>Micrococcus luteus</i> , <i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i> , and <i>Pseudomonas aeruginosa</i> , fungus like <i>Aspergillus flavus</i> , <i>Aspergillus niger</i> and <i>Candida albicans</i> .	[62]

Yoon *et al.* [64] reported the antibacterial effects of silver and copper nanoparticles using single representative strains of *Escherichia coli* and *Bacillus subtilis*, where copper nanoparticles demonstrated superior antibacterial activity compared to the silver nanoparticles. Ruparelia *et al.* [65] have compared the antibacterial effects of silver and copper nanoparticles against *E.coli*, *B.subtilis* and *S.aureus* in which copper nanoparticles showed better antimicrobial activity against *B.subtilis* than silver nanoparticles because the copper nanoparticles have greater affinity towards the surface active groups of *B.subtilis*, which leads to its better bactericidal effect. We have reported that the biosynthesized copper nanoparticles using *Dodonea viscosa* leaf extract exhibited more efficient antibacterial activity [66] than earlier studies. Copper nanoparticle polymer composite having antifungal and bacteriostatic properties has been investigated by

Cioffi *et al.* [67]. Sepiolite–copper nanoparticle composite has been evaluated for antibacterial activity by Esteban-Cubillo *et al.* [68]. Individual and synergistic activities of copper and silver ions on the inactivation of *Legionella pneumophila* has been evaluated by Lin *et al.* [69]. Similarly, Lin *et al.* [70] have investigated the antimicrobial activity of silver ions against *Mycobacterium avium*.

15.2.3 Zero-Valent Iron Nanoparticles

Commercial iron granules have been studied for the inactivation and removal of viruses [71]. The zero-valent iron nanoparticles in aqueous solution rapidly inactivated gram-negative *E.coli*, which was not observed in other types of iron compounds [72]. The nanoscale zero-valent iron (nZVI) particles have been reported to completely inactivate *Pseudomonas fluorescens* and *B.subtilis* [73].

15.3 Metal Nanoparticles for Heavy Metal and Dye Removal

Among the metal nanoparticles, zero-valent iron (ZVI) nanoparticles are the most commonly used nanoparticles for heavy metal sequestration due to their high reactivity. Since they can be synthesized easily and are inexpensive, ZVI nanoparticles are the most preferable. Zero-valent iron has been used for dechlorination of chlorinated solvents in contaminated groundwater [74, 75], reduction of nitrate to atmospheric N_2 [76–78], immobilization of numerous inorganic cations and anions [79–81, 75, 82–85], reduction of metallic elements [86], and the reduction of aromatic azo dye compounds [87, 88] and other organics such as pentachlorophenol [89] and haloacetic acids [90]. Similarly, ZVI nanoparticles are being used extensively for permeable reactive barriers (PRB) for *in situ* groundwater decontamination. The ZVI nanoparticles are reported in the treatment of acid mine water, which is from uranium leaching [91]. Green synthesized ZVI nanoparticles are used as Fenton-like catalyst for the degradation of cationic and anionic dyes [92].

Selvakumar *et al.* [93] reported the development of silver nanoparticles with yeast cells as adsorbent for arsenate removal. Similarly, Tuan *et al.* [94] reported the use of silver nanoparticles for the removal of *E. coli* and arsenate. There is a partial list of heavy metals and dyes treated by Ag, Cu and ZVI nanoparticles in Table 15.2. Silver nanoparticles are also being evaluated for the removal of dyes like methyl orange [95, 96], methylene

Table 15.2 List of heavy metals and dyes treated by Ag, Cu and ZVI nanoparticles and composites.

S.No	Metal Nanoparticles	Heavy Metal	Reference
1	Copper hexacyanoferrate	cesium	[107]
2	Silver	Hg(II)	[108]
3	Silver nanoparticles on amidoxime fibers	methyl orange	[95]
4	Silver	mercury (II) ions and hydrogenperoxide	[109]
5	Silver	Sunset yellow	[98]
6	Silver	methyl orange dye	[96]
7	Silver	Methylene Blue	[97]
8	Silver	As(III)	[110]
9	Iron	arsenic	[111]
10	Palladium, silver, and zinc oxide	Bromophenol red	[99]
11	Iron–silver	Cr(VI)	[112]
12	Copper (II) oxide	Arsenic	[113]
13	Zero-valent iron (ZVI) nanoparticles	chromium	[114]
14	Silver	Biofouling, resistance and virus removal	[115]
15	Carbonized yeast cells containing silver	As(V)	[93]
16	Zero-valent iron	Uranium	[91]
17	Iron	aqueous cationic and anionic dyes	[92]
18	Zinc sulfide doped with manganese, nickel and copper	organic dyes	[104]
19	Copper oxide incorporated mesoporous alumina	As(III) and As(V)	[105]

Table 15.2 (*cont.*)

S.No	Metal Nanoparticles	Heavy Metal	Reference
20	Silver	<i>Escherichia coli</i> and As(V)	[94]
21	Ni/Fe nanoparticles	Polychlorinated biphenyls	[116]
22	Silver	12 yellow	[117]
23	Zero-valent iron (ZVI)	Reactive Black 1 (RB1).	[118]
24	Copper ferrite	Arsenate	[119]

blue [97], sunset yellow [98], and bromophenol red [99]. Amidoxime fibers surface coated with silver nanoparticles were evaluated for the photodegradation of methyl orange [95]. Silver nanoparticles capped by mercaptosuccinic acid supported on activated alumina have been used for the removal of mercury from water [100]. Silver nanoparticle-based reduction of aromatic–nitro compounds have been investigated by Pradhan *et al.* [101]. Heavy metal ions removal by naked and monolayer protected silver nanoparticles has been investigated by Bootharaja and Pradeep [102] by X-ray photoelectron spectroscopic studies. Semiconductor AgBr/Ag₅P₃O₁₀ heterojunctions have been developed by Song *et al.* [103] for enhanced photocatalytic activity. Copper nanoparticles are generally used to alloy with other metallic elements for removal of heavy metals and degradation of dyes. Pouretedal *et al.* [104] reported the use of zinc sulfide doped with copper and other elements for the photodegradation of methylene blue and safranin dye. Copper oxide incorporated alumina has been used to remove As(III) and As(V) from wastewater [105]. Copper oxide nanoparticles have been reported for the removal of As(III) and As(V) in a wide pH range [106].

15.4 Multifunctional Hybrid Nanoparticles – Ag, Cu and ZVI

Metal nanoparticles are currently being explored for their multifunctional action to create smart materials with two or more different actions. Earlier nanomaterials were being developed to serve a problem of bacterial inactivation or sensing or heavy metal removal or superhydrophobicity. Recently research has been going on that focuses on making/developing

products utilizing nanotechnology to impart different functions, viz multitasking at the same time. For example, Li *et al.* [120] have developed silver nanoparticle–PVDF membrane which has the dual effects of anti-fouling and superhydrophilicity. Earlier, Chauchan *et al.* [121] from NPL India have reported the use of amine-functionalized gold nanoparticles for single-step sensing and removal of cadmium, cobalt and mercury ions from wastewater. In our study we have reported the use of biosynthesized nanoparticle–membrane composites [31, 30] for better biocompatibility and antimicrobial activity.

Hybrid silver, copper and ZVI nanoparticle clusters were developed and patented [122] to treat different industrial effluents (tannery, textile, pharmaceutical) and sewage. These hybrid clusters contain less silver and more copper and ZVI to reduce the cost of treatment. The hybrid clusters were found to disinfect microorganisms and remove excess salts, chlorides, fluorides, heavy metals and dyes from the effluent. A large number of textile industries were located in Tirupur, a town in the state of Tamil Nadu, India. Textile effluents were being released periodically on a daily basis directly into the groundwater table and nearby Noyyal River, thereby polluting them. Drinking water and water for agriculture were severely affected, leading to the ban of all dyeing industries in Tamil Nadu by the Supreme Court of India. A lot of people were rendered jobless due to the closure of textile dyeing units, and subsequently, textile industries in 2012. These actions have led those of us from Madurai Kamaraj University and Anna University to form teams for developing cost-effective effluent treatment strategies. Our work resulted in the development of hybrid nanoparticle clusters, and the treatment of effluents was demonstrated before the State Pollution Control Board (PCB) and the High Court Bench in Madurai; the nanotreatment method was approved by the PCB and was evaluated by the agriculture department of Tamil Nadu. The treatment cost is 150 rupees / 3 US dollars for 1500 liters of effluent. Currently the ban has been revoked provided there is zero discharge from the industries.

In our study we used the biosynthetic approach for the synthesis of hybrid nanoparticles using readily available plants to make the nanotreatment cost-effective and biocompatible. Figure 15.1 shows the atomic force microscopy image (3D) of the hybrid nanoparticles. The HRTEM images at different scales and SAED pattern of the hybrid nanoparticles are depicted in Figure 15.2. Different dye effluents were treated and evaluated (Figure 15.3). Press reports of the work done in Tirupur and Madurai using nanotreatment are depicted in Figure 15.4.

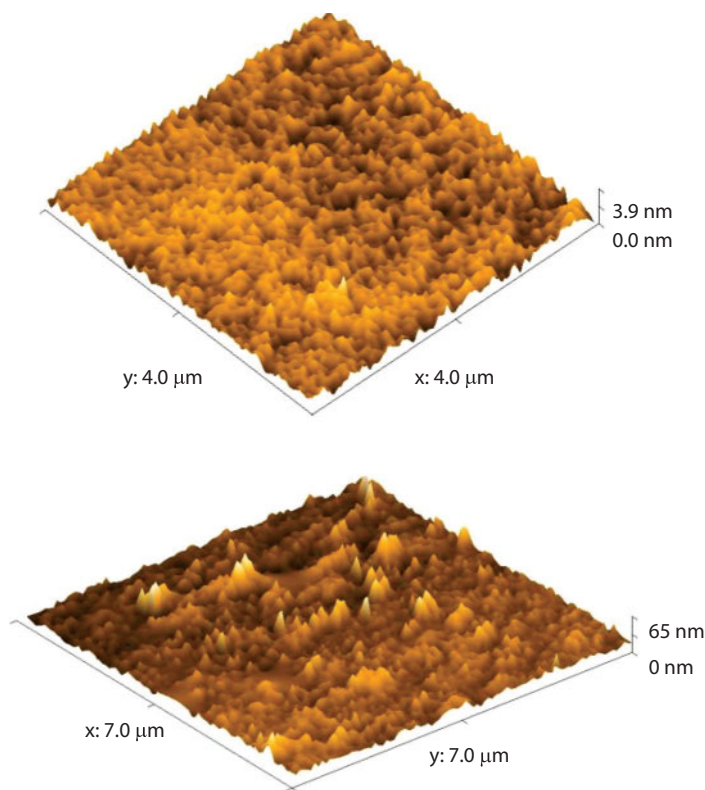


Figure 15.1 Atomic force microscopy images of hybrid Ag, Cu and ZVI nanoparticles evaluated for wastewater treatment [122].

15.5 Mechanism of Action

Antimicrobial activities of metallic nanoparticles are due to their high aspect ratio (size-to-surface ratio). The nanoparticles interfere with cellular processes once entering the microbes. Also, the nanoparticles surface adhesion with the microbial cell surface leads to its immobilization [28]. The zero-valent iron nanoparticles-based reduction process of pollutants is a redox process in which the metal acts as an electron donor for the reduction of oxidized species. In normal conditions, due to their high reactivity, ZVI nanoparticles are exemplary in nanoremediation but are easily oxidized when exposed to air, leading to the formation of iron oxides which are less reactive [35]. This can be stopped by adding a small secondary catalyst like silver or copper, which leads to accelerated reduction.

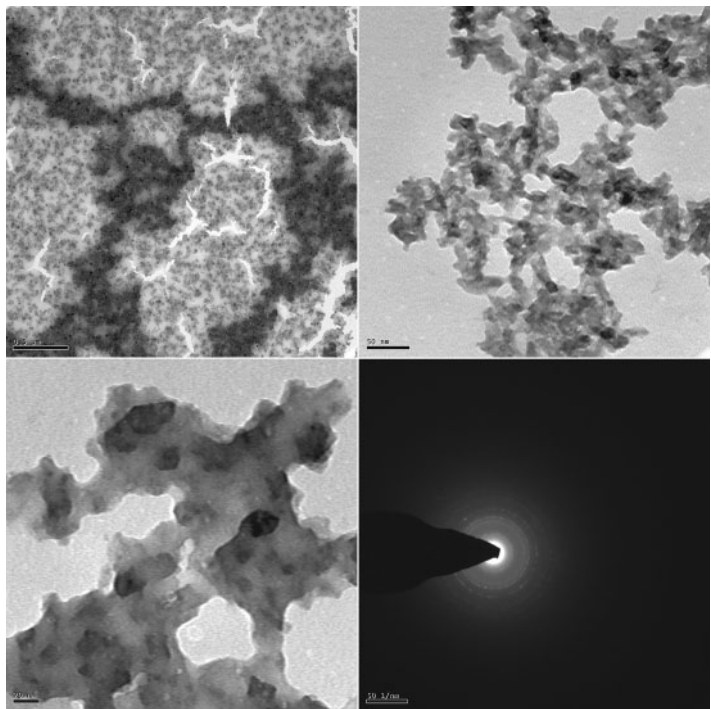


Figure 15.2 High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) pattern of Ag, Cu and ZVI nanoparticles as clusters used for wastewater treatment [122].

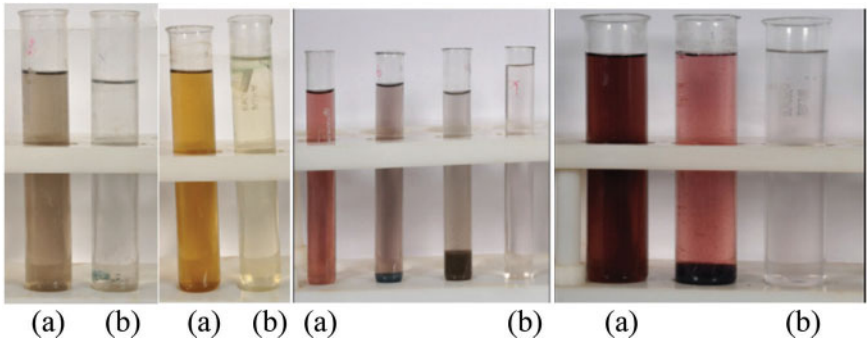


Figure 15.3 Photographic images of different dye effluent being treated by hybrid nanoparticles: (a) untreated effluent and (b) treated effluent.



Photo-Fenton-like processes are also being pursued for wastewater treatment by ZVI nanoparticles using solar irradiation [118].

The sequestration of mercury by silver nanoparticles is by amalgamation on the surface of nanoparticles [100]. The zero-valent form of heavy metals is easily adsorbed by noble metal nanoparticles, especially silver, gold and copper.

15.6 Concluding Remarks and Future Trends

In this chapter, we have discussed the role of silver, copper and zero-valent iron nanoparticles individually and as hybrids for wastewater treatment. Metallic nanoparticles when used in low concentrations would be very useful in nanoremediation. We have also discussed a case study where nanoparticles were directly put to use as treatment strategy for realtime applications. The multifunctionality of such nanoparticles in microbial inactivation and heavy metal removal has been evaluated. We are also developing more such products by carrying out application-oriented research which is the need of the hour. In the future, hybrid nanoparticles with many more functionalities will be made available, enhancing the potential of nanotechnology in changing this world.

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Iron Oxide Materials for Photo-Fenton Conversion of Water Pollutants

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Abstract

The Fenton process, based on the Fenton reaction discovered in 1894, is used to treat a large variety of water pollutants. Iron and hydrogen peroxide are used to generate hydroxyl radicals that react with the pollutants, oxidizing them into carbon dioxide and water. One of the drawbacks of the typical homogeneous Fenton process is the presence of large quantities of dissolved iron in the effluent after treatment. The resulting ferric hydroxide sludge requires further separation and disposal, which makes the process relatively expensive. In order to overcome this problem, recent research has focused on the development of iron oxide catalysts, like the heterogeneous photo-Fenton process under UV-Vis irradiation. In this chapter, we will describe the preparation and characterization of nanostructured iron oxide materials and their use for the treatment of wastewater containing critical and emerging pollutants, such as metalaxyl (a phenylamide pesticide), using this photo-assisted process.

Keywords: Photo-Fenton, water pollutants, metalaxyl, iron oxide, gold nanoparticles

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16.1 Introduction

The need for clean water has increased with population growth and with the intensification of agricultural and industrial activities. It is very important to protect the natural sources of water from pollutants and to develop new technologies for wastewater treatment. Several organic pollutants are highly toxic and those accumulated in the ecosystems are being included in new worldwide directives on water quality standards, including pesticides, pharmaceuticals, antibiotics and hormones [1].

Advanced oxidation processes (AOPs) based on the ability of hydroxyl radicals ($\text{HO}^\bullet$) to promote rapid oxidation reactions have been extensively investigated as possible solutions for the oxidative degradation of persistent organic pollutants. Henry John Horstman Fenton (1854–1929), a British chemist, discovered in 1894 that several metals have special oxygen transfer properties, which improve with the use of hydrogen peroxide [2]. In fact, some metals have a strong catalytic activity to generate highly reactive hydroxyl radicals ($\text{HO}^\bullet$). Since then, the iron-catalyzed hydrogen peroxide reaction has been called Fenton's reaction. Fenton's reagent is thus the result of the reaction between hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}), producing $\text{HO}^\bullet$, which are non-selective strong oxidants.

Nowadays, Fenton's reaction is used to treat a large variety of water pollutants, such as phenols, formaldehyde in formalin-derived effluents, pesticides, etc., and has proven to be more efficient than other photocatalytic routes for degradation of pharmaceuticals, insecticides and persistent pesticides [1]. In the typical homogeneous Fenton process, Fe^{2+} can be regenerated by the reduction of Fe^{3+} species with H_2O_2 , Eq. 16.2, but the formation of Fe^{3+} , Eq. 16.1, is faster than Fe^{2+} regeneration, Eq. 16.2. The presence of large quantities of dissolved iron in the solution after the treatment limits the management of the Fenton process, because the resulting ferric hydroxide sludge requires further separation and disposal, which makes the process relatively expensive.



A way to overcome this limitation is to assist the process with UV-Vis radiation (the so-called photo-Fenton process) activating an iron redox cycle involving intermediate complexes that under irradiation lead to Fe^{2+} and hydroxyl radicals, or even to other radicals depending on the reacting ligand [3, 4]. The development of heterogeneous iron oxide catalysts, to use

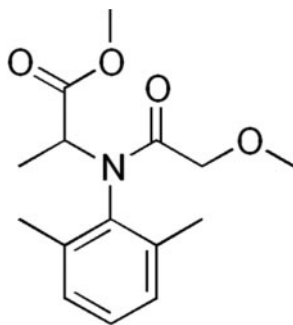


Figure 16.1 Chemical formula of metalaxyl.

in the heterogeneous photo-Fenton process under UV-Vis irradiation, is also a promising route.

In this chapter, we describe the preparation and characterization of nanostructured iron oxide materials and their use for the treatment of simulated wastewater containing critical and emerging pollutants. One of them is metalaxyl (Figure 16.1), that is, methyl N-(methoxyacetyl)-N-(2, 6-xylyl)-DL-alaninate (IUPAC name: 2-[(2,6-dimethylphenyl)- (2-methoxy-1-oxoethyl) amino]propanoic acid methyl ester; CAS: 57837-19-1), a phenylamide fungicide with systemic function.

In this work, we report the use of nanostructured iron oxides prepared by calcination of iron nitrate (precursor) at different temperatures and calcination times, alone or loaded with gold, as photo-Fenton catalysts for the degradation of metalaxyl.

16.2 Experimental

16.2.1 Iron Oxide Supports

Several iron oxide samples were prepared by calcination of Fe^{3+} nitrate trihydrate (reagent, $\geq 98\%$, Sigma Aldrich) at 300°C and 500°C and heating times varying from 30 min to 96 h in N_2 (with a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$). Hereafter, those samples will be referred to as Fe-temp-time (for example Fe-300-1, meaning Fe_2O_3 prepared at 300°C for 1 h). A list of all samples prepared is displayed in Table 16.1. A commercial Fe_2O_3 support (99.0%) from Fluka (Fe-com) was also used for comparison purposes. This sample was also heat treated for comparison. Fe-com-300-5 means that the sample originates from a treatment of the commercial material at 300°C for 5 h in N_2 ($50 \text{ cm}^3 \text{ min}^{-1}$).

16.2.2 Au/Iron Oxide Materials

Gold loading was carried out by double impregnation (DIM), which is similar to traditional impregnation (the support is impregnated with a solution of HAuCl_4 using sonication), but using a second impregnation step with addition of an aqueous solution of Na_2CO_3 (1 M), under constant ultrasonic stirring [5–8]. The resulting solid is washed repeatedly with distilled water for chloride removal (which is well known to cause sinterization of Au nanoparticles, thus turning them inactive [5, 8–10]), and dried in the oven at $\sim 110^\circ\text{C}$ overnight.

16.2.3 Characterization Techniques

The materials were analyzed by adsorption of N_2 at -196°C , in a Quantachrome NOVA 4200e apparatus for the textural characterization. Temperature programmed reduction (TPR) experiments were performed in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments). X-ray diffraction (XRD) analysis was carried out in a PAN'alytical X'Pert MPD equipped with a X'Celerator detector and secondary monochromator ($\text{Cu K}\alpha = 0.154 \text{ nm}$, 50 kV, 40 mA). The collected spectra were analyzed by Rietveld refinement using PowderCell software, in order to determine the grain size. Further details can be found elsewhere [5–8]. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDXS) were carried out on a FEI Tecnai F30 instrument.

16.2.4 Chemical Reagents for Photo-Fenton Experiments

A pesticide formulation consisting of metalaxyl ($\text{C}_{15}\text{H}_{21}\text{NO}_4$) as active compound (ca. 45% wt.) was used as model pollutant. Iron (III) oxide ($\text{Fe}_2\text{O}_3 \geq 99.0\%$, Fluka) and reagent grade hydrogen peroxide (H_2O_2 , 30% w/w) were used in the photo-Fenton experiments. Sulfuric acid (98%, Sigma–Aldrich) was used for pH adjustment. Methanol ($\geq 99.8\%$, Prolabo) and milli-Q water were used for high performance liquid chromatography (HPLC).

16.2.5 Photo-Fenton Experiments

An aqueous solution of the commercially available pesticide was prepared to a metalaxyl concentration of 150 mg L^{-1} . The solution pH (7.2) was adjusted to 2.8 with H_2SO_4 because it is well known that Fenton reactions perform better at pH values in the range of 2.5–3.0.

The photo-Fenton-like experiments for screening of catalysts were performed in a small quartz cylindrical reactor filled with 7.5 mL of the aqueous model solution. The UV-Vis irradiation source consisted of a Heraeus TQ 150 medium-pressure mercury-vapor lamp. A DURAN® glass cooling jacket with water recirculation was used to operate with near-UV and visible light (main emission lines at 365, 436 and 546 nm). The operating temperature was around 30°C, because this can be an important parameter in the Fenton reaction. Preliminary experiments with a commercial sample were performed in order to optimize the reaction parameters, with the ideal concentrations of the iron oxide catalyst and H_2O_2 equal to 1 g L^{-1} and 230 mg L^{-1} , respectively. In a typical run, the solution was magnetically stirred and continuously purged with an oxygen flow, the ideal amount of catalyst was loaded into the reactor along with the pesticide solution, and the time zero for the reaction was defined as the time when H_2O_2 was added simultaneously with switching-on the lamp. The total irradiation time for each experiment was 120 min.

16.2.6 Product Analysis

The concentration of metalaxyl was monitored by HPLC with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450) and a solvent delivery pump (L-2130). A gradient method at a constant flow rate of 1 mL min^{-1} was used in a Purospher Star RP-18 column ($250 \text{ mm} \times 4.6 \text{ mm}$; $5 \mu\text{m}$ particles). At first, the column was equilibrated with a A:B (70:30) mixture of milli-Q water (A) and methanol (B), followed by a linear gradient run to A:B (20:80) in 30 min and finally with isocratic elution during 2 min. The quantification was based on the chromatograms taken by measuring the concentration of each compound at its maximum absorbance value. This absorbance was found to be linear over the whole range considered (maximum relative standard deviation of 2%).

16.3 Results and Discussion

16.3.1 Characterization of Samples

16.3.1.1 BET Surface Area

The characterization results obtained by N_2 adsorption at -196°C are displayed in Table 16.1. For the samples obtained from nitrate decomposition, the surface area decreases with increasing calcination time, above 1 h. The same happens with increasing temperature from 300 to 500°C . Heat

Table 16.1 Particle sizes (determined by XRD), BET surface areas (obtained by adsorption of N₂ at –196°C) for the iron oxide samples (adapted from [8]).

Fe ₂ O ₃ samples	BET surface area (m ² g ⁻¹)	Particle size (nm)
Fe-com	6	63
Fe-com-300-5	8	40
Fe-300-0.5	91	–
Fe-300-1	109	17
Fe-300-12	80	20
Fe-300-24	68	–
Fe-300-96	37	27
Fe-500-1	24	30
Fe-500-96	13	–

treating the commercial sample does not affect the surface area (although the particle size decreases, as determined by XRD, as shown ahead). The highest value was thus obtained for the Fe-300-1 sample, which is one order of magnitude larger ($\sim 100 \text{ m}^2 \text{ g}^{-1}$) than that of the commercial sample ($\sim 10 \text{ m}^2 \text{ g}^{-1}$). Preparing the sample at 500°C (Fe-500-1) causes the surface area to decrease 4 times ($\sim 25 \text{ m}^2 \text{ g}^{-1}$).

We found that loading the materials with gold did not significantly change either the surface area or the particle size of the Fe₂O₃ support; therefore, these results are not shown for simplicity.

16.3.1.2 XRD

Figure 16.2 and Table 16.1 show selected XRD results obtained for the Fe₂O₃ samples. The same phase (hematite, α -Fe₂O₃, rhombohedral, R-3c, 01-073-2234) was identified for all samples, either nitrate prepared or the commercial material, with differences only in particle size (ranging from 17 to 63 nm).

For nitrate prepared samples, particle size increases with increasing calcination time (ranging from 17 to 27 nm, for 1 h to 96 h calcination time, respectively) and calcination temperature (from 17 to 30 nm for 300°C and 500°C, respectively), as seen in Table 16.1. Gold was not detected by XRD, possibly due to the low loading and low particle size. Addition of gold produced no structural changes in the iron oxide phase on the XRD spectra with respect to that of the parent supports.

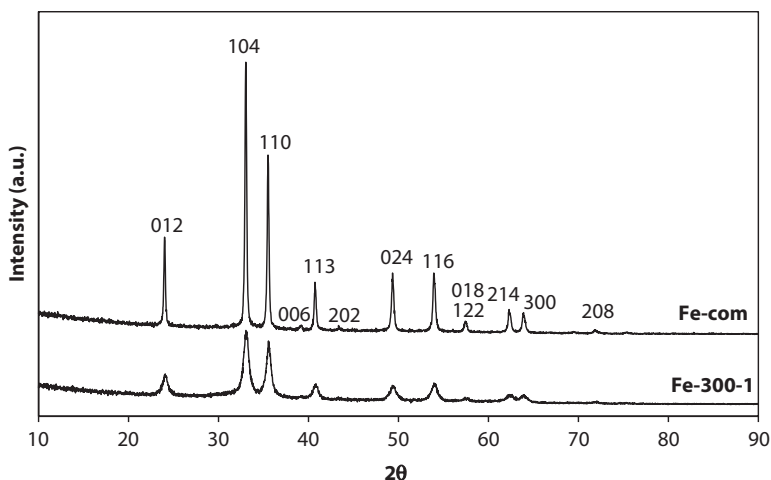


Figure 16.2 XRD spectra of commercial Fe_2O_3 (Fe-com) and Fe_2O_3 sample prepared from iron nitrate at 300°C during 1 h (Fe-300-1) with Miller indexes identified for $\alpha\text{-Fe}_2\text{O}_3$ (hematite).

16.3.1.3 TPR

The TPR results shown in Figure 16.3 indicate that the different iron oxides were reduced in several stages. According to the literature [8, 11–13], the peak at $\sim 300^\circ\text{C}$ can be attributed to the reduction of the hydroxylated iron oxide species and the peak at $\sim 400^\circ\text{C}$ to the reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4). At $\sim 600^\circ\text{C}$ the reduction of Fe_3O_4 to FeO (wustite) occurs and finally the reduction to Fe, above 800°C , but in some cases this last peak overlaps with the previous one. In this work, two peaks above 800°C were observed, indicating that the reduction of Fe_3O_4 to FeO (or of FeO to Fe) possibly occurs in two stages.

The intensity of the first peak decreases as the calcination time increases, and is neither present in the Fe-com spectrum nor in the Fe-500 samples, demonstrating that these samples do not contain hydroxylated species. Increasing the calcination temperature shifts the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ transition peak to higher temperatures, but the peak of the Fe_3O_4 to FeO transition is not much affected. That is observed by comparing the sample treated at 300°C with those treated at 500°C for 1 h.

The presence of gold shifted the first peak to lower temperatures as expected from literature [8, 11–13] (an example is shown in Figure 16.4 for the Fe-com sample, pure and loaded with gold). The subsequent reduction to metallic iron, at higher temperatures, was less influenced by the presence of gold (Figure 16.4), as also expected from literature [8, 11–13].

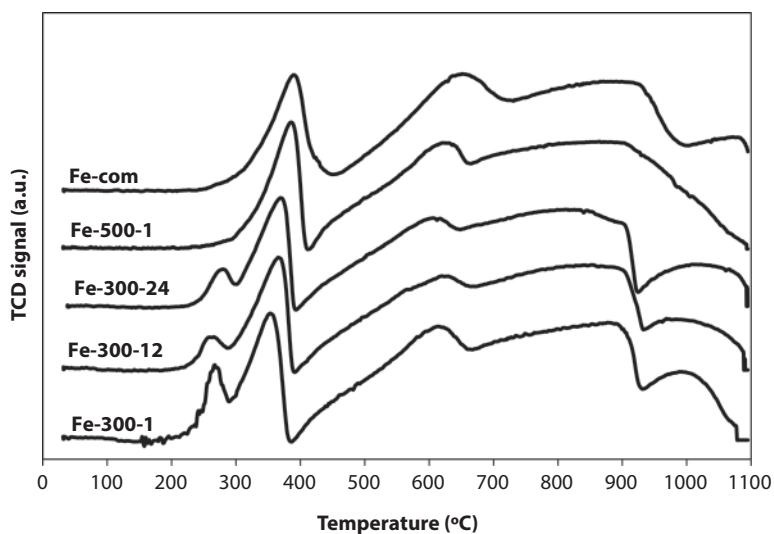


Figure 16.3 TPR spectra of Fe_2O_3 samples prepared from iron nitrate at 300°C during 1, 12 and 24 h and at 500°C during 1 h, and commercial sample (adapted from [8]).

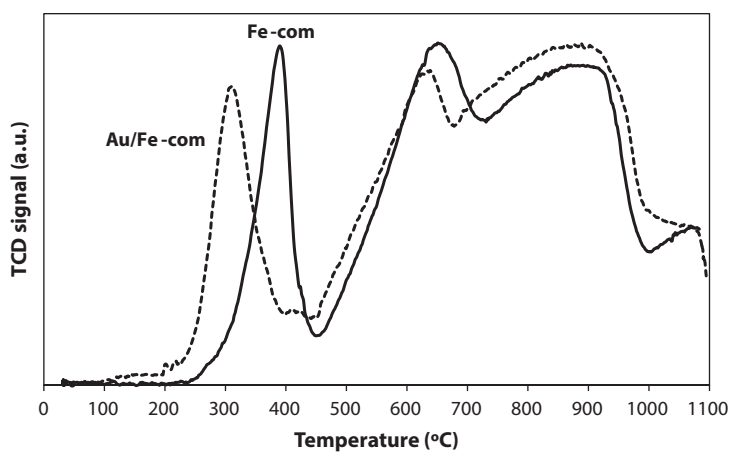


Figure 16.4 TPR spectra of commercial Fe_2O_3 sample alone (Fe-com) and loaded with gold (Au/Fe-com).

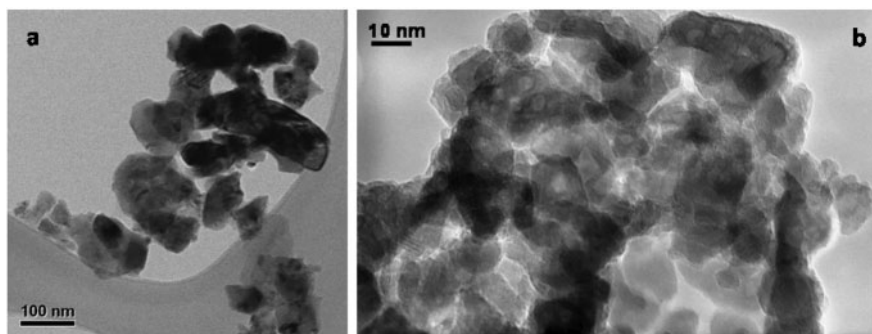


Figure 16.5 HRTEM images of Fe-com (a) and Fe-300-1 (b).

16.3.1.4 HRTEM/EDXS

Figure 16.5 shows HRTEM images of Fe-com (a) and Fe-300-1 (b), respectively. Fe-300-1 is much more porous than Fe-com, as expected from the BET surface area measurements (Table 16.1), since Fe-300-1 has ~10 times more surface area than the commercial material. Fe-com (Figure 16.5a) shows the larger particles, likely due to the high temperature used during the preparation (commercial) process, whereas a smaller size is observed in the Fe_2O_3 nanostructured catalyst (Figure 16.5b), as also determined by XRD (Table 16.1). The samples prepared from nitrate have a sponge-like appearance with pores similar to nanoparticles (Figure 16.5b).

The Fe-com and Fe-300-1 samples loaded with gold were also analyzed by HRTEM, as shown in Figure 16.6. Gold nanoparticles are seen as darker spots (this was confirmed by EDXS). The size of gold nanoparticles was higher on the commercial support (average 11.8 nm) than on the nanostructured support (average 7.4 nm). Similar values were obtained in the literature for catalysts prepared by different methods [8, 11–13]. EDXS results confirmed the gold loading of 1% wt. Au.

16.3.2 Photo-Fenton Catalytic Experiments

Figure 16.7 shows the percentage of metalaxyl degradation after 120 min of irradiation, using Fe-300 materials obtained under different calcination times up to 24 h. The best performance was obtained with Fe-300-1, which is most likely related with its highest surface area (and, consequently, lower nanoparticle size, as seen in Table 16.1), and highest amount of hydroxylated species (as seen by the TPR analysis in Figure 16.2). As an example, Figure 16.8 shows the degradation of metalaxyl obtained after 120 min

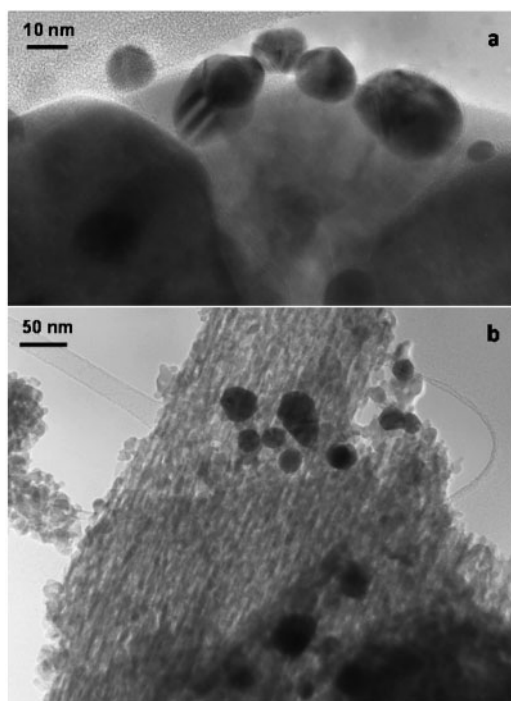


Figure 16.6 HRTEM images of Fe-com (a) and Fe-300-1 (b) loaded with gold. Gold nanoparticles are seen as darker spots.

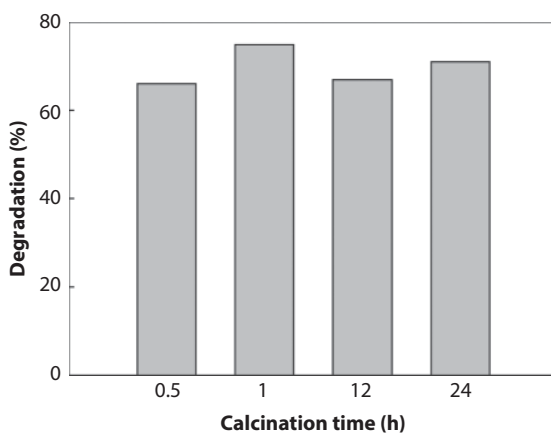


Figure 16.7 Degradation of metalaxyl after 120 min of irradiation with Fe-300 materials obtained at different calcination times.

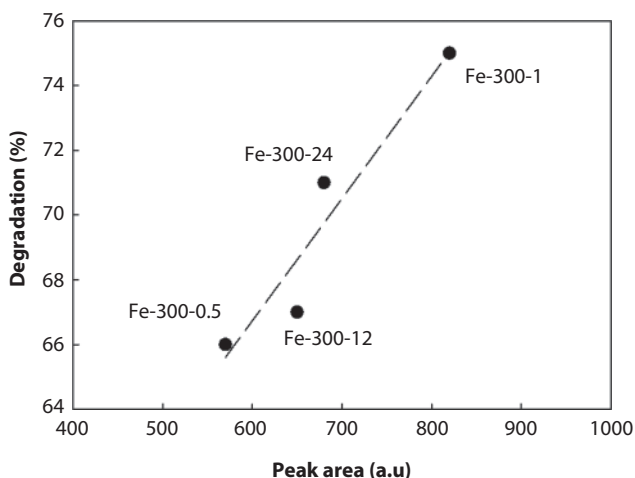


Figure 16.8 Degradation of metalaxyl after 120 min of irradiation for Fe-300 materials vs the area of the TCD signal (in TPR analysis) corresponding to the hydroxylated iron species peak.

versus the TPR peak area of hydroxylated species, indicating that the presence of hydroxylated species could be relevant for this process, as already observed with other photocatalytic driven processes [14, 15].

For comparison purposes, reactions using Fe-300-1 and commercial Fe_2O_3 material (Fe-com) were performed and also compared to previously obtained results [16] using a hydrothermally prepared bismuth doped iron oxide, BiFeO_3 (hereby referred to as BFO). A peroxidation reaction in the absence of any Fe_2O_3 catalyst was also performed (labelled as H_2O_2 in Figure 16.9). It can be observed that photo-Fenton-like process (i.e., using Fe-based heterogeneous catalysts and H_2O_2) is more effective for metalaxyl degradation than the simple photo-assisted peroxidation reaction (i.e., using only H_2O_2). The commercial material (Fe-com) produced a slight increase in the efficiency when compared with the non-catalytic degradation process, the lab-prepared materials being those presenting higher catalytic activity. Metalaxyl conversion after 120 min of irradiation varied as follows: Fe-300-1 (75%) > BFO (61%) > Fe-com (43%) > H_2O_2 (36%). Therefore, the Fe_2O_3 material obtained at calcination temperature of 300°C during 1 h proved to be the most effective catalyst for metalaxyl degradation, most likely due to its morphological/textural properties (BET surface area and particle size) and surface chemistry (presence of hydroxylated groups).

Figure 16.10 shows the results obtained for metalaxyl degradation using Fe-com and Fe-300-1 catalysts loaded with Au nanoparticles. Different effects resulting from the addition of gold to Fe_2O_3 were observed. For the

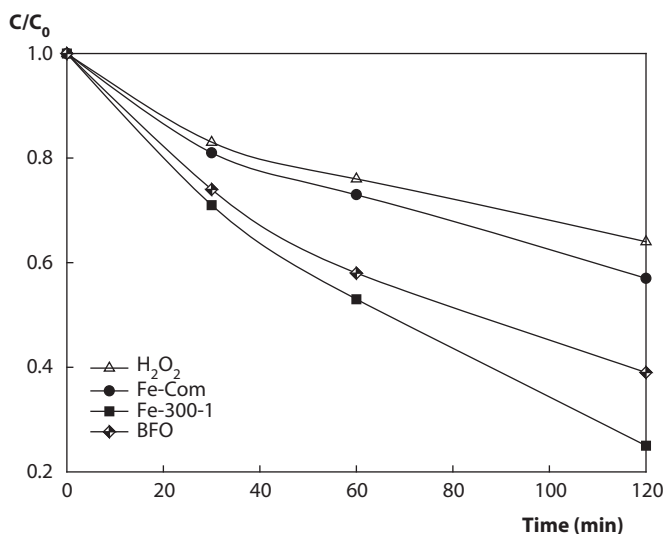


Figure 16.9 Normalized metalaxyl concentration (C/C_0) during photo-Fenton experiments ($C_0 = 150 \text{ mg L}^{-1}$ and $\text{pH} = 2.8$) using 230 mg L^{-1} of H_2O_2 in non-catalytic conditions (labeled as H_2O_2) and in catalytic conditions using 230 mg L^{-1} of H_2O_2 and 1 g L^{-1} of Fe-com, Fe-300-1 and BFO [16] catalysts.

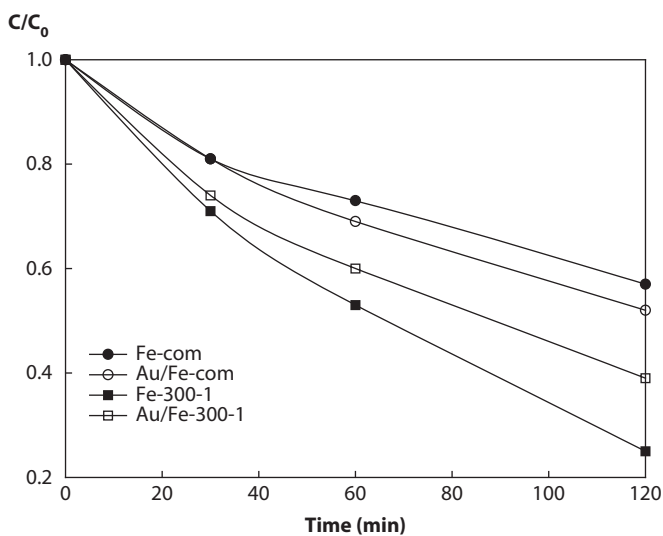


Figure 16.10 Normalized metalaxyl concentration (C/C_0) during photo-Fenton experiments ($C_0 = 150 \text{ mg L}^{-1}$ and $\text{pH} = 2.8$) using 230 mg L^{-1} of H_2O_2 and 1 g L^{-1} of Fe-com and Fe-300-1 catalysts alone or loaded with gold.

commercial material, the presence of Au produced an increase in metalaxyl conversion of 12%, while a decrease of 19% was observed when comparing Fe-300-1 with the respective Au-loaded material.

It has been reported that Au nanoparticles can act both as electron traps (when using UV radiation) or as electron donors (under visible light irradiation) in Au/TiO₂ materials [17]. Gold exhibits a characteristic surface plasmon band in the visible spectral region (at around 550 nm), due to the collective excitation of electrons in the gold nanoparticles [18, 19]. On the other hand, hematite Fe₂O₃ is a semiconductor material with a narrow band gap (approximately 2.2 eV), which absorbs in the UV-Vis spectral range (200–800 nm) [20]. Since the experiments were performed at $\lambda \geq 365$ nm, Fe₂O₃ absorbs most of the light under such conditions. In this case, the main reasonable rationalization of the photocatalytic mechanism assumes direct photoexcitation of Fe₂O₃, leading to the generation of electrons in the semiconductor conduction band and holes in the valence band. The electrons in the conduction band will move to the gold nanoparticles acting as electron buffer, avoiding undesired electron/hole recombination. Meanwhile, the trapped electrons on Au nanoparticles may be scavenged by H₂O₂ to produce highly reactive hydroxyl radicals (HO•), which can attack the metalaxyl molecule. This is most likely the main mechanism when using Au/Fe-com material. On the other hand, the negative effect observed for Au/Fe-300-1 catalyst may be related to a decrease in the number of hydroxylated sites at the surface of the Fe₂O₃ material due to its blockage by the metal nanoparticles. As discussed previously, the presence of a large amount of hydroxylated groups is believed to be one of the most important features of this material, besides its high surface area. Nevertheless, Au/Fe₂O₃-300-1 catalyst still shows higher efficiency than Fe-com.

16.4 Conclusions

Iron oxide samples prepared by decomposition of iron nitrate, at several temperatures and heating times, proved to be active supports for the photocatalytic degradation of metalaxyl, when compared to a commercial iron oxide support. Gold was loaded by a double impregnation method. The best results were obtained for the sample produced by decomposition of nitrate at 300°C for 1 h, which showed the largest surface area, lowest particle size and largest amount of hydroxylated iron species. In fact, the quantity of hydroxylated iron species seems to play a major role in this photo-Fenton process, since there seems to be a correlation between the

amount of hydroxylated species and the degradation of the active compound. Increasing the calcination time or temperature produced less active samples, with lower surface areas and a lower amount of hydroxylated species. Addition of gold improved the catalytic performance only in the case of the commercial iron oxide sample; however, when supported on iron oxide prepared from iron nitrate, the opposite occurred.

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Nanomaterials with Uniform Composition in Wastewater Treatment and Their Applications

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Abstract

Wastewater treatment is a worldwide environmental problem because various organic wastes, heavy metals, non-biodegradable materials are present at higher concentration in non-organic waste pollutants. The removal of these wastes from wastewater in an effective manner has become an important issue today. Clean and effective purification technology is needed to remove pollutants from wastewater. Towards this direction, innovative techniques have been adopted for the treatment of wastewater such as reverse osmosis, ultrafiltration and microfiltration. Additionally, nanotechnology techniques are innovative and effective for the purification of water through low-cost nanoscale adsorbents/nanofiltration. The present chapter deals with the advantages of nanotechnology where it can be easily used to reduce pollutants through the use of nanomaterial-modified nanostructures (nanoparticles, nanorods, nanoflowers, CNTs, etc.) as a nanofiltration membrane to achieve high quality pure water. The tools and methods for nanotechnology involving imaging, measuring, modeling and manipulating matter at the nanoscale level are extensively covered. There are also detailed explanations of the production, modification and shaping of structures used in industrial, health and environmental applications.

Keywords: Nanomembrane, nanofiltration, wastewater, heavy metals

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17.1 Introduction

Waste management/treatment is currently needed to achieve good quality water in order to defend against various diseases. Therefore, several operation plans are required due to the continuously increasing complexity of wastes, which operate at an enormous level such as in incineration plants. The treatment of wastewater is not only important for our own health but also to keep our environment clean and healthy. Without the proper wastewater treatment many ecosystems would be severely damaged. Once the treated water gets recharged back into the environment, it can be classified on the basis of sanitary, commercial, industrial, agricultural or surface runoff. The term wastewater needs to be separated into sewage, industrial, municipal, organic, bacteria and microorganism waste, to reduce the BOD (bio-chemical oxygen demand), organic matter and pollutants to an acceptable level and restore oxygen. Water that enters the sanitary sewer system during a storm, as well as groundwater enters through cracks in sewers. Primary, secondary, and tertiary treatment of water involves physical, biological, and physico-chemical methods respectively. After tertiary treatment, water can be suitable for release directly to a water purification plant. Treated wastewater can be reused as drinking water after it has been eliminated from the contaminants. A literature survey describes several sources of wastewater pollution [1].

- The source of wastewater usually is classified by its origin; the four most common types of groundwater pollution include municipal, agricultural, industrial and individual groundwater pollution. Arsenic poisoning of groundwater is currently a serious issue in Asian countries such as Bangladesh, India and Vietnam.
- Industrial pollution is the biggest source of wastewater pollution. Industry generates an incredible amount of waste, most of which is dumped into different water bodies.
- Many pesticides are highly toxic; these pesticides are a major source of wastewater pollution. Pesticides are a form of organic compound. In fact, there are some pesticides which are considered too dangerous for general public health.
- Marine waste, oil, radioactive (radioactive gases, liquids or particles), soil and chemical wastes can lead to wastewater contamination. These wastes easily enter into the food chain and cause a highly negative environmental impact.

- Most of the heavy metals are toxic at low concentrations; they have a great tendency to dissolve in water and wastewater. The discharge of wastewater containing high concentrations of heavy metals is received by water bodies and has serious adverse environmental effects.

The primary object of any wastewater treatment is to minimize or eliminate potential health risks. Untreated human and animal excretory product disturb the environment and ecosystem and the presence of these elements in the environment transmits various diseases. A variety of pathogenic organisms like bacteria, viruses, protozoa and helminthes cause diseases. Many reviews have been published on the range of these pathogenic organisms normally found in human excreta and wastewater [2]. Crude sewage water in prevalent areas can contaminate the environment and cause diseases such as diarrhea. The types of pathogens present in wastewater and these diseases are extremely harmful not only to a person's health but to their productivity, and to the welfare of the whole community.

Bacteria: Diarrhea is the most prevalent type of infection, with cholera the worst form. Typhoid, paratyphoid, intestine infection and other Salmonella type diseases are also caused by bacterial pathogens [3].

Virus: Hepatitis A virus, reoviruses and diarrhea-causing viruses (especially rotavirus) [4].

Protozoa: Diarrhea and dysentery, Giardia lamblia, Balantidium coli and Entamoeba histolytica are responsible for continued transmission of diseases [5].

Helminths: Serious illnesses, soil-transmitted (or gastrointestinal) helminths, causing ascariasis, trichuriasis and hookworm infection and elephantiasis disease [6].

Other than pathogenic diseases, there are several other diseases which are caused by polluted water such as waterborne, water washed, water based and water related.

Waterborne diseases: Water is the chief medium for the spread of these diseases and hence they are termed as waterborne diseases, and fecal-oral pathogens can be transmitted by water. Since these diseases are highly infectious, extreme care and hygiene should be maintained by people looking after an infected patient. Hepatitis, cholera, dysentery, and typhoid are

the more common waterborne diseases [7]. Therefore, waterborne diseases can be prevented by:

- Improving the quality of drinking water at the source (tap storage vessel).
- Boiling and filtering water at home.
- Protecting food from flies interrupts the faeces-flies-food route.
- Chlorination of water interrupts the faeces-fluids-food and drinking water route (at the community level).
- Water pipes should be regularly checked for leaks and cracks.

Water-washed diseases: These diseases are spread from person-to-person on unwashed hands and also increase the quantity of water available for washing, cleaning, etc., so water-washed diseases can be prevented by doing the following [8]:

- Regularly wash with soap and keep clothes, bedclothes and houses clean to prevent scabies.
- Keep store-bought drinking water safely in a clean container and environment.
- Wash hands with soap and water after doing household work, after visiting the toilet, before eating and after playing with or touching pets.
- Cover food properly and keep it safe from flies.
- Make sure your hands are clean before you handle food when cooking or serving food and before eating.

Water-based diseases: These diseases are spread by drinking contaminated water and are responsible for significant outbreaks of fecal-oral diseases such as cholera and typhoid; they include diarrhea, viral hepatitis A, cholera, dysentery and dracunculiasis (Guineaworm disease) [8].

- These diseases are only preventable by disinfecting contaminated water.

Water-related diseases: These diseases are spread by water-based insect vector, urine of certain mammals and cause malaria, filaria and dengue fever and leptospirosis [9]. They can be prevented by:

- Reducing the mosquito population.
- Destroying breeding sites of insects.
- Boiling all drinking water.
- Improving the quality of water supply and sanitation services.

Today, most of the organic wastes produced are from the municipal, industrial and agricultural sectors. Municipal waste, which is produced through human, biological and social activities, contains a large portion of organic waste readily available for treatment. Wastewater is not just sewage; water used in homes, restaurants, businesses, and industries that goes down drains or into the sewage collection system is wastewater as well. This includes water from baths, showers, sinks, dishwashers, washing machines, and toilets. Wastewater is contaminated by organic pollutants including microorganism, bacteria, dissolved solids (such as salts, pharmaceuticals, drugs, etc.), and toxins, industrial and municipal effluents. Approximately 95% of water is wastewater and the remaining 5% is receiving waters detrimental to ecosystems, and human health. Industrial wastes arise in many varieties and are the most difficult to biologically treat depending on their origin. Namely, many industries use chemicals in their production process in order to achieve product quality, and some of these chemicals are present in the waste stream, which is consequently difficult to treat. Industry is a huge source of water pollution, it produces pollutants that are extremely harmful to people and the environment [10].

The agriculture waste materials can be utilized for the production of biogas. The proper management of waste from agricultural operations can contribute in a significant way to farm operations. Waste management helps to maintain a healthy environment for farm animals and can reduce the need for commercial fertilizers, while providing other nutrients needed for crop production. Other aspects of agricultural production are required for application and management of agricultural waste on farms. However, the primary reason behind managing agricultural waste is that it makes good sense both environmentally and economically. The reuse of animal waste in farming operations can reduce the quantity and hauling costs of commercial fertilizer. The contribution of animal waste increases the organic matter contents of soils, which not only increases nutrient availability for crops but also improves the water-holding capacity and tilt of soil. In general, garden soils tend to contain higher concentrations of lead and zinc than agricultural soils. Good waste management reduces the instances of well water contamination and minimizes surface water pollution [11]. The benefits of reusing organic materials are shown in the following points:

- Creates jobs.
- Builds healthy soils.
- Reduces the need to use pesticides and fertilizers.
- Creates energy.

- Conserves water.
- Saves fossil fuels.
- Reduces greenhouse gas emissions.

17.1.1 Biosorbents

Biosorbents have been examined and used for the removal of diverse types of pollutants from water [12–19]. Selective biosorbents are used for the removal of Cu such as activated carbon (ACs), obtained by pyrolysis of cow bone, cassava peel in the presence of chloride zinc [20, 21], crosslinked magnetic chitosan–diacetylmonoxime Schiff's base (CSMO) resin adsorption on Cu^{2+} , Co^{2+} and Ni^{2+} ions [22]. The presence of tetracycline suppresses the adsorption of copper on chitosan, which could be ascribed to competition of tetracycline with the functional groups in chitosan for the copper ions to form tetracycline–Cu complexes and the competition of tetracycline with copper ions for adsorptive sites at chitosan surface [23], the microbeads, modified resin amberlite XAD-16 modified by 3-((2, 6-dichlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (DC PIMI), use sorption of Cu^{2+} , Zn^{2+} and Mn^{2+} metal ion [24], and ion-imprinted polymers. A novel comb-type grafted hydrogel system of net-[PP-g-AAc]-g-4VP was synthesized by gamma radiation in three steps. In the first step, sensitive Aac copolymer grafted onto PP film was obtained by radiation grafting of acrylic acid (AAc) onto polypropylene (PP) films in aqueous solution at radiation doses of 10kGy with a ^{60}Co source [25]. With the use of vapor–solid (VS) reactions, anthracene nanowires and perylene nanorods could be prepared [26]. By the VS deposition, the synthesis of single-crystal copper tetracyanoquinodimethane (TCNQ-Cu) nanowires on prefabricated electrodes demonstrated the possibility of integration of organic nanowires into devices [27]. Nanophoto-catalyst goethite and hematite nanomaterials (nano-goethite and nano-hematite) are effective materials for the removal of Cu (II) ions in an aqueous stream. Copper phthalocyanine (CuPc) nanoribbons could grow from β -phase nanocrystals predeposited on the SiO_2/Si substrate in a physical vapor transport system [28–30]. The CNTs adsorbed Cu^{2+} onto modified carbon nanotubes [31].

Numerous investigations have studied Cu uptake in batch and continuous systems using biosorbents such as brown alga *fucus vesiculosus*, *Sargassum fluitans* brown seaweed biomass, raw rice husk and olive pomace [32–35]. Conventionally, biosorption studies have focused on batch mode systems, but fixed-bed column is the most operative pattern for

industrial applications. Recently, the fixed-bed column studies showed the interest in the industrial applications [36]. According to literature survey, biosorption is a cost effective process and is applied as a substitute for water and wastewater treatment. Biosorbents are inexpensive material and is present in the form of agriculture materials and originates in nature. The enormous studies of biosorbent via the biosorption is published in many journals. Actually, biosorption process is a passive physico-chemical process, interaction between ions solution and charged species living (microorganisms) or non-living (macrophytes) [37]. The non-living organism/dead cells do not show metabolic activity and living cell/microorganisms display metabolic activity and uptake metal ions, in a phenomena called bioaccumulation [38]. The cell wall of microorganism containing polysaccharide, proteins, lipids and other substances have many functional groups such as carboxylates, amines, phosphate, sulfhydryls, hydroxyls; imidazoles, bacterial cell wall composed of peptidoglycans, which creates linear chains of disaccharides N-acetylglucosamine- β 1, 4-N-acetylmuramic acid with peptide chains, for example algae and yeast. But the biomass of fungi cell wall is very soft due to cell wall of fungi containing chitin and chitosan which employed for interaction of metal ions in column applications. Cells immobilization increases rigidity, strength and porosity of the microorganism which responsible to binding with metal ions [39]. The immobilization process is based on supporting culture activity such as entrapment of microorganisms in a polymeric matrix, which bind to solid surface and formed stable aggregates. The immobilization binding cover by natural mineral-sepiolite and silica gel in bacteria cells (algae, yeast, bacteria and fungi). In addition, platinum and palladium metal ions have been selective for biosorption of algae, cholera, vulgaris and yeast [40]. The metal biosorption is a living cells process and is categorized in a two-step process. In the first step, metal ions are adsorbed on the surface of cells by interaction between metals and functional groups displayed on the surface of the cells. Before gaining access to the cell membrane and cell cytoplasm all the metal ions come across to the cell wall. The cell wall consists of a variety of polysaccharides and proteins and hence offers a number of active sites capable of binding metal ions. In the second step, due to active biosorption, metal ions penetrate the cell membrane and enter into the cells. Algae, bacteria, fungi and yeast have proved to be potential metal sorbents for preconcentration and separation of different metals in static or dynamic modes before determination by atomic spectrometric techniques [41]. Biosorption of nickel on protonated and deactivated yeast was studied with respect to temperature and

initial metal ion concentration by Padmavathy [42]. The removal of Ni(II) ions by the fermentation of industrial waste such as *Corynebacterium glutamicum* biomass was examined [43]. For the biosorption of nickel, *Oedogonium* green filamentous alga [44], *Punica granatum* (pomegranate) peel waste [45] and the pomace waste of an olive oil factory act as potential biosorbent [46]. Subbaiah *et al.* studied and reported the use of *Acacia leucocephala* bark as adsorbent material and checked the effect of parameters such as pH, initial metal ion concentration, adsorbent dosage, contact time and temperature. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to the kinetics of adsorption. The data were fitted with Langmuir and Freundlich isotherm models [47]. Jayakumar *et al.* prepared carboxymethyl chitosan-graft-d-glucuronic acid membranes by grafting d-GA onto CMCS in the presence of 1-ethyl-3-(3 dimethylaminopropyl) carbodiimide (EDC) and reported the bioactivity of the metal uptake (Ni^{2+} , Zn^{2+} , Cu^{2+}) behavior of CMCS-g-d-GA in detail for tissue engineering and environmental applications [48].

17.1.2 Metals and Metal Oxide

Nickel (Ni) is a silvery-white, hard, malleable, and ductile metal. Nickel alloy is made by melting and mixing two or more metals such as sulphur (millerite), arsenic (mineral niccolite) to form nickel glance (NiAsS). Nickel and nickel compounds are more toxic for animal species, micro-organisms and plants. Most compounds are water soluble and when released into the environment, adsorb to sediment or soil particles and become immobile. Beside these, nickel is released into air in the form of nickel fumes (dust and gas) by power plants and trash incinerators. From the nutritional point of view, nickel is an essential in trace amount and used for many industrial and consumer applications. The nickel exposure in general is by oral intake through water and food, as a contaminant in drinking water. The amount of nickel is enhanced when people eat vegetables from polluted soils in large quantities. The major use of nickel is in the preparation of alloys. Nickel is as an ingredient and found in steel household appliances (like coffee makers, toasters, and pots and pans), medical equipment (X-ray machines), jewellery, rechargeable batteries, catalysts and other chemicals, coinage, plating and other food products contain small amounts of nickel; chocolate and fats are known to contain extremely high quantities. Nickel can cause more serious health problems. For example, people

who smoke have a higher nickel fumes uptake while breathing, which shows the toxic effects on respiratory tract and immune system which causes pneumonitis. Large quantities of Ni have the following consequences:

- Causing cancers: lung cancer, nose cancer, larynx cancer and prostate cancer
- Lung embolism
- Respiratory problems
- Asthma and chronic bronchitis
- Skin rashes mainly from jewellery called nickel allergy
- Heart disorders

According to U.S. Department of Health and Human Services (DHHS) and International Agency for Research on Cancer (IARC), nickel metal and nickel compounds are carcinogenic for humans and these compounds are known as human carcinogens. Nickel sensitivity, once acquired, appears to persist indefinitely [49].

After Ni metal, arsenic is the second most toxic metal commonly present in soil and contaminated water. As per the World Health Organization (WHO), the allowable limit of arsenic in water is 10g/l as total arsenic. The arsenic species As(V) creates more toxicity in the environment as compared to As(III) [50, 51]. Chakravarty *et al.* investigated adsorption mechanisms for As(III) and As(V) from appropriate adsorption isotherms. Finally, ferruginous manganese ore (FMO) has been used for the removal of arsenic from contaminated groundwater samples [52]. Activated carbon and activated alumina have been separately used for removing As(V) from groundwater by adsorption techniques [53, 54].

Many authors have surveyed low-cost adsorbents and their sorption efficiencies and adsorption behavior in presence of other impurities. Viraraghavan *et al.* used iron oxide-coated *Aspergillus niger* biomass to examine the removal of arsenic As(III) and As(V) from an aqueous solution; the iron oxide treatment significantly enhanced the efficiency of arsenic removal. Some commercially available adsorbents for agricultural waste such as char, carbons, coconut husk, carbons, biosorbents, etc., exhibited great performance for the removal of arsenic from water and wastewater [55–57].

Chromium compounds are harmful inorganic water pollutants. They pose a great threat to surface and groundwater which is more

dangerous for human health. The variety of contaminated water such as industrial water and sewage water are major concerns to the rapid development and proliferation of water pollutants. Beside these, heavy metals, volcanic and weathering of rock exhibited great potential in environmental science or nature. Chromium compounds exist in two oxidation states: (i) trivalent chromium Cr (III) which is essential element in trace amount and (ii) Cr(VI) hexavalent form which are more toxic and carcinogenic for humans.

The excess amount of discharged chromium (VI) ions form dyes and pigments valuable to the metal cleaning, plating, leather and mining industries. The world Health Organization standard set the maximum concentration level of toxic chromium (VI) ions present in drinking water as 0.05 mg L^{-1} . The precipitation, membrane filtration, solvent extraction, ion exchange, activated carbon adsorption, electro-deposition, and various biological processes have been employed for the removal of chromium ions from contaminated waters. The treatment of contaminated wastewater depends on the physical parameter such as pH, temperature, flow volume, biological oxygen demand (BOD) and the economic point of view of government agencies [58-66].

Recently, various naturally available adsorbents like wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal from used tires, soot, hazelnut shells, coconut shell charcoal, banana peels, seaweed, dead fungal biomass, cyanobacterium, and green alga were used for the removal of chromium [67-75]. Low cost fertilizer industrial waste material (carbon slurry) was used for the removal of hexavalent chromium from aqueous solution [76]. Large numbers of biosorbent materials such as algae, bacteria, fungi, and agricultural products are used to remove chromium. Cell walls are responsible for biosorption for dead biomaterial; compositions of cell walls present in various functional groups are responsible for hexavalent chromium sorption from industrial and municipal effluents [77].

Transition metals such as Mn, Fe, Co, Ni, Cu and Zn have been synthesized in the oxide form inside the mesopores of CMK-3. The size of the particle is in the range of nanoscale and was confirmed by X-ray diffraction pattern and TEM. Few reports have been published on synthesis of metal oxalate nanorods using the solid-state route; Ni(OH)_2 , Co(OH)_2 and Fe_3O_4 were obtained in the form of $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in NaOH solution via the hydrothermal route. The Co_3O_4 nanoparticles and cobalt oxalate nanorods were obtained via thermal treatment method using convenient solvothermal route. Nanorods of copper,

cobalt and magnesium oxalate have also been prepared by the direct solid-state reaction of metal salt and oxalic acid in the presence of surfactant [78–80].

Semiconductor nanoparticles conjugated with organic molecule (folic acid) and metal oxides, such as TiO_2 and CeO_2 , are linked using trimethoxysilane as spacer-linker. These particles exhibit electronic and optical activity and high efficiency photoluminescence. Spacer ligands such as 4-aminothiophenol, tridecylamine and 3-aminobenzoic acid are used in the synthesis and assembly of various nanoparticles of gold and silver controlled pH at room temperature. Metal oxide nanostructure-organic molecules are significantly used as templates, structural units and hosts. For example: 1) Wrapping of organic molecules is used in ultrathin amorphous metal oxide films to produce novel nanocomposites and microporous materials which are synthesized by self-assembly of polyoxometalates; 2) copper-catalyzed azide-alkyne cycloaddition reaction for “click” chemistry has been used to chemically assemble photoactive heterojunctions between metal oxide nanoparticles, using WO_3 and TiO_2 as a model system, and; 3) highly-synthesized crystalline metal and metal oxide nanoparticles, such as Cu/CuO , $\text{Co/Co}_3\text{O}_4$, ZnO , Mn_2O_3 , MgO and CdS/CdO , embedded in a carbon matrix showed promising H_2 and CO_2 adsorption properties depending on the environment by the controlled thermolysis of metal organic frameworks (MOFs) [81–84]. Several reports have shown the unique relationship between the nanoparticle size and the distance between the secondary building units inside the MOF precursors. The chemical linkages of metal oxide nanoparticles were determined via X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). Various polyfunctional organic molecules used in shape-controlled synthesis of nanoparticles were confirmed by transmission electron microscopy (TEM). The variety of nanostructures (i.e., nanoparticles, nanorods, nanoflowers, microflowers, nanobelts) prepared for the different applications were synthesized with the use of zinc acetate dihydrate and zinc nitrate at various concentrations [85]. Capping molecules have also been used to direct the nanostructures such as hydroxylamine hydrochloride and hydrazine hydrate. At room temperature, needle-shaped nanorods have been prepared via a sonochemical method [86]. The annealing of hydrozincite powder and conversion to zinc oxide nanoparticles have also been studied. The effect of refluxing time on the morphology of nanorods was studied in 6 to 24 h. The nanostructures have also been used, for example, for the sensing of urea and glucose; a thick film of

zinc oxide nanostructures was prepared on aluminum sheet and their sensing capacity was checked [87]. The behavior of zinc oxide and its growth were checked with the effect of pH alteration. The synthesis and behavior of its nanostructures have been applied for anticancer and antibacterial studies [88]. Metal oxides such as CuO, Cu₂O, ZnO and NiO nanoparticles are used for the removal of pathogenic microorganisms such as *E. coli* and *S. aureus* in the tertiary stage of wastewater treatment [89].

17.1.3 Organic Materials

17.1.3.1 Composite Materials

Generally, composite materials are naturally occurring materials that are prepared by the combination of two or more materials which have different chemical and physical properties with shape, volume and interface. But nanocomposite materials differ from conventional composite materials due to multiple combinations of materials with two or three dimensions, exceptionally high surface area, high volume ratio to reinforcing phase, and different morphology and structure. Nanocomposite materials are highly adequate and novel materials because of their wonderful types of bonding and the force of attraction present between matrix and filler components [92, 93].

These materials are formed by different chemical compositions and dissimilar components, both mixed at the nanometer scale; the ability of these newly obtained materials opens up possibilities for the development of advanced and more reactive materials with unique properties, as a result of their nanometric dimensions. Nanocomposite materials exhibit properties entirely not dissimilar to properties of parent components and refer to nanomaterials such as nanoparticles, nanotubes/nanostructures, nanowires and nanorods [90–94].

Nanocomposites have received great attention and exhibit super performance in various fields. They are very attractive due to the fact that a small size/amount of nanoparticles and nanostructure can lead to great improvement in the fire resistant property of nanocomposite. Lots of research articles have proven the popularity of nanomaterials and nanotechnology, which are highly significant and useful in our everyday life. The inorganic components are based on their dimension. Nanocomposites materials morphology can be classified as zero-dimensional nanomaterials such as nanoparticle of (Mo₃Se₃⁻)_n chains

and clusters [95–97]; one-dimensional nanomaterials such as nanowire and nanotube [98]; two-dimensional nanomaterials such as silicate layers and materials such as clays, metal oxides, metal phosphates, and chalcogenides; three-dimensional nanomaterials such as zeolites [99–101].

The key concept of nanocomposites is that they are not specifically employed within the shape of the particle, but in the nanoparticle characteristics to tailor the engineering morphology to achieve a desired property from the resultant composite materials [1]. Recently many studies have been conducted on the preparation and characterization of organic-inorganic hybrid polymeric composites due to their excellent properties in the form of physical and chemical modifications. Some inorganic particulate-filled polymers [102] such as glass bead filled polyvinyl chloride (PVC/GB) composite, calcium carbonate filled PVC (PVC/CaCO₃) composite and hollow glass bead filled polypropylene (PP/HGB) composite were proven to have maximum sound absorption and high insulation properties; and Lee *et al.* [103] observed the effect of sound insulation on ABS/carbon-black composites.

17.1.3.2 Carbon Materials

Nanostructured materials, carbon nanotubes and their related organic and inorganic compounds play a major role as adsorbent in the solid phase extraction process [104]. These materials exhibit great properties such as hydrophobicity, high adsorption capacities with surface areas. Literature survey reported a variety of materials of environmental samples for used in preconcentration-separation methods [105]. The preconcentration and separation of organic analytes show good performance for quantitative analysis (10–30 mg) of nanotubes-loaded membrane filter in different medium and cellulose acetate membrane disc also used for heavy metals ions with bucky tubes [106].

The natural zeolites show adsorption of anions and organics in aqueous solution from water and wastewater by using several methods such as acid treatment, ion exchange, and surfactant functionalization, making the modified zeolites achieve higher adsorption capacity for organics and anions. Zeolites are crystalline hydrated aluminosilicates built from silicon, aluminum, oxygen and cations interconnected with tetrahedral oxygen bridge used as adsorbents. The sorbents depend on the shape of the framework, which consists of tetrahedral networks atoms or molecules. The framework contains cages, cavities, or channels, which allows small

molecules to easily enter. Zeolites remove metals ions cesium, strontium and thorium from aqueous solutions [107, 108]. The main advantage of synthetic zeolites when compared with naturally occurring zeolites is that they can be engineered with a wide variety of chemical properties and pore sizes. They are stable at higher temperatures and it is reported that an alumina coating improves both the uptake capacity and surface area [109]. Due to their high affinity for water pollutants they prove to be a promising adsorbent, but there are a few disadvantages, which include clogging of the bed during scale-up operations, and fungal and microbial growth.

17.2 Experimental

17.2.1 Material Synthesis

Narasimhulu used biomass of *Pseudomonas* species to investigate biological adsorption capacity and it was found to be the highest for Ni followed by Cd(II), Cu(II) and Cr(VI). The heavy metal concentrations have been determined by the use of atomic absorption spectrophotometer [110].

Dalal *et al.* studied the removal of nickel, cadmium and lead from industrial waste and investigated the use of tea-waste as an adsorbent estimated by AAS (Atomic Absorption Spectroscopy). The analyses were performed using different amounts of adsorbent in the solution. The analysis of this study indicates that tea-waste is one of the best natural adsorbents of heavy metals as it has a very low cost and 100% absorption efficiency [111].

In a study by Pajany *et al.*, the adsorption of arsenate on iron oxyhydroxides depends on the pH value, They conducted sorption experiments of arsenic on commercial hematite and goethite. The main physico-chemical properties relative to the reactivity of a mineral powder are: the grain size, the specific surface area, the acid-base surface acidity constants (pK_{a1} and pK_{a2}) corresponding to the protonation and deprotonation of the surface sites, and the point of zero charge (PZC) (i.e., the average of the pK_a values). The grain size (D50) was determined by laser granulometer (Mastersizer 2000, Malvern Instruments). The specific surface area was determined by the Brunauer Elmet Teller nitrogen adsorption method (BETeN2). The obtained results indicate that in comparison with goethite, hematite is a good adsorbent because the pH range related to the maximum sorption of As is larger than for goethite, and; (ii) the goethite allows an efficient sorption capacity for a larger range of initial concentration than hematite [112].

Parson *et al.* studied the nanoadsorbents Fe_3O_4 , MnO_4 , and MnFe_2O_4 synthesized Fe(II) (from FeCl_2) and Mn(II) (from MnSO_4), in solution containing Mn(II) (from MnSO_4) which was titrated with NaOH solution to the metal solution in 4 h and investigated for sequestering As from aqueous solutions. The synthesized nanoadsorbents had the crystal structure of magnetite, hausmannite and Jacobsite, respectively. The adsorption capacity and the time required for the adsorption of As(III) and (V) by three nanoadsorbents were determined in a pH range of 2 to 6. In addition, the possible dissolution of the nanoadsorbents was measured by the release of Fe and Mn in aqueous solution. The average grain size of the nanoadsorbents was determined before and after treatment with 1000 ppm of As(III) and (V) and a combination of 500 ppm of each As species. The microwave-assisted hydrothermal synthesis technique was used to speed up the ripening process for the nano-materials [113].

Wang and Zhao evaluated the feasibility of using biological methods for the remediation of arsenic contaminated soils and groundwater. Arsenic removal was enhanced by the addition of Fe-bearing solids (or solutions) and a carbon electron donor (e.g., sucrose, molasses, methanol, acetate, and methanol, etc.). Biodegradable environmentally benign products such as biosurfactants and natural organic matter (e.g., humic and fulvic acids) were used to increase arsenic availability to microbes [114].

Budinova *et al.* investigated the preparation of activated carbons with high adsorption activity towards As(III) and Mn(II) ions from aqueous solutions, using an agricultural residue as carbon precursor (i.e., bean pods). The biomass waste was submitted to pyrolysis in the presence of water vapor, and obtained porous material used for the removal of toxic heavy metals. The result indicates that apart from the porosity, an outstanding factor in the adsorption of arsenic and manganese ions is the basic character of the carbon surfaces. The presence of basic oxygen functionalities on the carbon surface seem to be necessary for enhancing the amount adsorbed via ion-exchange and/or complexation with the ionic species in solution [115].

Changa *et al.* studied the removal of arsenic via several natural and synthetic metal oxides; activated alumina showed the greatest adsorption capacity for both As(III) and As(V), on the basis of the removed amount of arsenic by unit kg of adsorbent over the entire pH ranges. The used alternative metal oxides of ICS were activated alumina (AA), sericite (SC) and iron sand (IS). In the column test, different combinations of each metal oxide and MLS were applied in a single column to elucidate the best column system for the efficient treatment of

both As(III) and As(V) at the same time [116]. In another report, the γ -Fe₂O₃ nanoparticles were synthesized with iron chloride and urea in deionized water under continuous stirring for 45 min at 90°C and were characterized [117].

Hristovski *et al.* showed the method of packed bed columns (PBC) for arsenate removal by aggregated metal oxide nanoparticles. For this, batch experiments were conducted for commercial nanopowders (TiO₂, Fe₂O₃, ZrO₂ and NiO) and were characterized with Freundlich adsorption isotherm for arsenate removal in all water matrices [118].

In another study, Cao *et al.* [39] reported that titanate nanoflowers, which have high surface areas, show accessibility property for the removal of heavy metal ions from the water system. The analysis were confirmed by Langmuir, adsorption kinetics and pseudo-second-order reactions [119].

The Mg(OH)₂ and the composite of Mg(OH)₂/Al₂O₃ nanotube were arrays prepared in the pores of AAO (anodic alumina oxide) for the removal of nickel ions from wastewater [120].

17.3 Effects of Pollutants on Health and the Environment

17.3.1 Sources of Nanomaterials

Human beings are commonly affected by tiny nanoparticles in terms of smoke, dust, ash, etc. The construction of nanomaterials and their building materials of nanostructures are chemical and biological, as well as physical. The body has adapted to protect against these particles. Several studies have shown a strong correlation between pollutants, such as air pollution, and respiratory and cardiovascular diseases such as cancers. The size, shape, and agglomeration of nanoparticles affect human health, depending on such factors as genetics, and can be easily translocated through the circulatory, lymphatic, and nervous systems to many tissues and organs, including the brain (Figure 17.1) [121].

17.3.2 Chemical Composition of Nanomaterials

Nanostructured materials have reached such a level that they do not need much of an introduction on their synthesis and application due to their specific chemical, surface and microstructural properties [122, 123]. Research achievements are aimed at synthesizing dimensionally controlled particles in large quantities and understanding their properties in order to

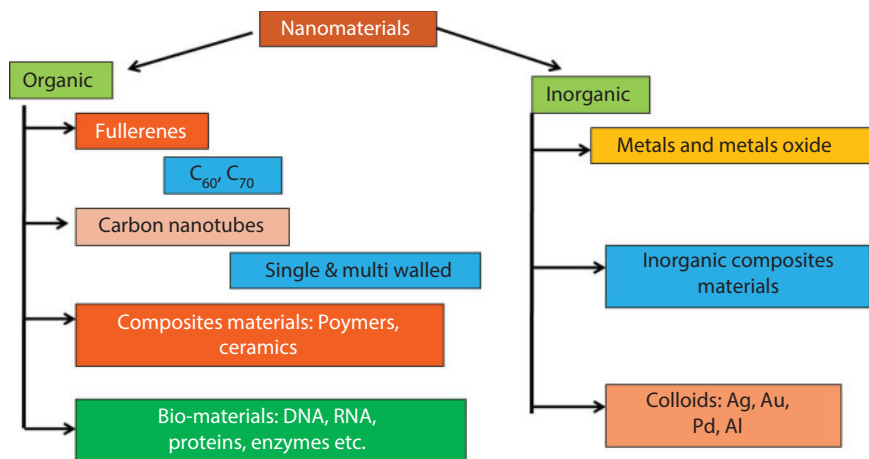


Figure 17.1 Types of nanomaterials.

explore new applications [124–127]. Several methods are being employed to prepare nanoparticles, such as evaporative decomposition of solution, template-assisted method, wet chemical method, gas phase reaction and many more [128–131], with structure varying from nanowires, nanobelts, nanobridges, nanonails, nanoribbons, nanotubes, nanorings, nanorods to microflowers and columnar hexagonal-shaped rods/bars [132–138]. Additionally, the old known techniques such as metal organic chemical vapor deposition (MOCVD), spray pyrolysis, ion beam-assisted deposition, laser ablation, sputter deposition, template-assisted growth and chemical vapor deposition have also been investigated for the synthesis of nanostructures [139–146]. Chemical routes were equally investigated to explore the synthesis of nanostructures with the use of various precursors such as ZnCl_2 , $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for the nanoparticles of zinc oxide [147]. For the metal oxide nanostructures, usually the metal salt of the precursors are used to prepare for the nanostructures formations. In the case of metal nanostructures, metal precursors are used.

17.3.3 Characterization of the Nanomaterials

The synthesized nanostructured materials are characterized with various techniques and studied with different configurations such as X-ray diffraction pattern (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), High-resolution TEM, Ultra-high resolution FESEM and TEM, atomic force microscopy

(AFM), energy dispersive X-ray spectroscopy (EDX), and bonded states of surface characterization X-ray photoelectron spectroscopy (XPS). The UV-visible and photoluminescence (PL) spectroscopy were used to know the optical property of the grown materials. The chemical composition and functional states of the molecules were observed by the Fourier infrared spectroscopy, etc.

17.3.3.1 *X-ray Diffraction*

X-ray diffraction is a useful technique for the crystallographic structure of the material. When an electromagnetic wave enters a crystal it gets scattered by the electrons inside, but due to the periodicity associated with the arrangement of atoms of a crystal for certain angles of incidence (θ) there will be constructive interference between the scatterers (planes of atoms). Nevertheless, for most of the angles, destructive interferences lead to the cancellation of the diffracted beam. With knowledge of the wave length (λ) of the radiation and by measuring the angles at which the constructive interferences occur (called Bragg angle θ_B), it is possible to understand the geometrical ordering of the atoms inside the crystals. The peaks in an X-ray diffraction pattern are related to the unit cell dimensions. The relation of the crystal structure with the above two parameters is expressed by the Bragg equation given below:

$$n\lambda = 2d \sin\theta \quad (17.1)$$

where the integer n is the order of the diffracted beam, λ is the wavelength of the incident X-ray beam, d is the distance between adjacent planes of atoms (the d -spacings), and θ is the angle of incidence of the X-ray beam [148–150]. The X-ray diffraction is the knowledge of determining the arrangements of atoms within crystal from the manner in which a beam of X-ray is scattered from the electrons within the crystals.

17.3.3.2 *Field Emission Scanning Electron Microscopy*

The field emission scanning electron microscope (FESEM) is an incredible tool for seeing micro- and nanostructures. The FESEM microscope creates the magnified images by using electrons instead of light waves. The object is scanned in a high electrical field gradient. In order to be observed with a FESEM, objects are first made conductive for current. This is done by coating them with an extremely thin layer (1.5–3.0 nm) of gold, platinum or osmium oxide (OsO_4). For the structural analysis, a small piece of the substrate/powder which contains the deposited products was pasted on the



Figure 17.2 Field emission scanning electron microscopy (FESEM).

sample holder using the carbon tape. Adhesive silver paste was used to stick the powder samples and a thin layer of gold or gold-platinum was coated on the surface of the powder sample using an ion beam sputtering system to avoid charging the specimen. The object is inserted through an exchange chamber into the high vacuum part of the microscope and anchored on a moveable stage. The object can be moved in a horizontal and vertical direction, and can be repositioned in the chamber left-right axis, or forward and backward. In addition, the object can be tilted, rotated and moved (Figure 17.2).

17.3.3.3 (TEM)

The transmission electron microscope (TEM) (Figure 17.3) operates on the same basic principles as the light microscope but uses electrons instead of light. Transmission electron microscopy uses electrons as “light source” and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope, hence it provides an extreme resolution, far beyond the possibilities afforded by visible light. One can see the objects to the order of a few angstroms (10^{-10} m) [151, 152].

Transmission electron microscopy is a complementary tool to conventional crystallographic methods such as X-ray diffraction. A crystalline material interacts with the electron beam—mostly by diffraction rather



Figure 17.3 Transmission electron microscope (TEM).

than absorption. If the planes of the atoms in the crystals are aligned at a certain angle to the electron beam, the beam is transmitted strongly; while at other angles, the beam is diffracted, sending electrons in another direction. In TEM, the specimen holder allows the user to rotate the specimen to any angle in order to establish the desired diffraction conditions; while an aperture placed below the specimen allows the user to select electrons diffracted in a particular direction. The resulting image shows strong diffraction contrast, which highlights the faults in the crystal structure very clearly, which is very important.

For TEM analysis, the powder/metal oxide samples were ultrasonically dispersed in the solvent (methanol/ethanol) depending upon the condition for 5–10 min. The carbon-coated copper grid was placed in the ultrasonically dispersed powder sample for 1 min and removed from the ethanol and dried at room temperature. The dried carbon-coated copper grid which was examined for the morphological analysis operates at an accelerating voltage 200kV.

17.3.3.4 Photoluminescence (PL) Measurements

The optical properties of metal oxide nanostructures were investigated by photoluminescence (PL) at room temperature. Room temperature PL spectra of nanostructures typically consist of a UV emission and possibly one or more visible bands due to defects and/or impurities. The UV

emission generally originates from the direct recombination of the free excitons through an exciton-exciton collision process and is called near-band-edge emission (NBE), while the appearance of the visible emission, also known as deep-level emission, is due to impurities and structural defects (oxygen vacancies) in the nanostructure crystals. Green emission is the most commonly observed defect emission in nanostructures. Several different hypotheses are proposed regarding the origination of green emission, [158]. But the commonly cited mechanism regarding green emission suggests that intrinsic defects, especially oxygen vacancies, play a key role in this emission; also, this emission is generated by the recombination of electrons in singly occupied oxygen vacancies with photo-excited holes in the valence band. The photoluminescence (PL) measurements of the nanostructure can be measured using a He-Cd laser line of 325 nm as an excitation source with the excitation power of 30 mW at room temperature and low temperature in the range of 13–270 K.

17.3.3.5 Raman-Scattering Measurements

Raman measurement involves a nondestructive effective analysis tool. It is a form of vibrational spectroscopy, much like infrared (IR) spectroscopy. A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wave numbers, cm^{-1}). This difference is called the Raman shift. Note that because it is a difference value, the Raman shift is independent of the frequency of the incident radiation [159, 160]. A typical Raman spectrum is made up of three basic parts: the laser, the collection device, and the spectrograph. A laser, which must exhibit good wavelength stability and low background emission, is used to excite Raman spectra because it gives a coherent beam of monochromatic light. Secondly, the probe, which collects the scattered photons, filters out the Rayleigh scatter and any background signal from the fiber optic cables, and sends the Raman scatter to the spectrograph. Lastly, a detector records the intensity of the Raman signal at each wavelength.

17.3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transforms spectroscopy is a measurement technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies

which are characteristic of that molecule. Fourier transforms spectroscopy analysis can be applied to minute quantities of materials, whether solid, liquid, or gaseous. When the library of FTIR spectral patterns does not provide an acceptable match, individual peaks in the FTIR plot may be used to yield partial information about the specimen. Single fibers or particles are sufficient enough for material identification through FTIR analysis. Organic contaminants in solvents may also be analyzed by first separating the mixture into its components by gas chromatography, and then analyzing each component by FTIR. The FTIR analysis usually takes place at room temperature in the range of $400\text{--}4000\text{cm}^{-1}$ [161, 162].

17.3.3.7 *X-ray Photoelectron Spectroscopy (XPS)*

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is used to determine quantitative atomic composition and surface chemistry analysis. It is a surface analysis technique with a sampling volume that extends from the surface to a depth of approximately 50–70 Angstroms. X-ray photoelectron spectroscopy is an elemental analysis technique that is unique in providing chemical state information of the detected elements, such as distinguishing between sulfate and sulfide forms of the element sulfur. The process works by irradiating a sample with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. It can also be used to analyze the change in surface chemistry of a material after chemical or physical treatments. X-ray photoelectron spectroscopy is used to determine: 1) what elements and the quantity of those elements that are present within ~10 nm of the sample surface; 2) what contamination, if any, exists in the surface or the bulk of the sample; 3) the empirical formula of a material that is free of excessive surface contamination; 4) the chemical state identification of one or more of the elements in the sample; 5) the binding energy (BE) of one or more electronic states, and; 6) the thickness of one or more thin layers (1–8 nm) of different materials within the top 10 nm of the surface [163].

17.3.4 **Effective and Advanced Technology Used for Water Purification [8]**

The removal of contaminants is possible with conventional water treatment processes by using effective, advanced tools and technology. There are many methods and techniques that are applied for accurately measuring

and monitoring contaminants. Wastewater treatment is categorized into three main processes:

1. Physical processes comprising screening or straining, sedimentation, flocculation and filtration.
2. Chemical treatment using adsorption, coagulation, ion exchange, and precipitation.
3. Biological treatment processes with dispersed growth system such as activated sludge and fixed-film reactors.

1. Physical treatment processes

a. Screening or straining

Screening/straining is the first operation in the physical treatment process in sizes between 20 to 40 μm for surface and wastewater. The screening depends on bar spacing because of their size, and it acts as a physical barrier which cannot pass pollutants and affect the loss of velocity head.

b. Sedimentation

Sedimentation is the second operation in the physical treatment process which depends on the difference between densities of solids; large particles settle than small particles due to gravity.

c. Flocculation

The flocculation process is used for small suspended solid particles ($>50 \mu\text{m}$) with low specific gravity and low settling velocity which cannot be easily separated by sedimentation.

d. Filtration

The filtration technique is used to remove particles such as the fine particles of perlite as well as hard and porous material in suspension.

2. Chemical treatment process

a. Coagulation

The coagulation process involves destabilizing solid particles which are present in wastewater so that agglomeration is improved.

b. Precipitation

Some chemical species are present in solution and several factors are involved in the precipitation process such as concentration of ionic metals, pH of the solution, etc.

c. Ion exchange

During the ion exchange process different types of materials can be subsequently used for organic species/sludge which are present in wastewater.

d. Electrochemical treatment

The electrochemical treatment process involves organic contaminants from aqueous streams which are toxic/non-biodegradable pollutants present in wastewater.

e. Advanced oxidation treatment

Advanced oxidation treatment is commonly employed for the oxidation of certain molecules such as O_3 , H_2O_2 , TiO_2 , UV radiation, electron-beam irradiation and ultrasound in textile wastewater.

f. Centrifugation

Centrifugal separation can be used to eliminate costly unpre-served filters. For applications such as aluminum rod breakdown using viscous oil, entire centrifuge filtration systems are used.

g. Distillation

In the distillation process liquid components are separated by vaporization and condensation processes, eliminating traces of ammonia and N-containing compounds from wastewater.

h. Carbon-based and zeolite-based adsorption

Carbon and zeolite-based adsorption methods can be employed to explore the possibility of reducing the chemical oxygen demand (COD), and the suspended solid and oil particles concentration in wastewater.

3. Biological treatment processes

This type of process is accomplished in several steps such as aerobic, anaerobic (hydrolysis, acidogenesis, acetogenesis and methanogenesis) and nitrification. It enhances the process for easily degradable chemical pollutants in wastewater.

17.3.5 Wastewater Treatment by Membranes

There are various types of membranes that have been used to purify the wastes from water such as reverse osmosis, nanofiltration (Nf), ultrafiltration, microfiltration, etc. [164]. These techniques are successfully utilized to purify wastewater (Figure 17.4).

Reverse Osmosis (RO): Reverse osmosis purifies water by removing salts such as calcium, magnesium, sodium ion, chloride ion, copper ion, as well as bacteria. This technique can be employed to remove the constituents which have a molecular weight of greater than 150–250 daltons [164–166].

Nanofiltration (NF): Nanomembrane filtration is a process which removes contaminants from water to produce pure water. It removes bivalents such

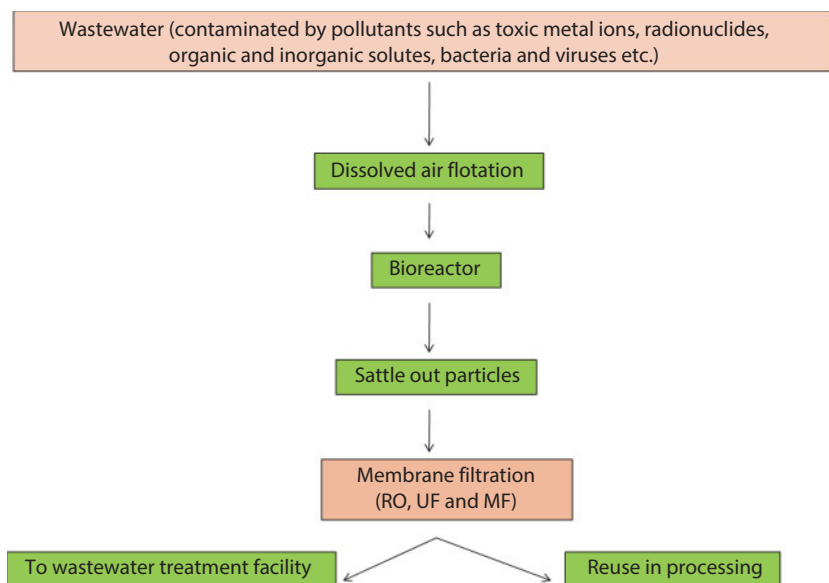


Figure 17.4 Purification process of wastewater treatment.

as calcium, magnesium and sulphates. For this reason, NF membranes are talented in removing turbidity and microorganisms [167, 168].

Ultrafiltration (UF): The ultrafiltration membrane is potentially applicable in many areas such as high water flux, high water purity, membrane fouling, and high mechanical, chemical and thermal stability [169].

Microfiltration (MF): Microfiltration is a process which permeates micrometer-sized particles present in water. Microfiltration separates larger size particles such as suspended solids, fixed solids and microorganisms. The membranes exhibit high porosity and have distinct pores. Microfiltration membranes are usually made up of ceramics, teflon, polypropylene, or other plastics. Microfiltration shows its best performance in fermentation, biomass clarification and an anaerobic process with a cross-flow microfiltration (CFMF) unit [170–172].

17.4 Summary and Future Directions

In this chapter we have tried to summarize in detail the techniques and treatment processes that use macro- and nanomaterials for the purification of water such as biosorbents, nanostructures of metals, metal oxide, carbon and organic materials, and their characterizations. Additionally,

we have also described the applications of nanomaterials and the effective advanced technologies used for the purification of water.

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