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# Removal of heavy metals and cyanide from gold mine wastewater

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## Abstract

**This paper reviews the technology and biotechnology to remove heavy metals (such as copper, arsenic, lead and zinc) and cyanide from contaminated wastewater. The paper places special emphasis on gold mine wastewater and the use of low cost materials as sorbent. Various biological as well as physicochemical treatment processes are discussed and compared on the basis of costs, energy requirement, removal efficiency, limitations and advantages. Sorption using natural plant materials, industrial and agricultural waste has been demonstrated to have the potential to replace conventional methods for the removal of heavy metals because of its cost effectiveness, efficiency and the local availability of these materials as biosorbent. The parameters affecting sorption, such as initial ion concentration, pH, sorbent dosage, particle size and temperature, are discussed. The overall treatment cost of metal and cyanide contaminated wastewater depends on the process employed and the local conditions. In general, technical applicability, cost-effectiveness and plant simplicity are the key factors in selecting the most suitable treatment method.**

**Keywords:** removal; sorption; heavy metal; cyanide; gold mine wastewater

## NOTATION

| | |
|---|---|
| $C$ | Metal ion concentration (mg L$^{-1}$) |
| $C_{eq}$ | Metal ion concentration at equilibrium (mg L$^{-1}$) |
| $C_i$ | Concentration of component i in solution (mg L$^{-1}$) |
| $q$ | Uptake capacity (mg g$^{-1}$) |
| $q_i$ | Uptake capacity of component $i$ |
| $q^0{}_i$ | Phase concentration of a single adsorbed component in equilibrium with $C^0{}_i$ (−) |
| $q_{\max}$ | Langmuir maximum uptake capacity (mg g$^{-1}$) |
| $q_t$ | Uptake capacity at time t (s) |
| $a,b$ | Langmuir isotherm parameters for single component system (−) |
| $a_i, b_i$ | Langmuir isotherm parameters for multicomponent system (−) |
| $K, n$ | Freundlich isotherm constants (−) |
| $k$ | Boltzmann constant (J K$^{-1}$) |
| $Y_i$ | Solute concentration of component i in the solid phase (−) |
| $CIL$ | Carbon-in-leach |

## INTRODUCTION

The term heavy metal refers to metallic elements with relatively high densities that are toxic at low concentrations. Heavy metals have atomic weights between 63.5 and 200.6, and specific gravity higher than 5.0.[1] Heavy metals are classified into three main groups as toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn etc.), precious metals (such as Pd, Pt, Ag, Au, Ru, etc.) and radionuclides (such as U, Th, Ra, Am, etc.).[2] Contamination of wastewaters by toxic metal ions is a worldwide environmental problem. The main sources of pollution are mining and electroplating industries discharging a variety of toxic metals such as Pb, Cu, Ni, Zn, As, and Cd ions into soils and water bodies.[3] Gold mine wastewater generally contains heavy metal pollutants (such as Cu, As, Fe, Zn, Pb, etc.) and cyanide at elevated concentrations. The toxicity of both metals and cyanide pollution is long lasting as these pollutants are non-biodegradable.[4,5]

### Gold mine wastewater production

Gold is generally extracted from ores or concentrates by the alkaline cyanidation (Elsner) process (Fig. 1). The gold-bearing ore is crushed and ground to approximately 100 microns. Next, it is transported to a leaching plant where lime, cyanide and oxygen are added to the ground and slurried ore. The lime raises the pH, while the oxygen and cyanide oxidize and complex the gold:):

$$4\mathrm{Au} + 8\mathrm{NaCN} + \mathrm{O_2} + 2\mathrm{H_2O} \longrightarrow 4\,\mathrm{Na[Au(CN)^2]} + 4\mathrm{NaOH} \quad (1)$$

The cyanide solution thus dissolves the gold from the crushed ore. Next, the gold-bearing solution is collected. Finally, the gold is precipitated out of the solution.

The common processes for recovery of the dissolved gold from solution are carbon-in-pulp, the Merrill-Crowe process, electrowinning and resin-in-pulp (Teeter S and Houck T, unpublished).

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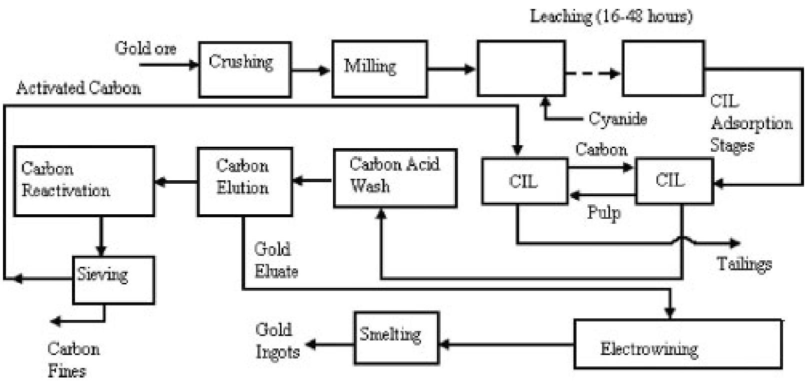

**Figure 1.** Schematic diagram of the cyanidation process of gold extraction.

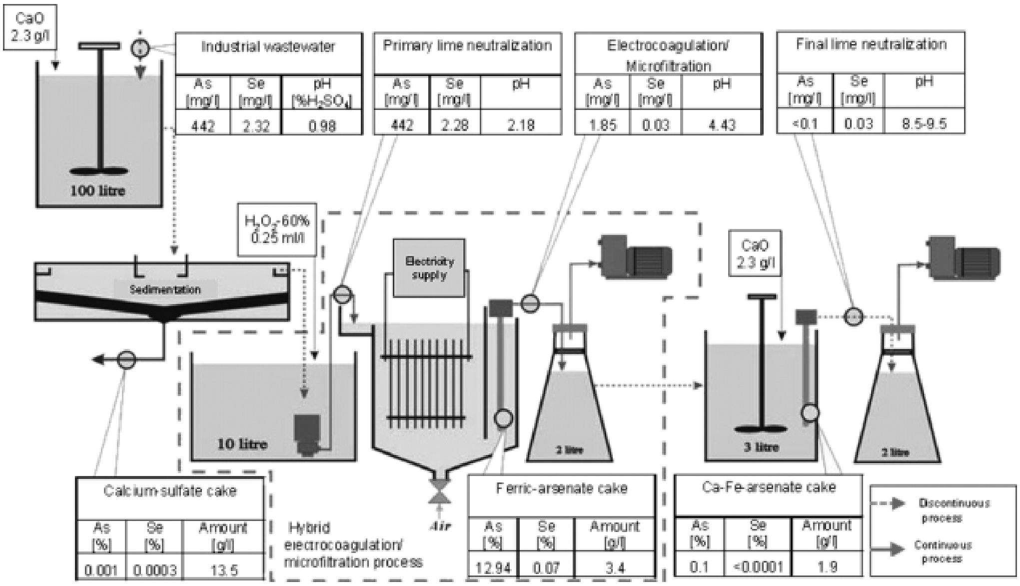

**Figure 2.** Experimental set-up and results of different stages of industrial wastewater treatment including hybrid electrocoagulation/microfiltration.[30]

In the carbon-in-pulp (CIP) technique, the gold cyanide complex is adsorbed onto activated carbon (Fig. 1) until it comes to equilibrium with the gold in solution. Because the carbon particles are much larger than the ore particles, the coarse carbon can be separated from the slurry by screening using a wire mesh. The gold-loaded carbon is then removed and washed before undergoing 'elution' or desorption of gold cyanide at high temperature and pH. The rich eluate solution that emerges from the elution process is passed through electrowinning cells where gold and other metals are precipitated onto the cathodes. Smelting of the cathode material further refines the gold and produces gold ingots suitable for transport to a refinery.[6]

Mercury amalgamation and gravity concentration are the other processes for obtaining gold concentrate from gold ore.

The tailings (Fig. 1), contaminated with metal and cyanide ions, are usually stored in tailings ponds, with the potential for groundwater contamination and high risk of failure, which can lead to spillage of the toxic metals and cyanide-bearing solution into the environment. The types of heavy metals present depend on the nature of the gold ore. Acid mine drainage is another type of mine effluent, which is produced when sulphide ores are exposed to the atmosphere as a result of mining and milling processes where oxidation reactions are initiated. Mining increases the exposed surface area of sulphur-bearing rocks allowing for excess acid generation beyond the natural buffering capabilities found in host rock and water resources. Collectively, the generation of acidity from sulphide weathering is termed acid mine drainage (AMD). Concentrations of common elements such as Cu, Zn, Al, Fe, As and Mn all dramatically increase in waters with low pH.[7] Table 1 shows the characteristics of a typical goldmine wastewater.

**Table 1.** Composition of a typical gold mine wastewater from Ghana

| Parameter | Typical gold mine wastewater | Wastewater standards (Ghana EPA[8]) |
|---|---|---|
| PH | 7.40 | 6-9 |
| Conductivity ($\mu S\ cm^{-1}$) | 5600 | 750 |
| TDS ($mg\ L^{-1}$) | 2900 | 50 |
| TSS ($mg\ L^{-1}$) | 22 | 50 |
| Temperature (°C) | 31.3 | <40 |
| Cyanide ($mg\ L^{-1}$) | 9 | 0.2 |
| As ($mg\ L^{-1}$) | 7.350 | 0.2 |
| Fe ($mg\ L^{-1}$) | 0.114 | 2.0 |
| Pb ($mg\ L^{-1}$) | 0.140 | 0.1 |
| Cu ($mg\ L^{-1}$) | 5.063 | 1.0 |
| Zn ($mg\ L^{-1}$) | 0.042 | 2.0 |

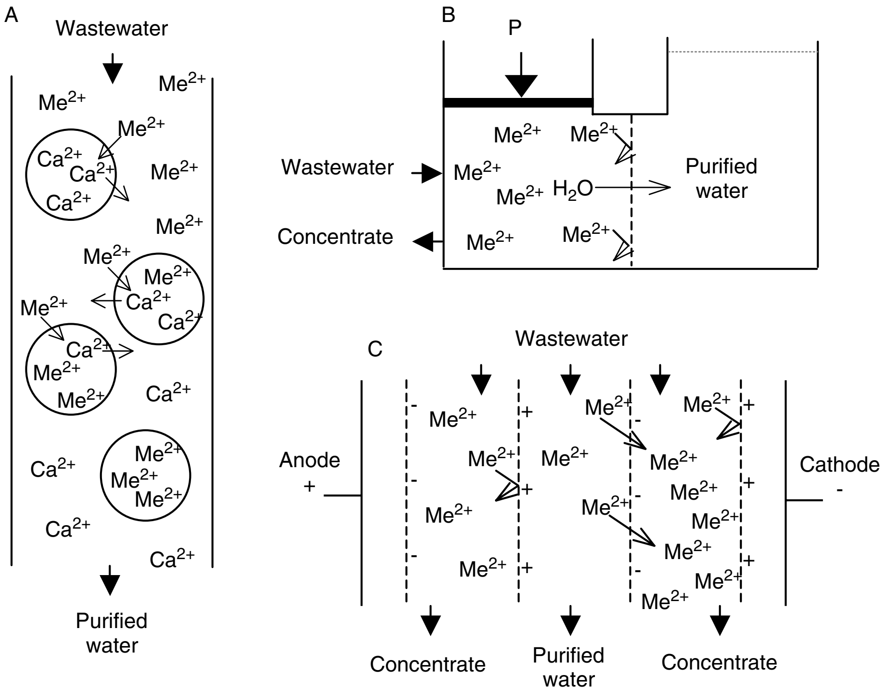

**Figure 3.** Schematic representation of physicochemical process to remove metals $Me^{2+}$ from solution: ion-exchange (A); reversed osmosis or ultrafiltration (B); and electrodialysis (C).

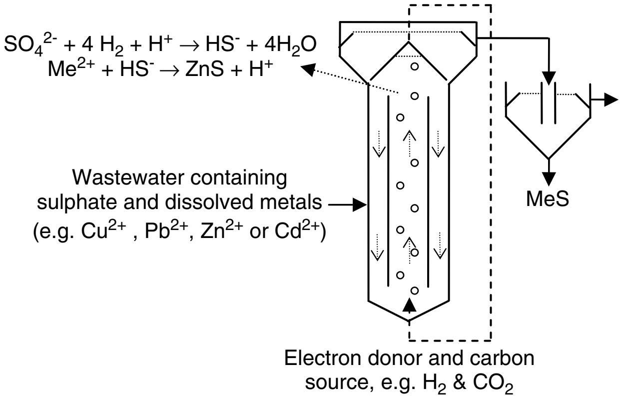

**Figure 4.** Schematic representation of a hydrogen-fed sulphate-reducing gas-lift bioreactor and settler treating wastewater polluted with heavy metals.

## Health and environmental risks of heavy metal and cyanide

Heavy metal pollution is one of the important environmental problems today.[2] These heavy metals are of special concern due to their toxicity, bioaccumulation tendency and persistency in nature.[1,9,10] The removal of heavy metals from water and wastewater is important in terms of protection of public health and environment due to their accumulation in living tissues through the food chain as a non-biodegradable pollutant.[11,12] Heavy metals (such as lead, copper and arsenic) are toxic to aquatic flora and fauna even in relatively low concentrations.[13]

The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous system problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney.[14,15] Arsenic dissolved in water is acutely toxic and leads to a number of health problems, including disturbances to the cardiovascular and nervous system functions and eventually death.[16] Other heavy metals (such as Hg, Cd, Se, Pb, Ni, Zn, etc.) produce similar health effects when injected in significant quantities.

Cyanide is acutely toxic to humans. Toxicological studies have indicated that short-term exposure to high levels of cyanide causes rapid breathing, tremors and other neurological effects; while long-term exposure causes weight loss, thyroid effects, nerve damage and death.[17,18] Skin contact with liquids containing cyanide may produce irritation and sores. Clearly, heavy metal and cyanide pollution of the environment is of paramount concern due to their health risk to humans and threats to the ecosystem.

## Regulatory discharge limits for wastewater containing heavy metals and cyanide

Gold mining operations result in contamination of soils and water with tailings that release toxic metals such as Cu, As, Pb, Mo, Fe, Ni and Zn.[19] Various regulatory bodies have set the maximum prescribed limit for discharge of toxic heavy metals into the

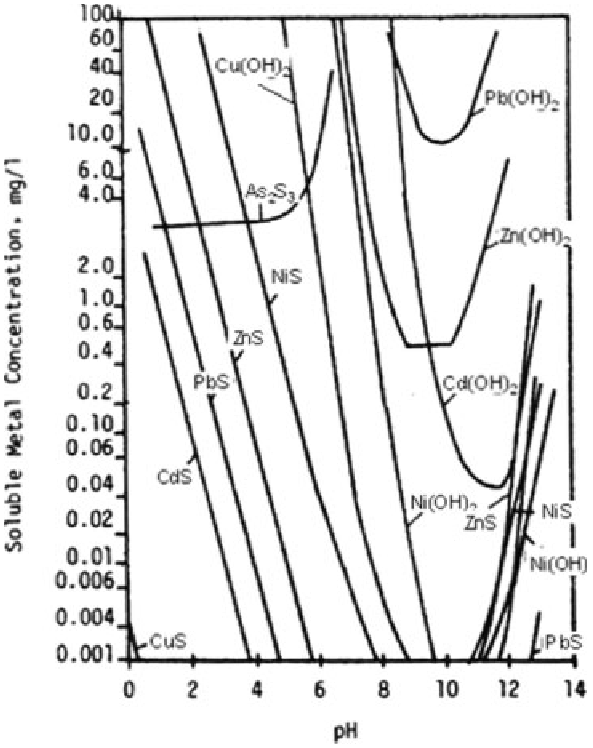

**Figure 5.** Comparison between the equilibrium concentrations of metal hydroxides and metal sulphides.[69]

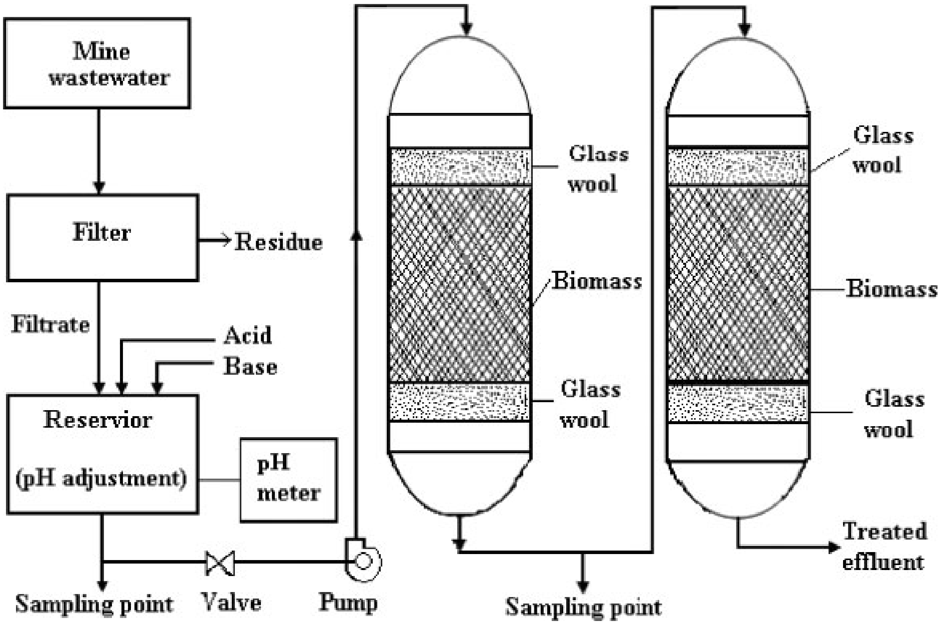

**Figure 6.** Schematic diagram of a two-stage process for heavy metal removal by sorption.

aquatic ecosystem. Table 2 shows the maximum contaminants level (MCL) values set by the US EPA and the position in the Comprehensive Compliance Environmental Response, Compensation and Liability Act (CERCLA), 2005 list of priority chemicals of some of the toxic heavy metals.[20,1] Nevertheless, metal ions are discharged into water bodies at much higher concentrations than the prescribed limit by industrial activities such as gold mining, thus leading to health hazards and environmental degradation.[21]

## Scope of this paper

The purpose of this paper is to review the relevant parts of technology and biotechnology to remove heavy metals and cyanide from wastewater. The paper places special emphasis on gold mine wastewater and the use of low cost materials as sorbent. Biosorption is giving prominence as an emerging technology that has been shown to be effective in removing contaminants at very low levels.

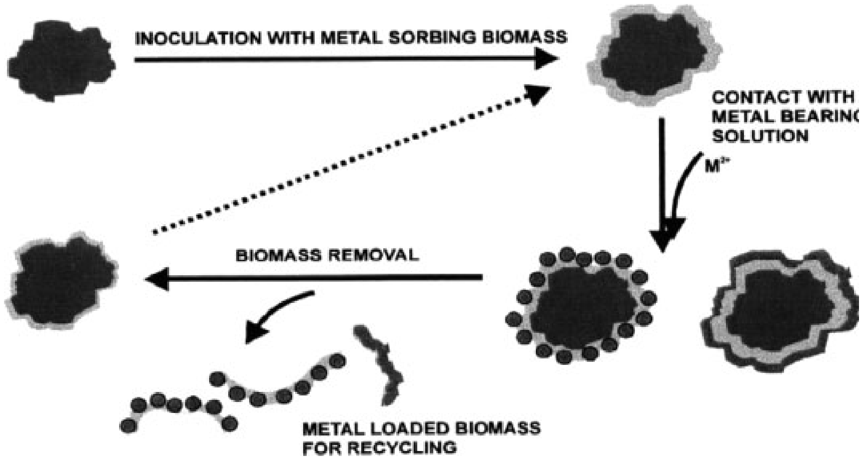

**Figure 7.** MERESAFIN concept: schematic presentation of metal binding and precipitation to biofilms on sand grains, and biofilm regeneration, in an Astrasand moving-bed sand filter.[219]

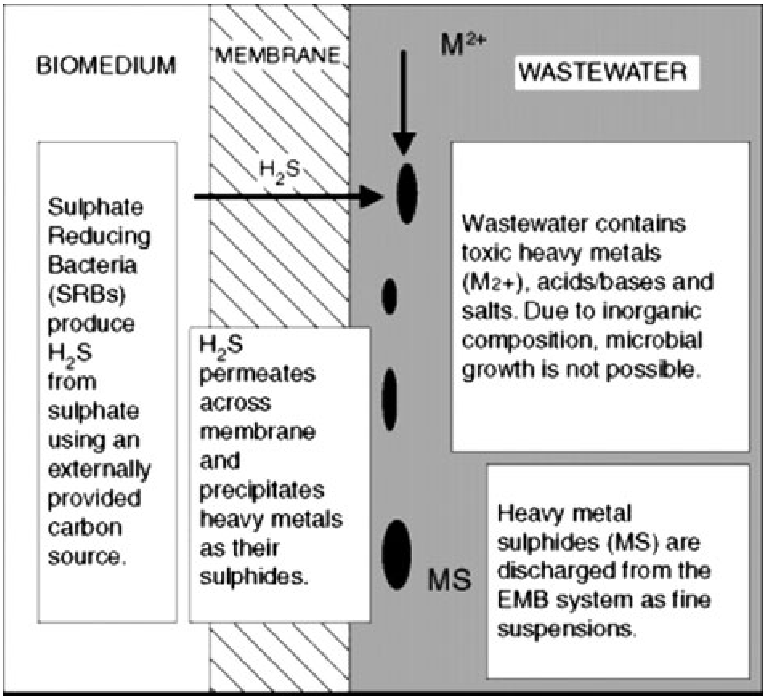

**Figure 8.** EMB–SRB system.[220]

## TREATMENT OF GOLD MINE WASTEWATER

The undesirable effects of heavy metals and cyanide pollution can be avoided by treatment of the wastewater prior to discharge.[22] In view of their toxicity and in order to meet regulatory safe discharge standards, it is essential to remove heavy metals and cyanide from gold mine wastewater before it is released into the environment. This helps to protect the environment and guarantee quality public health. The available treatment methods are reviewed below.

### Heavy metal removal and recovery

*Physicochemical heavy metal removal methods*

The conventional methods for removing heavy metal ions from wastewater include chemical precipitation, coagulation–flocculation, flotation, filtration, ion-exchange, reverse osmosis, membrane-filtration, evaporation recovery and electrochemical technologies.[23–29] Mavrov *et al*.[30] used a hybrid process of electrocoagulation and membrane filtration (MF) to remove heavy metals from industrial wastewater. Figure 2 shows the experimental set-up and a summary of the results of their study. Although these treatment methods can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application (see Table 3). Figure 3 shows the schematic representation of physicochemical process to remove metals from solution by ion-exchange, reverse osmosis, ultrafiltration and electrodialysis.

Precipitation is most applicable among these techniques and considered to be the most economical.[22] However, this technique produces a large amount of sludge precipitate that requires further treatment. Reverse osmosis and ion-exchange can effectively reduce the metal ions, but their use is limited due to a number of disadvantages such as high materials and operational cost, in addition to the limited pH range for the ion-exchange

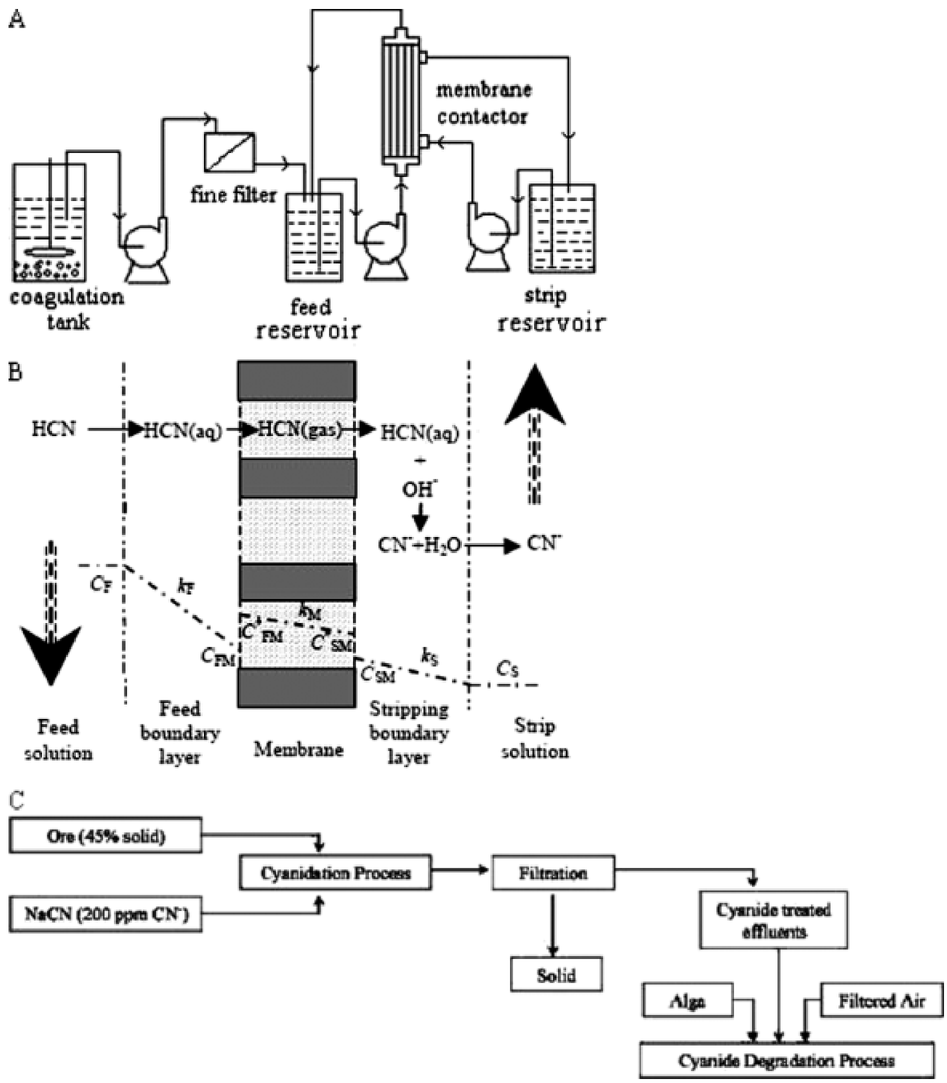

**Figure 9.** (A) Schematic diagram of cyanide recovery from wastewater in an integrated gas-filled coagulation–membrane reactor.[225,226] (B) Illustration of cyanide recovery by gas-filled membrane absorption.[225,226] (C) Bioprocess flow diagram for algal treatment of cyanide contaminated wastewater from cyanidation process of gold extraction (Gurbez *et al.*[18])

resin.[23,31] Table 4 gives performance characteristics of some conventional heavy metal removal and recovery technologies while Table 5 summarizes research work on heavy metal removal using physicochemical techniques.

*Biological heavy metal removal methods*

In recent years, research attention has focused on biological methods for the treatment of metal- bearing effluents. There are three principal advantages of biological technologies for the removal of pollutants. First, biological processes can be carried out *in situ* at the contaminated site. Second, bioprocess technologies are usually environmentally benign (no secondary pollution). Third, they are cost effective.[60–62]

*Sulphide precipitation combined with biological sulphate reduction.* Sulphate reduction is mediated by a diverse group of prokaryotes that can gain energy for growth and maintenance from the reduction of sulphate to sulphide.[63] For sulphate reduction an electron donor is required. Sulphate reducers are able to use a wide range of electron donors, including hydrogen, formate, methanol, ethanol, fatty acids and sugars.[64] Sulphate reduction only occurs when electron acceptors with a higher redox potential (e.g. oxygen and nitrate) are absent. In nature, such conditions are found in marine and fresh-water sediments.[65]

Sulphate reduction in anaerobic bioreactors treating organic wastes has long been regarded as an unwanted side process due to the loss of electron donor and inhibition of the methanogenic process by sulfide.[66] However, currently biological sulphate reduction is an established biotechnological process for the treatment of inorganic wastewaters containing oxidized sulphur compounds and heavy metals.[67,68] The wastewater and an electron donor are fed into a reactor containing immobilized sulphate-reducing microorganisms. In this bioreactor, sulphate is reduced and the dissolved metals precipitate with the biologically produced sulphide (Fig. 4). The formed insoluble metal sulphides can subsequently be separated from the water phase in a settler. Figure 5 compares the equilibrium concentrations of metal hydroxides and metal sulphides.

**Table 2.** Ranking of heavy metals in the CERCLA list of priority chemicals (2005), according to their health and environmental risk, and discharge standards for industrial wastewater in the USA

| Heavy metal | Rank | Standards (USA) (mg $L^{-1}$) |
|---|---|---|
| Arsenic (As) | 01 | 0.01 |
| Lead (Pb) | 02 | 0.015 |
| Mercury (Hg) | 03 | 0.002 |
| Cadmium (Cd) | 08 | 0.005 |
| Chromium (Cr (VI)) | 18 | 0.01 |
| Zinc (Zn) | 74 | 5.0 |
| Manganese (Mn) | 115 | 0.05 |
| Copper (Cu) | 133 | 1.3 |
| Selenium (Se) | 147 | 0.05 |
| Silver (Ag) | 213 | 0.05 |
| Antimony (Sb) | 222 | 0.006 |
| Iron (Fe) | – | 0.3 |

Due to the low equilibrium concentrations of sulphide precipitates, most metals can be removed to very low concentrations (Fig. 4).[69] In addition, the high volumetric conversion rates (Table 6) allow for compact treatment systems. Moreover, the metal sulphide content of the produced sludge is high −95%.[70] Often this metal sludge can be reused in the metallurgical industry.[69] The gas-lift bioreactor (Fig. 3) is the most suitable bioreactor type for sulphate reduction with gaseous electron donors. In this system, the transfer of gas to the liquid is optimized and the sludge is partly retained in the bioreactor by a three phase separator. At a zinc refinery in Budel (the Netherlands) and at the Kennecott cupper mine (Utah, USA), hydrogen-fed sulphate-reducing gas-lift bioreactors are applied to remove metals from wastewater.[67]

### *Heavy metal sorption and biosorption*

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on the metal binding capacities of various biological materials. Biosorption has been demonstrated to possess the potential to replace conventional methods for the removal of heavy metals,[62] because of its cost effectiveness, efficiency and availability of biomass as biosorbent.[90,91] Wang and Chen[2] and Gadd and White[92] defined biosorption as the removal of metal and metalloid species, compounds and particulates from solution by biological material. Ahluwalia and Goyal[28] overviewed the major advantages and disadvantages of biosorption over conventional treatment of heavy metal contaminated wastewater. Natural and plant materials, industrial and agricultural wastes are receiving attention as low cost sorption materials. Figure 6 shows a schematic diagram of a two-stage process for heavy metal biosorption.

*Sorption by microorganisms.* Microorganisms include all prokaryotes (archaea and bacteria) and some eukaryotes (fungi and microalgae). Like all organic matter, microbial cells can take up dissolved metals. However, the sorption capacities and affinities can differ greatly between non-microbial and microbial biomass and between the microorganisms themselves.[62]

Two microbial metal-uptake processes are distinguished: bioaccumulation and biosorption. During bioaccumulation, the metals are accumulated intracellularly. For the transportation of metals across the cell membrane, the microorganisms need to be alive and metabolically active.[93] Biosorption is the binding of metals to organic mater; it is a passive metabolic independent process. In the case of microorganisms, metals are mainly bound to functional groups on the outside of the cells wall. These functional groups include carboxyl, amine, phosphonate and hydroxyl groups.[94]

The following binding mechanisms contribute to biosorption: ion exchange, complexation, adsorption, electrostatic interaction, and precipitation.[95,96] Non-viable microbial biomass frequently exhibits a higher affinity for metal ions than viable cells, probably due to the absence of competing protons produced during metabolism.[97] Sorption capacities of unaltered microorganisms exceeding 100 mg $g^{-1}$ have often been observed. Potent metal biosorbents under the class of bacteria include species from the genera *Bacillus, Pseudomonas* and *Streptomyces*; and important fungal biosorbents include *Aspergillus, Rhizopus* and *Penicillium.*[63] Due to the high presence of alginate in the cell wall, algae (single or multicelluar) form excellent biosorbents as well. The sorption capacity of a microbial sorbent can be increased by chemical pretreatment or by genetic modification.[98] Chemical pretreatment can remove impurities blocking binding sites or introduce new or enhanced binding groups into the cell wall.

In addition to sorption by the cell wall, metals can bind to inorganic compounds (e.g. sulphide, bicarbonate or phosphate) or extracellular polymeric substances (EPS), compounds excreted by metabolically active microorganisms.

*Sorption using non-living biomass.* Most of the biosorption studies have been and continue to be carried out on microbial systems; chiefly bacteria, microalgae and fungi, and with toxic metals and radionuclides.[90] However, practically all biological materials have an affinity for metal species. The process of biosorption using non-living biomass is a rapid phenomenon and involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ions). Due to the higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms.[99] The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

*Sorption using inorganic and natural sorbents.* Both industrial by-products and natural materials locally available in certain regions can be employed as low-cost adsorbents. Due to its metal-binding capacity, natural materials such as zeolite and clay have been explored for treating metal-contaminated wastewater. Babel and Kurniawan[100] studied Cr(VI) uptake from artificial wastewater using natural zeolite. According to them, NaCl treated zeolite had better removal capabilities (3.23 mg $g^{-1}$) for Cr(VI) ions than as-received zeolite (1.79 mg $g^{-1}$) at an initial Cr concentration of 20 mg $L^{-1}$. These results suggest that the Cr adsorption capacities of zeolite varied, depending on the extent of chemical treatment.[37] The results were significantly lower than those of Peric *et al.*[101] (Table 7). They also noted that metal removal by zeolite was a complex process, involving ion exchange and adsorption.

Another low-cost mineral that has a high cation exchange capacity (CEC) in solution is clay. There are three types of clay relevant for sorption: montmorillonite, bentonite and kaolinite. Of the three, montmorillonite has the highest CEC.[106] A number of studies on metal uptake using montmorillonite have been

**Table 3.** Advantages and limitations of physicochemical treatments of industrial wastewater

| Type of treatment | Target of removal | Advantages | Disadvantages | References |
|---|---|---|---|---|
| Reverse osmosis | Organic and inorganic Compounds | High rejection rate, able to withstand high temperature | High energy consumption due to high pressure required (20–100 bar), susceptible to membrane fouling | Potts *et al.*[32], Kurniawan *et al.*[33] |
| Electrodialysis | Heavy metals | Suitable for metal concentration less than 20 mg $L^{-1}$ | Formation of metal hydroxide, high energy cost, can not treat a metal concentration higher than 1000 mg/l | Bruggen and Vandecasteele[34], Ahluwalia and Goyal[28] |
| Ultrafiltration | High molecular weight compounds (1000–10 000 Da) | Smaller space requirement | High operational cost, prone to membrane fouling, generation of sludge that has to be disposed off | Vigneswaran[35] |
| Ion exchange | Dissolved compounds, cations/anions | No sludge generation, less time consuming | Not all ion exchange resins are suitable for metal removal, high capital cost | Vigneswaran[35], Ahluwalia and Goyal[28], Kurniawan *et al.*[33] |
| Chemical precipitation | Heavy metals, divalent metals | Low capital cost, simple Operation | Sludge generation, extra operational cost for sludge disposal | Ahluwalia and Goyal[28], Bose *et al.*[36], Wingenfelder *et al.*[37] |
| Coagulation–flocculation | Heavy metals and suspended Solids | Shorter time to settle out suspended solids, improvedsludge settling | Sludge production, extra operational cost for sludge disposal | Shammas[38], Semerjian and Ayoub[39], Ayoub *et al.*[40] |
| Dissolved air flotation | Heavy metals and suspended Solids | Low cost, shorter hydraulic retention time | Subsequent treatments are required to improve the removal efficiency of heavy metal | Lazaridis *et al.*[41] |
| Nanofiltration | Sulphate salts and hardness ions such as Ca(II) and Mg(II) | Lower pressure than RO (7–30 bar) | Costly, prone to membrane fouling | Ahn *et al.*[42] |
| Electrochemical precipitation | Heavy metals | Can work under both acidic and basic conditions, can treat effluent with a metal concentration higher than 2000 mg/l | High capital and operational costs | Subbaiah *et al.*[43] |
| Membrane electrolysis | Metal impurities | Can treat wastewater with metal concentration of less than 10 mg $L^{-1}$ or higher than 2000 mg $L^{-1}$ | High energy consumption | Kurniawan *et al.*[33] (2006) |

conducted. The adsorption of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) ions on Na-montmorillonite using column operations was investigated by Abollino *et al.*[105] The results of this and other works are shown in Table 7.

*Biosorbent for heavy metal removal.* Since all biological materials have affinity for metals, and indeed other pollutants, the kinds of biomass potentially available for biosorption purposes are enormous. All kinds of microbial, plant and animal biomass, and derived products, have received investigation in a variety of forms and in relation to a variety of substances.[90,107] Strong biosorbent behaviour of certain micro-organisms towards metallic ions is a function of the chemical composition of the microbial cells. This type of biosorbent consists of dead and metabolically inactive cells. A common rationale for such studies is to identify highly-efficient biosorbents that are cost-effective, i.e. cheap. This will, in theory, provide new opportunities for pollution control, element recovery and recycling.[90]

A large quantity of materials has been investigated extensively as biosorbents for the removal of heavy metals or organics. Tables 8, 9 and 10 summarize the research works on metal uptake by agricultural waste and plant materials, bacterial and algal biomass, and industrial waste sorbents respectively.

Cost is an important parameter for comparing the sorbent materials. A biosorbent is considered low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry.[90,27] Some of the reported low cost biosorbents includes sawdust, bark/tannin-rich materials, coconut husk and shells, peat moss, seaweed/algae, dead biomass etc.[27] Perhaps research should employ those biomass types that are efficient, cheap, easy to grow or harvest. Attention should be given to biomass modifications and/alteration of the bioreactor configuration and physico-chemical conditions to enhance biosorption. In this regard, the potential of plant materials and agricultural wastes as biosorbents should be exploited much more.

**Table 4.** Performance characteristics of some conventional heavy metal removal and recovery technologies[44]

| | Performance characteristics | | | | |
|---|---|---|---|---|---|
| Technology | pH change | Metal selectivity | Influence of suspended solids | Tolerance to organic molecules | Metal working level (mg $L^{-1}$) |
| Adsorption (e.g. GAC*) | Limited tolerance | Moderate | Fouled | Can be poisoned | $<10$ |
| Electrochemical | Tolerant | Moderate | Can be engineered to tolerate | Can be accommodated | $>10$ |
| Ion exchange | Limited tolerance | Some selectivity (e.g. chelating resin) | Fouled | Can be poisoned | $<100$ |
| Precipitation as hydroxide | Tolerant | Non-selective | Tolerant | Tolerant | $>10$ |
| Solvent extraction | Some tolerant systems | Metal-selective extractants available | Fouled | Intolerant | $>100$ |

* Granular activated carbon.

*Sorption mechanisms.* Biosorption is made possible by the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical uptake pathways. Due to the interaction of several factors on specific biosorbents, it is almost impossible to propose a general mechanism. Although, several metal-binding mechanisms have been put forward, e.g. chemisorption by ion exchange, coordination and/or chelation, complexation, physical adsorption etc., the actual mechanism of metal biosorption is still not fully understood.[156,157]

*Chemisorption mechanism.* Ion-exchange is an important concept in biosorption, because it explains many observations made during heavy metal uptake experiments.[98] Ion-exchange is a reversible chemical reaction where an ion within a solution is replaced by a similarly charged ion attached onto an immobile solid particle.[158] Romero-Gonzalez *et al*.[159] claimed that cadmium biosorption on *Saccharomyces cerevisiae* followed an ion-exchange mechanism. Tan and Cheng[160] examined the mechanism involved in the removal of five heavy metals, namely, Cu(II), Ni(II), Zn(II), Pb(II) and Cr(III) by *Penicillium chrysogenum,* and concluded that ion-exchange was the dominant mechanism.

Ahmady-Asbchin *et al*.[3] noticed that in the biosorption of copper ions on *Fucus serratus*, the bond between the copper ions and the surface functional groups of the biomass formed as soon as calcium ions were released from the surface. This ion-exchange process is one of the well-known surface reactions, which represents a great degree of complexity, primarily due to its multi-species nature. Kuyucak and Volesky[161] reported that ion-exchange plays a role in the biosorption of cobalt by marine algae (*Ascophyllum nodosum*). In bacterial biosorption, the bacterial cell wall is the first component that comes into contact with the metal, where the solute can be deposited on the surface or within the cell wall structure.[62] Since the mode of solute uptake by dead or inactive cells is extracellular, the chemical functional groups of the cell wall play vital a role in biosorption.

*Involvement of functional groups in metal binding.* Another frequently encountered metal binding mechanism is chelation, which can be defined as a firm binding of metal ions with an organic molecule (ligand) to form a ring structure.[156] Various functional groups including carboxylic, hydroxyl, sulphate, phosphate, amides and amino groups can be considered possible for sorption. Among these groups, the amino group is the most effective for removing heavy metals, since it does not merely chelate cationic metal ions but also absorbs anionic species through the electrostatic interaction or hydrogen bonding. As they are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations.[163]

According to Ahalya *et al*.[126], in the biosorption of Fe(III) by the husk of *Cider arientinum*, carboxyl as well as amino groups were involve in the metal uptake. Golag and Breitenbach[164] indicated that carboxyl groups on the cell wall peptidoglycan of *Streptomyces pilosus* were responsible for the binding of Cu(II). The contribution of amine groups in the Cu(II) adsorption by *Mucor rouxii* was verified by Majumder *et al*.[165] Altun and pehlivan[166] revealed that chelation and ion-exchange were mainly behind Cu(II) adsorption from aqueous solution by walnut, hazelnut and almond shells.

Agricultural and plant waste materials, such as coconut husk and shell, are usually composed of lignin and cellulose as the main constituents. Other components present in the metal binding process are hemicellulose, lipids, proteins, simple sugars, starches, water, hydrocarbons and many more compounds that contain a variety of functional groups.[21] The presence of these functional groups and their complexation with heavy metals during biosorption has been reported by different researchers using spectroscopic techniques.[167]

*Sorption isotherms and models.* Among all phenomena governing the mobility of substances in aqueous porous and aquatic environments, the transfer of substances from a mobile phase (liquid or gas) to a solid phase is a universal phenomenon. That is the reason why the 'isotherm', a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of this substance in the environment.[168] These retention/release phenomena are sometimes strongly kinetically controlled, so that time-dependence of the sorption isotherm must be specified.

Models have an important role in technology transfer from a laboratory scale to industrial scale.[168] The equilibrium of the sorption process is often described by fitting the experimental points with models (Table 10), usually used for the representation of isotherm

**Table 5.** Summary of heavy metal removal data by physicochemical treatment methods

| Treatment method | Metal | Initial metal conc. (mg $L^{-1}$) | pH | Removal efficiency (%) | Power consumption (kWh $m^{-3}$) | References |
|---|---|---|---|---|---|---|
| Chemical precipitation | Zn(II) | 450 | 11.0 | 99.77 | NA | Cherernnyavak[45] |
| | Cd(II) | 150 | 11.0 | 99.76 | NA | |
| | Mn(II) | 1085 | 11.0 | 99.30 | NA | |
| | Cu(II) | 16 | 9.5 | 80 | NA | Tünay and Kabdalsi[46] |
| Electrochemicalcoagulation/ Membrane Filtration | As | 442 | | 99.90 | NA | Mavrov *et al.*[31] |
| | Se | 2.32 | | 98.70 | NA | |
| Ultrafiltration | Cu(II) | 78.74 | 8.5–9.5 | 100 | NA | Juang *et al.*[47] |
| | Zn(II) | 81.10 | 8.5–9.5 | 95 | NA | |
| | Cr(III | 200 | 6.0 | 95 | NA | Aliane *et al.*[48] |
| Nanofiltrattion | Ni(II) | 2000 | 3–7 | 94 | NA | Ahn *et al.*[43] |
| Reverse osmosis | Cu(II) | 200 | 4-11 | 99 | NA | Mohammad *et al.*[49] |
| | Cd(II) | 200 | 4-11 | 98 | NA | |
| Froatation | Cu(II) | 3.5 | 5.5 | 98.26 | NA | Rubio *et al.*[50] |
| | Ni(II) | 2.0 | 5.5 | 98.6 | NA | |
| | Zn(II) | 2.0 | 5.5 | 98.6 | NA | |
| | Zn(II) | 50 | 7-9 | 100 | NA | Matis *et al.*[51] |
| Electrodialysis | Ni(II) | 11.72 | NA | 69 | NA | Tzanetakis *et al.*[52] |
| | Co(II) | 0.84 | NA | 90 | NA | |
| Membrane electrolysis | Cr(VI) | 130 | 8.5 | 99.6 | $7.9 \times 10^3$ | Martınez *et al.*[53] |
| | Ni(II) | 2000 | 5.5 | 90 | $4.2 \times 10^3$ | Orhan *et al.*[54] |
| Electrochemical precitipation | Cr(VI) | 570-2100 | 4.5 | 99 | 20 | Kongsricharoern and Polprasert[55] |
| | Cr(VI) | 215-3860 | 1.5 | 99.99 | 14.7–20 | Kongsricharoern and Polprasert[56] |
| | Ni(II) | 40 000 | NA | 85 | $3.43 \times 10^3$ | Subbaiah *et al.*[44] |
| Ion exchange | Ni(II) | 100 | | 90 | NA | |
| | Cr(III) | 100 | 3-5 | 100 | NA | Rengaraj *et al.*[57] |
| | Ni(II) | 100 | | 90 | NA | Sapari *et al.*[58] |
| | Cu(II) | 100 | | 100 | NA | |
| | Cr(VI) | 9.77 | NA | 100 | NA | Kabay *et al.*[59] |

NA=Not Available.

sorption equilibrium. Appropriate models can help in understanding process mechanisms, analyze experimental data, predict answers to operational conditions and process optimization.[62] As an effective quantitative means to compare binding strengths and design sorption processes, employing mathematical models for the prediction of the binding capacity can be useful.[60,168] Examination and preliminary testing of the solid–liquid sorption system are based on two types of investigations: (a) equilibrium batch sorption tests and (b) dynamic continuous flow sorption studies. The two widely accepted and linearised equilibrium adsorption isotherm models for a single solute system are the Langmuir and the Freundlich isotherms (Table 11).

Surface complexation models provide molecular descriptions of metal adsorption using an equilibrium approach that defines surface species, chemical reactions, mass balances and charge balances. Such models provide information on stoichiometry and reactivity of adsorbed species.[173] In order to use a surface complexation model, the adsorption mechanism and types of surface complexes must be specified for all adsorbing metal ions. This may necessitate independent experimental determination of the adsorption mechanism using spectroscopic techniques, including Raman and Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, electron spin resonance (ESR) spectroscopy, and X-ray absorption spectroscopy (XAS), which includes X-ray absorption near edge (XANES) and extended X-ray fine structure (EXAFS) spectroscopy, and X-ray reflectivity.[90] Most of these techniques have been used, but only in a small number of biosorption studies. Evaluation of equilibrium sorption performance needs to be supplemented with process-oriented studies of its kinetics and eventually by dynamic continuous flow tests.

*Parameters affecting sorption.* The investigation of factors affecting the efficiency of heavy metal sorption is of great interest for the industrial community. The efficiency is strongly influenced by the physico-chemical characteristics of the solutions, such as pH, temperature, initial metal concentration, presence of other ions and sorbent dosage.[156] These factors are important in evaluating the maximal sorption performance of any sorbent.

*pH.* The solution pH is a crucial factor in heavy metal sorption. The pH value significantly influences the dissociation of the sorbent and the solution chemistry of the heavy metals, i.e.

**Table 6.** Sulphate reduction rates achieved during different reactor runs with various electron donors

| e-donor | Temp (°C) | Reactor concept | Volumetric activity ($gSO_4^{2-}$ $L^{-1}$ $day^{-1}$) | Reference |
|---|---|---|---|---|
| Hydrogen | 30 | Gas-lift bioreactor | 25 | van Houten *et al.*[71] |
| Hydrogen | 30 | Gas-lift bioreactor | 30 | van Houten *et al.*[72] |
| Hydrogen | 55 | Gas-lift bioreactor | 8 | van Houten *et al.*[73] |
| Hydrogen | 30 | Gas-lift bioreactor | 13 | van Houten *et al.*[74] |
| Hydrogen | 30 | Gas-lift bioreactor | 5 | Bijmans *et al.*[75] |
| Synthesis gas | 30 | Gas-lift bioreactor | 7 | van Houten *et al.*[76] |
| Synthesis gas | 35 | Packet bed reactor | 1.2 | du Preez *et al.*[77] |
| CO | 35 | Packet bed reactor | 2.4 | du Preez *et al.*[77] |
| CO | 50-55 | Gas-lift bioreactor | 0.2 | Sipma *et al.*[78] |
| Formate | 30 | Membrane bioreactor | 29 | Bijmans *et al.*[79] |
| Methanol | 65 | Expanded granular sludge bed | 15 | Weijma *et al.*[80] |
| Ethanol | 35 | Fluidized bed | 5 | Kaksonen *et al.*[81] |
| Ethanol | 8 | Fluidized bed | 0.6 | Sahinkaya *et al.*[82] |
| Ethanol | 33 | Expanded granular sludge bed | 21 | de Smul and Verstraete[83] |
| Acetate | 35 | Packed bed | 65 | Stucki *et al.*[84] |
| Acetate | 33 | Expanded granular sludge bed | 10 | Dries *et al.*[85] |
| Molasses | 30 | Upflow anaerobic sludge bed | 4.3 | Annachhatre and Suktrakoolvait[86] |
| Molasses | 31 | Packed bed | 6.5 | Maree and Strydom[87] |
| Sucrose | 55 | Upflow anaerobic sludge bed | 1 | Lopes *et al.*[88] |
| Sucrose | 30 | Upflow anaerobic sludge bed & Completely stirred tank reactor | 1 | Lopes *et al.*[89] |

**Table 7.** Heavy metal uptake by natural materials through sorption

| Sorbent | Metal | Initial Metal Conc. (mg $L^{-1}$) | Adsorbent dosage (g $L^{-1}$) | pH | Adsorption Capacity (mg $g^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| Natural zeolite | Zn(II) | 65.4 | 10 | 6.5 | 13.06 | Peric *et al.*[101] |
| Kaolinite | Cd(II) | 200 | 20 | 6.0 | 3.04 | Ulmanu *et al.*[102] |
| | Cu(II) | 200 | 20 | 6.0 | 4.47 | |
| Betonite | Cd(II) | 200 | 20 | 6.0 | 9.27 | Ulmanu *et al.*[102] |
| | Cu(II) | 200 | 20 | 6.0 | 18.16 | |
| Pyrite fines | Cr(VI) | 100 | 20 | 5.0–6.5 | 10.00 | Zouboulis and Kydros[103] |
| Ball clay | Ni(II) | 100 | 20 | 6.0 | 0.41 | Chantawaong *et al.*[104] |
| | Cu(II) | 100 | 20 | 5.0 | 1.60 | |
| | Cd(II) | 100 | 20 | 6.5 | 2.24 | |
| | Zn(II) | 100 | 20 | 6.5 | 2.88 | |
| | Cr(III) | 100 | 20 | 4.0 | 3.60 | |
| Na-montmorillonite | Cd(II) | 112 | 1274 | 5.5 | 5.20 | Abollino *et al.*[105] |
| | Cr(III) | 52 | 1274 | 5.5 | 5.13 | |
| | Cu(II) | 63.5 | 1274 | 5.5 | 3.04 | |
| | Ni(II) | 58.7 | 1274 | 5.5 | 3.63 | |
| | Zn(II) | 65.4 | 1274 | 5.5 | 3.61 | |

metal speciation, hydrolysis, complexation by organic and/or inorganic ligands, redox reactions and precipitation are all pH dependent.[156,120,174,175,176] Competition between cations and protons for binding sites means that sorption of metals like Cu, Cd, Ni, Co and Zn is often reduced at low pH values.[90,177] Due to the importance of pH in sorption; many researches were conducted on its effect on the removal of various heavy metals.

Nuhoglu and Oguz[178] reported that the removal of Cu(II) from aqueous solution increased as pH was increased, and that the maximum adsorption occurred at a pH of 7.7. Pino *et al.*[169] noted that the removal of cadmium and arsenic by green coconut shell increased from 69% at pH 4 to 98% at pH 7. Cu(II) adsorption onto activated rubber and wood sawdust was found to be pH-dependent and maximum removal was observed at pH 6.[109] The optimum pH for As(III) removal (96.2%) by activated alumina was reported to be 7.6.[179] Yu *et al.*[110] showed that the greatest increase in the sorption rate of Cu(II) on sawdust was observed in the pH range 2 to 8. During the biosorption of Cu(II), Pb(II), Zn(II), and Cd(II) by Nile rose plant, Abdul-Ghani and Elchaghaby[180] found out that the sorption efficiencies were pH-dependent, increasing with increasing pH from 2.5 to 8.5, except for Pb(II). Other researchers, including Anurag *et al.*,[23] Pehlivan *et al.*,[130] Sari and Tuzen[144] and

**Table 8.** Data on biosorption of heavy metals using different agricultural and plant biosorbents

| Biosorbent | Metal | Initial metal conc. (mg $L^{-1}$) | Optimum pH | Temp (°C) | Adsorption capacity (mg $g^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| Calcinated wheat by-product | Cu(II) | 10.0 | 6 | 20 | 8.40 | Gherbi *et al.*[108] |
| $H_3PO_4$-activated rubber wood sawdust | Cu(II) | 20 | 6 | 30 | 3.75 | Kalavathy *et al.*[109] |
| Sawdust | Cu(II) | 10 | 8 | 23 | 1.90 | Yu *et al.*[110] |
| Coconut coir | Cr(VI) | | | | 6.30 | Gonzalez *et al.*[111] |
| Submerged aquatic plant (*Myriophyllum spicatum*) | Cu(II) | 10.00 | 5-6 | 25 | 10.37 | Keskinkam *et al.*[112] |
| | Pb(II) | | | | 46.49 | |
| | Zn(II) | | | | 15.59 | |
| Melon seed husk | Cd(II) | 10-50 | NA | 29 | 23.30 | Okieimen and Onyenkpa[113] |
| | Cu(II) | | | | 11.40 | |
| Zr(IV)-loaded orange waste gel | As(III) | | 9-10 | 30 | 130.00 | Biswas *et al.*[114] |
| | As(V) | | 2-6 | | 88.00 | |
| Agarose | Cu(ii) | 25-200 | 2 | 35 | 238.00 | Anurag *et al.*[23] |
| Coconut shell carbon (CSC) | Cr(VI) | 20 | 6 | NA | 2.18 | Babel and Kurniawan[115] |
| $HNO_3$-Treated CSC | Cr(VI) | 20 | 4 | NA | 10.88 | Babel and Kurniawan[115] |
| Sawdust | Cr(VI) | 100 | 2 | NA | 15.82 | Dakiky *et al.*[116] |
| Banana peel | Cu(II) | 25 | 6.8 | NA | 4.75 | Annadurai *et al.*[117] |
| | Zn(II) | | | | 5.80 | |
| Rice husk | Cd(II) | 50 | NA | NA | 2.00 | Ajmal *et al.*[118] |
| Crab shell | Cu(II) | 500 | 6 | NA | 243.9 | Vijayaraghavan *et al.*[119] |
| | Co(II) | | | | 322.6 | |
| Grape stalk | Cu(II) | 5-300 | 5.2 | 20 ± 1 | 42.92 | Vijayaraghavan *et al.*[119] |
| | Ni(II) | | | | 38.31 | |
| Lignin | Pb(II) | 0.2–2.5 | 5.5 | 20 | 1293.75 | Guo *et al.*[120] |
| | Cu(II) | 0.2–2.5 | | | 22.86 | |
| | Cd(II) | 0.2–2.5 | | | 25.43 | |
| | Zn(II) | 0.2–2.5 | | | 11.18 | |
| | Ni(II) | 0.2–2.5 | | | 6.00 | |
| Moringa | As(III) | 1-100 | 2-12.5 | NA | NA | Kumari *et al.*[121] |
| | As(V) | | | | | |
| Cassava waste | Cd(II) | 112.4 | 4-5 | NA | 18.05 | Abia *et al.*[122] |
| | Cu(II) | 63.5 | | | 56.82 | |
| | Zn(II) | 65.4 | | | 11.06 | |
| Peanut hulls | Cu(II) | 32 | NA | NA | 10.17 | Brown *et al.*[123] |
| | Cd(II) | 32 | | | 6.00 | |
| Peanut hulls | Cu(II) | 80 | 6-10 | NA | 65.57 | Periasamy and Namasivayam[124] |
| Cocoa shell | Cd(II) | 28.10 | 2 | NA | 4.94 | Meunier *et al.*[125] |
| | Cr(III) | 13 | 2 | | 2.52 | |
| | Cu(II) | 15.9 | 2 | | 2.87 | |
| | Ni(II) | 14.7 | 2 | | 2.63 | |
| | Zn(II) | 16.4 | 2 | | 2.92 | |
| Bengal gram husk | Fe(III) | 25 | 2.5 | NA | 72.16 | Ahalya *et al.*[126] |
| Pecan shell | Cu(II) | 500 | 3.6 | | 95.00 | Shawabkeh *et al.*[127] |
| Orange peel | Ni(II) | 1000 | 6.0 | | 158.00 | Ajmal *et al.*[128] |
| Fish scale | As(III) | 20-100 | 4.0 | 20 | 2.48 | Rahaman *et al.*[129] |
| | As(V) | | | | 2.67 | |
| Barley straws | Cu(II) | 10 | NA | 25 ± 1 | 4.64 | Pehlivan *et al.*[130] |
| | Pb(II) | 10 | | | 23.20 | |
| *Lessonia Nigrescens* | As(V) | 50-600 | 2.5 | | 45.20 | Hansen *et al.*[131] |
| Sawdust | Cu(II) | 10 | 6.3 | 23 | 7.50 | Larous *et al.*[132] |
| Unmodified coconut husk | As(III) | 2000 | 5.0 | 30 | 944.00 | Igwe and Abia[133] |
| Modified coconut husk | As(III) | 2000 | 5.0 | 30 | 952.5 | Igwe and Abia[133] |

NA = Not available.

**Table 9.** Heavy metal uptake by bacterial and algal biomass

| Bacterial/Algal species | Metal | Adsorption capacity (mg g$^{-1}$) | Reference |
|---|---|---|---|
| *Bacillus sp* | Pb(II) | 92.30 | Tunali *et al.*[134] |
| *Streptomyces rimosus* | Fe(III) | 122.00 | Selatnia *et al.*[135] |
| *Streptomyces rimosus* | Zn(II) | 80.00 | Mameri *et al.*[136] |
| *Thiobacillus ferrooxidans* | Zn(II) | 82.60 | Celaya *et al.*[137] |
| *Bacillus sp* | Hg(II) | 7.90 | Green-Ruiz[138] |
| *Bacillus cereus* | Pb(ii) | 36.71 | |
| | Cu(II) | 50.32 | |
| *Enterobacter sp* | Cu(II) | 32.50 | Lu *et al.*[139] |
| | Pb(II) | 50.90 | |
| | Cd(II) | 46.20 | |
| *Pseudomonas putida* | Cu(II) | 96.90 | Usla and Tanyol[140] |
| | Pb(II) | 270.40 | |
| *Pseudomonas stutzeri* | Cu(II) | 22.90 | Nakajima *et al.*[141] |
| *Bacillus licheniformis* | Cr(IV) | 69.40 | Zhou *et al.*[142] |
| *Bacillus thuringiensis* | Cr(IV) | 83.30 | Sahin and Ozturk[143] |
| *Inonotus hispidus* | As(III) | 51.90 | Sari and Tuzen[144] |
| | As(V) | 59.60 | |
| *Ulva lactuca* | Pb(II) | 34.70 | Sari and Tuzen[145] |
| | Cd(II) | 29.20 | |
| *Spirogyra insignis* | Cu(II) | 19.30 | Romera *et al.*[146] |
| | Zn(II) | 21.10 | |
| | Pb(II) | 51.50 | |
| | Cd(II) | 22.90 | |
| | Ni(II) | 17.50 | |
| *Spirogyra sp* | Cu(II) | 133.30 | Gupta *et al.*[147] |
| *Ascophyllum nodosum* | Cd(II) | 215.00 | Holan *et al.*[148] |

Rahaman *et al.*,[129] also reported similar trends in pH influence on biosorption of heavy metals such as copper, arsenic and lead.

*Temperature.* Depending on the structure and surface functional groups of a sorbent, temperature has an impact on the adsorption capacity within the range 20–35 °C.[181,95] It is well known that a temperature change alters the adsorption equilibrium in a specific way determined by the exothermic or endothermic nature of a process.[156] Higher temperatures usually enhance sorption due to the increased surface activities and kinetic energy of the solute. However, physical damage can be expected at higher temperatures.[182,183] It is always desirable to evaluate the sorption performance at room temperature, as this condition is easy to replicate.

The impact of temperature on the adsorption isotherm of Cu(II) and Cd(II) by corncob particles at a certain pH was explored by Shen and Duvnjak[184]. They found that the uptake of metal ions increased at higher temperature. Igwe and Abia[133] noted that temperature and particle size are very crucial parameters in biosorption reactions. They investigated the effects of these two parameters on the biosorption of As(III) from aqueous solution using modified and unmodified coconut fibers and found that the most suitable temperature was 30 °C.

*Ionic strength.* Another important parameter in biosorption is the ionic strength, which influences the adsorption of solute at the biomass surface. Industrial wastewater often contains ions other than heavy metal ions, e.g. $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$, which may interfere with heavy metal ion uptake by biomass. As a general trend, metal uptake is found to decrease with increasing ionic strength of the aqueous solution as a result of more electrostatic attraction and change of the metal activity.[156,185,186,120]

It was found that uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of manganese, cobalt, copper, cadmium, mercury and lead in solution.[187] In contrast, the presence of $Fe^{2+}$ and $Zn^{2+}$ was found to influence uranium uptake by *Rhizopus arrhizus*,[193] and cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper.[188] Anions like $CO_3{}^{2-}$ and $PO_4{}^{2-}$ may clearly affect sorption through the formation of insoluble metal precipitates. Chloride may influence sorption through the formation of complexes, e.g. $CdCL_3{}^-$.[90]

*Metal concentration.* The initial ion concentration can alter the metal removal efficiency through a combination of factors, i.e. availability of functional groups on the specific surface and the ability of surface functional groups to bind metal ions (especially at higher concentrations). Higher initial concentration of heavy metal ions results in a high solute uptake.[156,189] According to Arief *et al.*,[156] the initial concentration acts as a driving force to overcome mass transfer resistance to metal transport between the solution and the surface of the biomass.

A number of studies on the effect of the initial metal ion concentration have been undertaken in the past. Ajmal *et al.*[190] found out that when the initial Cu(II) concentration was increased from 5 to 50 mg L$^{-1}$, the amount adsorbed increased from 8.8 to 96 mg L$^{-1}$, showing that adsorption of Cu(II) depends upon the initial concentration because the amount of Cu(II) adsorbed increased with increasing initial concentration. Gulnaz *et al.*[191] also investigated the effect of initial Cu(II) ion concentrations between 100 and 400 mg L$^{-1}$ at 20 °C and pH 4. They determined that the biosorption capacity of dried activated sludge for the $<$0.063 mm particle size range was 76, 256 and 243 mg g$^{-1}$ for 100, 200 and 400 mg L$^{-1}$ initial Cu(II) concentrations, respectively. This indicated that the initial Cu(II) concentration is an important parameter for biosorption of Cu(II) by dried activated alumina. Anurag *et al.*[23] also investigated the effect of initial concentration (25–200 mg L$^{-1}$) on biosorption of Cu(II) by agarose gels at 35 °C and reported that the removal was highest (70%) at an initial Cu(II) concentration of 25 mg L$^{-1}$. They explained that because at higher concentrations, more ions compete for limited binding sites on the agarose gels, the rate of adsorption decreases, resulting in a lower adsorption percentage.

*Adsorbent dosage.* The amount of biomass in the solution also affects the specific metal uptake. For lower values of biomass concentrations, there is an increase in the specific uptake.[91,192] Gadd *et al.*[192] suggested that an increase in biomass concentration leads to interference between the binding sites. By increasing the adsorbent dosage, the adsorption efficiency increases even though the amount adsorbed per unit mass decreases. In principle, with more adsorbent present, the available adsorption sites or functional groups also increase. In turn, the amount of adsorbed heavy metal ions increase, which results in an improved adsorption efficiency.[193,194,195,156,170]

*Adsorbent size.* The size of the biosorbent also plays a vital role in biosorption. Smaller sized particles have a higher surface area, which in turns favours biosorption and results in a shorter

**Table 10.** Heavy metal uptake by industrial waste through sorption

| Sorbent | Metal | Initial metal conc. (mg $L^{-1}$) | Adsorbent dosage (g $L^{-1}$) | pH | Adsorption capacity (mg $g^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| Sewage sludge | Cd(II) | 40 | 10 | 5.5–6.0 | 16.00 | Zhai *et al.*[149] |
| Olive cake | Cr(VI) | 100 | 2.4 | 2.0 | 33.44 | Dakiky *et al.*[116] |
| Olive cake | Cd(II) | 100 | NA | 2.0–11.0 | 65.36 | Al-Anber[150] |
| Bagasse | Cd(II) | 14 | 10 | 6.0 | 2.00 | Gupta *et al.*[151] |
| Fry ash | Ni(II) | 12 | 10 | 6.5 | 1.70 | Gupta *et al.*[151] |
| Fish scale | As(III) | 20-100 | NA | 4.0 | 2.48 | Rahaman *et al.*[129] |
| | As(V) | 20-100 | | | 2.67 | |
| Iron slags | Cu(II) | 200 | 2 | 3.5–8.5 | 88.50 | Feng *et al.*[152] |
| | Pb(II) | 200 | 2 | 3.5–8.5 | 95.24 | |
| Red mud | Ni(II) | 400 | 7 | 9.0 | 160.00 | Zouboulis and Kydros[103] |
| Soya cake | Cr(VI) | 44 | 9.3 | 1.0 | 0.28 | Daneshvar *et al.*[153] |
| Anaerobic sludge | Cd(II) | 200 | 20 | 6.0 | 5.82 | Ulmanu *et al.*[105] |
| Brewery waste | Pb(II) | 33.1–1656 | NA | 4 | 85.49 | Chen and Wang[154] |
| | Ag(II) | 17.3–864 | NA | 4 | 42.77 | |
| | Sr(II) | 14.1–704 | NA | 4 | 72.29 | |
| | Cs(II) | 21.3–1064 | NA | 4 | 10.11 | |
| Tea factory waste | Cr(VI) | 50-400 | NA | 2.0–5.0 | 54.65 | Malkoc *et al.*[155] |

NA= Not available.

equilibrium time. Simultaneously, a particle for biosorption should be sufficiently resilient to withstand the application of pressure and extreme conditions applied during regeneration cycles.[196] Therefore, preliminary experiments are necessary to determine a suitable size for a biosorbent.

## Desorption

Desorption of loaded biomass enables reuse of the biomass, and recovery and/or containment of sorbed materials, although it is desirable that the desorbing agent does not significantly damage or degrade the biomass.[90,197] In some cases, desorption treatments may further improve sorption capacities, although in other cases there may be a loss of sorption efficiency. For operation of continuous flow systems, columns in parallel arrangements may allow sorption and desorption processes to occur without significant disruption. A successful desorption process requires proper selection of eluents, which strongly depends on the type of biosorbent and the mechanism of biosorption. Also the eluent must be non-damaging to the biomass, low cost, environmentally friendly and effective.

A variety of substances have been used as metal desorbents including acids, alkalines and complexing agents depending on the substances sorbed, process requirements and economic considerations. Akar and Tunali[26] studied the desorption of Cd(II) and Cu(II) using 10 mmol $L^{-1}$ HCL solution as desorbing agent. They reported that more than 95% of the adsorbed metal ions were desorbed from the biosorbent.

One of the main attributes of biosorption is the potential ability to regenerate the biomass. However, most published work aimed to evaluate the binding ability of biomass and factors affecting the process. Less attention has been paid to the regeneration ability of the biosorbent, which often decides the industrial applicability of a process. Thus, biosorption studies should emphasize the ability of biomass regeneration to improve process viability.

From the above review, although abundant natural materials of cellulosic nature have been suggested as biosorbents, very little work has been done in this respect. Indeed, a large amount of biological research on heavy metal removal has focused on the use of microorganisms such as bacteria. There is, therefore, the need to intensify research into the use of agricultural waste and plant material such as coconut husk, coconut shell carbon, and *Moringa oleifera seeds* (MOS) as low-cost and locally available biosorbents.

Another important observation from the literature reviewed so far is that most of the studies used laboratory scale batch sorption systems. Kratochvil and Volesky[198] pointed out that the limited understanding of the metal uptake mechanism has hindered the application of biosorption. While batch equilibrium sorption studies can provide useful information on relative biosorbent efficiencies and important physico-chemical factors that affect biosorption, they usually provide no information on the removal mechanism. As a consequence, the batch method is very useful as a preliminary experiment, but extrapolation to porous or fixed bed media requires other investigations in a continuous system.

Continuous mode of operation is preferred in large scale wastewater treatment applications owing to such advantages as simple operation, high yield, easily scaled up from laboratory-scale procedure and easy regeneration of packed bed.[199] Such laboratory continuous column studies, which can provide information on the effect of flow rate variation and metal uptake mechanism by the biosorbents, have received less attention. Table 12 shows data on biosorption of heavy metal in laboratory fixed-bed columns (FBC) and continuous stirred tank reactors (CSTR).

In a continuous process, Pümpel *et al.*[219] employed metal biosorbing or bioprecipitating bacteria to remove heavy metal from wastewater. The MEtal REmoval by Sand Filter INoculation (MERESAFIN) process is based on the inoculation of a sand filter with metal biosorbing or bioprecipitating bacteria. In this system, bacteria grow in a biofilm on a supporting material. During contact with heavy $Zn^{2+}$-containing wastewater, the biofilm in the EMB-SRB system adsorbs the metals. The metal-loaded biomass is then removed from the supporting material and the residual biomass on the substratum can be reused, after re-growth, for a subsequent

**Table 11.** Frequently used adsorption models

Single-component adsorption models

| Models | Equation | Advantages | Disadvantages | References |
|---|---|---|---|---|
| Langmuir | $q = \frac{q_{\max} bC_{eq}}{1 + bC_{eq}}$ | Interpretable parameters | Not structured: monolayer sorption | Pino *et al.*[169] |
| Freundlich | $q = KC_{eq}{}^{1/n}$ | Simple expression | Not structured: no leveling off | Amuda *et al.*[170] |
| Combination (Langmuir – Freundlich) | $q = \frac{q_{\max} bC^{1/n}{}_{eq}}{1 + bC^{1/n}{}_{eq}}$ | Combination of the above equations | Unnecessarily complicated | Vijayaraghavan and Yun[62] |
| Radke and Prausnitz | $\frac{1}{q} = \frac{1}{aC_{eq}} + \frac{1}{bC_{eq}{}^{\beta}}$ | Simple expression | Empirical: uses three parameters | Gavrilescu[171] |
| Reddlich-Petterson | $q = \frac{aC_{eq}}{1 + bC_{eq}{}^{n}}$ | Approaches Freundlich at high concentrations | No special advantage | Gavrilescu[171] |
| Brunnauer (BET) | $q = \frac{BCQ^0}{(C_s - C)[1 + (B - 1)C/C_s]}$ | Multilayer adsorption: inflection point | No 'total capacity' equivalent | Gavrilescu[171] |
| Dubinnin-Radushkevich | $\frac{W}{W_0} = \exp\left[-k\left(\frac{\varepsilon}{\beta}\right)^2\right]$ | Temperature-independent | No limited behaviour in Henry's law regime | Gavrilescu[171] |
| | | Multicomponent adsorption models | | |
| Langmuir (Multicomponent) | $q_i = \frac{b_i q_{mi} C_i}{1 + \sum_{i=1}^{N} b_i C_i}$ | | | Goel *et at.*[172] |
| Combination of Langmuir and Freundlich | $q_i = \frac{a_i C_i{}^{1/n_i}}{1 + \sum_{i=1}^{N} b_i C_i{}^{1/n_i}}$ | | | Gavrilescu[171] |
| IAST: Ideal Adsorbed Solution Theory | $\frac{1}{q_t} = \sum \frac{Y_i}{q_t{}^0}$ | | | Limousin *et al.*[168] |
| SCM: Surface Complexation Model | $q \approx f(C_{eq})$ | | | Limousin *et al.*[168] |

NA: Not Available.

**Table 12.** Data on heavy metal biosorption in fixed-bed column (FBC) and continuous stirred tank reactor (CSTR)

| Biosorbent (Reactor type) | Metal | Initial ion conc. (mg $L^{-1}$) | pH | Temp (°C) | Adsorbent dosage (g) | Packing height (cm) | Flow rate (mL $min^{-1}$) | Uptake capacity (mg $g^{-1}$) | % Removal | References |
|---|---|---|---|---|---|---|---|---|---|---|
| Silica-gel matrix **(FBC)** | Ni(II) | 100 | 6.5 | 25 ± 2 | 0.08 | 19.0 | 0.5-5.0 | 50.03 | NA | Akar *et al.*[199] |
| Seaweed **(FBC)** | Ni(II) | 10 | 2.6 | NA | NA | 22.9 ± 0.3 | 25.0 | 0.53 ± 0.04 | 90 | Brady *et al.*[200] |
| | Zn(II) | 10 | 2.6 | NA | NA | 22.9 ± 0.3 | 25.0 | 0.35 ± 0.03 | 90 | |
| | Al(II) | 10 | 2.6 | NA | NA | 22.9 ± 0.3 | 25.0 | 0.97 ± 0.03 | 74 | |
| | Sb(II) | 10 | 2.6 | NA | NA | 22.9 ± 0.3 | 25.0 | 0.92 ± 0.09 | 67 | |
| Seaweed (*S. ilipendula*) **(FBC)** | Cu(II) | 35 | 5 | NA | | 41 | 15.0 | 38.00 | NA | Volesky *et al.*[201] |
| Poly acrylamide gel immobilized *S. platensis***(FBC)** | Cu(II) | 0.1 | 6 | NA | 2.00 | NA | 2.0 | 250.00 | NA | Vannela and Verma[202] |
| *R. arrhizus* **(FBC)** | Cr(VI) | 100 | 2 | 25 | NA | 10.0 | 1.2 | 85.90 | 57.7 | Sag *et al.*[203] |
| | Fe(III) | 100 | 2 | 25 | NA | 10.0 | 1.2 | 37.80 | 33.6 | |
| Calcium-treated anaerobic biomass **(FBC)** | Pb(II) | 40 | 4 | NA | 11.00 | 1.5 | 1.5 | 160.00 | NA | Hawari and Mulligan[204] |
| | Cu(II) | 40 | 4 | NA | 11.00 | 1.5 | 1.5 | 90.84 | NA | |
| | Cd(II) | 40 | 4 | NA | 11.00 | 1.5 | 1.5 | 91.90 | NA | |
| | Ni(II) | 40 | 4 | NA | 11.00 | 1.5 | 1.5 | 52.65 | NA | |
| Residual brewer *Saccharomyces cerevisiae* immobilized in volcanic rock **(FBC)** | Cr(III) | 300 | 4.3 | | 61.80 | 120.0 | 15.0 | 48.00 | NA | Ramirez *et al.*[205] |
| | Cr(VI) | 200 | 1.7 | | 61.80 | 120.0 | 15.0 | 60.00 | NA | |
| *Posidonia oceaica***(FBC)** | Cu(II) | 1.02 | 6.0 | 22 ± 1 | 0.90 | 10.0 | 0.7 | 41.50 | NA | Izquierdo *et al.*[206] |
| | | 1.98 | | | 0.96 | 9.8 | 0.7 | 44.83 | NA | |
| | | 10.62 | | | 1.00 | 9.9 | 0.7 | 55.17 | NA | |
| | | 20.07 | | | 0.97 | 10.1 | 0.7 | 56.25 | NA | |
| | | 41.40 | | | 0.87 | 10.0 | 0.7 | 56.02 | NA | |
| *Sargassum fluitans* seaweed biomass **(FBC)** | Cu(II) | 2-3 | 2.5-3.5 | NA | | 20 | 7.5 | 75 | NA | Kratochvil *et al.*[207] |
| Quaternized wood chips **(FBC)** | Cr(VI) | 9.07 | 4.3 | 28 ± 2 | 1.10 | 7.0 | 50.0 | 27.03 | 75.3 | Low *et al.*[208] |
| *Cladosporium cladosporioides* biomass beads **(FBC)** | Au | 10 | 4.0 | | 3.00 | 10.0 | 0.13-0.4 | 110.00 | 80 | Pethkar and Paknikar[209] |

**Table 12.** (*Continued*)

| Biosorbent (Reactor type) | Metal | Initial ion conc. (mg $L^{-1}$) | pH | Temp (°C) | Adsorbent dosage (g) | Packing height (cm) | Flow rate (mL $min^{-1}$) | Uptake capacity (mg $g^{-1}$) | % Removal | References |
|---|---|---|---|---|---|---|---|---|---|---|
| Crab shell particles **(FBC)** | Ni(II) | 100 | 4.5 | | 31.00 | 15.0 | 5.0 | 24.74 | 59.88 | Vijayaraghavan *et al.*[210] |
| | | | | | 41.00 | 20.0 | | 24.77 | 67.63 | |
| | | | | | 51.00 | 25.0 | | 25.57 | 71.82 | |
| Olive stone **(FBC)** | Cr(III) | 10 | 4.0 | 25 | 5.00 | 4.0 | 2.0 | 0.33 | 40.40 | Calero *et al.*[211] |
| | | 25 | | | 10.00 | 8.9 | 4.0 | 0.53 | 25.40 | |
| | | 50 | | | 15.00 | 13.4 | 6.0 | 0.82 | 21.50 | |
| *Sargassum Wightii* | Cu(II) | 100 | 4.5 | NA | 7.05 | 15 | 5 | 51.7 | 61.7 | Vijayaraghavan and Prabu[212] |
| | | 100 | | | 9.38 | 20 | 5 | 51.9 | 70.9 | |
| | | 100 | | | 11′73 | 25 | 5 | 52.6 | 74.7 | |
| | | 100 | | | 11.73 | 25 | 10 | 51.8 | 71.3 | |
| | | 100 | | | 11.73 | 25 | 20 | 48.9 | 72.4 | |
| | | 75 | | | 11.73 | 25 | 5 | 49.3 | 72.1 | |
| | | 50 | | | 11.73 | 25 | 5 | 48.4 | 67.3 | |
| Marine algae (*Gelidium*) Composite material **(FBC)** | Cd(II) | 25 | 4.7 | 20 | 10.70 | 15.0 | 4.1 | 19.00 ± 2 | NA | Vilar *et al.*[213] |
| | Cd(II) | 25 | 4.6 | 20 | 9.20 | NA | 4.0 | 7.90 ± 0.3 | NA | |
| S. fruitans biomass **(FBC)** | Cu(II) | 35.00 | 5.0 | NA | 33.00 | 38.0 | 10.0 | 61.5 | NA | Kratochvil *et al.*[213] |
| *Hydrilla verticillata* **(FBC)** | Cd(II) | 10.00 | 5.0 | 25 ± 2 | 0.50 | NA | 10.91 | 15.00 | 98.00 | Bunluesin *et al.*[215] |
| *A. hydrophila* **(FBC)** | Cr(VI) | 103.9 | 1.5 | 30 | 13.30 | 19.0 | 2.0 | 44.62 | 78.58 | Hasan *et al.*[216] |
| Algae *Gelidiun* | Cd(II) | 19.5 | 5.3 | 20 | 10 | Not Applicable | 35.5 | 12.40 | NA | Vilar *et al.*[213] |
| Composite material **(CSTR)** | Cd(II) | 20.4 | 5.4 | 20 | 10 | Not Applicable | 35.5 | 6.80 | NA | |
| Algae *Gelidiun* | Cu(II) | 25-6 | 4.3 | NA | 10 | Not Applicable | 35.5 | 53.9 | NA | Vilar *et al.*[217] |
| | Pb(II) | 25.6 | 4.8 | | 10 | | 35.5 | 36.4 | | |
| Composite material **(CSTR)** | Cu(II) | 25-6 | 4.3 | NA | 10 | Not Applicable | 35.5 | 16.0 | NA | |
| | Pb(II) | 25.6 | 4.8 | | 10 | | 35.5 | 20.0 | | |
| Grape stalk **(CSTR)** | Cr(VI) | 10 | 3 | 30 | 10 | Not Applicable | NA | | | Escudero *et al*[218] |

NA= Not available.

treatment cycle. Figure 7 shows the schematic presentation of metal binding and precipitation to biofilms on sand grains, and biofilm regeneration, in an Astrasand moving-bed sand filter. Chuichulcherm *et al.*[220] studied the removal of $Zn^{2+}$ from wastewater using sulfate-reducing bacteria (SRB) in an extractive membrane bioreactor (EMB). The continuous EMB-SRB system removed more than 90% (w/v) of the $Zn^{2+}$ ions present in the wastewater. The concept is illustrated in Fig. 8.

It is also worth noting that considerable information is available on the biosorption of single-component systems, but many industries discharge effluents contain several components. Thus, knowledge of how one metal influences another is necessary for pilot reactor design. A successful laboratory scale continuous column bioreactor is key to the design and operation of an on-site pilot scale reactor that uses the real gold mine wastewater; and ultimately, the design and operation of full scale industrial reactors based on low-cost agricultural/plant waste as biosorbent. Thus, current research must focus on column and pilot scale studies using multi-component metal ion solutions or actual industrial effluents.

## Cyanide removal

The wastewaters from gold ores cyanidation processes are treated by several methods.[221] Cyanide treatment processes are classified as destruction-based process versus physical processes of cyanide recovery and activated carbon sorption. In a destruction process, either chemical or biological reactions are utilized to convert cyanide into other less toxic compounds. There are several destruction or recovery processes that are well proven to produce effluents or slurries with low levels of cyanide.[222–224] Shen *et al.*[225] and Han *et al.*[226] used gas-filled membrane reactor (see Fig. 9(A) and (B)) to recover cyanide from wastewater. They concluded that both the feed and membrane side mass transfer coefficients contributed to the overall mass transfer coefficient.

### *Chemical cyanide removal processes*

In general terms, cyanide is successfully removed by alkaline chlorination and oxidation.[227] Chlorination of cyanides can result in highly toxic intermediates (e.g. cyanogen chloride) and other toxic organo-chlorines that can be formed. These compounds, together with residual chlorine create additional environmental problems.[3] The process also produces sludge, which requires licensed disposal. Another disadvantage is that it is relatively expensive due to the quantity of chlorine required.[17] Most cyanide destruction processes (e.g. sulphur dioxide/air and hydrogen peroxide) operate on the principle of converting cyanide into less toxic compounds through an oxidation reaction.

In order to keep operational costs as low as possible, effluents are frequently only partially treated to the cyanate ($OCN^-$) phase or in many cases non-reacted metal cyanide containing effluents are directly discharged without treatment.[228] Some of the more important chemical processes are discussed in the following section.

*Sulfur dioxide/air.* The sulfur dioxide and air process was developed by INCO in the 1980s.[229] The process utilizes $SO_2$ or a derivative and air in the presence of a soluble copper catalyst to oxidize cyanide to the less toxic cyanate. The resulting effluent is usually stored in tailing ponds.

$$SO_2 + O_2 + H_2O + CN^- \xrightarrow{Cu^{2+}\,catalyst} OCN^- + SO_4{}^{2-} + 2H^+ \tag{2}$$

The primary advantage of the INCO process is in the treatment of tailings slurry, but it is also widely used for the treatment of process solutions.

*Hydrogen peroxide.* The hydrogen peroxide treatment process chemistry is similar to that described for the INCO process, but hydrogen peroxide is used rather than sulphur dioxide and air. With this process, soluble copper is also required as a catalyst and the end product of the reaction is cyanate:

$$H_2O_2 + CN^- \xrightarrow{Cu^{2+}\,catalyst} OCN^- + H_2O \tag{3}$$

The primary application of the hydrogen peroxide process is with solutions rather than slurries due to the high consumption of hydrogen peroxide in slurry applications. The process is typically applied to achieve effluent cyanide levels suitable for discharge. It is a simple process capable of operating over wide pH ranges, while producing environmentally acceptable effluents without increasing total dissolved solids as do other chemical processes.[222]

*Alkaline and breakpoint chlorination.* Alkaline chlorination was at one time the most widely applied of the cyanide treatment processes, but it has been gradually replaced by other chemical processes and is now used only occasionally. The cyanide destruction reaction is a two-step process, the first step involving conversion to cyanogen chloride (CNCl), followed by a second step of hydrolysis of the cyanogen chloride into cyanate:

$$Cl_2 + CN^- \longrightarrow CNCl + Cl^- \tag{4}$$

$$CNCl + H_2O \longrightarrow OCN^- + Cl^- + 2H^+ \tag{5}$$

If additional chlorine is added to attain breakpoint, this process can also oxidize thiocyanate and ammonia to nitrogen gas. In this event, these two cyanide related compounds must be removed from the treated effluent.

Although chemical and physical processes can be employed to degrade cyanide and its related compounds, they are often expensive and require special equipments and maintenance. The biological treatment of effluents has been described as an appealing inexpensive and environmentally friendly alternative to the chemical approach due to a much safer operation, free from hazardous chemicals and the final effluent is devoid of highly toxic products.[227]

### *Biological cyanide removal processes*

Although biological treatment of cyanide is a relatively new phenomenon in the gold mining industry, there are several literature references to it dating from the 1950s.[230,231,229,227,232] Castric and Strobel,[233] Mosher and Figueroa[234] demonstrated cyanide degradation in solutions using a pure culture of *Bacillus megaterium*. The applicability of biological treatment processes for cyanide solutions in the mining industry is primarily for waste streams with temperatures above 10 °C.

Biological treatment processes have recently become more widespread in the mining industry due to the success of the plant installed at Homestake Lead (USA) in the 1980s. In this plant, an aerobic attached growth biological treatment is used to remove cyanide, thiocyanate, cyanate, ammonia and metals from tailings impoundment decant solution prior to discharge into a trout fishery. The plant has been operating successfully for over 15 years, producing high-quality effluent.[222] At the Homestake Gold Mine in South Dakota, a biofilm process was developed and patented to biologically treat cyanide-containing wastewater without the addition of carbon. The plant was designed to treat 20,818 $m^3$ per day of combined mine tailings and impoundment water using a rotating contactor.[207]

Chergui *et al*.[235] studied the biosorption of a hexacyanoferrate(III) complex by dead biomass of *Pleurotus mutilus* and observed that biosorption was affected by pH and particle size. Recent studies by Gurbuz *et al*.[18] have also demonstrated the ability of *Scenedesmus obliquus* to biodegrade cyanide from gold mine wastewater. In this study, gold mill effluents containing WAD cyanide concentration of 77.9 mg $L^{-1}$ was fed to a batch unit to examine the ability of *S. obliquus to* degrade cyanide. The result shows a reduction in cyanide concentration to 6 mg $L^{-1}$ in 77 h. Figure 9(C) shows a schematic representation of the cyanidation and algal treatment unit. Treatment of cyanide- bearing wastewater by simultaneous adsorption and biodegradation was done by Dash *et al*.[232] Dash *et al*.[17] extensively reviewed the biotreatment of cyanide in industrial wastewater. They concluded that the continuing generation of large volumes of cyanide-bearing wastes from various industries which contaminate soils and water suggests that novel processes are required to alleviate the serious environmental consequences of cyanide pollution.

From the above review on cyanide treatment of gold mine wastewater, the use of chemical, physical and biological processes have been established. However, the biological treatment processes have been largely limited to the use of microorganisms only. There is no report in the literature on the use of agricultural waste and plant materials as biosorbent for the removal of cyanide from gold mine wastewater. These materials are available in abundance as waste in developing as well as developed countries. There is, therefore, a need for research into the use of these low-cost materials to remove cyanide from solutions.

## CONCLUSIONS

Pollution of the environment with heavy metals is widespread and often involves large volumes of wastewater. Remediation strategies for gold mine wastewater must be designed to support high throughput while keeping costs to a minimum. Biosorption is an alternative to traditional physicochemical means for removing toxic metals from wastewater.

Biosorption has a future as it can quickly (rapid intrinsic kinetics) and effectively sequester dissolved metals out of dilute complex solutions with high efficiency. These characteristics make biosorption an ideal candidate for the treatment of high volumes of low concentration complex gold mine wastewater. However, preparing biosorption for application as a process requires a strong chemical engineering background, and an understanding of the sorption operation is a must.

It is therefore important to continue fundamental research into a better understanding of the mechanism of biosorption. In this regard, it is necessary to focus current research on column studies to determine the physico-chemical conditions necessary for pilot scale plant design and operation. Pilot scale studies are crucial for scaling the process to industrial level, which is the ultimate aim of all biosorption research. The potential of plant materials and agricultural waste as low-cost biosorbents should be exploited much more.

For industrial application of biosorption, regeneration of the biosorbents is important to keep process costs down, and it gives the possibility of recovering metal ion extracted from the liquid phase. Attention should be given to biomass modifications and alteration of bioreactor configurations to enhance biosorption. Research should employ those biomass types that are efficient, cheap, and easy to grow or harvest. The successful design of hybrid reactors and the regeneration of spent biosorbents is key to the commercialization of biosorption.

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