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*Review Article*

# Nanoparticles Used for Extraction of Polycyclic Aromatic Hydrocarbons

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This article offers a review on the application of nanoparticles (NPs) that have been used as sorbents in the analysis of polycyclic aromatic hydrocarbons (PAHs). The novel advances in the application of carbon NPs, mesoporous silica NPs, metal, metal oxides, and magnetic and magnetised NPs in the extraction of PAHs from matrix solutions were discussed. The extraction techniques used to isolate PAHs have been highlighted including their advantages and limitations. Methods for preparing NPs and optimized conditions of NPs extraction efficiency have been overviewed since proper extraction procedures were necessary to achieve optimum analytical results. The aim was to provide an overview of current knowledge and information in order to assess the need for further exploration that can lead to an efficient and optimum analysis of PAHs.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a large group of organic compounds containing two or more fused benzene rings connected in linear, angular, or cluster arrangements. They have high melting and boiling points, low volatility, and are relatively insoluble in water. Their solubility decreases with increasing number of aromatic rings. They are highly soluble in organic solvents and are lipophilic. PAHs with more than five rings occur as solids, whereas those with less than five rings occur in the vapour and particulate phases [1]. These compounds are ubiquitous in the environment and can originate from both natural and anthropogenic sources. Globally, the major contributors to environmental PAHs include burning coal and biofuels, vehicle emissions, and biomass burning (agricultural waste, deforestation, and wildfires) [2, 3]. Recently, PAHs have received considerable attention as significant pollutants that contaminate our environment. More than 80% of inputs of PAHs to the environment are influenced by atmospheric deposition as reported by the Federal Environmental Agency of Germany [4]. They show high persistency and low biodegradability in the environment. In addition, PAHs are present in environmental matrices in trace levels, and due to their lipophilic property, they show high affinity for organic matter. The behaviour and toxicity of individual PAHs in the environment depend on their size, and the smallest ones (less than three benzene rings) are more soluble in water and can break down quickly via dissolution, volatilisation, and microbial degradation which make them acutely toxic to fish and aquatic organisms [5]. PAHs with 3 to 5 benzene rings are less water soluble and accumulate in the tissues of aquatic organisms and stick to solid particles. Larger-size PAHs (greater than 5 benzene rings) do not break down quickly and can persist for years especially in sediments [6]. Some of these larger compounds are known to cause cancer and affect DNA [7]. Alkylated PAHs have also been shown to be more toxic than the parent compounds (nonalkylated PAHs), and they are formed during the diagenesis process and usually coexist with their parent compounds in the environment [8]. More than 100 PAHs have been characterised in nature, and 16 of which were classified as priority pollutants due to their wide distribution and toxicity (Figure 1) [9]. The U.S. Environmental Protection Agency (US EPA) has classified PAHs into three groups based on their carcinogenic tendencies (Table 1) [10]. Group B2 consists of

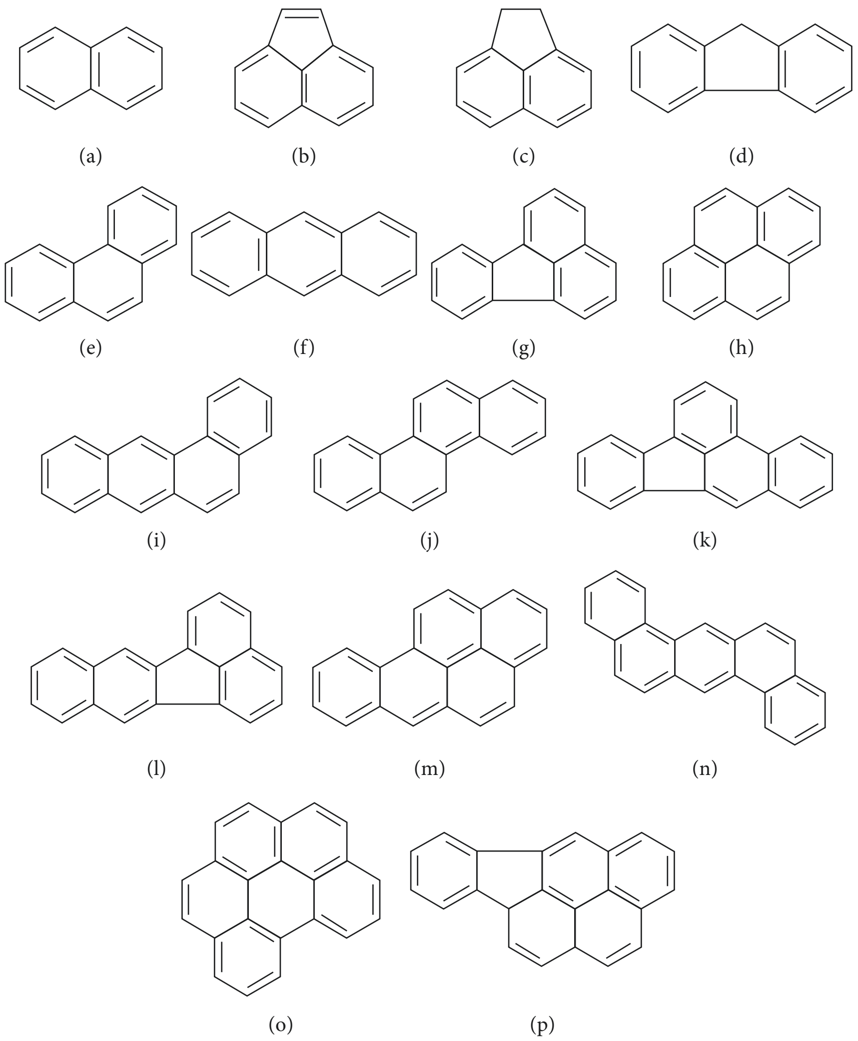


Figure 1: Chemical structure of the 16 PAHs listed in US EPA priority pollutants: (a) naphthalene; (b) acenaphthylene; (c) acenaphthene; (d) fluorene; (e) phenanthrene; (f) anthracene; (g) fluoranthene; (h) pyrene; (i) benzo(a)anthracene; (j) chrysene; (k) benzo(b)fluoranthene; (l) benzo(k)fluoranthene; (m) benzo(a)pyrene; (n) dibenzo(a,h)anthracene; (o) benzo(g,h,i)perylene; (p) indeno(1,2,3-cd)pyrene.

Table 1: EPA classification of PAHs.

| PAH | EPA classification |
|---|---|
| Acenaphthylene | D |
| Anthracene | D |
| Benzo(a)anthracene | B2 |
| Benzo(b)fluoranthene | B2 |
| Benzo(k)fluoranthene | B2 |
| Benzo(g,h,i)perylene | D |
| Benzo(a)pyrene | B2 |
| Chrysene | B2 |
| Dibenzo(a,h)anthracene | B2 |
| Fluranthene | D |
| Fluorene | D |
| Indeno(1,2,3-cd)pyrene | B2 |
| Naphthalene | C |
| Phenanthrene | D |
| Pyrene | D |

substances that are probable human carcinogens, group C contains substances with possible carcinogenic effects in humans, and group D contains substances not classifiable as to human carcinogenicity. US EPA has also developed toxicity equivalence factors (TEFs) based on carcinogenicity for the quantification of the PAHs toxicity level (Table 2) [11]. Furthermore, these compounds are known to induce the formation of cancer after chronic exposure [12]. In addition, exposure to high levels of PAHs has been shown to produce immunosuppressive effects causing oxidative stress during its metabolism [13]. Among all PAHs, benzo(a) pyrene is the greatest carcinogen based on a number of studies demonstrating the carcinogenicity in human and animal species. It has been found that human exposure to different PAH mixtures containing benzo(a)pyrene increases the cancer risks in the lung and skin [14].

Different regulatory agencies have defined the maximum allowable level of PAHs in the environment due to their adverse effects on human health [15]. The Occupational Safety and Health Administration (OSHA) permissible exposure level for PAHs in the workplace is 0.2 $mg/m^3$ for eight hours of workday [16]. The annual mean target value of benzo(a)pyrene of 0.7 to $13 \times 10^{-7}$ $mg/m^3$ was established by European countries [17]. The World Health Organization

Table 2: Toxicity equivalent factors (TEFs) of PAHs [11].

| PAH | TEF |
|---|---|
| Acenaphthylene | 0.001 |
| Anthracene | 0.01 |
| Benzo(a)anthracene | 0.1 |
| Benzo(b)fluoranthene | 0.1 |
| Benzo(k)fluoranthene | 0.1 |
| Benzo(g,h,i)perylene | 0.01 |
| Benzo(a)pyrene | 1 |
| Chrysene | 0.01 |
| Dibenzo(a,h)anthracene | 5 |
| Fluranthene | 0.001 |
| Fluorene | 0.001 |
| Indeno(1,2,3-cd)pyrene | 0.1 |
| Phenanthrene | 0.001 |
| Pyrene | 0.001 |

Table 3: Maximum allowable concentrations (MACs) of PAHs in water and soil [9].

| PAH | MAC (water) (ppm) | MAC (soil) (ppm) |
|---|---|---|
| Pyrene | 3.0 | 3.0 |
| Naphthalene | 3.0 | 1.0 |
| Phenanthrene | 3.0 | 3.0 |
| Benzo(h,g,i)perylene | 3.0 | 3.0 |
| Benzo(a)pyrene | 0.005 | 0.3 |
| Anthracene | 3.0 | 3.0 |
| Fluoranthene | 3.0 | 3.0 |
| Acenaphthene | 3.0 | 3.0 |
| Acenaphthylene | 3.0 | 3.0 |
| Benzo(a)anthracene | 0.005 | 0.15 |
| Benzo(b)fluoranthene | 0.005 | 0.3 |
| Dibenzo(a)anthracene | 0.005 | 0.3 |
| Fluorene | 3.0 | 3.0 |
| Indeno(1,2,3-ghi) pyrene | 0.005 | 0.3 |
| Indene | 3.0 | — |

(WHO) recommended a health-based guideline value of $1 \times 10^{-6}\,\mathrm{mg/m^3}$ benzo(a)pyrene for an ambient air [18]. US EPA has defined the maximum allowable concentration of PAHs in soil and water, as shown in Table 3 [9]. Due to their ecological risks, toxicity, and adverse health effects in humans, the monitoring and detection of PAHs from the environment has attracted worldwide concern.

## 2. PAHs Extraction Techniques

As mentioned, PAHs are released to the environment through natural and anthropogenic sources. Human exposure to PAHs is usually through water, air, food, and soil. Exposure routes include inhalation, ingestion, and dermal contact in both occupational and nonoccupational settings (Figure 2). The analysis of water samples requires isolation of PAHs from the sample matrix before instrumental analysis. PAHs have low solubility in water, and thus, they are usually present in trace quantity in water samples (sea, rivers, lakes, surface and groundwater, industrial waste, and drinking water). Different extraction techniques have been applied to isolate PAHs from water samples [19], among them include solid phase extraction (SPE) [20, 21], solid-phase microextraction (SPME) [22, 23], dispersive microsolid phase extraction (D-$\mu$-SPE) [24], stir bar sorptive extraction (SBSE) [25, 26], cloud point extraction (CBE) [27], liquid-liquid extraction (LLE) [28], and dispersive liquid-liquid microextraction combined microsolid-phase extraction (DLLME/SPE) [29]. Owing to their presence in trace quantity, the extraction method of PAHs from water samples should be of high enrichment factors for the target analyte in order to be in a detectable level of the instrument used for analysis [30]. An effective method should provide good accuracy, low limit of detection, and high recovery of the target analyte. Table 4 shows the limit of detection and recovery percent of different PAHs extraction techniques from water samples. The most commonly used methods for preconcentration of PAHs in drinking water are SPE and LLE [33–35] and have been recommended by US EPA (methods 8310 and 8100).

On the contrary, it has been reported that SPME is suitable for extraction of low-molecular-weight (less than four rings) PAHs associated with airborne particles [36]. The extract from airborne particulate matter represents a complex matrix in trace amounts which contain $N_2$, $O_2$, sulfur heterocompounds, and saturated hydrocarbons which lead to difficulties in identification of PAHs [37]. To eliminate interference that affects PAHs detection, a cleanup procedure was recommended after liquid extraction [38]. The analysis of PAHs in the solid samples also required pretreatment extraction to transfer PAHs into a solvent. Different methods have been used for extraction of PAHs from soil and sediments, and some of them are soxhlet extraction [39], pressurised fluid extraction, microwave extraction [40], ultrasonic extraction [41], solid-phase microextraction, and micellar solid-phase microextraction [42, 43]. Table 5 shows a summary of the main techniques for the extraction of organic compounds from environmental matrices [44]. Most of the extraction techniques are nonselective and produce an extract with a large amount of the matrix effect; therefore, a cleanup step is necessary to isolate PAHs from the matrix effect prior to instrumental determination [45]. The choice of the extraction method depends mainly on the sample matrix, operation cost, simplicity of operation, and availability of the standardised method. Some of the standardised methods for the determination of PAHs in various matrices are presented in Table 6. Although these techniques provide good accuracy and low limits of detections, they are often time-consuming and some of them generate large solvent wastes (Table 4). In this regard, a new adsorbent attached to nanoparticles (NPs) has gained a great consideration as a novel extraction technique focused on the isolation of PAHs as target analytes from complex matrices. NPs with a structural characterisation ranging from 1 to 100 nm in size have become of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. NPs are unique because of the following properties: presence of a large surface area, high absorption capacity, quantum effect production, ability to form suspensions, quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles, and superparamagnetism

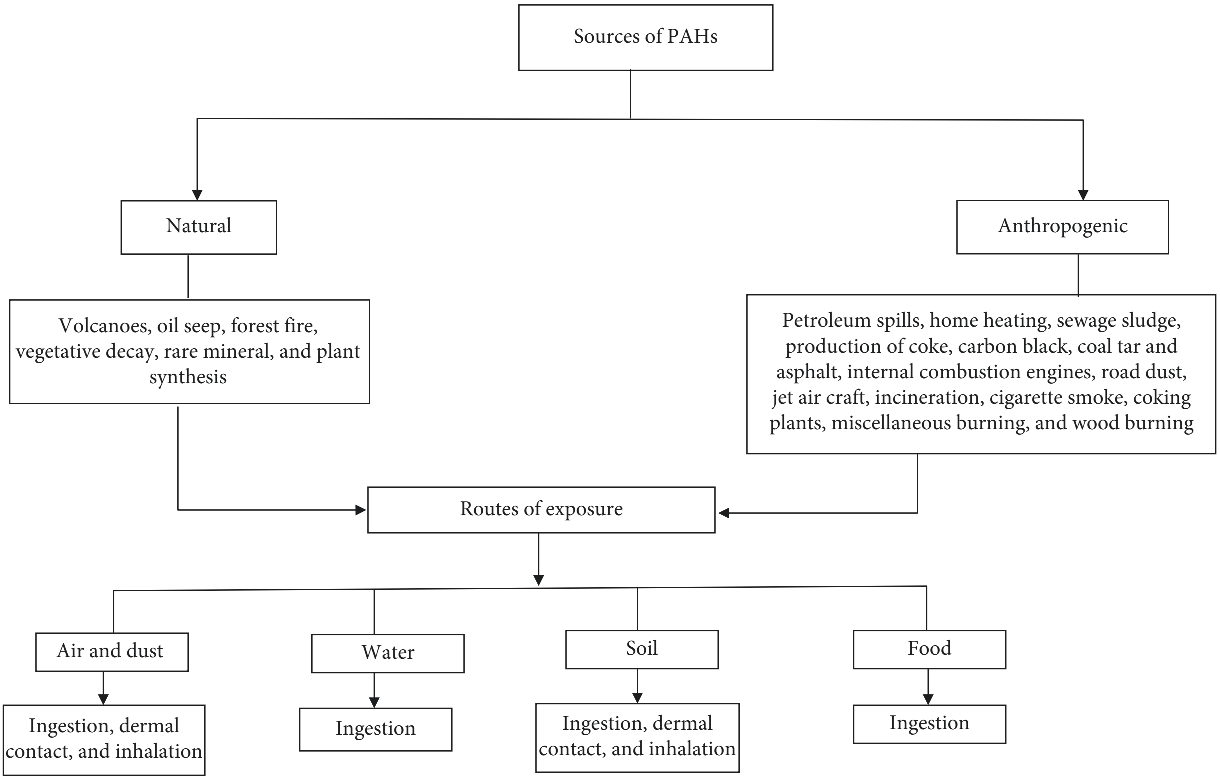


Figure 2: Sources and routes of exposure of PAHs to human.

Table 4: Some PAHs extraction techniques.

| Sample matrix | Technique | Advantage | Limitation | Limit of detection | Recovery (%) | Ref |
|---|---|---|---|---|---|---|
| Retention pond water | SPE | Easy automation, analyzed many samples in parallel, requires no human intervention | Adsorption of PAHs on to the wall of extraction vessels, large solvent volume, involves many steps | 0.5–5 ng/L | 40–95 | [31] |
| Surface water | LLE | Extracts PAHs both dissolved in the water and adsorbed upon any suspended particles in the sample | Use of large volumes of solvents and numerous pieces of laboratory glassware, time-consuming, not easy to automate | 0.1–14 ng/L | 80–120 | [32] |
| Water | D-$\mu$-SPE | Low cost, solvent minimization, materials used were more convenient in handling | Solvent type, significant effect of extraction and desorption time on the method performance | 0.013–0.73 ng/ml | 84–110 | [24] |
| Seawater | SPME | Solvent minimization, involved few steps, minimum sample volume, easy preparation | Limited capacity of the fiber, potential contamination of the SPME needle | 0.1–0.35 ng/g | 75.6–107 | [22] |
| Sea water | SBSE | | Further sample preparation, e.g., by pH adjustment, back extraction, and derivatisation required for extraction of certain compounds | 0.01–0.04 ng/L | 58–70 | [25] |

in magnetic materials [47]. NPs have amorphous or crystalline form, and their surfaces can act as carriers for gases or liquid droplets. Owing to their distinctively large surface area, high sorption capacity, favorable thermal features, and the possibility for surface functionalisation, NPs have shown great promise in analytical application especially in sample treatment. The physicochemical properties of NPs can be controlled through surface modification, insertion of suitable components, or structural design. In addition, multifunctional NPs (hybrid NPs) have exceptional properties due to their combination of targeting specificity, magnetic properties, and analytical capability [47]. On the contrary, the adsorption process is a promising technology owing to its low cost, high efficiency, and simplicity of operation for removing trace levels of organic and inorganic pollutants from effluents. In the adsorption mechanism, the adsorbate is accumulated on the adsorbent surface through molecular interaction and diffusion of sorbate molecules from the surface into the

Table 5: Classification of the main extraction techniques, characteristics, and applications [44].

| Techniques | Characteristics | Analyte |
|---|---|---|
| Soxhlet | It has been so far applied for organic compound extraction from solid matrices due to its high extraction efficiency | PAHs, polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs), among others |
| Ultrasound-assisted extraction (UAE) | Ultrasound energy has also been widely used for the leaching of organic and inorganic compounds from solid matrices | Pharmaceutical, endocrine disruptor, compounds (EDCs), perfluorochemicals (PFCs), antibiotics, tetrabromobisphenol-A (TBBPA) PAHs, phthalate esters (PEs), PCBs, nonylphenols (NPs), nonylphenol ethoxylates (NPEOs), and pharmaceuticals and personal care products |
| Pressurized liquid extraction (PLE) | Pressure is applied to allow the use of extraction solvents or mixtures at temperatures higher than their normal boiling point. The increase on the extraction temperature can promote higher analyte solubility by increasing both solubility and mass transfer rate | Perfluorinated acids (PFAs), perfluorosulfonates (PFSs), and perfluoroctanesulfonamide PAHs |
| Microwave-assisted extraction (MAE) | Uses microwave energy to heat the sample-solvent mixture. This technique reduces the extraction times and the extractant amount for the extraction of organic compounds from solid matrices | PAHs in airborne particles, 17-estradiol (E2), estriol (E3), 17-ethinyl estradiol (EE2) |
| Supercritical fluid extraction (SFE) | Is an alternative extraction method with the advantages of reduced solvent consumption and extraction time compared with the classical extraction techniques. Carbon dioxide is commonly used as fluid, and methanol is added as an organic modifier when polar compounds are extracted | PAHs in marine sediment |
| Solid-phase microextraction (SPME) | It is used specifically for the extraction of low-molecular-weight organic compounds, from liquid, air, and solid matrix | PAHs or polybrominated biphenyls (PBBs) |

Table 6: Standardized methods for PAHs determination in various matrices [46].

| Matrix | Method | Comments |
|---|---|---|
| Food | ISO/CD TR 24054 | Animal and vegetable fats and oils–determination of PAHs–method using GC/MS |
| Food | EN ISO 15753 : 2006 | Animal and vegetable fats and oils–determination of PAHs |
| Food | EN ISO 15302 : 2007 | Animal and vegetable fats and oils–determination of benzo(a)pyrene–reverse phase HPLC |
| Primary smoke product | Collaborative study validation. JRC-IRMM | Validation of two methods for the quantification of PAHs in primary smoke condensate: report on the collaborative trial |
| Water | EN ISO 17993 : 2002 | Determination of 15 PAHs in water by HPLC with fluorescence detection after LLE |
| Drinking water | EPA method 525 | Determination of organic compounds in drinking water by liquid-solid extraction and GC/MS |
| Wastewater | EPA method 610 | PAHs : LLE extraction and HPLC-FID or GC-FID |
| Wastewater | EPA method 652 | PAHs and other chemical residues: LLE and GC/MS |
| Sediment water | EPA method 8272 | Parent and alkyl PAHs in sediment pore water by SPME and GC/MS |

interior of sorbent materials either by monolayer or by multilayer [48]. The adsorption process is generally classified as physisorption in which an adsorbate is attached to the surface by weak Van der Waals forces and chemisorption in which adsorbate is tethered to the surface through covalent bonding or due to electrostatic attraction [49].

## 3. Methods for Preparing Nanoparticles

The synthetic methods for preparing NPs were classified as either the bottom-up method which involves building up of the atom or molecular constituent using chemical or biological procedures or the top-bottom method which involves making a smaller structure from a uniform piece of material using a physical (mechanical) or chemical means to create nanostructures [50]. However, the top-bottom approach for the generation of uniform NPs faces some difficulties like the introduction of an internal stress, structural defect, and contaminations in addition to the consumption of energy to maintain high pressure and temperature used in synthetic procedures. Although the bottom-up approach produces NPs with more precise structures, shape, size, and chemical composition with low cost for high volume, the use of toxic solvents and generation of hazardous by-products are its drawbacks [51]. Table 7 presents different methods used in the synthesis of NPs including their advantages and limitations. Different routes with various strategies have been applied for the synthesis of NPs, and these include chemical, physical, and biological routes (Figure 3). The chemical route is fast and inexpensive and can produce a large number of NPs, but this route leads to the creation of a non-ecofriendly environment since toxic chemicals were used to stabilise and cap NPs. Fabrication of NPs by using the physical method is usually expensive and time- and energy-consuming and involves complex experimental instrument in comparison with biological methods which are easy, cost-effective, and ecofriendly [52]. The green synthesis (biosynthesis) of NPs is a bottom-up approach that uses microbes, enzymes, or phytochemicals for the reduction of metal compounds into their respective NPs [53]. The green method is easy and efficient, eliminates the use of toxic chemicals, consumes less energy, and produces safer products and by-products. The biological method is used in various areas such as pharmaceuticals, cosmetics, foods, and medical applications.

Recently, there is a greater interest in green synthesis of NPs [54–56]. Gold NPs were synthesized by using plant extracts as both the reducing and capping agents [57]. Pomegranate peels extract was used as a reducing and capping agent for the synthesis of proanthocyanidin-functionalised gold NPs via the hydrothermal method [58]. Also, iron oxide NPs (IONPs) were synthesized at room temperature by using pomegranate peel extracts for removal of pyrene and benzo(a)pyrene from water samples with a removal rate of 98.5 and 99%, respectively [59]. Metal and metal oxide NPs have been widely used for the isolation of PAHs. Metal oxide NPs are usually prepared by hydrothermal synthesis which can easily be obtained through the hydrothermal treatment of peptised precipitates of a metal precursor with water [60, 61]. The hydrothermal method can be useful to control grain size, particle morphology, crystalline phase, and surface chemistry through regulation of the solution composition, pressure, solvent properties, additives, and aging time [62]. Carbon-based nanomaterials including graphene, fullerene, and nanotube have been used as adsorbents for PAHs due to their availability, ease of preparation, stable structure, and high sorption capacity. Graphene NP can be prepared from distinct carbon-containing precursors by the chemical method. A reaction of potassium with $CO_2$ led to the formation of 3D honeycomb-like structured graphene [63]. Surface oxygen groups can be introduced to graphene edges (Figure 4). PAH-based metal complexes can be prepared by the inclusion of heteroatoms (Ru or Pd) (Figure 5). These heteropolyaromatic compounds result from the $FeCl_3$ catalysed oxidative cyclodehydrogenation of 1,2-dipyramidyl-3,4,5,6-tetra-(4-tert-butylphenyl) benzene. Three new C-C bonds are formed that lock the two pyrimidines in a molecular platform comprising eight fused aromatic rings flanked by two remaining uncyclised phenyl rings [65]. Oxidation of graphene produces graphene oxide (Figure 6). Using $\pi$–$\pi$ stacking interaction and van der Waals' forces, adsorption of pollutant on the graphene oxide nanosheet (GONSs) can be realised (Figure 7) [66]. Carbon nanotubes (CNTs) are members of the fullerene structural family, and they can be single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) [67] (Figure 8). CNTs can be prepared by decomposition of hydrocarbon molecules on a metal catalyst surface, and the formed CNT hangs down from the catalyst particle and captures it in the growth process (Figure 9). The CNT growth is accompanied by a charge of catalyst particle "spherical-elongated-spherical" [64]. Also, CNTs can be prepared from ethanol using iron or cobalt acetate as the catalyst, and horizontally or vertically ordered arrays of CNTs can be obtained on $SiO_2$ from xylene as the carbon source and ferrocene as the catalyst [64]. CNTs can be functionalised to introduce various functional groups that provide new adsorption sites. Hydroxyl and carbonyl groups can be easily introduced to CNTs via oxidation.

Novel approaches in improving the use of NPs include incorporating a magnetic material such as $Fe_3O_4$. The method includes the use of adsorbents attached to NPs that can be separated by a magnetic field. The surface modification of magnetic NPs (MNPs) with a suitable coating is very important to get an efficient extraction of the target analyte and prevents agglomerisation/aggregation of MNPs by van der Waals' forces or magnetostatic interaction [69]. The magnetic particles in nanoscales can be synthesized by different methods such as chemical (coprecipitation of hydroxides), hydrothermal synthesis, sol-gel transformation, and ball milling [70]. A novel approach for the preparation of the SPE sorbent (1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane) (TBCD)/MNP was developed. The four benzyl groups provide the TBCD functionalised $Fe_3O_4$ with strong adsorption capacity for PAHs due to their $\pi$–$\pi$ stacking interaction which increases the selectivity of the synthesized material to the target analyte [71]. The TBCD/MNP was prepared by a bottom-up chemical strategy, TBCD was chemically bonded to the surface of prepared MNPs through the quaternisation reaction, as illustrated in Figure 10, and the extraction process scheme is illustrated in Figure 11.

## 4. Nanoparticles for Extraction of PAHs

The search for a suitable adsorbent that can effectively isolate PAHs from environmental samples is a priority and that is because PAHs are hydrophobic and tend to coextract with a large amount of matrix effects, have a very low charge, and exist in the environment as mixtures and in trace amounts. The synthesis of nanosorbents coated with functional

Table 7: Advantages and disadvantages of some methods of preparing NPs.

| Method | Advantages | Disadvantages |
|---|---|---|
| Vapour-phase process | High-purity NPs yielded by the clean process | Limited mass of prepared material, high price of product, agglomeration |
| Milling process | Production of large quantities of crystal powders | Contamination from milling media and atmosphere, difficult to control product morphology |
| Sol-gel method | Very practical, low cost, precise stoichiometry control | High cost of raw materials, health hazard of organic compounds, amorphous final products, need final calcinations at high temperature |
| Hydrothermal and solvothermal process | Efficient and available for many kinds of nanomaterials, synthesis of complex inorganic compounds | Need capping agents and surfactants which affect some properties of the product, large amount of solvent used, high pressure |
| Flame synthesis | Solvent free, product required no subsequent postprocessing, less process waste | Agglomeration of NPs |
| Chemical precipitation | Simplicity, yields final products of near-perfect stoichiometry without high temperature treatment | Use of a lot of chemicals, potentially hazardous waste, postprocessing treatments required to improve purity of the end-product |
| Biological methods: plants | Easy scaled up for large synthesis of NPs, no need of high temperature, energy, pressure, and toxic chemical, reduces cost of microorganism isolation and their culture media | Cannot be manipulated as the choice of NPs through optimized synthesis through genetic engineering, produces low yield of secreted proteins which decrease the synthesis rate |
| Enzymes/microorganism | Cost-effective, biocompatible<br>Bacteria have ability to reduce heavy metal ions and are easy to handle and manipulate | Difficult to control size and shape, monodispersed particles, low rate of production, time-consuming culturing of microorganism |

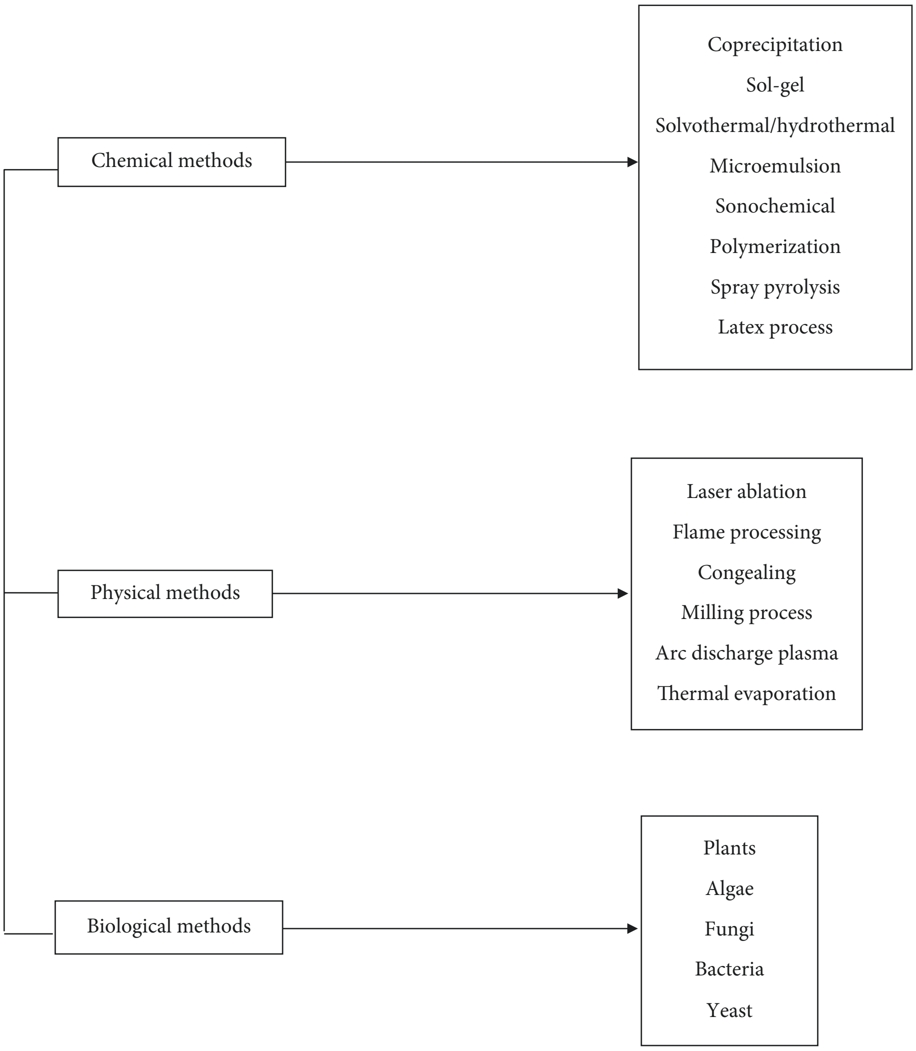


Figure 3: Different routes for synthesis of nanoparticles.

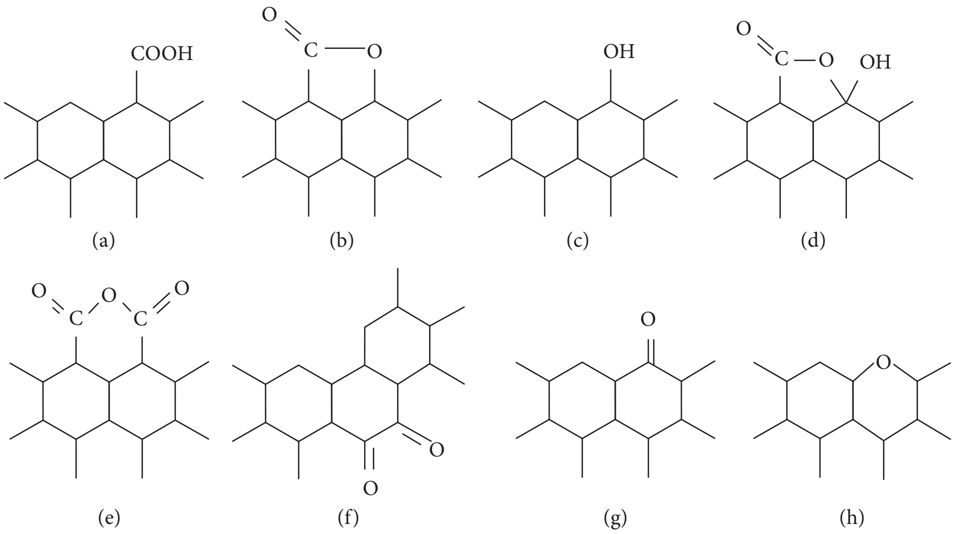


Figure 4: Surface oxygen groups on graphene edge: (a) carboxyl; (b) lactone; (c) hydroxyl; (d) lactol, (e) carboxylic anhydride; (f) quinone; (g) carbonyl; (h) ether.

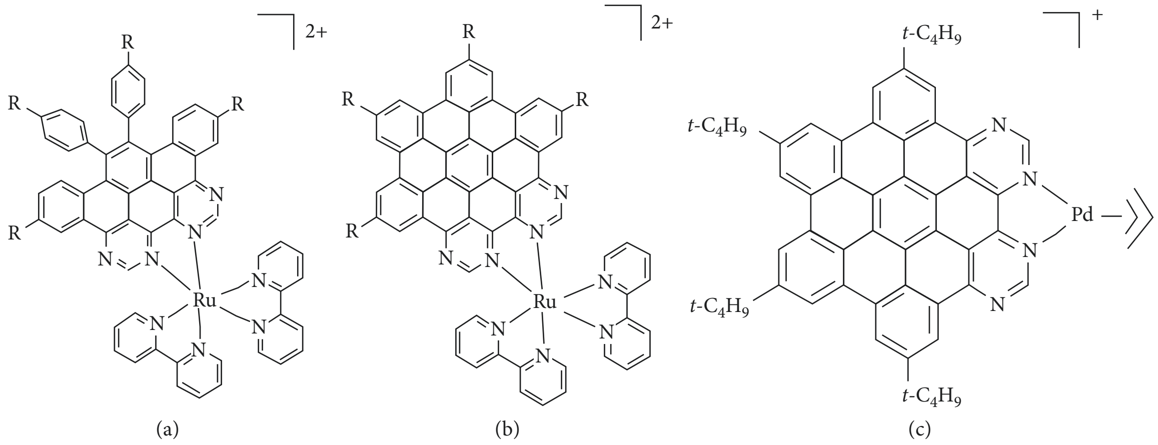


Figure 5: (a, b) Ruthenium and (c) palladium-graphene complex [64].

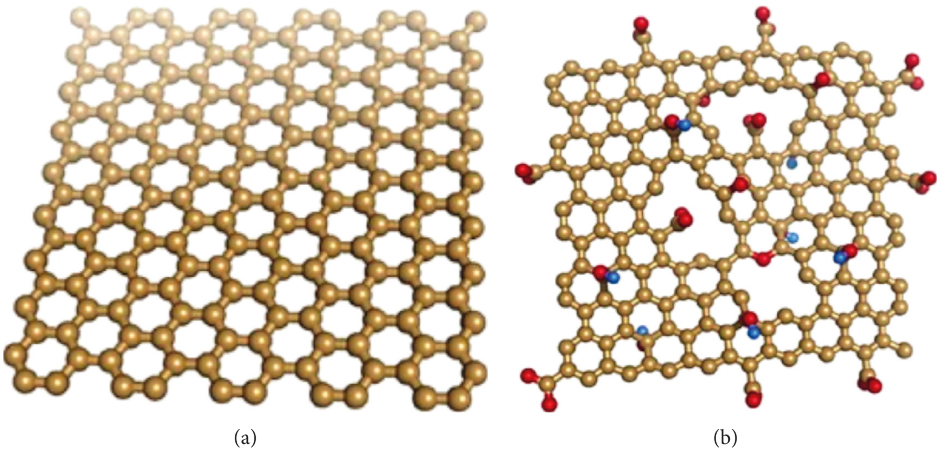


Figure 6: Schematic structure of graphene (a) and graphene oxide (b) [49].

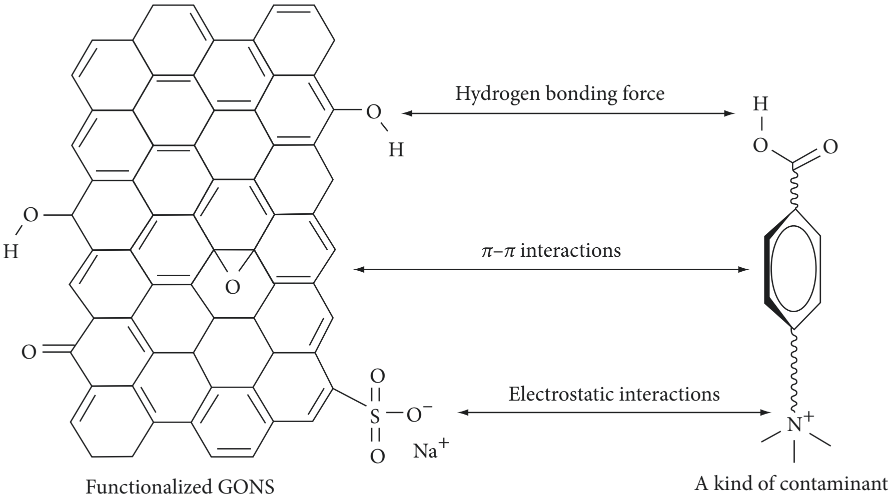
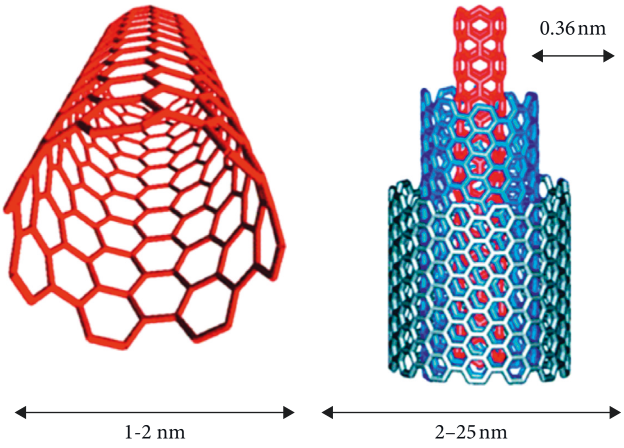


Figure 7: Schematic representation of possible interactions between GONSs and pollutants [66].



(a)

(b)

Figure 8: Schematic of (a) SWCNTs and (b) MWCNT [68].

organic moieties and the fabrication of molecular imprinted polymers for PAHs forms part of the progress in the analysis of PAHs [72]. Different NPs adsorbents have been investigated and applied for isolation of PAHs from a sample matrix, and these include mesoporous silica NP, carbon NP, metal and metal oxide NP, and magnetic and magnetised NP. Some properties of these nanoparticles adsorbents are summarised in Table 8.

*4.1. Mesoporous Silica NP.* Mesoporous silica NPs (MSNPs) are chemically and thermally stable nanomaterials having pores in the range of 2–50 nm. The unique properties of MSNPs make them highly attractive in many diverse fields of science, industry, and technology [73, 74]. These nanomaterials are synthesized by condensation reactions of tetraethyl orthosilicate in the presence of a surfactant such as cetyltrimethylammonium bromide under acidic or basic catalysis [75]. MSNPs are considered excellent carriers for drug delivery because of their textural properties which increase the loading amount of drug inside the pore channels, and drug diffusion kinetics can be controlled due to the functionalised silanol group [76, 77]. MSNPs have been applied for isolation of PAHs from environmental water samples. Different surfactants have been found to increase adsorption capacity values such as dodecylamine and tetramethylammonium [78, 79]. Cyclodextrin-functionalised MSNPs was used for removal of 5 PAHs from aqueous solution with adsorption capacities of 0.3 and 1.56 $\text{mg·g}^{-1}$ [80]. Recently, the magnetised form of mesoporous silica has been applied for the adsorption of pyrene [81]. Magnetised silica NPs using cholesterol as a functionalising agent was applied for extraction of 7 PAHs, and the limit of detection (LOD) was between 0.50 and 1.0 $\text{ng·g}^{-1}$ [82]. *N*-methylimidazole-coated MSNPs was also used for extracting 13 PAHs with an extraction efficiency of 75–102% [83]. Silica has been applied in surface modification due to its availability, cheapness, good chemical stability, biocompatibility, and flexibility. In different methods of extraction of PAHs by using magnetic NP ($Fe_3O_4$), the

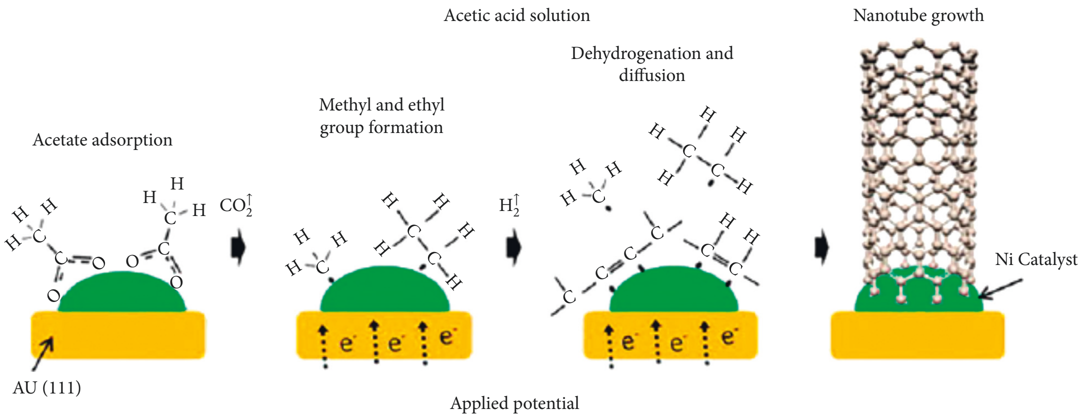


Figure 9: Proposed mechanism for SWCNT growth on Au supporting Ni nanocatalyst by the electrochemical process [64].

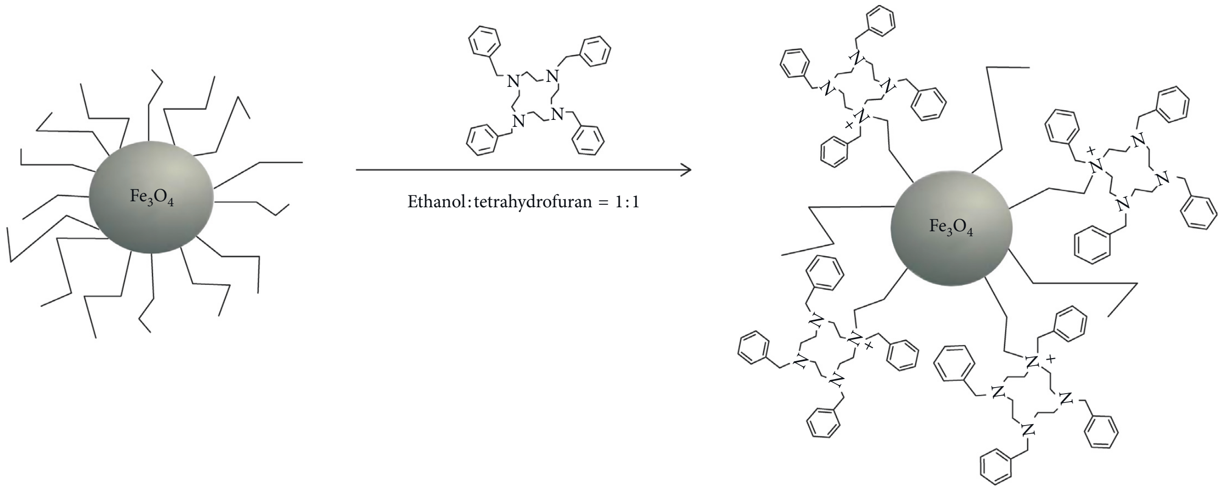


Figure 10: Preparation scheme of $Fe_3O_4$/TBCD MNP [71].

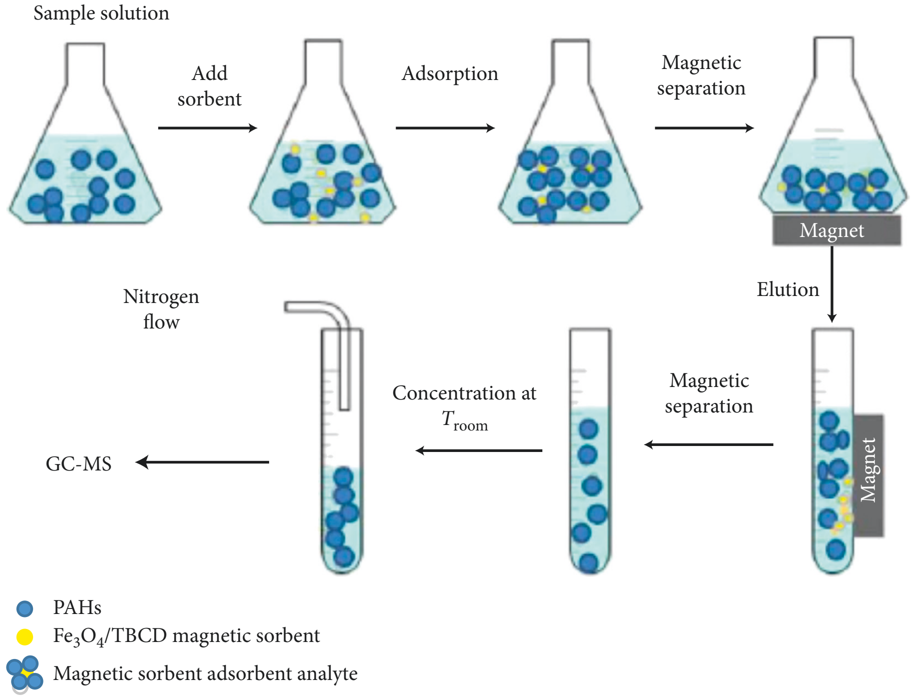


Figure 11: Scheme of the extraction process of PAHs by $Fe_3O_4$/TBCD MNP [71].

Table 8: Some properties of nanoparticles adsorbents for PAH extraction.

| Nanoparticles adsorbents | Properties |
|---|---|
| Mesoporous silica | High surface area, specific pore size, 2D-hexagonal and 3D-cubic structural characteristics, and high chemical stability |
| Metal and metal oxides | Porous structure<br>Large surface area<br>Thermal, mechanical, and chemical stabilities<br>High adsorption capacity<br>High affinity for an analyte |
| Carbon NPs | Pore structure<br>High surface area, high mechanical strength, and chemical stability |
| Magnetic and magnetized NPs | Small size<br>High surface area<br>No agglomeration after separation from matrix solution |

unprotected particles can easily be oxidised under harsh extraction conditions and lose magnetism when used in long term, and silica has been chosen as the most ideal substance to solve this problem [84, 85].

*4.2. Metal and Metal Oxide NPs.* Unfunctionalised metal and metal oxide NPs have been used in the extraction of PAHs from environmental samples. Gold and titanium oxide NPs have been reported with the recoveries of 83.3–100% and LOD value of 0.9–59 ng$\cdot$L$^{-1}$, respectively [86, 87]. Among the metals and metal oxides which have been used for the isolation of PAHs are gold and silver NPs due to the ease of preparation and strong affinity to PAHs which allow extraction and preconcentration of these compounds from drinking water [88, 89]. Silane-based 3-mercaptopropyltrimethoxysilane and thiolated agents have been reported for functionalising gold NPs [90]. The thiol-based coated NPs recorded LODs of 0.8–60 ng$\cdot$L$^{-1}$ for 16 PAHs with a total recovery of 44.6–90.5%. Gold immobilised magnetic mesoporous silica NPs were applied for extraction of PAHs from seawater samples, and the results indicated good recovery efficiencies ranging from 91.4 to 104.2% with a detection limit in the range 0.002–0.004 $\mu$g$\cdot$L$^{-1}$ [91]. Several kinds of modified Au and Ag substrates have been developed to adsorb PAHs close to the surface of the metal for the label-free surface-enhanced Raman spectroscopy (SERS) detection. Among these are thio-functionalised $Fe_3O_4$@Ag core-shell magnetic NPs [92], humic acid-modified Ag NPs [93], and Ag NPs functionalised with dithiocarbamate [94]. However, excessive modifying reagents may adsorb PAHs and reduce the sensitivity of SERS. Au NPs decorated with glycidyl methacrylate-ethylene dimethacrylate (GMA-EDMA) were reported for SERS detection of anthracene, phenanthrene, and pyrene in water samples with LODs of $0.93 \times 10^{-7}$, $4.5 \times 10^{-7}$, and $1.1 \times 10^{-7}$, respectively [95]. Inorganic-organic hybrid nanocomposite has been used as a fiber coating for SPME of PAHs. It is composed of ZnO NPs, polythiophene, and hexagonally ordered silica (ZnO/PT/SBA-15) [96]. The material was successfully applied in HS-SPME due to its thermal stability, and detection limits were found between 8.2 and 20 pg$\cdot$mL$^{-1}$. Table 9 shows some metal and metal oxide NPs used in the extraction of PAHs. To enhance the selectivity of metal and metal oxide NPs, they can be functionalised with organic frameworks. This involves incorporating metal ions or metal oxides into organic ligands that have an affinity for the target analyte. The organic ligand acts by providing interaction sites for PAHs while the metal and metal oxide NPs increase the surface area of the interaction. When organic ligand functionalised metal and metal oxide NPs also contain magnetic components, the adsorption can be achieved by dispersing them in solution and then can be easily separated from the matrix by applying an external magnet.

*4.3. Carbon NPs.* Carbon-based nanomaterials form a diverse group of nanomaterials, and these include graphene, carbon black, graphene oxide, and carbon nanotubes. All have been reported as sorbents in the analysis of PAHs (Table 10). Application of carbon NPs (CNPs) in SPE and SPME has shown higher extraction yields and thermal stability compared to other materials such as polydimethylsiloxane (PDMS) and PDMS/divinylbenzene [110]. The characteristic structures and electronic properties of CNPs allow them to interact strongly with organic molecules via hydrogen bonding, $\pi$–$\pi$ stacking, and electrostatic and van der Waals' forces. Depending on the synthesis process, multiwalled carbon nanotubes (MWCNTs), fullerene, graphene platelets, or carbon nanohorns can be generated [111]. The surface of CNPs can be modified with oxygen-containing groups such as carboxylic, carbonyl, and hydroxyl to make them more hydrophilic materials suitable for sorption of relatively low-molecular-weight and polar compounds [112]. Fullerene has been applied successfully in headspace in-tube extraction of eight PAHs with LODs ranging from 10 to 300 ng$\cdot$L$^{-1}$ [113]. Carbon black was used to adsorb benzopyrenes with well-known toxic properties on its surface, and this is due to its hydrophobic character [114]. Graphene is a two-dimensional nanomaterial composed of a single layer of carbon atoms and can be chemically functionalised through graphene oxide with ease. Owing to the similarity in the chemical structure, it is common to treat graphene as the parent form of graphite, fullerenes, and carbon nanotubes. Graphene nanomaterials have been used for the adsorption of phenanthrene [115], and in this manner, graphene nanosheets and graphene oxide show better adsorption capacities than those of carbon nanotubes

Table 9: Some metal and metal oxide NPs used in the extraction of PAHs.

| Nanoparticles | No. of PAHs | Matrix | Extraction technique | Detection method | Amount of sorbent | Extraction time (min) | Recovery (%) | LOD (ng·mL$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| ZnO/Pt/SBA-15 | 7 | Water | HS-SPME | GCMS | — | 30 | — | 0.0082–0.02 ng·mL$^{-1}$ | [96] |
| Green IONPs | 2 | Water | Semipilot plant | HPLC | 90 mg | 150 | — | 98.5–99 ng·mL$^{-1}$ | [59] |
| UiO-66 | 9 | Rain water, lake water | SPME | GC | 40 mg | 40 | 87.7–108 | 10–30 ng·L$^{-1}$ | [97] |
| Ag NPs | 16 | Underground water | SPME | GC-FID | — | 60 | 74.9–122 | 0.6 ng·mL$^{-1}$ | [98] |
| CTAB/$TiO_2$ | 8 | Water | $\mu$-SPE | HPLC | 90 mg·L$^{-1}$ | 60 | 75–114 | 0.026–0.82 $\mu$g·L$^{-1}$ | [99] |
| PEDOT@Au NPs | 5 | Water | SPME | GC | 0.05 M PEDOT, Au NPs/PEDOT 10/1 | 40 | 89.9–112 | 2.5–25 ng·L$^{-1}$ | [100] |
| Ag NPs/$TiO_2$/Ti | 6 | Soil | UAE/SPE | HPLC-FID | — | 90 | 70.32–115.51 | 0.0015–0.4 ng·g$^{-1}$ | [101] |
| $TiO_2$ nanotube | 4 | Water | SPME | GC | — | 60 | 70.83–119.28 | 0.1 $\mu$gL$^{-1}$ | [102] |
| Au NPs | 1 | Drinking water | SPE | LETRSS | 950 $\mu$L | 5 | 87.5–96.5 | 0.05–0.2 ng·mL$^{-1}$ | [103] |

Table 10: Some CNPs used in the extraction of PAHs.

| Nanoparticles | No. of PAHs | Matrix | Extraction technique | Detection method | Amount of sorbent (mg) | Recovery (%) | LOD () | Ref. |
|---|---|---|---|---|---|---|---|---|
| G-FeCo | 2 | Water | MSPE | GCMS | 4 | — | 0.002–0.2 ng·mL$^{-1}$ | [104] |
| MWCNT | 16 | Surface water | FI-SPE | GCMS | 25 | 72–93 | 0.001–0.15 $\mu$g·L$^{-1}$ | [105] |
| MWCNT | 16 | Water | SPE | GCMS | 150 | 70–127 | 2.0–8.5 ng·L$^{-1}$ | [106] |
| GO/$SiO_2$ | 14 | Cigarette smoke | SPE | GCMS | 100 | 73–116 | 0.05–0.36 ng/cig | [107] |
| Gr/$SiO_2$ | 6 | Water, milk | SPE | HPLC | 30 | 89–115 | 0.0029–0.052 $\mu$g·L$^{-1}$ | [108] |
| MWCNT/PVA | 3 | Water | SPE | HPLC | 15% | 89–98 | 5–8 ng·L$^{-1}$ | [109] |

and granular activated carbon in the presence of synthetic organic contaminants [116]. Despite its high adsorption capacity, graphene tends to aggregate, and some researchers tried to combine it with other nanomaterials to solve this problem. Zhao et al. [117] introduce hydrophilic sulfonic acid groups to the surface of graphene which increased the adsorption capacity for naphthalene (2.326 mmol·g$^{-1}$) and 1-naphthol (2.407 mmol·g$^{-1}$) [117]. Graphene oxide contains many oxygen functional groups such as epoxy and hydroxyl groups which enable good dispersion of it in many solvents compared with graphene [118]. Graphene oxide nanosheet bonded with silica-coated $Fe_3O_4$ microparticles and graphene oxide surface modified with 2-phenylethylamine were reported for the extraction of 10 PAHs from aqueous matrices with an LOD value of 0.005–0.1 $\mu$g·L$^{-1}$ [119]. Graphene oxide embedded in silica fiber was also reported for extraction of PAHs from river and pond water with an LOD value of 0.005–0.08 $\mu$g·L$^{-1}$ [120]. A significant advantage of graphene is that it can be synthesized from graphite, a very common and cheap material without using a metal catalyst.

Carbon nanotubes (CNTs), especially multiwall CNTs (MWCNTs), have attracted great attention in different research fields as sorbent materials due to their physical and chemical properties and hydrophobic and $\pi$–$\pi$ interactions with PAHs [121, 122]. MWCNTs have been used as sorbents packed inside a porous polypropylene membrane in SPE microcolumns for monitoring PAHs in water samples [123, 124]. The results show an LOD of 4.2–46.5 ng/L [125]. Also, MWCNTs have been combined with polyvinyl alcohol cryogel (MWCNTs/PVA) to form composites used for extraction and preconcentration of PAHs in water samples [109]. Despite the wide uses of MWCNTs composites in PAHs extraction, different limitations were reported, and these include technically complex and longtime of preparation with high costs, in addition to their agglomeration due to their high hydrophobic nature which hinders the PAHs adsorption processes [126, 127]. Recently, the combination of MWCNTs composite and MNPs can be promising to overcome these limitations [128]. MWCNT oxide immobilised on pyrrole MNPs ($Fe_3O_4$@PPy-MWCNT) have been used in MSPE for extraction and preconcentration of five PAHs from environmental water samples with LODs of 0.1–0.3 $\mu$g·L$^{-1}$ [129]. Another composite made by caging $Fe_3O_4$ NPs and MWCNTs into calcium alginate beads was used for extraction of benzo(a) anthracene, benzo(a)pyrene, and benzo(a)fluoranthene from water samples with LODs of 5, 5, and 10 ng·L$^{-1}$, respectively [130]. On the contrary, CNTs may affect bioavailability and toxicity of organic contaminants in the environment [131–133]. Recent studies have reported the influence of MWCNTs on the fate of PAHs and other organic contaminants. MWCNTs minimise the toxicity of highly bioavailable PAHs in a sandy loam soil and increase pyrene degradation in a sandy clay loam soil [134]. A novel application of CNPs is the combination of magnetisation and functionalisation of their surface with organic groups that have an affinity for PAHs. As mentioned, the major challenge with the application of CNPs is their tendency to aggregate in aqueous solutions due to the hydrophobic nature of their surfaces. Coating on other NPs materials such as silica and magnetite or the incorporation of a small hydrophilic group such as sulfonic acid can be used to solvate CNPs.

*4.4. Magnetic and Magnetised NP.* Another new trend is to couple different NPs with a magnetic material such as magnetite $Fe_3O_4$ and maghemite Y-$Fe_2O_3$. This technique is based on the use of magnetic nanoparticles (MNPs) which provide rapid extraction ability and excellent efficiency. The method includes the use of adsorbents attached to nanoparticles that can be separated by a magnetic field. The surface modification of MNPs with a suitable coating is very important to get an efficient extraction of target analytes and prevent agglomerisation/aggregation of MNPs by van der Waals' forces or magnetostatic interaction [69]. Metal/metal oxides, silica, or graphene organic functionalised framework can be dopped with $Fe_3O_4$. The coating of nanomaterials by inorganic substances (e.g., silica, $MnO_2$, graphene, and carbon nanotubes) and organic substances (e.g., molecularly imprinted polymers, chitosan, polypyrrole, and surfactants) stabilises the magnetic shell and prevents their oxidation providing different applications. Different organic functional groups such as 1,3,5-triformylphloroglucinol, styrene-divinylbenzene, tert-butyl methacrylate, octadecyl-3-methylimidazolium, and 1,3,5-benzenetricarboxylic acid have been used as modifiers for NPs surface due to their affinity for PAHs. $Fe_3O_4$ magnetic NPs modified with polyfuran (PFu/$Fe_3O_4$) was used as an adsorbent for the magnetic solid-phase extraction of some PAHs in water and urine samples, the LODs range was 0.02–0.05 ng·mL$^{-1}$, and the relative recovery was between 87.3 and 99.2% [135]. Some drawbacks of reported modified sorbents include tedious preparation and time-consuming and usually involve toxic reagents. Fats and oils were used as economical and ecofriendly hydrophobising agents in modifying the surface of MNPs. Among them is the palm fatty acid used to functionalise MNPs (MNP-FA) [136] (Table 4). Also, another green method used for the reduction of PAHs in marine sediment was enhanced by using magnetic bamboo biochar [137]. Wood biochar supported by magnetite NPs ($Fe_3O_4$-WB) was found as an efficient catalyst for the removal of high-ring PAHs with the highest degradation rates for the 6-, 5-, and 4-ringed PAHs being 90, 84, and 87%, respectively [138]. Polydopamine coated $Fe_3O_4$ NPs ($Fe_3O_4$/PDA) has been successfully used as an adsorbent for determination of trace PAHs in environmental samples. $Fe_3O_4$/PDA adsorbents are environmentally friendly and simple, and no toxic materials or organic solvents were used [139]. Magnetic and magnetised NPs are the most used nanosorbents in the isolation of PAHs (Table 11). Magnetic NPs can be attached to the desired molecules, conferring magnetic properties to the targets and then with a rapid and simple separation by using an external magnetic field.

## 5. Optimisation Conditions of NP Efficiency

Several parameters such as desorption solvent, type and amount of adsorbent, pH, and ionic strength can affect the extraction efficiency of NPs. In order to obtain quantitative recoveries, selection of an appropriate desorption solvent to elute the target analytes from adsorbent is necessary. Organic solvents like hexane, acetone, methanol, toluene, dichloromethane, ethyl acetate, acetonitrile, and a mixture of them have been used for desorbing PAHs. The effect of desorption solvent volume should be investigated to improve the elution of an analyte from the adsorbent. Nonpolar organic solvents were found to improve the recovery toward PAHs with a higher ring number [144]. In the extraction of PAHs from water samples by using synthesized MWC nanotube oxide immobilised in the pyrrole magnetic NPs, seven organic solvents which had a broad range of polarities were used for desorption of the adsorbed PAHs. 2-Propanol was chosen as the best elution solvent [129]. In another study where a nanocomposite consisting of silica-coated magnetite and phenyl functionalised graphene oxide used for extraction of PAHs from an aqueous matrix, a mixture of acetonitrile : tetrachloroethylene (CAN : $C_2Cl_4$) has shown a better elution capability toward all PAHs [119]. Acetonitrile was selected as the best desorption solvent for 6 PAHs extracted from water samples by using polydopamine-coated $Fe_3O_4$ NP ($Fe_3O_4$/PDA) [71].

Type and amount of nanomaterials will also influence the analyte desorption. For PAHs, MWCNTs composites were described as less prone to aggregation than single-walled CNTs [128, 145]. Other studies show that $Fe_3O_4$/CNS/PPy sorbent exhibits the higher extraction efficiency for PAHs compared to the $Fe_3O_4$/PPy sorbent [141]. The main advantages of NPs adsorbents are the large surface area and high extraction capacity. Therefore, better extraction capacity can be achieved with fewer amounts of NPs compared to microsized sorbents. In many studies, it has been observed that the peak area of PAHs increases as the amount of nanosorbent increases. This is due to accessible active sites of adsorbents for interaction with the analyte; after that, the extracted amount of PAHs was almost constant; hence, the suitable amount of NPs can be optimised [136]. In another study where the silica-based organic-inorganic nanohybrid material ($NH_2$-SBA-15) was used

Table 11: Some magnetic and magnetised NPs used in the extraction of PAHs.

| Nanoparticles | No. of PAHs | Matrix | Extraction technique | Detection method | Amount of sorbent (mg) | Extraction time (min) | Recovery (%) | LOD | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| MNP-FA | 4 | Leachate, sludge | MSPE | HPLC-DAD | 15 | 15 | 81.1–119.3 | 0.01–0.05 $ng \cdot mL^{-1}$ | [136] |
| $Fe_3O_4$-CTAB | 15 | Water | SPE | UPLC-FLD | 50 | 5 | 59.23–87.95 | 0.4–10.3 $ng \cdot mL^{-1}$ | [140] |
| $Fe_3O_4$-PDA | 6 | Water | SPE | HPLC | 20 | 5 | 76–107 | 0.51–1.92 $ng \cdot L^{-1}$ | [139] |
| $Fe_3O_4$/MWC/alginate composite | 3 | Water | MSPE | HPLC-FID | 200 | — | 92–97.7 | 0.005 $ng \cdot mL^{-1}$ | [130] |
| $Fe_3O_4$/CNS/ppy | 5 | Water | MSPE | GC-FID | 20 | 10 | 88.9–99 | 0.01–0.05 $ng \cdot mL^{-1}$ | [141] |
| $Fe_3O_4$@ppy-MWCN | 5 | Water, soil | MSPE | GCMS | 13 | 3 | 85.4–106.8 | 0.001–0.003 $ng \cdot mL^{-1}$ | [129] |
| $Fe_3O_4$/MWCN | 7 | Water | MSPE | UHHPLC | 5 | 5 | 76.4–106.5 | 0.025–0.73 $ng \cdot mL^{-1}$ | [128] |
| $Fe_3O_4$@$SiO_2$-GO-PEA | 10 | Water | MSPE | GC-FID | 30 | 5 | 0.005–0.1 | 71.7–106.7 $ng \cdot mL^{-1}$ | [119] |
| $Fe_3O_4$@Agcore@shell | 5 | Water | MSPE | HPLC-UV | 50 | 20 | 0.02–0.1 | 82.4–109 $ng \cdot mL^{-1}$ | [142] |
| COF-LZUI@ | 6 | Water | MSPE | HPLC | 5 | 30 | 90.9–107.8 | 0.2–20 $pg \cdot mL^{-1}$ | [143] |
| PEI@ $Fe_3O_4$ | 6 | Soil | MSPE | HPLC | 5 | 30 | 85.1–105 | | |
| Magnetic Au-$NH_2$-MCM-4 | 5 | Seawater | DLLME | GC-FID | 30 | 5 | 91.4–104.2 | 0.002–0.004 $\mu g \cdot L^{-1}$ | [91] |

for removal of naphthalene, acenaphthylene, and phenanthrene from wastewater, the removal efficiency was increased significantly as the adsorbent amount increased due to the increase in the contact surface of the adsorbent and greater availability of adsorbent [146].

Effect of salt concentration is commonly studied in many extraction methods in order to enhance enrichment performance. This can be achieved by decreasing the solubility of the analytes in the aqueous phase and enhancing their partitioning onto the sorbent or organic phase. The solubility of PAHs decreases with increasing molecular weight or number of aromatic rings [147]. Higher recoveries were obtained for PAHs with four or more aromatic ring at a lower amount of salt. In contrast, the PAHs with a lower number of rings (3 rings) and high amount of salt result in better extraction efficiency. It has been observed in another study that the adsorption capacity of pyrene increased when the concentration of KCl increased. This result was attributed to the salting-out effect. Since the adsorption mechanism of pyrene was mainly caused by hydrophilic interaction, as the ionic strength increased, the solubility of pyrene and the activity coefficients in solution decreased which induce the adsorption of pyrene [148].

The effect of pH on extraction efficiency was studied. The pH ranges of 3–11 have been studied for PAHs, and no significant effect of pH on extraction efficiency was observed [119]. PAHs exist as neutral molecules in aqueous solutions and $\pi$–$\pi$ interactions between adsorbent and PAHs are not affected by changing the pH value. On the contrary, NPs functionalised with palm fatty acid (MNP/FA) and high recoveries of four selected PAHs were obtained at pH 6.5 and lower recoveries were observed when pH was higher or lower. This can be explained by considering the charged species and charge density on the surface of the nanosorbent [136]. It has also been observed that the adsorption capacity of pyrene onto SBA-15 and MCM-41 decreased when the pH values increased in a single system. This result was explained by the electrostatic interaction between adsorbents and contaminants. The change of pH values affects the electrical conductivity of the surface of SBA-15 and MCM-41 greatly. Pyrene has an electron-rich $\pi$-ring; therefore, the electrostatic attraction between pyrene and the two adsorbents is weakened, resulting in a decrease in the adsorption capacity for pyrene [148]. The pH of the solution affected the surface charge of the adsorbents and the degree of ionisation and speciation of different pollutants. The removal rate of 3 PAHs (naphthalene, acenaphthylene, and phenanthrene) was increased at a lower pH, and this is due to the formation of $NH^{3+}$ on the surface of the nanohybrid adsorbent ($NH_2$-SBA-15). Consequently, the electrostatic interaction between surface charges of the adsorbent and PAHs increased due to the $\pi$-electron-rich character of PAHs [146].

## 6. Conclusion

Recently nanotechnology is one of the most active areas in modern science and its development is impacting human life. Novel applications of NPs are renovated in various fields such as health, environment, drug-gene delivery, biomedical food and feed, mechanics, optics, and chemical and space industries. NPs are known to have unique properties owing to their high surface area and sorption capacity; they have been successfully applied in the isolation of PAHs from sample matrix solutions. The extraction techniques used to isolate PAHs have been highlighted including their advantages and limitations. Different methods for NPs synthesis have been discussed in this paper, and it is necessary to develop the nonhazardous and green biological methods for NPs synthesis. Challenges in the application of adsorbents for PAHs are related to the lack of functional groups on

PAHs that can be targeted. Nanosorbents that have been applied in the analysis of PAHs were reviewed, and these include mesoporous silica NPs, CNTs, metal and metal oxides, novel advancements of NPs functionalised with organic groups that have a high affinity for PAHs, and application of magnetic and magnetised NPs to improve extraction efficiency. One of the most important issues that need more investigation is how to make safe disposal of NPs. The effect of the prolonged exposure to NPs on human health and the environment needs to be assessed completely before their large-scale production. The small size of NPs allows them to easily access the skin, lung, and brain and causes adverse effects [149]. Green synthesis of NPs can be developed as an alternative to produce more environmentally friendly NPs.

## Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this article.

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