



Nanotechnology to remove polychlorinated biphenyls and polycyclic aromatic hydrocarbons from water: a review

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Abstract

Persistent pollutants cause adverse effects to human and environmental health. Most polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) are toxic and stable in the environment, yet their removal is rarely targeted by conventional remediation methods. Alternatively, nanotechnology appears promising for contaminant removal. Indeed, nanomaterials have unique size-dependent properties due to their high specific surface area. Nanomaterials also possess fast dissolution properties, strong sorption, supermagnetic characteristics and quantum confinement. This manuscript reviews the application of nanotechnologies for the removal of PCB and PAH from contaminated water sources.

Keywords Carbon nanotubes · Iron oxides · Nanomaterials · Photocatalytic nanocomposites · Polychlorinated biphenyls · Polycyclic aromatic hydrocarbons

Introduction

As the world's population and industrialization continue to grow, so does the demand for clean water. Expanding industrial output along with uncontrolled waste discharge, however, has led people to lose harmony with their immediate environment (Al-Qodah and Al-Shannag 2017; Karataş and Karataş 2015). This has resulted in serious water contamination problems around the world due to the increasing amounts of pollutants that are being discharged into water bodies. Persistent pollutants are an important category of environmental pollutants given that they can remain unrecognized either because they are not commonly monitored or because of the limits imposed by the available detection methods (Geissen et al. 2015; Mahamadi 2019). These pollutants, which can be synthetic or naturally occurring chemicals, are of a rising concern given their potential to cause adverse ecological and/or negative human health impacts (Geissen et al. 2015).

Persistent organic pollutants are extremely diverse in nature and are classified into more than 20 classes (Geissen et al. 2015). Few of the prominent categories are: pharmaceuticals, pesticides, disinfection by-products, and industrial chemicals (Ritter et al. 1995). Among vastly encountered pollutants are aromatic hydrocarbons which can be chlorinated, such as in the case of polychlorinated biphenyls and organochlorine pesticides such as dichlorodiphenyltrichloroethane, polybrominated diphenyl ethers, and hexachlorocyclohexane, or non-chlorinated, such as in the case of the combustion by-products that are presented as polycyclic aromatic hydrocarbons (Han and Currell 2017; Lammel et al. 2015).

The potential serious environmental and human health risks posed by such pollutants have led to the initiation of treaties including the United Nations' Aarhus Protocol, Stockholm Convention (UNEP 2009). These treaties were aimed at eliminating or at least restricting the production and use of such polluting chemicals. The lack of knowledge on the behavior of these pollutants in the environment and the lack of optimized analytical and sampling techniques have both entailed urgent actions at multiple levels related to water purification technologies (Aparicio et al. 2017; Geissen et al. 2015; Tobajas et al. 2017).

PCB and PAH are known to be highly stable chemical compounds. Although their hydrophobicity limits their water solubility, their high toxicity is usually aggravated by the

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accumulation of these compounds in the living tissues over time. Even when present in low amounts in water, these contaminants will have significant environmental impact (Henriquez-Hernandez et al. 2017; Petrie et al. 2015), in particular that conventional water treatment processes are not effective in the treatment of these contaminants (Ncibi et al. 2017).

Due to their hydrophobic nature, PCB and PAH tend to accumulate in very high concentrations in sediments of aquatic environments by being adsorbed onto the sediments and the sediment organic matter. As a consequence, natural water sources are affected by the continuous release of these pollutants, even when the overlying water body undergoes treatment. PCB and PAH can also easily accumulate in food chains, especially in the fatty tissues given their high fat solubility, and thus their toxicity effects can easily be transferred to humans through the ingestion of these food resources (Unyimadu et al. 2017). Accordingly, there is a need to develop efficient technologies for treating and managing waters laden with such pollutants which are deemed to be cost-effective, reliable, sustainable, and environmentally friendly options (Capodaglio 2017; Ugya and Fidelis 2016).

One of the recently introduced technologies that present promise in the treatment of contaminated water is nanotechnology. Nanotechnology holds great potential to bring water treatment one step forward to enhance the quality of water supply (Bhati and Rai 2017; Mahamadi 2019; Qu et al. 2013). The present review addresses recently introduced nanotechnologies for the treatment of two major groups of pollutants, namely PCB and PAH, and highlights the limitations in their application and identifies areas for further study to arrive at sustainable field applications.

Polychlorinated biphenyls and polycyclic aromatic hydrocarbons in water

PCB are a group of compounds composed of around 209 individual chlorinated hydrocarbons containing different numbers of chlorine atoms per molecule (Baqar et al. 2017). Due to their bioaccumulation and resistance to biodegradation, the discharge of these polluting compounds into water causes a serious threat to the environment as well as to public health (Samia et al. 2018; Yu et al. 2012). These compounds were widely used in plasticizers, different coatings, inks, glues, fire retardants, insecticide extenders, as well as paints. PCB are relatively heat stable and can withstand both acids and alkalis, which render them of value in an extensive variety of applications including transformers, capacitors, and lubricants (Afghan and Chau 2017). Environmental contamination occurs as a result of the discharges from the various industrial activities where PCBs are used (Selene and Chou 2003; Xu et al. 2012).

Ecological exposure to PCB has been reported to cause carcinogenic, endocrinal reproductive neurotoxic, pathological, and immunological complications (Baqar et al. 2017). Due to health complications and environmental impacts, the use of PCB has been restricted or banned in many countries (EPA USEPA 1992). Consequently, their usage was limited to certain allowable levels and domains of production (Davies and Delistraty 2016).

PCB were first recognized to present a serious risk in the 1960s, and their production and use were consequently banned in several countries during the 1970s, mostly in developed countries that included the USA, UK, and Japan (Reddy et al. 2019). However, their hazardous character was not sufficiently recognized nor addressed in many other areas around the world (Quiroz et al. 2008). Despite the production ban and restrictions imposed, PCB are still being used in several developing countries and in a number of developed countries (Habibullah-Al-Mamun et al. 2019; Mahmood et al. 2014; Men et al. 2014; Starling et al. 2019) and consequently contributing to PCB pollution (Habibullah-Al-Mamun et al. 2019).

The incessant use and disposal of old materials that were dependent on PCB also contribute to environmental pollution (Habibullah-Al-Mamun et al. 2019). In this context, it deems necessary to control the discharge of PCB into the environment and also arrive at water treatment technologies that will effectively and sustainably eliminate any PCB that may be present in water sources.

PAH are among the organic compounds that have aroused attention for their potential carcinogenic effects (Kumar et al. 2016). PAH are hydrocarbons composed of 2 or more aromatic benzene rings that are ubiquitous in the environment (Abdel-Shafy and Mansour 2016; Manoli and Samara 1999; Sun et al. 2017). PAH are commonly used in many applications, such as in the production of dyes, pigments and plastics, wood preservatives, agrochemical production, and even in pharmaceutical industries (Abdel-Shafy and Mansour 2016).

The influx of PAH into the environment is severely impacted by anthropogenic processes, especially in aquatic environments where PAH are discharged into water bodies and ultimately accumulate in the sediments (Barra et al. 2008; De Almeida et al. 2018) at very high concentrations (703–3302 ng/g) (Mirza et al. 2012). The Environmental Protection Agency (EPA) lists PAH among the primary contaminants, of which 16 are considered priority pollutants, ranging from the two-ringed to six-ringed PAH (Ćirić et al. 2018).

PAH can enter the environment through different anthropogenic pathways, and thus are divided into two groups based on the source of the pollution, which is either petrogenic or pyrogenic. Petrogenic PAH contamination events result mainly from crude oil and oil-refined products

entering the aquatic ecosystem such as during accidental spills and contaminated runoff. Pyrogenic sources are also important given that they add to the existing pollution through the deposition of PAH that are produced from the incomplete combustion process of organic matter (Barakat et al. 2011; Richter-Brockmann and Achten 2018).

PAH are extremely stable, and thus can easily be transported over long distances in the form of gases given their apparent resistance to degradation when bonded onto atmospheric particulates, and ultimately deposit onto ecosystems including water bodies (Manoli and Samara 1999). Once settled, these hydrophobic contaminants would be adsorbed onto organic particulates and tend to persist given their slow natural biodegradation rate (Barakat et al. 2011; Yang et al. 2019). In view of the high toxicity of many PAH, their presence poses a high risk even at low concentrations. In addition, their tendency to accumulate in food chains could easily lead to human exposure (Srogi 2007).

After entering the aquatic environment, the behavior and fate of PAH depend on their physiochemical properties such as chemical stability, water solubility, and adsorbability (Djomo et al. 2004). Humans are prone to PAH exposure mainly through inhaling contaminated air, ingesting polluted water, and consuming contaminated food such as fish (Manzetti 2012). Many PAH are known to be carcinogenic and mutagenic, and as such exposure to PAH poses high health risks (Bortey-Sam et al. 2015). Some known carcinogenic PAH include benzo[a]pyrene, naphthalene, chrysene, and benzo[b]fluoranthene (Abdel-Shafy and Mansour 2016).

Nanotechnology for water treatment

Complementing conventional water treatment processes with nano-based technologies should offer novel opportunities in advancing the water treatment industries, particularly that current technologies have reached a state of saturation in providing adequate water quality, especially in the presence of persistent and emerging pollutants (De La Cueva Bueno et al. 2017; Teow and Mohammad 2017).

Nanomaterials exhibit intrinsic unique properties such as fast dissolution, high reactivity, and strong sorption, along with discontinuous properties including super magnetism, localized surface plasmon resonance, and quantum confinement effects (Baruah et al. 2015; Gehrke et al. 2015). Among the various types of nanomaterials that have been applied for water treatment are nanoadsorbents, nanometals and nanometal oxides, as well as membrane and photocatalytic processes (Baruah et al. 2015).

Nanoadsorbents present significant advantages because of their extremely high specific area and associated sorption sites, short intra-articular diffusion distance, tunable pore size and surface chemistry, as well as their high rates of

adsorption for inorganic compounds such as heavy metals and micro-pollutants (Anjum et al. 2016; Qu et al. 2013). The current research tends to focus on four different types of nanoadsorbents, namely metal-based nanoadsorbents, carbon-based nanomaterials, polymeric nanoadsorbents, and zeolites (Gehrke et al. 2015; Mhlanga et al. 2007).

Nanoscale metal oxides are reported as promising alternatives for use in the removal of heavy metals and radionuclides (Xue et al. 2016). They include nanosilver and nano-TiO₂, which are used for water disinfection, prevention of biofouling, and decontamination of organic compounds. Nanosilver exhibits bactericidal attributes with low human toxicity, but has limited durability (Kim et al. 2012), whereas nano-TiO₂ has high chemical stability along with a very long lifetime; however, it requires ultraviolet activation (Gehrke et al. 2015). Magnetic nanoparticles (magnetite Fe₃O₄) are used in groundwater remediation, particularly for removal of arsenic, and are simply recovered by the application of a magnetic field; however, they require stabilization (Kim et al. 2011). Nano-zero-valent iron has a short half-life due to its high reactivity and also requires stabilization, thus limiting its use for certain (specific) applications (Matlochová et al. 2013).

Carbon nanotubes have been found to be highly efficient in the adsorption of organic matter due to their large specific surface area and diverse contaminant-carbon nanotubes interactions and thus can aid in the removal of a variety of organic contaminants (Yang and Xing 2010). Drawbacks for carbon nanotubes include high production cost and possible health risks (Qu et al. 2013).

Polymeric nanoadsorbents used in the removal of organics and heavy metals have the highlighted advantage of bifunctional property, whereby the inner shell branches have the capacity to adsorb organics, whereas the outer shell adsorbs heavy metals (Yang et al. 2019). A downside for polymeric nanoadsorbents is their complex multistage production process (Tiwari et al. 2008).

Zeolites constitute a new versatile low-cost nanomaterial that can be used for wastewater treatment and water desalination (Duke et al. 2009; Sutisna et al. 2017). Zeolites present a charged, permeable, and thick polyamide active layer, which, combined with their porous structure, provide a high surface area characterized by hydrophilic pores that form potential paths for water flow (Duke et al. 2009; Qu et al. 2013; Yurekli 2016).

Membrane separation processes act as a barrier for different contaminants depending on the membrane pore size and the particular substance to be removed (Kusworo et al. 2018). In particular, nanofiltration membranes have been successfully used for removing hardness, color, odor, and heavy metals. They possess a high selectivity along with a charge-based repulsion mechanism but require considerable energy for operation and are prone to fouling (Han et al.

2013). Nanocomposite membranes, on the other hand, are a fouling resistant membrane filtration option that have thermal/mechanical robustness and are commonly applied for removal of micro-pollutants in reverse osmosis water treatment (Bhati and Rai 2017; Gehrke et al. 2015).

Photocatalysis is an oxidation process where organic contaminants are degraded by photocatalytic oxidation. This is achieved by combining ultraviolet light rays with a catalyst-coated filter. Photocatalysis has the advantages of high availability, limited toxicity, cost efficacy, and known material characteristics (Gehrke et al. 2015; Bai et al. 2017). TiO_2 nanoparticles are widely used as a photocatalyst because of their supermagnetic photocatalytic ultraviolet activity, low human toxicity, high stability, and low cost (Chong et al. 2010). In addition, the effectiveness of TiO_2 as a photocatalyst is highly increased when combined with other nanoparticles (Gehrke et al. 2012).

The aforementioned materials and processes were all investigated for the removal of persistent pollutants from aqueous solutions including contaminated water sources. Major findings in this context are discussed in the following sections, with the main focus directed at applications for the removal of PCB and PAH from water. As shown in Fig. 1, this manuscript attempts to evaluate the effectiveness of the most commonly employed nanotechnologies as specifically

applied to the treatment of the targeted pollutants. The aim of this work is to review nanomaterials on the removal of PCB and PAH from water resources. This review discusses removal approaches by carbon-based nanomaterials, iron oxide nanomaterials, photocatalytic nanocomposites, and some other miscellaneous nanomaterials.

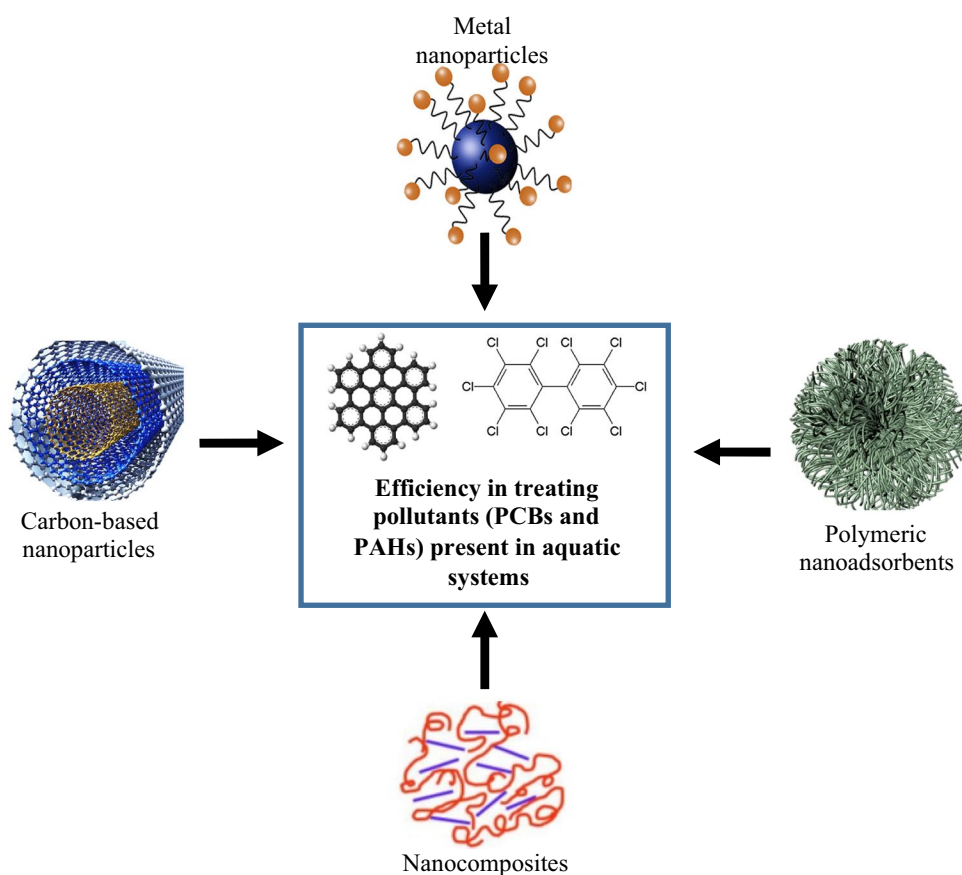
Carbon-based nanomaterials for the removal of polychlorinated biphenyls and polycyclic aromatic hydrocarbons

Different carbon-based nanomaterials have been tested for the removal of PCB and PAH from water and wastewater. Some of the highlighted carbon-based material in the literature includes carbon nanotubes, graphene oxides, and carbon-based nanomaterials coupled with different functional groups.

Carbon-based nanomaterials for the removal of polychlorinated biphenyls

Carbon nanotubes are considered among the most significant materials that helped prompt nanotechnological research (Ravelo-Perez et al. 2010). They have shown to

Fig. 1 Nanomaterials used for the removal of polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) from aquatic systems. These materials include: carbon-based nanomaterials such as carbon nanotubes and graphene oxides; nanoscale metallic oxides including TiO_2 and Fe_3O_4 ; nanocomposites covering photocatalytic nanocomposites; and polymeric nanoadsorbents. Other nanomaterials including nanocomposites of nanoscale zero-valent iron and nanoclays can be used as well



possess superb adsorption capacities which aid in the efficient removal of many organic contaminants from large volumes of wastewater (Wang et al. 2014b). Carbon nanotubes exhibit uniqueness with their massive specific surface area, external diameter, and huge mesoporous volume (Ye et al. 2007). In addition, they exhibit good conductivity, structural regularity, chemical inertness, and mechanical and thermal stability, which render them ideal as a coating material (Zhu and Diao 2011). Carbon nanotubes are further divided into two groups, single-walled and multi-walled carbon nanotubes, both of which have been tested for the removal of PCB and PAH from water (Yu et al. 2017). Furthermore, studies showed that functionalization of carbon nanotubes' surface with functional groups such as $-OH$, $-NH_2$, $-COOH$ improves their adsorption capacities (Patino et al. 2015; Sherlala et al. 2018).

For example, a study by Shao et al. (2011) grafted methyl methacrylate on multi-walled carbon nanotubes by using N_2 plasma technique (MWCNT-g-pMMA)-induced grafting. The interaction between the oxygen containing functional groups of methyl methacrylate on the walls of the multi-walled carbon nanotubes enhanced the removal of PCB from water. The application of this composite in large volumes of aqueous solutions showed more than 95% removal of PCB under ambient conditions in 24 h. The removal of PCB by the mentioned nanoadsorbent was found to be pH dependent, where the removal efficiency works best in a medium of pH 2–10 and decreases as pH exceeds 10 (Shao et al. 2011).

Mahdavian and Mousavi (2016) studied the removal of PCB by single-walled carbon nanotubes, where results showed complete removal of PCB using this nanomaterial at ambient conditions (Mahdavian and Mousavi 2016). In a study by Shao et al. (2010), β -cyclodextrin was grafted on to the walls of multi-walled carbon nanotubes. The synthesized nanomaterial exhibited high removal efficiency toward PCB (> 95%) at an adsorbent content of 0.04 g/L for 50 h contact and equilibrium time. This indicates that this nanocomposite has a very high adsorption capacity toward PCB, and it is pH independent (Shao et al. 2010).

Graphene oxide, a relatively novel carbonaceous nanomaterial, has demonstrated pronounced promise in several applications (Chen et al. 2012; Mahgoub 2019). Graphene oxide has gained attention due to its unique properties, especially given that it can be easily functionalized with a variety of functional groups (Thombal and Jadhav 2016). It is distinguished by its surface O-functionalities which increase its hydrophilicity while remaining stable under common environmental conditions (Balasubramani and Rifai 2018; Kim et al. 2010). Moreover, it has been shown that colloidal graphene oxide nanoparticles may act as effective contaminant carriers as well (Pavagadhi et al. 2013).

A study performed by Ren et al. (2018), for instance, highlighted the expediency of graphene-based nanomaterials

as an excellent adsorbent for PCB28 and as a promising nanomaterial for application in environmental remediation. Results of their study showed high efficiency (> 99%) of graphene nanomaterials toward the adsorption of PCB from aqueous solutions at very low concentrations of PCB. The efficiency of the removal is mainly attributed to the high surface area of adsorption exhibited by the nanomaterial. Nevertheless, the adsorption efficiency showed minimal or negligible impact of pH on the process, but, was found to be temperature dependent, where lower temperature aids the adsorption process (Ren et al. 2019).

Beless et al. (2014) studied the sorption of different PCB by graphene oxide and found that it can be used as a good sorbent for the removal of PCB from water. Beless et al. did not specify the percentage of removal of PCB from water but stated that the nanomaterial used has high sorption affinity toward PCB removal using Langmuir, Freundlich, and Polanyi–Dubinin–Manes (PDM) models, which showed similar results at ambient conditions (Beless et al. 2014).

Moreover, Tian et al. (2019) studied a hybrid version of graphene oxide and amino-functionalized polypropylene nonwoven graphene oxide (PP-g-DMAEMA/GO) with dual-scale channels structure, for fast removal of PCB from water. This overlapped and intertwined structure nanomaterial assured easy water permeation through the channels to achieve more than 85% removal of PCB from water with a concentration of 1 mg/L of PCB. The conditions for the removal were set at pH 6.5 at 25 °C with 3-h shaking for the assembly of graphene oxide sheets. The results showed a good fit to pseudo-first-order kinetic models. In addition to its fast and easy sorption of PCB, this composite could simply be recovered by washing with an ethanol solution (Tian et al. 2019).

On another note, carbon-based nanomaterials coupled with titanium (IV) exhibited a high PCB removal efficiency and was thus classified as one of the most promising candidates for photocatalytic applications. These materials have been widely used for wastewater treatment due to their electronic properties, viability, high photo-activity, chemical stability, and non-toxicity (Oturán and Aaron 2014; Westerhoff et al. 2011).

Carbon-based nanomaterials for the removal of polycyclic aromatic hydrocarbons

Multi-walled carbon nanotubes were used in a study by Paszkiewicz et al. (2018) for the selective extraction of PAH from an aqueous solution. It was observed that helical multi-walled carbon nanotubes exhibit high sorption abilities, up to 99%, toward PAH removal at very low concentrations. This is attributed to the structure and electronic properties of carbon nanotubes which allow interactions with PAH by

non-covalent forces such as π – π interactions (Paszkiewicz et al. 2018).

Though, non-functionalized carbon nanotubes provide efficient adsorption capacity, yet the possibility for their functionalization offers biocompatibility, high scalability, and large specific area for the removal of pollutants from contaminated aquatic ecosystems. A study by Rasheed et al. (2019) reported on the functionalization of $\text{TiO}_2/\text{SiO}_2$ on carbon nanotubes for the adsorption of PAH for water purification. Functionalized carbon nanotubes appeared to be efficient and good adsorbents for PAH with adsorption efficiencies of > 90%. This was attributed to the high interaction of carbon nanotube sheets with the aromatic rings of the PAH (Rasheed et al. 2019). In general, there is a smaller number of reported studies that have addressed the removal of PAH by carbon nanotubes (Akinpelu et al. 2019); however, a report by Ong et al. (2010) highlights the ability of carbon nanotubes to adsorb PAH from wastewater, and justifies their efficiency as adsorbents for PAH removal from aqueous solutions (Ong et al. 2010).

Graphene oxide nanoparticles gained wide attention due to their ability to remove different pollutants from water including PAH (Hussain et al. 2019). Several studies reported on the adsorption affinity of graphene oxides to PAH and their adsorbing power of a large range of PAH (Amin et al. 2014; Paixão et al. 2018; Wang et al. 2014a). A study by Zhao et al. (2011) reported an excellent performance of sulfonated graphene oxides in the adsorption of many organic contaminants, highlighting its effectiveness for the removal of PAH and their derivatives from water (Zhao et al. 2011). This effective adsorption attribute is ascribed to the graphene oxides' open-layered structure that has a completely accessible adsorption surface for organic molecules (Ji et al. 2013). Zhao et al. (2011) found that 95% of PAH and their derivatives can be absorbed on the surface of sulfonated graphene oxide at pH > 7. The main mechanism for the strong adsorption of organic molecule onto this material was attributed to the π – π interaction between PAH and surface electron of sulfonated graphene oxide nanoparticles, and was fitted into a Langmuir model (Zhao et al. 2011).

Wang et al. (2014a, b) studied the adsorption affinities of graphene oxide nanoparticles for a range of aromatic pollutants. Eight different aromatic hydrocarbons with different physiochemical properties were chosen. Results indicated that graphene oxide nanoparticles exhibited a strong adsorption affinity for all the tested compounds (~ 99%) owing to the dispersion of graphene oxide as single nanoflakes, which maximized the surface area of adsorption (Wang et al. 2014a). Likewise, Wang et al. (2014a, b) studied the adsorption of different PAH by graphene oxide nanosheets and investigated the potential adsorptive sites and molecular mechanisms of the mentioned nanomaterial. Results showed high adsorption affinity of PAH on graphene oxide

nanosheets irrespective of temperature and a specific pH range (Wang et al. 2014b).

Moreover, another study suggested the synthesis of a nano-reduced graphene oxide-hybridized polymeric high-internal phase emulsions (RGO/polyHIPEs) for the removal of PAH from water (Huang et al. 2018). This compound was characterized by an open-cell structure that improved the adsorption mechanism and performance of PAH removal, resulting in treated water having PAH content that is less than the limits set by the European Food Safety Authority for drinking water. This investigated nanomaterial showed 50–90% removal of PAH in 14 h at an increasing temperature (> 25 °C) (Huang et al. 2018).

A separate study by Huang et al. (2019) revealed that magnetic graphene oxide had excellent adsorption properties for the removal of PAH from water. The effects of several environmental factors were studied to optimize the removal mechanism. Results showed 98–100% removal of PAH by the suggested nanomaterial at pH 5 and initial concentration of 100 mg/L of PAH in water. The adsorption mechanism was attributed to the π – π interaction between PAH and magnetic graphene oxide, and the high adsorption capacity due to the large surface area and pore volume of the nanomaterial (Huang et al. 2019).

In summary, the flexibility of graphene oxide nanomaterials showed an obvious impact on the adsorption of PAH. Findings from these studies indicated that colloidal nanoparticles of graphene oxide are highly stable and thus are more important for environmental applications. This is due to possessing abundant active functional groups, which makes it an excellent adsorbent compared to other carbon nanoparticles in the case of PAH removal (Sherlala et al. 2018). Despite the excellent properties of graphene oxide, its high hydrophilic nature, extensive agglomeration, and difficulty in separation from wastewater are considered as drawbacks when suggesting graphene oxide for water treatment. In addition, some functional groups, when functionalized on graphene oxide nanosheets, showed selectivity to certain water pollutants, which demonstrated its ability to treat different aspects/pollutants in water treatment applications (Sherlala et al. 2018).

Nonetheless, assessment of the environmental risk of graphene oxide sheets must be carried out to identify any potential negative impacts and to better recognize their potential adsorption behaviors at a molecular level. Additionally, further studies are also required to better understand the adsorption behavior of graphene nanomaterials in pilot-scale studies that better reflect actual field applications.

Magnetic carbon nanomaterials coupled with metals are also prepared and explored for the removal of PAH from water. A magnetic adsorbent was prepared by integrating Fe_3O_4 nanoparticles on multi-walled carbon nanotubes by Abdar et al. (2016) to study its efficiency in PAH removal

from water samples. Results showed that at optimum conditions, pH 7 at room temperature, the suggested nanoadsorbent can remove up to 99% of PAH in 16 h. The proposed adsorbent could also be easily separated from the sample solution by applying an external magnetic field thus rendering the process to be efficient and environmentally friendly, and can be considered as a potential candidate for PAH removal from contaminated water resources (Abdar et al. 2016).

Overall, carbonaceous nanomaterials have proven their efficiency for the removal of both PCB and PAH due to their unique properties and the variety of forms through which they can be applied (Beless et al. 2014). However, almost all of these materials which demonstrated a high potential for water treatment are yet to be evaluated at the pilot-level scale. The limitation of studies targeting the removal of PAH and PCB is being restricted to a proof of concept under controlled laboratory environments in which most of the involved environmental variables are known and preset. When attempting to scale up a potential treatment approach, there are the additional environmental complexities that are most often uncontrollable, and in most cases unpredictable, which have to be accounted for. For example, application of a specific treatment for a contaminated water resource might simply fail. This might be due to the potential interaction of the adsorbent with nontarget pollutants and with naturally occurring organic matter, which might simply deplete the adsorbent's capacity very fast as compared to laboratory experiments, where the tested waters are usually quality controlled.

Table 1 summarizes the results of different studies addressing the use of carbon-based nanomaterials for the removal of PCB and PAH.

Iron oxide-based nanomaterials

Iron oxide nanomaterials are naturally found in the environment and have proved their efficiency in the removal of a number of persistent pollutants from aqueous solutions (Hassan et al. 2018). They particularly play a positive role in adsorption, which is a widely applied treatment process to remove pollutants from water. Adsorption has several advantages in terms of its effectivity, cost feasibility, flexibility, and simplicity as well as its insensitivity to toxic contaminants (Rafatullah et al. 2010). Because of their small size, iron oxide nanomaterials provide fundamental improvements to the adsorption processes due to their higher surface area (Gutierrez et al. 2017), and selectivity (Zhou et al. 2016). Iron oxide nanomaterials tend to present a favorable option for use in the control of PCB and PAH as is discussed in the following subsections.

Iron oxides for the removal of polychlorinated biphenyls

Iron oxide nanomaterials were investigated for PCB adsorption, particularly for the treatment of large water volumes and enhanced separation through the application of an external magnetic field (Huang et al. 2017). Moreover, studies have addressed the use of iron oxides in combination with other materials to boost the removal of organic pollutants (Mahpishanian et al. 2015; Saharan et al. 2014). For example, a synthesized magnetic nanomaterial with oxide graphene as a functional group, combined with Fe_3O_4 , was reported to achieve good PCB removal results (Geng et al. 2012; Yao et al. 2012). On this note, Zeng et al. (2013) tested Fe_3O_4 -grafted graphene oxide for the removal of PCB 28 from a volume of contaminated water solution using magnetic solid-phase extraction technique. Results of this study showed that 50 mg of the proposed nanoparticle required 30 min for 100% removal of PCB 28 from a 200 mL volume of water. Solution pH plays an important role in the adsorption of PCB 28 by the nanoparticles, and the sorption process was investigated in the pH range of 3–10. Sorption percentage was the highest in the pH range 3–8 and started decreasing at pH greater than 8. Further studies were done for the extraction of PCB 28 from the nanoparticles by hexane/dichloromethane, whereby 91% of the PCB 28 was recovered (Zeng et al. 2013). Similarly, Fe_3O_4 mixed with ammonium chloride and dispersed on graphene oxide sheets (Fe_3O_4 @PDDA/GOx@DNA) also resulted in high removal efficiencies (99.1%) for PCB from 100 mL water in 30 min (Gan et al. 2014).

Another example covers a compiled adsorbent in the form of a metal organic nanotube (Fe_3O_4 @Co-MONT) prepared by Li et al. (2016) for the removal of PCB from wastewater. This material was investigated as an adsorbent for PCB abstraction through magnetic solid-phase extraction. It exhibited strong magnetic properties toward the removal of PCB from environmental water samples resulting in almost 100% removal of PCB in 30 min. Moreover, the developed method showed reproducibility; in that, the synthesized nanoadsorbent was separated from the extracted PCB and regenerated for further use by exposing it to hexane for 5 min. These results render the process as a sustainable and efficient one (Li et al. 2016).

Coating iron with another metal, such as palladium (Pd), was shown to be effective in the adsorption of PCB from water solutions. Choi et al. (2008) studied the efficiency of a nanomaterial in the form of Fe/Pd bimetallic system for PCB adsorption. They found that almost all the PCB present in water were adsorbed by the aforementioned nanomaterial within 2 days of application at room temperature and pH 6.5 (Choi et al. 2008).

Table 1 Removal of polychlorinated biphenyls and polycyclic hydrocarbons by carbon-based nanomaterials

Nanomaterial	Size of nanomaterial (nm)	Target pollutant	Percentage of removal	Means of removal	Isotherm/kinetics	References
Methyl methacrylate on multiwalled-carbon nanotube (MWCNT-g-pMMA)	6.72	PCB	95	Adsorption	Langmuir model, Pseudo-first order	Shao et al. (2011)
Single-walled carbon nanotubes (SWCNTs)	–	PCB	100	Adsorption	–	Mahdavian and Mousavi (2016)
Multiwalled-carbon nanotubes grafted cyclodextrin (MWCNT-g-CD)	~ 0.79	PCB	> 95	Adsorption	Langmuir	Shao et al. (2010)
Graphene oxide	76 μm	PCB-28	99	Adsorption	Langmuir	Ren et al. (2018)
Graphene oxide	< 5	PCB	–	Adsorption	Langmuir, Freundlich, and PDM	Beless et al. (2014)
Amino-functionalized polypropylene nonwoven graphene oxide (PP-g-DMAEMA/GO)	2.7 μm	PCB	85	Adsorption	Pseudo-first order	Tian et al. (2019)
Multiwalled-carbon nanotube (MWCNTs)	60–100	PAH	99	Extraction	Pseudo-second order	Paszkiewicz et al. (2018)
TiO ₂ /SiO ₂ -carbon nanotubes	0.4	PAH	> 90	Adsorption	–	Rasheed et al. (2019)
Sulfonated graphene oxide	0.89–1	PAH	95	Adsorption	Langmuir	Zhao et al. (2011)
Graphene oxide	–	PAH	~ 99	Adsorption	Freundlich	Wang et al. (2014a)
Nano-reduced graphene oxide-hybridized polymeric high-internal phase emulsions (RGO/polyHIPEs)	–	PAH	50–90	Adsorption	–	Huang et al. (2018)
Magnetic graphene oxide	10–20	PAH	100	Adsorption	Dubinin and Astakhov	Huang et al. (2019)
Fe ₃ O ₄ -carbon nanotubes	–	PAH	99	Magnetic solid-phase extraction	–	Abdar et al. (2016)
Fe ₃ O ₄ -carbon nanotubes	–	PAH	–	Adsorption	Pseudo-first order	Zhang and Fang (2010)
Graphene oxide-Fe ₃ O ₄	–	Naphthalene	–	Extraction	–	Nazari et al. (2016)

Furthermore, studies showed that Fe₃O₄ mixed with beta-cyclodextrin provided a polymer that enhanced the removal of organic pollutants from aqueous solutions (Alsaiee et al. 2016; Li et al. 2013; Salipira et al. 2006). Wang et al. (2015) compiled Fe₃O₄ nanoparticles with cyclodextrin to prepare a core-shell magnetic nanoparticle. This nanoparticle is composed of a magnetic core with a silica-bonded cyclodextrin layer (Fe₃O₄@-CD). Results of the study showed that cyclodextrin enhances the binding capacity of the nanoparticles, thus, enhancing the removal of PCB from water with 100% removal in 30 min (Wang et al. 2015).

Additionally, bamboo charcoal-modified Fe₃O₄ nanosheets were successfully used for the removal of PCB from wastewater by achieving a 98.4% removal rate. (Zhao et al. 2013). Likewise, Liu et al. (2014) investigated

the efficiency of bamboo charcoal with iron oxide for the removal of PCB from water samples while applying solid-phase microextraction. The results indicated that this nanomaterial is a good nanomaterial for the removal of PCB from water by achieving almost 90% removal efficiency in 30 min (Liu et al. 2014).

Iron oxides for the removal of polycyclic hydrocarbons

Iron oxides have been also successfully used for the removal of PAH from water and wastewater. One application included the employment of carbon-coated Fe₃O₄ nanoparticles (Fe₃O₄/C) for the removal of PAH from aqueous solutions. In this context, Zhang et al. (2010) synthesized

this nanoparticle by a simple hydrothermal reaction. As a result of the combined strong adsorptive capability of carbon materials and the large surface area of nanoparticles, this composite showed to possess a high PAH adsorption capacity and attraction efficiency (~ 100%), without being affected by the physicochemical properties of the water, such as pH and salinity of the solution (Zhang et al. 2010).

Graphene/ Fe_3O_4 is another composite nanomaterial which was grafted onto polythiophene (PT) surface (G/ Fe_3O_4 @PT) in order to enhance the adsorption properties of the nanomaterial. The resulting nanomaterial exhibited effective PAH removal from water in a magnetic solid-phase extraction system, along with a high recovery of the synthesized nanomaterial. The prepared nanomaterial showed 95% PAH removal from 100 mL water volume in 4 min under ambient conditions. The nanomaterial also presented good reusability with at least 17 times regeneration while maintaining high removal efficiencies (Mehdinia et al. 2015).

Anthracene, a three-ringed PAH, for example, showed high adsorption levels onto two types of iron oxide nanoparticles, namely magnetite and goethite. This would propose a possible shift in the water treatment industry toward the use of such low-cost, efficient, and easily applied nanomaterial (Gupta et al. 2016). Nian et al. (2019) reported that graphitic carbon nitride (g-C₃N₄) coated with Fe_3O_4 nanoparticles (g-C₃N₄/ Fe_3O_4) demonstrated high affinity toward the adsorption of PAH. This high affinity, combined with the magnetic behavior of Fe_3O_4 , provided an effective nanomaterial for the removal of PAH by achieving 100% removal from 2 mL water solution contaminated with 200 ng PAH within 3 min. Tests resulted in low limits of detection of PAH and showed good linearity and high recovery of this nanomaterial (Nian et al. 2019).

Another study in which Fe_3O_4 particles were synthesized into wood biomass (Fe_3O_4 -wood biomass) also showed effective remediation of sediments contaminated with high PAH concentrations through chemical oxidation. The findings indicated that the Fe_3O_4 composite served as an activator and accelerated the removal of PAH (Dong et al. 2018). Moreover, iron oxide nanoparticles, coupled with chitosan, a polysaccharide polymer derived from the naturally occurring chitin, exhibited good PAH removal efficiency and was also suggested as a good candidate for water purification. Results of the proposed nanomaterial showed almost 96% removal of PAH from 2 µg/L PAH contaminated water (Nisticò et al. 2016).

It may be noted from the fore-mentioned studies that the advances in the use of iron oxides for PCB and PAH removal from water may provide opportunities for developing new nanomaterials and processes that will sustain high adsorptive capacities coupled with ease of operation. Additionally, such approaches will have extended life cycles and thus can be more efficient as remediation approaches compared to

conventional technologies. However, the main limitations to their direct application are related to the human and environmental risks accompanying their use, which have not been determined yet. In addition, the disposal of the spent adsorbents could pose an added hindering factor.

Another important aspect to consider is the cost of both preparing and applying these technologies. Although many of the base nanoparticles are relatively inexpensive to obtain or prepare, the modifications needed to optimize the adsorption capacity of the target pollutants, such as in the case of many of the aforementioned studies, add to the complexity and the resulting economic feasibility of pilot-scale, and possibly large-scale, applications in water treatment. Hence, the need for conducting comparative testing between different adsorbents is essential in addition to the focused studies on large-scale applications to allow for faster development of the technology for potential applications (Zhou et al. 2016).

Table 2 summarizes the results of different studies addressing the use of iron oxides nanomaterials for the treatment of PCB and PAH.

Photocatalytic nanocomposites

TiO_2 nanoparticles are considered to be one of the most promising and emerging photocatalysts used for water and wastewater purification (Sutisna et al. 2017; Lan et al. 2013). TiO_2 mainly acts through the production of highly reactive oxidants that enhance the pollutant removal process (Hai et al. 2013). In one study, TiO_2 nanodots fixed on carbon nanotubes (TiO_2 /Co@NCT) were found to be efficient in the removal of PAH reaching 98.48% removal within 15 min (Li et al. 2018). In yet another study, the use of crystalline TiO_2 synthesized nanoparticles revealed that photocatalysis was highly successful in the removal of PAH attaining around 95% removal within 120 min (Soni et al. 2017).

Removal of PAH was, moreover, found to increase by adopting noble metal doping into TiO_2 , mainly due to enhanced hydroxyl radical production (Liu et al. 2011). Doping of strontium (Sr) onto TiO_2 nanoparticles was effective in improving the nanoparticle removal efficiency by 40% resulting in nearly 100% removal of PAH from water solutions (Liu et al. 2011). $\text{Sr}(\text{OH})_2/\text{SrCO}_3$ nanocomposites doped in graphene oxide- TiO_2 exhibited strong photocatalytic activity for the degradation of phenanthrene. This degradation was attributed to the hybridization between the coupling of TiO_2 with $\text{Sr}(\text{OH})_2/\text{SrCO}_3$ and the electron transport in graphene oxide sheets. These results showed nearly 100% removal of PAH in the presence of 50 mg/L photocatalyst within 1-h contact time (Fu et al. 2018).

Photocatalysis of TiO_2 synthesized on graphene oxide sheets also showed an enhancement in the photocatalytic performance at higher PAH concentrations. The work

Table 2 Removal of polychlorinated biphenyls and polycyclic aromatic hydrocarbons by iron oxides nanomaterials

Nanomaterial	Size of nanomaterial (nm)	Target pollutant	Percentage of removal	Means of removal	Isotherm/kinetics	References
metal organic nanotube ($\text{Fe}_3\text{O}_4@\text{Co-MONT}$)	400	PCB	100	MSPE	Pseudo-second order	Li et al. (2016)
Metal grafted graphene oxide ($\text{Fe}_3\text{O}_4@\text{GO}$)	20	PCB 28	100	MSPE	Pseudo-second order	Zeng et al. (2013)
Fe_3O_4 with ammonium chloride dispersed on graphene oxide sheets ($\text{Fe}_3\text{O}_4@\text{PDDA}/\text{GOx}@DNA$)	3	PCB	99.1	MSPE	Langmuir	Gan et al. (2014)
Nano-Fe/Pd bimetallic	6–12	PCB	100	Adsorption	Pseudo-first order	Choi et al. (2008)
Fe_3O_4 beta-cyclodextrin	100–150	PCB	100	Adsorption	Langmuir	Wang et al. (2015)
Bamboo charcoal iron oxide ($\text{BC}@\text{Fe}_3\text{O}_4$)	–	PCB	98.4	SPME	–	Zhao et al. (2013)
Bamboo charcoal iron oxide ($\text{BC}@\text{Fe}$)	–	PCB	90	SPME	–	Liu et al. (2014)
Fe_3O_4 –carbon nanosheets	–	PAH	100	Hydrothermal	Freundlich	Zhang and Fang (2010)
Graphene/ Fe_3O_4 grafted onto polythiophene ($\text{G}/\text{Fe}_3\text{O}_4@\text{PT}$)	–	PAH	95	MSPE	–	Mehdinia et al. (2015)
Fe_3O_4 – FeOOH	–	Anthracene	–	Photodegradation	Pseudo-first order	Gupta et al. (2016)
Graphitic carbon nitride ($\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4$)	–	PAH	100	Adsorption	–	Nian et al. (2019)
Fe_3O_4 –chitosan	–	PAH	96	Sorption	Freundlich	Nisticò et al. (2016)
Graphitic carbon nitride ($\text{g-C}_3\text{N}_4/\text{Fe}_3\text{O}_4$)	–	PAH	80–99.8	MSPE	–	Wang et al. (2015)
Fe_3O_4 –wood biochar	–	PAH	90	Adsorption	–	Dong et al. (2018)

explored by Bai et al. (2017) indicated that almost 80% of PAH in water was removed by the prepared nanomaterial within 2 h of contact time with a concentration of 2 $\mu\text{g}/\text{mL}$ of PAH at ambient conditions. The removal mechanism was associated with π – π interaction between PAH molecules and the aromatic region of the nanomaterial. The results of the study suggest that this nanomaterial can be considered a possible candidate for PAH removal from aqueous solutions (Bai et al. 2017).

In this context, a study performed by Shaban et al. (2016) reported the photocatalytic efficiency of carbon-modified titanium oxide nanoparticles ($\text{CM-}n\text{-TiO}_2$) to be very high (93%) when applied to PCB contaminated water. The photodegradation results in this study revealed that the value of 0.5 g/L of nanomaterial dose is sufficient for the removal of high concentration of PCB under ambient condition for 24 h in acidic (pH 5) medium conditions (Shaban et al. 2016).

Table 3 summarizes the results of different studies addressing the removal of PCB and PAH using photocatalysis.

Other nanocomposites

Removal of polychlorinated biphenyls

Nanocomposites have shown unique advantages in the water treatment sector. They have advanced the way to a totally new generation of environmental remediation technologies (Soukupova et al. 2015). The synthesis of new nanocomposites has also attracted considerable interest. Due to their resilience, nanomaterials can sustain bending to large angles and straightening without undergoing damage (Camargo et al. 2009). Several studies targeted the removal of PCB from contaminated solutions through different mechanisms. These include supercritical fluid extraction with almost 95% PCB removal (Silva et al. 2012), and nanoscale zero-valent iron with almost 100% PCB removal (El-Temsah et al. 2016).

On this note, several nanomaterials were investigated for PCB removal, for instance, velvet-like magnetic carbon nitride nanocomposites ($\text{V-g-C}_3\text{N}_4$) were synthesized

Table 3 Removal of polychlorinated biphenyls and polycyclic aromatic hydrocarbons by photocatalysis

Nanomaterial	Size of nanomaterial (nm)	Target pollutant	Percentage of removal	Means of Removal	Isotherm/Kinetics	Reference
TiO ₂ nanodots fixed on carbon nanotubes (TiO ₂ /Co@NCT)	1–4 µm	PAH	98.48	Photocatalytic remediation	–	Li et al. (2018)
Nanometer TiO ₂	30	PAH	95	Photocatalytic remediation	Pseudo-first order	Soni et al. (2017)
Sr–TiO ₂	–	Phenanthrene	100	Photocatalytic degradation	Pseudo-first order	Liu et al. (2011)
Graphite oxide–TiO ₂ –Sr(OH) ₂ /SrCO ₃	–	Phenanthrene	100	Photocatalytic degradation	Pseudo-first order	Fu et al. (2018)
TiO ₂ –graphene oxide	20	PAH	80	Photocatalytic degradation	Pseudo-first order	Bai et al. (2017)
Carbon-modified titanium oxide nanoparticles (CM–n-TiO ₂)	–	PCB	93	Photocatalytic degradation	Langmuir	Shaban et al. (2016)

by chemical co-precipitation, and were used to develop a solid-phase extraction method for the separation of PCB from water samples. This nanomaterial is characterized by its large surface area, good dispersity, low solvent consumption, rapid analyte adsorption, and reusability. These results show that 100% removal of PCB was achieved for 3 µg/L of PCB in 3 s (Li et al. 2017a, b).

Gold nanoparticles scattered on graphene oxide sheets (RGO–AuNp) have also shown strong selectivity toward adsorption of PCB. Wu et al. (2017) investigated the removal of PCB 77 from water using this nanocomposite, and found that it can efficiently remove (100%) PCB 77 from water at very low concentration (1 µg/L). This nanocomposite was also tested on the removal of different kinds of PCB (other than PCB 77) and showed great potential (Wu et al. 2017).

Moreover, studies on nanoclays revealed high affinity of these materials toward PCB removal. This is attributed to their specific selectivity and to the large surface area of the nanoclays (Shariat and Raihan 2015). For instance, nanoscale zero-valent iron (NZVI) particles have also shown promising results for PCB removal due to their high reactivity and good mobility (El-Temsah et al. 2016; Sevcu et al. 2017). Sevcu et al. (2017) discussed an optimized removal of 97.5% of PCB from water after 24-h contact time by reporting that this PCB removal was obtained at pH values higher than 7.5 at room temperature with a concentration of 1 g/L of nanoscale zero-valent iron in the contaminated water (Sevcu et al. 2017).

Removal of polycyclic aromatic hydrocarbons

The elimination of PAH from water via a blend of adsorption–coagulation–flocculation processes using nano- and organo-modified nanoclays was adopted in a number of studies for a set of different reasons. Firstly, alums are known to be widely used for the removal of PAH (Zhao et al.

2011), and PAH can simultaneously adsorb onto surfactant reformed nanoclays (Ma et al. 2009). Secondly, organic clays can act as both a sorbent for PAH and a nucleus for flocculation, thus resulting in the formation of larger and more rapidly settling flocs (Olivella et al. 2011). Thirdly, the use of nanoclays helps the adsorption process of organic pollutants when present at low concentrations (Krupadam 2012). Fourthly, using modified clay minerals is relatively inexpensive when compared to the frequently used activated charcoal/carbon (Torabian et al. 2014).

To illustrate, PAH removal in a conventional water treatment process increased after the addition of alum combined with aluminum polychloride, and reached maximum removal (100%) upon the addition of nanoorganic clay (nanobentonite) or nanohalloysite (Shabeer et al. 2014). Alum–nanoclay material combinations were also shown to exhibit remarkable effects for the removal of PAH due to their acting as coagulation aids (Woo et al. 2014).

Furthermore, Chen et al. (2015) discussed the effectiveness of nanoscale zero-valent iron nanoparticles in eliminating PAH. They reported that the best removal efficiency (90%) was obtained at high temperatures (50–70 °C). The optimized condition was achieved with an initial concentration of 0.01 g/L of nanomaterial at 70 °C for 24 h contact time in an ex situ treatment of PAH contaminated water (Chen et al. 2015).

Li et al. (2017a, b) studied the use of nanoscale zero-valent iron coupled with silica oxides (Fe@SiO₂@PDA) for the removal of PAH. These results indicated that the supermagnetic characteristics and stability of these adsorbents were active factors effecting PAH removal. Almost complete removal (100%) of PAH was achieved at 30 °C after 10 h while using this nanomaterial. In addition to the high removal efficiency, this nanomaterial exhibited reusability, where the removal efficiency barely decreased after 10 cycles of treatment (Li et al. 2017b).

Other highlighted nanomaterials include magnetic nanoparticles (Torretta 2012). Two new magnetic and recyclable nanomaterial hybrids were recently developed, showing high efficiency (83–100%) PAH removal from water (Gutierrez et al. 2018). Also, by applying magneto-filtration, bismide perylene dopamine (PBI-DA) and bismide perylene 3-aminopropyltriethoxysilane nanomaterials proved to be very efficient in the removal of major carcinogenic PAH (Gutierrez et al. 2018). The nanomaterials studied by Kozhemyakina et al. (2010) presented high dispersity, stability, and absorbance in the aqueous media due to hydrophobic forces and the π – π interactions between the synthesized material and the PAH. However, this study was not conducted on contaminated water sources, and thus, further research is required to widen its applicability (Kozhemyakina et al. 2010).

Another study discussed the modification of magnetic nanoparticles with 3-mercaptopropyltrimethoxysilane (MPTMS) and grafted with allyl glycidyl ether and used it for the removal PAH from contaminated water (Torabian et al. 2014). Results of the conducted experiments depicted that the modified nanoadsorbents had good potential for the fast removal of PAH from large water volume samples, and also displayed a high adsorption capacity (> 90%) and an elevated chemical stability at pH 7 and room temperature (Torabian et al. 2014).

Overall, magnetic nanoadsorbents showed a good potential for the fast removal of PAH from water samples.

However, the fact that the successes of such applications are dependent on a multitude of factors influencing the removal rate, such as ease of synthesizing the nanocomposite, ease of application, and the cost of material, may lead to limiting the wide application of these nanocomposites.

It is to be noted that the current literature lacks information on the optimal conditions under which the different adsorbents, or their variations, are best suited. Not only each adsorbent has its specific set of optimized treatment conditions for sustaining high removal rates, but also their modified forms or the combined use of multiple adsorbent could substantially impact the efficiency of the removal of the target pollutants under different sets of operating conditions. Also, when the processes need to be scaled up for pilot-scale studies and field applications, the lack of information related to the optimized operating conditions might easily lead to erroneous results and ultimate failure of the treatment process. It may also increase the operational cost thus rendering the system diverse components unfeasible. Equally important, when designing a study dealing with the removal of persistent pollutants using nanomaterials, it is paramount to use naturally contaminated water instead of synthesized water which does not reflect the diverse components present in natural ecosystems.

Table 4 summarizes the results of different studies addressing the removal of PCB and PAH using different nanomaterials.

Table 4 Removal of polychlorinated biphenyls and polycyclic aromatic hydrocarbons by different nanomaterials

Nanomaterial	Size of nanomaterial (nm)	Target pollutant	Percentage of removal	Means of removal	Isotherm/kinetics	Reference
Nanoscale zero-valent iron (NZVI)	–	PCB	100	Adsorption	–	El-Temsah et al. (2016)
Velvet-like magnetic carbon nitride nanocomposites (V-g-C ₃ N ₄)	–	PCB	100	Adsorption	Langmuir and Freundlich	Li et al. (2017a)
Gold nanoparticles scattered on graphene oxide sheets (RGO-AuNp)	–	PCB 77	100	Adsorption	–	Wu et al. (2017)
Nanoclays	–	PCB	77	Adsorption	Langmuir and Freundlich	Shariat and Raihan (2015)
Nanoscale zero-valent iron (NZVI)	70	PCB	97.5	Degradation	Multipoint Brunauer–Emmett–Teller model	Sevcu et al. (2017)
Fullerenes C60	–	Naphthalene	100	Adsorption	Freundlich	Cheng et al. (2004)
Graphitic carbon nitride (g-C ₃ N ₄)	–	Nitro-PAH	100	Adsorption	–	Lin et al. (2015)
Nanoscale zero-valent iron coupled with silica oxides (Fe@SiO ₂ @PDA)	–	Phenanthrene Anthracene	100	Adsorption	Pseudo-second order	Li et al. (2017a, b)
Bismide perylene dopamine (PBI-DA)	196	PAH	83–100	Adsorption	Langmuir	Gutierrez et al. (2018)
Magnetic nanoparticles	–	PAH	100	Adsorption	Langmuir	Torabian et al. (2014)

Conclusion

This review addressed the current studies and findings related to nanotechnology as a developing treatment process for the removal of PCB and PAH from aqueous solutions. Several types of nanomaterials, as well as combinations thereof, were presented and critically discussed, where applicable, to evaluate their technical abilities in removing the targeted pollutants. Furthermore, an assessment of the limitations and gaps in the related studies were evaluated. These gaps mostly dealt with the supplementary studies needed to develop the use of these nanomaterials in a higher level of application, i.e., full-scale sustainable treatment processes.

Information about using nanotechnology in water matrices with a mixture of pollutants was found to be lacking in the studies reported in this review; thus, the potency of nanotechnology in the water treatment domain, and specifically for the removal of PCB and PAH, remains vague due to lack of sufficient information relevant to field sampling. In addition, most of the studies, both the experimental and the theoretical ones, lack information about potential human health and environmental impacts, a topic that deserves to be seriously addressed in future studies.

Moreover, on the technical stance, a discrepancy exists in the reported optimal conditions for achieving high removal efficiencies of the targeted pollutants. In future research, it is hence vital to focus on: (a) understanding the interaction between the optimal conditions of a certain parameter and the adsorbent, (b) investigating the extent to which interactions differ in case different adsorbents are used, (c) understanding the impacts of the operating conditions on the rate of adsorption, and (d) investigating the effect of a mixture of pollutants on the expected behavior of a certain adsorbent.

Consequently and in order to also alleviate the deficits related to the applicability of the proposed nanomaterials and their composites to real large-scale field applications, future studies should target to remediate the basic testing procedures by (a) including applications using naturally contaminated water samples; (b) determining the effects of different experimental conditions on removal efficiency to better reflect field conditions; (c) quantifying the impact of a mixture of different pollutants on the adsorption process; (d) determining the effect of water type and characteristics on the adsorption process; and finally, (e) evaluating the technological advantages and cost effectiveness related to nanotechnology compared to conventional water treatment processes, taking regeneration into account.

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