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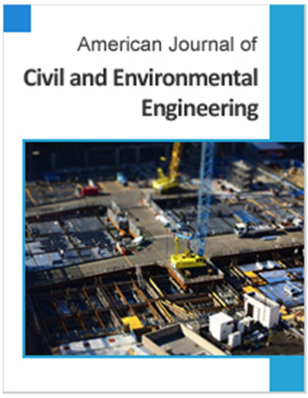

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Remediation of Soil and Groundwater Polluted by Polycyclic Aromatic Hydrocarbons: A Review

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Abstract

Water and soil pollution due to polycyclic aromatic hydrocarbons (PAHs) is a serious problem because of acute toxicities and carcinogenic nature of these pollutants. Several strategies have been applied to eliminate these dangerous pollutants from contaminated soil and groundwater. Among a variety of removing techniques, adsorption is the most popular and widely used. Adsorption has advantages over the other methods because of low price, simplicity of design, universal nature and ease of operation. Hence, this process meets the great attention from the researchers. This paper provides literature review about PAH, Emission sources and occurrence in the environment and PAH adsorption characteristics by various adsorbents such as activated carbon, bio-adsorbent, carbon nanotube, magnetic adsorbent, biochar and zeolite adsorbent. These adsorbents have been classified into seven different categories on the basis of their chemical nature. The results of this reviewed article showed that little attention has been paid to usage of novel adsorbents in PAH removal. Hence, few suggestions for future research are proposed.

1. Introduction

During the last century, strong human impact on PAH concentrations in the environment has been proved and PAHs compounds have been detected around the world even at the Polar Regions, and in the tropics which are far from industrial regions [1]. PAHs are a collection of over 100 different benzene ring chemical compounds [2]. Hence, due to slow migration and water insolubility, PAHs accumulate and remain in soil for a very long time [3]. Pollution of the environment with PAH compounds is extremely dangerous to live organisms. Also, plant uptake of PAHs compounds from contaminated media and PAHs permeation to ground water may lead to serious ecological and health-related consequences [4]. In recent years, extensive researches have been performed in the removal of PAHs from the environment with different chemical, physical and biological techniques [5-7]. Among these removal strategies, adsorption process as a physical technique has attracted a great deal of research attention recently. However, there is no a review article concerning usage of different adsorbents for PAH adsorption in soil and aqueous environment. Hence, the aim of this work is to review, evaluate, and compare different adsorbents, and highlights the need to continue research on PAH adsorption with novel adsorbents in environmental media, including surface soil and groundwater.

2. Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons (PAHs) are introduced in our environment in large quantities daily with little or no awareness. PAHs can be found in air, sediments, soils and water either in solution or adsorbed on particulate material. They are a group of several hundred individual organic compounds consisting of two or more fused aromatic rings.

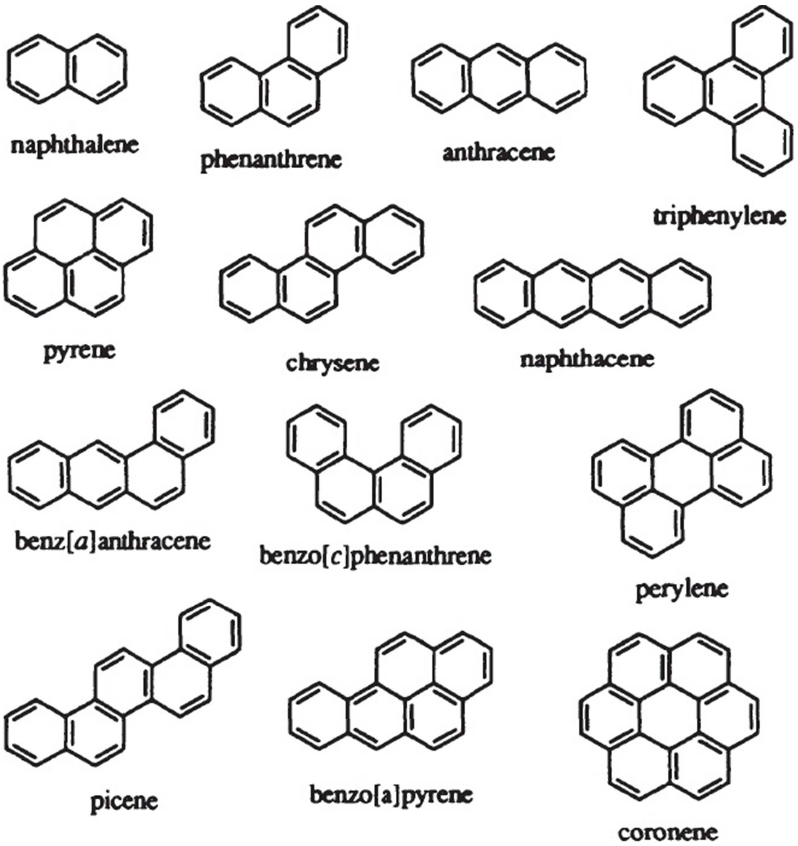

Figure 1. *Some common alternate PAH ring systems.*

Some of the more common PAHs are shown in Figure 1. PAH compounds formed of organic matters at high temperature under pyrolytic condition. Hence, incomplete combustion of fossil fuels, organic materials, and wood are the main source of PAHs. Also, they are found in petroleum [9]. Natural processes, such as volcanic eruptions and forest fires, contribute to an ambient existence of PAHs. They are classified by their melting and boiling point, vapor pressure, and water solubility. Table 1 shows physical and chemical characteristics of 16 priority PAHs, listed by the US EPA [1, 10].

Table 1. *Physical and chemical characteristics of 16 priority PAHs [1, 10].*

Characteristic	**Chemical formula**	**Molecular weight**	**Solubility in Water (mgr/L)**	**Boiling point (°C)**	**Vapor pressure (Pa)**
Naphthalene	$C_{10}H_8$	128.17	31	218	11.866
Acenaphthene	$C_{12}H_{10}$	154.21	3.8	96	0.500
Acenaphthylene	$C_{12}H_8$	152.20	16.1	265-275	3.866
Fluorene	$C_{13}H_{10}$	166.2	1.9	295	0.432
Anthracene	$C_{14}H_{10}$	178.2	0.045	340-342	$3.4*10^{-3}$
Phenanthrene	$C_{14}H_{10}$	178.2	1.1	340	$9.07*10^{-2}$
Fluoranthene	$C_{16}H_{10}$	202.26	0.26	375	$1.08*10^{-3}$
Pyrene	$C_{16}H_{10}$	202.3	0.132	393-404	$5.67*10^{-4}$
Benzo(a)anthracene	$C_{20}H_{12}$	228.29	0.011	438	$2.05*10^{-5}$
Chrysene	$C_{18}H_{12}$	228.28	0.0015	448	$1.04*10^{-6}$
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.3	0.0015	No Data	$1.07*10^{-5}$
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.3	0.0008	480	$1.28*10^{-8}$
Benzo(a)pyrene	$C_{20}H_{12}$	252.3	0.0038	495	$6.52*10^{-7}$
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.35	0.0005	No Data	$2.8*10^{-9}$
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	0.00026	550	$1.33*10^{-8}$
Ideno(1,2,3-c,d)pyrene	$C_{22}H_{12}$	276.3	0.062	530	$1.87*10^{-8}$

Health effects resulting from PAH exposure have been discussed extensively in recent years. Many PAHs are known to be mutagenic and carcinogenic, thus, increases risk of cancer and creates advance glycogen end product which leads to an increased risk of heart disease and diabetes. Consequently, the US Environmental Protection Agency has listed 16 PAHs as priority pollutants for remediation [11-13].

PAHs are lipophilic and nonpolar. Hence most of them are insoluble in water and persist in the environment. As a rule thumb, the aqueous solubility of PHAs decreases approximately logarithmically as molecular mass increases [14]. PAHs containing two or three benzene ring in their structure have low solubility in water. Hence they can attend in biodegradation reactions. PAHs with two to four rings volatilize and introduce in the air in gaseous form. PAHs compounds with five or more ring are neither soluble in water nor volatile; hence they are found in soil, sediment, oily compound and particulate phases in ambient air. Most of PAHs compounds are persistent organic pollutants (POPs) in the environment and are chemically inert. They can be decomposed under strong ultraviolet light or sunlight [15]. Hence, some of them may be lost during atmospheric sampling. In addition, PAHs can react with ozone, hydroxyl radicals, nitrogen and sulfur oxides, and nitric and sulfuric acids [10].

3. PAH Measurement Techniques

The exact measurement concentration of each PAH compounds containing in different samples (soil, water and gaseous forms) are performed in different stages which include sampling, extraction, concentration and analysis [16]. Low molecular weight PAHs are released in a vapor phase into the air environment, while high molecular weight PAHs containing five or more rings are adsorbed onto suspended particles. Therefore, sampling will be performed in different methods with special apparatus. Approaches for volatile organic compound include: solid-phase trapping, liquid trapping, headspace sampling, grab sampling, purge and trap, and thermal extraction. The most common methods for gaseous sampling are solid-phase and liquid trapping. In two techniques, a gaseous sample is passed through a tube packed with adsorbent (e.g., XAD-2 resin and polyurethane foam for PAH sampling) and the trapped aromatic compounds are eluted with a strong solvent [17]. For keeping samples, glass containers with bottle cap made of polytetrafluoroethylene (PTFE) have been used. Because PAH compounds are photoreactive, exposure to light should be minimized by using brown glass containers or clear containers wrapped tightly with an opaque material (e.g., clean aluminum foil). Also, samples should be stored in the dark, by refrigeration (4°C).

After sampling, PAHs are extracted using organic solvents such as mixtures of n-hexane, methanol and dichloromethane. As regards concentrations of PAH compounds in samples are low and sometimes are lower than detection limit of instrument, so, the extracted PAHs solutions have to be concentrated. Most common extraction technique is Soxhlet extraction [7, 18-19]. Gas chromatography, combined with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC), are often used to quantify the PAH compounds concentration [20-21].

4. Emission Sources and Occurrence in the Environment

As mentioned in section 2, PAHs emit into environment from different sources. They can be of anthropogenic or natural origin. Oil seeps from crude oil reservoirs, volcanoes, forest fires and erosion of ancient sediment are natural sources of PAH emission [22]. Thermal alteration or incomplete combustion of organic matters leads to formation of anthropogenic PAHs [23]. Anthropogenic PAHs sources include: combustion of fossil fuels, municipal and industrial waste incineration, coal tar, coke, asphalt, crude oil and municipal and industrial wastewater [24]. PAHs have been found around the world and these compounds transfer between these resources; for example leaching of PAHs from a soil resource into ground water, or PAHs transport of particulate soil into the atmosphere [1]. Table 2 shows the results of comparison of atmospheric PAHs concentrations in different studies around the world. As can be seen in this table, PAH compounds concentration in soil, water and atmosphere are not negligible in most areas and hence it is essential to clean up these hazardous compound. Since PAHs can have mutagenic/carcinogenic effects, they have to be removed from all environments [25].

Table 2. *Comparison of atmospheric PAHs concentrations in different studies around the world.*

Location	**System, Number of PAH**	**Method of Measurement**	**Concentration; Unit**	**Ref**
Hong Kong	Soil, 16	GC-FID	7 – 69.3 (rural); 49.2-410 (urban); ppb	Zhang et al., 2006 [26]
Oslo, Norway	Forest soil, 16	GC-Mass	0.01-2.6; ppm	Jensen et al., 2007 [27]
Yangtze River Delta region	Soil, 15	HPLC	8.6-3881; ppb	Ping, 2007
New England	Urban Soils, 17	GC-Mass	0.7; ppm	Bradley, 1994 [28]
Pyrenees and Tatra	Soils and sediment lakes, 24	GC-Mass	90-1900 (soil); 3000-12000 (sediment); ng/g	Grimalt et al., 2004 [29]
Wells at Coal Tar Site	Ground water, 11	GC-FID	mg/L	Mackay, and Schwend., 2001 [30]
Region of Mezirici,, Czeck	Soil, 16	HPLC	0.86-10.84 (urban/agricultural); 7.66-79.39 (forest soils); ppm	Placha et al., 2009 [31]

Location	System, Number of PAH	Method of Measurement	Concentration; Unit	Ref
Agbabu,, Nigeria	Soil, 12	GC-Mass	0.07±0.036 (dry season) and 0.69±0.19 (rainy season); ppm	Fagbote and Olanipekun, 2013 [32]
Tianjin and Beijing	Wastewater irrigated soils, 16	GC-Mass	1,304 to 3,369 (Tianjin), 2,687 to 4,916 (Beijing), µg kg^{-1}	Khan et al., 2008 [33]
Dagang Oilfield	Soil, 16	GC-Mass	Arable desert soil (mean 343.5), oil well areas (mean of 627.), urban and residential zones (mean 1856); µg kg^{-1}	Jiao et al., 2015 [34]
Abakaliki; Nigeria	Soil, 6	GC-Mass	0.0184 ± 0.02 to 0.1385 ± 0.2; mg/kg	Obini et al., 2013 [35]
Midway Atoll, North Pacific Ocean	Soil, 16	GC-ITMS	3.55 to 3200 with a mean concentration of 198; mg kg^{-1}	Yang et al., 2014 [36]
Southern Poland	Soil, 15	GC-Mass	384; ng / g	MalaWska et al., 2006 [37]
Caspian Sea	Sediments, 16	GC-FID	990 ± 33; µg/kg	Saravi et al., 2012 [38]
Shahrekord, Iran	Soil, 2 (phenanthrene and pyrene)	HPLC	24.14±6.8 and 50.67±20.42 (in vicinity crude oil transmission line site), 0.22±0.02 to 2.5±1 (storage reservoirs site), 32.24 ± 19.45 to 61.32±36.23 (areas exposed to	Arbabi et al., 2015 [39]
Guiyu, China	Soil, 16	GC-Mass	exhaust); mg/kg 44.8 to 3206 µg / kg 2.01-38.96 and 32.45-	Yu et al., 2006 [40]
Tehran, Iran	Drinking Water, 16	GC-Mass	733.10; ng/L	Rastkari et al., 2013 [41]
Five European countries	Atmosphere	GC-Mass	$5-1.2*10^3$ ng $SPMD^{-1}$ day^{-1} (semipermeable membrane devices)	Soderstrom et al., 2005 [42]

Removal of PAH compounds can be performed through chemical (e.g. chemical degradation [5, 6], physical (e.g. adsorption) and biological processes [43]. Hence, in the next section, application of absorption process with different absorbents for removal of PAH compounds will be discussed in details.

5. Absorption Technique

Absorption methods provide a simple and universal approach to remove organic pollutants from the aquatic environment effectively [44]. Due to low cost, simplicity of design, ease of operation and insensitivity to toxic pollutants, the adsorption process have been extensively used for removal of PAH compounds [45]. There are two types of adsorption; physical and physico-chemical adsorptions. Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding without any electron exchange between adsorbent and adsorbate while chemical adsorption originates from the chemical bond between adsorbent and adsorbate [46]. In physical adsorption, activation energy is not required [47]; so equilibrium time will be very short. Pore structure and the specific surface and chemical nature of the surface area are the most important properties of adsorbent [48]. Major types of adsorbents which have been used for removal of organic materials from contaminated soil and water are activated carbon, bio-based adsorbents, carbon nanotube adsorbents, zeolite adsorbents, magnetic adsorbents and biochar adsorbents. Published papers on adsorption can be divided into three main parts. The first part deals with possibility of adsorption with the adsorbent and determination of adsorption efficiency. The second part discusses the effect of process parameters on adsorption efficiency and the last one explains kinetics of adsorption. Hence, this article is primarily attempting to describe these three viewpoints for every type of adsorbent based on results which have been published in the literature. In the next subsections, applications of different adsorbents for the removal of PAH compounds will be reviewed and few suggestions for future researches are proposed.

5.1. Activated Carbon Adsorbents

Commercial activated carbon is a well-known adsorbent which is widely used as industrial adsorbent for removal of a broad spectrum of organic pollutants from aqueous solutions [49-50]. Also, activated carbon as a potential adsorbent can be applied for in situ soil remediation but published researches in this area are scarce. The principle of the technique is that activated carbon adsorbents are usually porous solids with high degree of surface reactivity and adsorption occurs mainly on the pore walls inside particles. Activated carbon is generated by chemical or steam activation of any carboneous materials with high concentration of carbon [51]. Totally, the removal of PAH compounds from water on activated carbon mainly occurs by a π–π electron-donor-acceptor mechanism. Various factors, such as the chemical properties of the molecules, molecular size, the hydrophobic nature of the adsorbate and the characteristics of the activated carbon have effect on removal efficiency [52]. Effect of variables properties such as adsorbent dosage, the initial phenanthrene concentration, contact time and pH value on kinetic and isotherm of the adsorption process have been investigated by Moradirad et al. (2014) [53]. Their results indicate that adsorption capacity become notably greater with an increase in contact time and initial phenanthrene concentration. Also, pH doesn't play a key role in the process of phenanthrene adsorption. In this study, adsorption process showed a strong correlation with Fraundlich isotherm models. In other research, the removal of three PAHs (naphthalene, fluorene and acenaphthene) from aqueous solution onto activated carbon have been carried out by Haro et al. (2011) to study the effect of molecular size of the hydrocarbons on adsorption rate [54]. Their results showed that the rate of adsorption was strongly dependent on the molecular size of the hydrocarbons, so that diffusion of PAH compounds with smaller size through boundary layer is more favored. Also, the interactions between PAH compounds and the activated carbon are to be controlled by two factors, aromaticity and water solubility. Totally, as the number of aromatic rings in the polycyclic hydrocarbon increase (fluorene > naphthalene = acenaphthene), the adsorbate–carbon interactions will be more favored. Smol et al. (2014) have studied on the efficiency of adsorption process of six PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene) using activated carbon [55]. PAHs removal of 98.1% is recorded for the activated carbon in this research. High adsorption capacity with activated carbon for PAH removal is achievable. Gupta (2015) have been studied on process parameters on removal of phenanthrene from water using activated carbon developed from orange rind [56]. Results showed that the adsorption of naphthalene rises with the increase in shaking time, initial concentration of phenanthrene and adsorbent dose. Increase in pH of the solution has an adverse effect on the adsorption capacity of the adsorbent. Also, the adsorption data were described by traditional Langmuir and Fraundlich adsorption isotherms. Adsorption of naphthalene on activated carbons with different surface and textural heterogeneities has been explored by Ania et al. (2007) [57]. The results of this article confirmed that the adsorption strongly depends on the pore size distribution of the adsorbent, being enhanced in those pores of narrower dimensions. In addition, the hydrophobic/hydrophilic character of the adsorbent has effect on adsorption because it dominates the undesirable competitive adsorption of water. Hence, adsorbents with a high non-polar character will be more effective for PAH compound.

Adsorption isotherm data for 11 polycyclic aromatic hydrocarbons from water onto activated carbon have been explored by Waiters et al. (1984) [58]. In this study, two different forms of the Langmuir equation are observed and it may be due to the occurrence of multistep adsorption process. Because adsorption onto the more active sites occurs first and it followed by additional adsorption onto lower energy surfaces.

The influence of the organic solvent polarity on adsorption of naphthalene, anthracene, and pyrene onto activated carbon from non-aqueous media has been studied by Dowaidar et al. (2007) [59]. Their data reveals that adsorption of PAHs onto activated carbon depends on the chemical structure of the solvent and the solvent aromaticity. As PAHs are able to form $\pi - \pi$ complex between π - electrons of benzene rings and active sites on an activated carbon surface, therefore aromatic solvents (with high affinity for activated carbon) inhibit PAHs adsorption. Also, for polar solvents with low affinity to activated carbon, the adsorbent sites are more available for the PAHs molecules. In Table 3, application of active carbon for removal of PAH compounds from soil and aqueous solution is reviewed.

Table 3. *Application of active carbon for removal of PAH from soil and aqueous solution.*

Adsorbate	**Isotherm of adsorption**	**Main Observations**	**Sources**
fluoranthene, benzo(a)anthracene, phenanthrene	Langmuir isotherm model, Dubinin– Radushkevich isotherm models, pseudo-second-order kinetics model	For phenanthrene 58.843 (mg/g)	Liu et al., 2014 [60]
11 PAHs	Langmuir equation	The adsorption of PAH onto activated carbon is much stronger than soils, sediments, and other hydrophobic organics.	Walters and Luthy, 1984 [58]
Naphthalene (NA), Phenanthrene (PH), and pyrene (PY)	Freundlich isotherm for NA, Generalized isotherm for PH and BET isotherm for PY	The adsorption of PAH compounds onto rice husk carbon is very favorable compared to AC	Yakout and Daifullah, 2013 [61]
naphthalene, fluorene and acenaphthene	Langmuir–Freundlich model	The overall adsorption rate is related to PAH molecular Dimensions	Haro et al., 2011 [54]
naphthalene, fluorene, pyrene, anthracene, acenaphthene, fluoranthene	pseudo-first-order reaction model	The sorption process with activated carbon is a more complex process than the one observed for hyper-cross-linked polymers	Valderrama et al., 2007 [62]
16 US EPA	No data	removal efficiencies of PAHs were about 76–91%	Zhou et al., 2004 [63]
Phenanthrene	Langmuir adsorption isotherm	Adsorption capacity was found to be 70.92 mg/g	Gupta, 2015 [56]
naphthalene and pyrene	Langmuir equation	Maximum adsorption capacity decrease with increasing temperatures, thus confirming the occurrence of physisorption and its exothermic behavior.	Murillo et al., 2011 [64]
anthracene	Langmuir equation	Maximum adsorption capacity of 0.14 mg/g is achieved for active carbon	Khames Saad et al., 2013 [45]
Naphthalene	Pseudo-second-order model	A coal with low ash content and less than 10% volatile content, is the best materials for the preparation of coal based active carbon for naphthalene adsorption.	Liu et al., 2015 [65]
Phenanthrene, naphthalene, pyrene	pseudo-second-order model	The equilibrium adsorption amounts were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and 78.18 mg/g for naphthalene.	Xiao et al., 2014 [66]
Naphthalene	Freundlich model	coal-based activated carbon modified by microwave induction is a low-cost and fast adsorbent for removal naphthalene from aqueous solutions	Ge et al., 2015 [67]

5.2. Bio-adsorbents

Due to acidic nature and high porosity, activated carbon has been extensively used as an adsorbent for the removal of pollutants. However, it is costly and challenging in regeneration which leads to increase the cost of waste water treatment. Hence, there is a great demand for such type of adsorbent which is cheaper with high adsorption capability [68]. Bio-adsorbents such as fruit wastes, coconut shell, tannin-rich materials, sawdust and other wood type materials, rice husk, fertilizer wastes, chitosan and seafood processing wastes, seaweed and algae, are promising resources for environmental technology if used in the purification of waters and treatment of wastewaters [68-69]. Bio-adsorbents have several advantages such as high sorption capacities, good modifiability and recoverability, insensitivity to toxic substances, simple operation in the treatment processes [70].

Also, absorption capacity of bio-adsorbent can be improved by chemical and physical modification. Chen and Xi (2014) have studied on removal of PAHs (naphthalene, acenaphthene, phenanthrene and pyrene) from aqueous solution by raw and acid hydrolyzed plant residue materials (bamboo wood, pine wood, pine needles and pine bark) [71]. Their results showed that the sorption isotherms of PAHs to raw bio-adsorbents and hydrolyzed bio-adsorbents were respectively linear and nonlinear. Also, compared to raw bio-adsorbent, the sorption capacity of acid hydrolysis plant residues was enhanced greatly due to the increase of aromaticity and the decrease of polarity of the sorbents. Budhwani (2015) have investigated on removal of PAH (anthracene, acenaphthene and naphthalene) present in Tyre Pyrolytic Oil using bio-adsorbent including sawdust, coconut fiber, neem bark, chitin, activated charcoal [72]. It was observed that for any PAH compound, the adsorption capacity is directly proportional to lignin content. Also, the uptake capacity of PAHs followed the order: activated charcoal> saw dust > coconut fiber > chitin. Adsorption of naphthalene from aqueous solution onto fatty acid modified (e.g., capric acid, lauric acid, palmitic acid, and oleic acid) walnut shells was explored by Zhu et al. (2016) [73]. Oleic acid grafted walnut shell showed the maximum partition coefficient compared with other modified sorbents, because its low polarity and high aromaticity imposed significant effects on the adsorption capacity of sorbents. Malt spent rootlets (MSR), by product of beer industry, is used for as adsorbents of phenanthrene from aqueous solutions (Vallili, 2013) [74]. Results exhibited that sorptive properties of MSR are not competitive with the traditional sorbents (e.g., activated carbons. Hence, the pyrolysis of raw MSR performed to increase surface area and porosity. This chemical treatment contributed to a significantly increased sorption capacity for phenanthrene. Table 4 exhibits maximum adsorption capacities and adsorption efficiency of some bio-adsorbent for PAH removal.

There are many bio-adsorbents which have been used in adsorption process to eliminate different pollutants from contaminated water and soil. These bio-adsorbents can be modified by chemical and physical treatment to improve adsorption properties. Also, combination of these bio-adsorbents can be used to increase adsorption capacity. Hence, bio-adsorbents have great potential for PAH removal in water and soil remediation in future research studies.

Table 4. *Maximum adsorption capacities and adsorption efficiency of some bio-adsorbent for PAH removal.*

PAH compound	**Adsorbent**	**Adsorption capacities (mg/g) or adsorption efficiency (%)**	**Source**
Phenanthrene	Tea leaf residue	80%	Xi and Chen, 2014 [75]
phenanthrene	Wood chips, ryegrass roots, orange peels, bamboo leaves, and pine needles	90%	Chen et al., 2011 [76]
Mixture of thirteen aqueous PAHs	Cork waste	Over 80%	Olivella et al., 2011 [77]
Phenanthrene, naphthalene, and acenaphthene	Soybean Stalk–based Carbon	Removal efficiencies of phenanthrene, naphthalene, and acenaphthene were 99.89, 100, and 95.64%, respectively.	Kong et al., 2010 [78]
Acenaphthene	Activated carbon produced from rice husk	Max adsorption: 5.554; Min adsorption: 1.386	Alade et al., 2012 [79]
Naphthalene, anthracene, and pyrene	Rice straw (RS) and sugarcane bagasse (SB)] from bioethanol production process	3.61, 1.01, and 0.86 mg/g SB and 3.35, 0.77, and 0.73 mg/g RS for pyrene naphthalene, anthracene, respectively	Younis et al., 2014 [80]
Pyrene	Palmitoyl Grafted cellulose (PMC) Nano absorbent	0.25 g of PMC removed 92% pyrene	Jadhav et al., 2015 [81]
Naphthalene, phenanthrene and pyrene	Fibric peat Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin	Adsorption capacity for naphthalene, pyrene and phenanthrene respectively are 291µg/g, 803 µg/g, 280 µg/g	Tang et al., 2010 [82]

5.3. Carbon Nanotube Adsorbents

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. CNTs are composed of graphite sheets rolled up into a tube like structure. There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). They have novel properties such as high aspect ratio, large accessible external surface area, high reaction activity and layered structures that make them potentially useful in a wide variety of applications in wastewater treatment for removing many kinds of organic and inorganic contaminants from aqueous solutions [83-85]. Removal of inorganic and organic compounds from contaminated water and soil by CNTs has been reviewed [86-87].

Due to nonpolar graphene sheets, CNTs are hydrophobic in nature. Hydrophobicity of graphene sheet leads to be used as third generation carbonaceous adsorbent. Strong *π-π* interactions between aromatic pollutants (such as naphthalene, pyrene, and benzene and so on) and the grapheme sheet of non-functionalized CNTs have extensively been recognized as a major driving force for absorption in a simple PAH– CNTs aqueous solution. However, CNTs have been known as better adsorbent media compared to activated carbon due to appropriate physicochemical properties and well known uniformed atomic structure [88]. Gotovac et al. (2007) have been studied on adsorption behaviors of PAHs (tetracene and phenanthrene) with single wall carbon nanotube (SWNTs) [89]. X-ray photoelectron spectroscopy confirmed that tetracene and phenanthrene molecules efficiently coated the SWCNT external surfaces. The remarkable difference between the adsorption amounts of tetracene and phenanthrene was observed such that tetracene adsorption was six times greater than that of phenanthrene. Because tetracene molecules, which have four benzene rings align with the SWCNT surface, while phenanthrene had only 2.5 rings in alignment. A difference in the amount of contact between the molecule and the tube surface was made due to the nanoscale curvature effect of the tube surface. In other research, adsorption of chrysene and benzo[a]pyrene on multiwalled carbon nanotubes and their equilibrium adsorption isotherms was investigated by zakeri et al. (2009) [90]. They reported that amount of chrysene adsorbed is small compared with the adsorbed amount of benzo[a]pyrene. This difference associated with the molecular size and geometry difference between the molecules. Benzo[a]pyrene is a five ring molecule with a large *π*-electron system which makes it more suitable for adsorption by *π-π* interactions with carbon nanotubes than chrysene (Sheng et al., 2010) [91]. The interaction between SWNTs and polycyclic aromatic hydrocarbons (polyacene series and polyphenyl series) by using a fluorescence model based on the adsorption/desorption equilibrium of SWNTs and PAHs has been studied by Debnath et al. (2008) [92]. Their result show that PAHs of polyphenyl series bind more strongly to the surface of SWNTs bundles than that of polyacene series due to the higher number of carbon and hydrogen. Also, the binding energy between SWNTs and different PAHs as a function of molecular weight of corresponding PAHs molecules are obtained by usage of this model. The batch equilibrium approach was used to examine the influence of MWNTs on the sorption behaviors of three PAH (naphthalene, fluorene, and phenanthrene) in soil by Shibin et al. (2013) [93]. PAH sorption on MWNTs followed the trend, naphthalene < fluorene < phenanthrene, which follows the same trend of their increasing hydrophobicity. Despite of the fact that CNTs have unique chemical and physical characteristics as an adsorbent media for elimination of PAH from contaminated water and soil; few research articles have been published in this area.

5.4. Zeolite Adsorbents

Zeolites are hydrated aluminosilicate minerals that contain alkaline and alkaline-earth metals. They are microporous minerals which are widely used as commercial adsorbent due to their unique structural chemistry (e.g. Si/Al ratio, pore size) and high specific surface area [94, 96]. Zeolites modified with cationic surfactants have been introduced as effective adsorbents for removal of organic compounds [97-99]. Adsorption of PAHs including benz[a]anthracene, fluoranthene, fluorene, pyrene and phenanthrene on zeolites modified with stearyl dimethyl benzyl ammonium chloride (SDBAC) have been determined by Lemic et al. (2007) [100]. Adsorption efficiency of modified zeolite depended on the hydrophobicity of the non-polar organic compound, as at a concentration of 20 μg/dm^3, the adsorption index for benz[a]anthracene was 100%. Results showed that the adsorption of PAHs was a competitive process and firstly adsorption sites had been occupied with the less hydrophobic compounds. Leaching characteristics of anthracene and phenanthrene adsorbed on oil shale ash particles and pyrene adsorbed on zeolite NaA was evaluated by Irha and Teinemaa (2015) [101]. The ash and zeolite have similar specific surface area with different characteristics of pores. Results showed that adsorption capacity of ash for PAH was four times less than that of zeolite. Also, PAHs adsorbed on ash particles leached more readily than those on zeolite. The adsorption behavior of naphthalene on the hydrophobic zeolite from water–butanol solution has been investigated by Chang et al. (2004) [102]. Their results showed that simple kinetic model of the pseudo second-order equation has been successfully applied to predict the adsorption of naphthalene on the zeolite. The effectiveness of different filter media including calcite, zeolite, sand, and iron filings for the removal of PAHs (naphthalene or phenanthrene) from storm water runoff have been explored by Reddy et al. (2013) [103]. Results showed that all of the filter media removed more than 90% of selected PAHs from the storm water runoff. Table 5 exhibits different applications of zeolites for PAHs removal.

Table 5. *Applications of zeolites for PAH compounds removal.*

Adsorbate	Adsorbent	Main Observation	Source
Phenanthrene	Cetylpyridinium bromide - modified zeolite (SMZ)	The main mechanism for phenanthrene adsorption onto monolayer SMZ bilayer SMZ are respectively hydrophobic interaction organic partitioning.	Li et al., 2014 [95]
Anthracene, phenanthrene, and pyrene	Zeolite derived from incinerator waste (ash)	Performance of zeolite incinerator ash (1 mg/kg) in removing 98. 97, and 96% of anthracene, phenanthrene, and pyrene, respectively	Mateen et al., 2014 [104]

Adsorbate	Adsorbent	Main Observation	Source
Naphthalene	Clinoptilolite zeolite chemically modified with 2-naphtol	The optimum pH value for sorption of the naphthalene zeolite was in acidic pH. Naphthalene adsorption by the zeolite follows Langmuir model.	Panahi et al., 2015 [105]
Naphthalene	NaY zeolite modified with Ni and Cs salts	The adsorption of naphthalene occurs via a π interaction of the d orbitals of Ni^{2+} with the electrons in the aromatic rings	Thomas et al., 2010 [106]
Fluoranthene and Anthracene in smoke	NaA zeolite	Reduction of PAHs in smoke by zeolites was not limited to the removal of PAHs themselves, but related to the suppression of thermal formation of PAHs in a burning cigarette.	Ying et al., 2006 [107]

5.5. Magnetic Adsorbents

Magnetic nanoparticles have been used extensively in research for wastewater treatment and soil remediation. Large removal capacity, fast kinetics, magnetism and high reactivity for contaminant removal are main characteristics of magnetic nanoparticles. Their sole properties originated from their extremely small particle size and high surface-area-to-volume ratio [108]. Magnetite nanoparticles including (Fe_3O_4), maghemite nanoparticles (g-Fe_2O_3) and nano zero-valent iron have been attracted the attention of researchers for treatment of polluted water and soil [109-110]. The presence of functional groups on magnetic adsorbents is the main issue which has to be considered in PAH removal from wastewater with magnetic adsorbents because these functional groups create π - π interaction between PAHs and magnetic adsorbent. The separation of contaminated bio-adsorbent from wastewater in a continuous flow system is most important problem in adsorption process using bio-adsorbents. Magnetic bio-adsorbents have great potential for separation the suspended bio-adsorbents from water. Hence, possibility of extensive usage of magnetic bio-adsorbents in treatment of wastewater is strongly suggested [110-111]. Nevertheless, a few research studies have been performed to remove PAH with magnetic adsorbents.

Modified and grafted magnetic nanoparticles respectively with 3-Mercaptopropytrimethoxysiline (MPTMS) and allyl glycidyl ether for coupling with beta naphtol have been used as a novel nano-adsorbent to remove anthracene and pyrene from contaminated water by Torabian et al. (2015) [112]. The aromatic rings of 2-naphtol enables adsorption process by the reaction of π - π between PAHs and the coupled -grafted-modified magnetic nanoparticles. Effects of temperature, contact time, pH, salinity and initial concentration of PAHs have been studied on the adsorption capacity of the two PAHs on grafted magnetic nanoparticles. Their results revealed that neutral pH was ideal for the adsorption process and also increasing the concentration of PAHs, lead to an increase in removal capacity due to more π - π interaction. High temperature had a negative effect on sorption due to increased molecular mobility, so the optimum temperature could be at room temperature. Addition of NacL led to high PAH removal due to salting out effect. In other research, coal-based magnetic activated carbon (MAC) was used in sediment to reduce the chemical and biological availability of organic contaminants (Han et al., 2015) [113]. Results showed that after three months, 98% of PAH removed by magnetic activated carbon from river sediment.

5.6. Biochar Adsorbent

Biochar is made from biomass via pyrolysis. Pyrolysis is the thermal decomposition of materials in the absence of oxygen [114]. Biochar is used as a soil conditioning and remediation. Numerous studies have been conducted to develop biochar application for water and wastewater treatment [115]. Wheat straw biochars produced at 400, 600 and 800^{0C} were used to selectively adsorb PAH compounds (phenanthrene, fluoranthene and pyrene) from soil washing effluents by Li et al. (2014) [116]. It is demonstrated that biochar can remove 71.8–98.6% of PAHs and they have much higher sorption affinity for PAHs. A graphene/biochar composite was synthesized through thermal pyrolysis of graphene pretreated wheat straw by Tang et al. (2015) [117]. Graphene coated on the surface of biochar was used as adsorbent to remove phenanthrene from aqueous solution. Results showed that compared to biochar, graphene/biochar composite has larger surface area, more functional groups, greater thermal stability, and higher removal efficiency of phenanthrene and mercury. Partitioning and surface sorption were dominant mechanisms for phenanthrene sorption. Influence of biochar and activated carbon on the freely dissolved concentration of total PAHs in sewage sludge has been studied by Oleszczuk et al. (2012) [118]. Results showed that depending on the dose, the reduction of freely dissolved PAHs ranged from 0% to 57% for biochar adsorbent.

The results of numerous studies indicate that biochars has great potential for removal heavy metals and organic pollutants from soil and water, but researches have been found that during biochar pyrolysis process, dangerous PAH compounds may be produced. In the case of high levels of these contaminants in biochar, there is the risk of their release in water and soil [119-120].

6. Conclusion

Large quantities of polyaromatic compounds can be released into the environment through various routes such as incomplete combustion of fossil fuels, volcanic eruptions, forest fires, and oil spillage. Different strategies have been used to clean up PAH compound from soil, sediment and groundwater. Adsorption is the most popular process for elimination of PAH compounds. In this review paper, various adsorbents such as activated carbon, bio-adsorbent, carbon nanotube, magnetic adsorbent, biochar and zeolite adsorbent which have been used for PAH removal in water and soil have reviewed.

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