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Strategies for mitigation of polychlorinated biphenyls (PCBs): A review

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Abstract

Polychlorinated Biphenyls or PCBs belong to a broad family of chlorinated hydrocarbons and find use across industrial and commercial applications including hydraulic and electrical equipments, plastics, paints, rubber products, dyes, pigments and carbonless copy paper etc. PCB residues persist in the ecosystem and bioaccumulate in food chain due to their persistent nature and resistance against natural breakdown agents. Global case studies suggest widespread contamination of the toxicant. So it becomes the need of an hour to remove polychlorinated biphenyls entirely from the environment. Stepwise, physical, chemical and ecological remediation strategies have been applied but some lacuna in efficient mitigation was felt by various researchers in each of the methods. Therefore, combination of multiple technologies have been suggested. The current review provides the detailed descriptions on the different physical and chemical methods used for removal of PCBs including incineration, natural attenuation, supercritical water oxidation, ultrasonic radiation, bimetallic systems, nZVI, etc as well as the combination of multi techniques that have been used till date e.g. nZVI with metal combo and bimetallic metal combination etc. It also depicts the future prospects and acceptability of these methods for removal of the polychlorinated biphenyls from the ecosystem to help us achieve a green sustainable world.

Keywords: Remediation, polychlorinated biphenyls, incineration, multi technologies

Introduction

Polychlorinated biphenyls (PCBs) are the member of chlorinated aromatic hydrocarbons, which have been started using for industrial purposes since the year 1929 when Monsanto in USA had taken initiatives for manufacturing of PCBs under trade name Aroclors. The physicochemical properties(electric insulation, thermal and chemical stability etc) of PCBs makes them eligible for a broad spectrum of applications particularly in coolants, paints, floor finishing, carbonless copy paper makings, electrical transformers etc. They have been classified into Aroclors (Aroclor 1100 and 1200 series) and Congeners. Approximately 209 congeners are there as named by IUPAC according to the no of chlorine atom substitution in the biphenyl rings. Highly chlorinated congeners usually possess high octanol-water partition coefficients (Kow) and therefore often found in organic matter especially in soils and sediments. Moreover, widespread contamination is the result of partitioning of PCBs between aquatic and solid phase, present in multiple compartments due to the hydrophobicity and vapor pressure of PCBs. When PCBs are released into the environment at once, they could bioaccumulate within the food chain, due to their high affinity for organic materials. PCBs have been considered as persistent organic pollutants (POPs) under Stockholm Convention having high toxicity and undesirable effects on the ecosystem ^[1]. Furthermore, they have been found in different body tissues, blood, breast milk and liver, mainly due to consumption of meat, fish, and dairy products ^[2]. Consequentially, they have been associated with chronic effects in humans including immune system damage, decreased pulmonary function, bronchitis, and hormonal interferences leading to carcinogenicity ^[3]. In US and many other countries, different physical, chemical, combined remediation approaches have been established for complete elimination of PCBs but most of the solutions are pretty disruptive. unsustainable and they aggravate transfer of PCBs to various sections of the environment, rather than ridding them ^[4]. Therefore the current review aims at the effectiveness of the prevailing physical and chemical approaches for mitigating PCBs as well as their future perspectives.

PCB Contamination Scenario

PCBs have different sources of exposure into the environment such as by evaporation/volatilization of paints, plastics and coatings, downright leakages into sewers and streams, dumping in non-secured landfills followed by other disposal techniques like ocean dumping etc. This leads to contamination of various matrices of water, soil, air and biota. Despite stringent regulations, few PCBs are dumped illegally either by ignorance or by negligence. Approximately, 1/3rd of total PCBs manufactured in United States (US) have already entered into the environment ^[5] and this further continue to rise via dumping of aged electrical appliances like transformers, capacitors etc. Due to the hydrophobicity and persistent nature of PCBs, they have been detected in soil, sediments, air, milk, wildlife, water, fish, plants, human adipose tissues and blood samples at significant concentrations since the year 1966 [6]. More surprisingly, residues of PCBs have been detected in the snow deposits in Antarctic where no industrial activity was reported ^[7]. This contamination leads to the adverse health effects both for human and biota. PCBs are considered as carcinogenic to human by the National Toxicology Program (NTP) and International Agency for Research on Cancer (IARC). Starting from endocrine disrupting effects, PCBs hamper neuron developments and reproductive normalities in human. Besides human, every component of the ecosystem e.g. birds, aquatic animals etc have been identified with higher quantity of PCBs.

Remediation strategies

Mitigation of this cumbersome PCB pandemics is one of major issues that plagued the researchers for decades. Apart from traditional technologies, some of the multi technologies have been mentioned in various literatures. A bunch of physicochemical approaches for removal of PCBs have been mentioned in this section.

Traditional Technologies:

A bunch of conventional methods have been tried for mitigating PCBs like physical approaches, thermal incineration, photolysis, adsorption on activated carbon etc.

Incineration

Conventionally, thermal destruction is a widely used remediation approach in which PCBs react with oxygen at a very high temperature of 850°-1350 °C to form water, CO2 and HCl in an incinerator. However, during fire or incineration, more toxic derivatives PCDD/Fs may be produced as PCBs are the precursors of PCDD/Fs^[8]. Usually, this formation takes place during cooling of gases after incineration. The rate of this by products formation depends on gas temperature, existence of chlorine and presence of a catalyst. Moreover, some modern incinerators are there which can be able to withstand higher temperatures and provides dioxin removal facility that further leads to removal of problems of dangerous emissions. Advanced incineration plants are constructed throughout with dioxin removal facilities such as selective catalytic reduction ^[9]. Again, presence of Sulphur as well as combination of extreme temperatures, high heating value fuel, available oxygen and greater residence times prevent the formation of PCDD/Fs viz temperatures greater than 700 °C can result in 99% destruction for PCBs without any of the toxic by-products formation ^[10].

Photodegradation/Photolysis

Another possible remediation technology is the photolysis of PCBs. Advancement in research depicted use of catalysts to enhance rate of photolysis. Among them, TiO₂ based catalysts have shown greater photocatalytic degradation such as nafion coated TiO2 particles (Nf/TiO2), carbon-modified titanium dioxide (CM-n-TiO2) nanoparticles and platinum loaded TiO2 (P25) catalysts etc [11]. Again, graphitic carbon nitride (g-C3N4), a non-metal π conjugated polymeric semiconductor, was reported for the photocatalytic degradation of PCBs because it has some unique properties of chemical and thermal stability, low-cost, non toxicity, re-usability, optoelectric property, molecular tunability, and visible light responsive nature. Besides, TiO2/gC3N4, graphene/g-C3N4, ZnO/g-C3N4, MoS2/g-C3N4, Bi2WO6/g-C3N4 are considered as supported photocatalysts that have already displayed stupendous degradation property than metal-free gC3N4 photocatalysts [12].

Advanced Oxidation Process

One example of advanced oxidation process is the rapid destruction of PCBs by Fenton's reaction in aqueous solutions. In Fenton's reaction, combination of H₂O₂ with Fe^{2+} generates hydroxyl radicals (HO·) may be in presence or absence of light. However, in most cases, ·OH are effective only under acidic conditions. But sulfate radicals (SO4⁻⁻) are more powerful oxidants as compared to •OH radicals due to its high redox potential (2.5- 3.1 V) and a wide pH range of 2.0-8.0 ^[13]. Besides, high water solubility, subsurface stability, cost effectiveness and benign end products proved SO4⁻⁻ as a brilliant choice among AOPs for mitigating PCBs from contaminated soil, sediment and groundwater. However, chloride ion, being the major product of reaction of chlorinated organic contaminants on oxidation with SO4⁻⁻, decreases the reactivity of sulfate radical system ^[14]. More recently, different AOPs were reported for PCBs decomposition in which sulfate radicals were generated by a variety of metals including Fe(II), Fe(III), V(III), V(IV) and V(V) and some nanomaterials. Most of sulfate radical systems showed effective performance towards removal of PCBs ^[15].

Capping and Natural Attenuation

Capping is also an age old practice including the covering of the contaminated soil. It is a means of not destroying the material but here it isolates the contaminant from the environment. In order to make it more reusable some sort of soil amendments are mixed with it leading to the land farming technology. Again sorption into organic matter, biodegradation, dilution of the chemical, chemical reactions to destroy them and evaporation leads to monitored natural attenuation which is seldom used in PCB waste remediation.

De-chlorination by Chemical Reagent

PCBs can be destroyed using chemical reagents with high temperatures and pressures. Different chemical reagents have been used and amidst them most common are Zn and Mg/acidic or basic solution, Fenton's reagent, and lower valent metals (alkali metal in alcohol) ^[16]. About 90 years back, dehlaogenation was first implemented using chemical reagents e.g commercially phenol was used to dehalogenate furans and dlPCBs. Dehalogenation of congeners proved to be more efficient than biological treatments because of its rapidity ^[17].

A study on PCB elimination was held using Ca in ethanol under room temperature and normal atmospheric pressure for 24 hr and interestingly it depicted about 98% reduction in levels of toxic PCBs¹⁸. Ryoo *et al.*, (2007) ^[19] developed an elimination technique in which KOH, aluminium and polyethylene glycol 600 have been used for PCB disposal. Results of the technique showed that on an average, PCB remediation efficiency stood about 78% at 100 ^oC with 2 h, which enhanced to 99% at 150 ^oC and 4 h, particularly for PCB-77, PCB-118, PCB-123, PCB-169, and PCB105. Recently, Nah *et al.* (2008) ^[20] implemented fine metal powder, glycol and alkali to mitigate PCBs from waste insulating oil resulting in a removal efficiency of 99.9% for total PCB concentration. Further, some studies reported that a combination of chemical solutions and catalysts i.e., catalytic hydro dehalogenation, can result in a higher dechlorination performance ^[21]. Extensive research has been conducted on catalytic hydro dehalogenation of PCBs. Such a combination of chemical solution and catalysts could allow PCB dehalogenation in short times under mild conditions (e.g., ambient temperature) with low energy requirement ^[22].

| Bimetallic systems | Compounds | Operating Conditions | Findings | References |
|-----------------------|--|--|---|------------|
| Al/Pd | 2- chlorobiphe-nyl | 50 mL solution of 2-PCB was added into a 100 mL serum bottle with 5.0 g/L of Al/Pd loading and fixed on a horizontal shaker (180 rpm) at ambient temperature | 2-PCB was completely dechlorinated into BP within 60 min by the 1.43 wt.% of Al/Pd | 23 |
| Fe/Pd | Tetrachlorobiphenyl (TeCB), PCB77, Aroclor 1254 | PCBs combined 5 g of Pd/Fe were placed in a vial with 500 ml of ethanol and isopropanol solution and shaken for 16 h. The degradation was initiated by injecting 25 μL of Aroclor 1254 (100 mg L-1) into 1 mL of solution per vial containing 1 g/L as Fe of a certain type of nanoparticles. Polypyrrole film (16.2 cm²) containing Pd nanoparticles was added to 20-mL solution of PCB 77 | TeCB was completely transformed to biphenyl in 9 h. Aroclor 1254 was resulted in a 24% reduction within 100 h, 85% of PCB 77 degraded within 2 hrs | |
| Mg/Pd | 2-Monochlorobiphenyl 3- Monochlorobiphenyl 4- | 0.25 g of Mg/Pd and 10 mL of PCB solution were added into 20 mL vials and were shaken for 2 min. Analysis was done in GC/DSQ. The contaminated substrate was mixed with Mg/Pd and contacted intimately by tumbling at 20 rpm. PCB extracts (0.5 mL) were spiked with 10 μL of 200 ppm D-8 naphthalene in DCM and analysed in a GC/MS | monochlorinated congeners in water was PCB-003 > PCB- $002 > PCB-001$ | 27-28 |

Activated Carbon based removal of PCBs

A widely used method for mitigating hazardous inorganic and organic chemicals is adsorption using Activated carbon. They have highly porous structure and this helps in increasing surface area (500-2,500 m²/g) for adsorption and further chemical reactions. Amidst the naturally occurring, cost effective and renewable method, coconut shell, hardwood, rice husk, bamboo, lignite, bark husk, maize cob, peanut hull, sawdust, coir pith, and pall fiber etc have been conventionally used as activated carbons ^[30]. Furthermore, depending on the size of pores, activated carbon can be differentiated into three categories including macropores, mesopores and micropores (diameter < 50 nm)^[31]. Morphology of activated carbon also plays a significant role in adsorption of organic pollutants. Based on the morphological features, they can be classified as powdered activated carbon (PAC), granular activated carbon (GAC), activated carbon fibers (ACFs), bead activated carbon (BAC), and carbon nanotubes (CNTs) etc. At the Hunters Point Sipyard near San Franscisco, a pilot study depicted that for a period of 60 months, approximately 73% of the PCBs have been transferred from sediments to the aqueous bodies just due to addition of activated carbon (3.7% dry wt.) into the sediment ^[32]. The removal efficiency of GAC and PAC was evaluated by Vasilyeva et al. (2010) [33] in a soil previously contaminated with PCBs. Kjellerup and Edwards (2013)^[34] applied sequestration methodology using granular activated carbon for elimination PCBs from contaminated sediments. Recently, biochar provided 89% reduction in PCBs bioavailability in historically contaminated sediments [35].

Furthermore, a bunch of auxiliary techniques have been implemented along with activated carbon including microwave decomposition and/or catalysts [36]. Some of the approaches multi-technology are; PCB 29(2,4,5trichlorobiphenyl) remediation form contaminated soils using microwave and granular activated carbon ^[37], Simultaneous adsorption and dehalogenation of congeners through synthesis of reactive nano-Fe/pd bimetallic system impregnated activated carbon ^[38], substituted chlorines of high-chlorinated PCB congeners by activated carbon impregnated with Fe coupled with Pd. It is of note that considerable studies have been done on PCB remediation inoculating combination of activated carbon and anaerobic bacterial biofilm wherein activated carbon served as a microbial inoculum delivery system. This opened the door towards the purposeful usage of combination technologies for outstanding success ^[39]

Modern Technology for PCB waste Remediation Supercritical Water Oxidation

It is a technology which occurs in water at temperatures and pressures above the critical point (647 K and 22.064 MPa)^[40]. This supercritical condition transform water from a polar to non polar solvent due to loss of hydrogen bonds. Therefore, solubility of PCBs in supercritical water start increasing. Example of some efficient commercially used SCWO system includes an operating condition of 550–650 ^oC ,250 bar pressure and most importantly it proved to be highly efficient, achieving over 99% PCB destruction ^[41]. Weber *et al.* (2002) ^[42] also documented over 99% PCBs destruction under

supercritical water with an alkaline environment. In presence of excess oxygen also, SCWO is capable of 93% decomposition of decachlorobiphenyl ^[43]. Marulanda and Bolaños (2010) ^[40] showed in a study that about 99.6% of the mixture of PCBs and hydrocarbons was destroyed from PCBcontaminated oil of a large scale mineral PCB transformer with 350% excess oxygen at about 539 ^oC. Researchers have analysed SCWO extensively and concluded that salt accumulation over the surface of equipment is a major problem which further requires high maintenance cost and other operational maintenance procedures.

Ultrasonic Radiation

Ultrasonic radiation is one of most promising technology for PCB remediation in which acoustic cavitation takes the major role^[44]. Acoustic cavitation is a mechanical activation process that destroys the attractive forces of molecules in the liquid phase and thus it allows bubble growth through vapor diffusion of solutes ^[45]. The energy present inside the bubbles will therefore release and lead to an increase in the temperatures and pressures in the microscopic regions. This finally results in chemical excitation and chemical bond breaks. So, PCB degradation can be carried out effectively using this method and simple handling conditions like low temperatures and fast reaction times added an extra flavour to it. Ultrasonic radiation shows very high PCB removal efficiencies of greater than 90% from environmental matrices ^[46]. Furthermore, Rodríguez and Lafuente (2008) ^[47] evaluated the dechlorination of PCB mixtures with ultrasonic radiation system having temperature of 40 °C with a hydrazine hydrochloride/palladium (HZ/Pd) catalyst. About 80-90% degradation of 2-chlorobiphenyl, 4-chlorobiphenyl and 2,2' -dichlorobiphenyl in aqueous solutions was observed by Okuno et al,(2000) [48] in about 30-60 min with 200 kHz ultrasound. A laboratory scale application of UR on 4chlorobiphenyl contaminated sediments depicted that more than 90% of the analyte in the aqueous, homogeneous solution was decomposed at 20 kHz ultrasound with power density of 460 W/L after 20 mins [49]. Recently introduction of ultrasound assisted chemical process (UACP) promotes a new horizon in PCB remediation technique. In a study, Chen et al. (2013)^[50] dechlorinated Aroclor 1260 by using a combination of ultrasonic irradiation and radical generations via di-tertbutyl peroxide as radical initiator. Results showed that UACP is more effective for PCBs remediation with 97% removal within 3 h. But it is a costly and not easy to be operated, moreover requirement of higher energy is also a constraint behind adoption of this technique for PCB removal.

PCBs removal by Electrokinetic Remediation

Electrokinetic remediation, an in-situ method, removes persistent organic pollutants from various environmental matrices including soil by using low-level direct current as a "cleaning agent" ^[51]. This often consists an external, direct current source, along with an anode and cathode immersed in the electrolytic solution. When the direct current is applied, the organic pollutants driven by ionic migration or electrophoresis will move towards the favourable electrodes. Other technologies like nZVI dehalogenation when coupled with electrokinetic remediation established a new stage in PCB remediation ^[52]. PCBs have been eliminated also from contaminated soil using electrokinetic energy coupled with nano Pd/Fe bimetallic nanoparticles ^[53]. They found that though the degradation was little bit slow as PCBs were strongly bound to the soil particles, high electroosmotic flow facilitates nano Pd/Fe transport. Gomes et al. (2014) [54] proposed the use of electrodialytic remediation combined with nZVI particles as a cost-effective way to remediate PCB contaminated soil. Electrodialytic remediation consists of the electrokinetic movement of ions for elimination of heavy metals ^[55]. They also used two surfactants namely saponin and Tween 80 in this study to increase PCB desorption and removal from contaminated soil. The outcome of the experiment exhibit that the removal efficiencies of highly chlorinated PCB congeners (penta-, hexa-, hepta-, and octachlorobiphenyl) ranges between 9 and 96%. Chun et al. (2013) ^[56] introduced an inventive approach for the effective dehalogenation of PCBs in contaminated sediment using electrical stimulation, which supplies electron acceptors and donors to PCB dechlorinating microorganisms. They experimented out that the concentration of weathered PCBs declined 40-60% from its original concentrations which was about 20 mg/kg dry sediments, in microcosms subjected to electric current than that of PCBs observed in control reactors.

nZVI with another Metal combination

Nano zero valent iron in combination with other metals can be a potential alternative for remediating PCBs as it can also be capable of overcoming the deficiencies due to individual treatments ^[57]. For the past few years, nZVI has been proved efficient in treating wide spectrum of contaminants like chlorinated & brominated methanes, trihalomethanes, chlorinated ethenes and benzenes, and some other polychlorinated hydrocarbons ^[58]. nZVI particles when covered with metals, becomes efficient in reducing the activation energy barriers as well as increasing the dechlorination reaction rates ^[59]. Additionally, increase in surface area and surface reactivity of metal coated NZVI added an extra flavour in rapid dechlorination process ^[60]. Zhuang et al. (2011) [61] evaluated palladized nZVI for mitigation of 2,3,4-trichlorobiphenyl (PCB-21) and the results suggested that the degradation rate of PCB-21 (normalized rate constant of 10-1) by using Pd/nFe was 3 orders of magnitude faster than that of PCB-21 when using unpalladized ZVI (normalized rate constant of 10-4). Le et al., (2015) [62] developed an integrated remediation system for dehalogenation of Aroclor 1248 using bimetallic nanoparticles Pd/nFe and biodegradation via burkholderia xenovorann LB400 whereas Horvathova et al., 2019 [63] developed an effective comparison study of bionanoremediation and nano-bioremediation using nZVI and bacteria O. anthropi from the sediment. In the first study, The dehalogenation efficiencies of tri-, tetra-, penta-, and hexachlorinated biphenyls were 99, 92, 84, and 28%, respectively while in second case about 77% degradation was found for hexa congeners by nano bioremediation strategy.

Biofilm Covered Activated Carbon

During early 1970s biofilm covered activated carbon particles was found efficient in removing organic pollutants64. Since then, the combined application of activated carbon and bacterial biofilm gained popularity as a practiced remediation technique for wastewater treatment, water purification, and elimination of organic contaminants ^[65]. Recently a report suggested that biofilm treatment along with activated carbon adsorption can significantly treat naphthenic acids in oil sand process affected waters (OSPW). The results of these successful experiments have emphasized the acceptance of the combined application as a viable tool for mitigating PCB-contaminated sediment as suggested by the USEPA.

Moreover, a bench scale study on PCB bioaugmentation in liquid wastes showed that with the use of GAC, one can be able to remove about 62% of PCBs ^[66]. Additionally, bioaccumulation of PCBs in clams, worms, and amphipods can be reduced by treating the sediment with 1-5% (w/w) of GAC as indicated by a field study. During 1- and 6-month experimental time period, sediments treated with 3.4% of coke activated carbon exhibited 85 and 92% reductions in aqueous equilibrium PCB concentrations respectively ^[67]. But due to scarcity of microorganisms, a combined application of adsorbent sequestration and bioaugmentation through biofilm covered activated carbon systems is suggested to increase the biodegradation of low concentration PCBs in sediment. Kjellerup and Edwards (2013) [34] suggested that the biofilm covered activated carbon system generally has a removal efficiency of over 60% because of simultaneous adsorption and biodegradation. A compact space between biofilms with large cell density and activated carbon surface enables the degradation by allowing microorganisms to exploit PCBs as an electron acceptor. Additionally, the microorganism nested within adherent biofilm achieve a high toxic pollutants resistivity [68]. Moreover, a biofilm coated activated carbon systems has the ability to maintain long solid retention times which results in biodegradation of persistent organics at a low growth rate ^[69].

Magnetic Composites for PCB removal

Magnetic nanomaterials were extensively investigated for adsorption of PCBs from water and wastewater treatment plants, with an effective separation via application of an external magnetic field ^[70]. nZVI particles having diameter of <100 nm and a core-shell structure are highly reactive with water and oxygen to form an outer hydroxide layer in aqueous conditions. This outer oxide layer further promotes transfer of electrons from the metal through the oxide conduction band or localized band thus could serve as an adsorbent for PCBs. Dehalogenation of alkyl halides (RX) was reported in 1994 by Schreier and Reinhard [71], who depicted that Fe powder in oxygen free and buffered water can be efficient for the process but it was difficult to predict outcomes. Since then, a novel 3 step mechanism was adopted for dehalogenation purposes [72]. In acidic environment electrons can directly transfer from Fe^0 to the PCB molecules and produces Fe^{2+} . Further in a study, iron oxides and V₂O₅/TiO₂ have been used together for effective removal of more than 95% of 10 different PCB congeners which have concentrations at a range of up to 1 mg/kg filter cake or soil ^[73]. Long et al. (2014) ^[74] experimented out that dehalogenation of Aroclor 1260 in soil can be increased by practising anaerobic composting with nZVI. To eliminate out TrCB and TeCB from water effectively, Liu et al. (2014) [75] used thermal desorption technique along with nZVI at different temperature conditions (300° - 600 °C). But scientists also reported some cases related to toxic impact of nZVI. Some composite materials like a

synthesized magnetic nanomaterial having oxide graphene as a functional group along with Fe₃O₄ also proved to be efficient to remove PCB contamination ^[76-77]. Zeng et al. (2013) ^[78] further experimented out the efficacy of Fe₃O₄grafted graphene oxide for removal of PCB 28 from a volume of contaminated water through magnetic solid-phase extraction technique. Results of further experiments suggested that 91% of the PCB 28 can be extracted from the hexane/dichloromethane. nanoparticles by Likewise, dispersion of a mixture of Fe₃O₄ and ammonium chloride on graphene oxide sheets (Fe₃O₄@PDDA/ GO_x@DNA) also showed high removal efficiencies (99.1%) for PCB from 100 mL water in 30 min [79]. Li et al. (2016) [80] developed a compiled adsorbent, metal organic nanotube (Fe₃O₄@Co-MONT) for the removal of PCB from wastewater. Choi et al. (2008) [38] observed the efficacy of Fe/Pd bimetallic nanomaterial system for PCB adsorption and they found that it adsorbed almost 100% PCB present in water within 2 days of application at room temperature and pH 6.5. Further studies exhibits that Fe₃O₄ along with betacyclodextrin resulted a polymer that increase the removal of PCBs from water with 100% removal in 30 min^[81]. Zhao et al. (2013)^[82] found that bamboo charcoal-modified Fe₃O₄ nanosheets can be successfully used for the removal of PCB from wastewater by achieving a 98.4% removal rate. Some photocatalytic nanocomposites are also found to be potent in removal of PCBs from various matrices. TiO₂ nanoparticles showed promising result for purification of waste water through photocatalysis ^[83]. Besides, its ability to remove Pthalic acid esters, Shaban et al. (2016) [84], found that the photocatalytic efficiency of carbonmodified titanium oxide nanoparticles (CM-n-TiO2) is very high (93%) when subjected to PCB contaminated water. The results of the photodegradation experiment confirmed that the value of 0.5 g/L of nanomaterial dose is ample for the remediation of high concentration of PCB under favourable condition for 24 h in acidic (pH 5) media. Other nanocomposites such as velvetlike magnetic carbon nitride nanocomposites (V-g-C₃N₄), synthesized by chemical co-precipitation, may also work effectively. The above mentioned materials were used to formulate a solid-phase extraction method to extract out PCB from water samples and the results showed that 100% removal of PCB was achieved for 3 µg/L of PCB within 3 s ^[85-86]. Wu et al. (2015) ^[87] reported that graphene oxide sheets scattered with gold nanoparticles (RGO-AuNp) exhibits high selectivity toward adsorption of PCB 77. Moreover, several studies on nanoclays revealed high affinity of these materials toward PCB remediation. Sevcu et al. (2017) [88] sought out an optimized removal method for PCB (97.5%) from water after 24h contact time. They basically carried out the PCB removal process at pH values higher than 7.5 in room temperature with a concentration of 1 g/L of nanoscale zerovalent iron in the contaminated water.

Table 2: Nanomaterials used for Effective Removal of PCBs with Mechanism of Removal [97]

| Nanomaterial | % removal | Mechanism | Isotherm | References |
|--|-----------|------------|--------------------------------------|------------|
| Methyl methacrylate on multiwalled-carbon nanotube(MWCNT- gpMMA) | 95% | Adsorption | Langmuir model, Pseudo-frst order | 89 |
| Multiwalled-carbon nanotubes grafted cyclodextrin (MWCNT-g-CD | >95% | Adsorption | Langmuir model | 90 |
| Graphene Oxide | 99% | Adsorption | Langmuir, Freundlich and PDM | 91-92 |
| Amino- functionalized polypropylene nonwoven graphene oxide (PP-g-DMAEMA/GO | 85% | Adsorption | Pseudo-1 st Order | 93 |
| Single-walled carbon nanotubes (SWCNTs) | 100% | Adsorption | - | 94 |
| metal organic nanotube (Fe3O4@Co-MONT) | 100% | MSPE | Pseudo 2 nd Order | 80 |

| Bamboo charcoal iron oxide (BC@Fe) | | SPME | - | 82 |
|--|-------|-------------------------------|------------------------------|----|
| Fe3O4 with ammonium chloride dispersed on graphene oxide sheets (Fe3O4@PDDA/ GOx@DNA) | 99.1% | SPME | Langmuir | 79 |
| Metal grafted graphene oxide (Fe3O4@GO) | 100% | MSPE | Pseudo 2 nd Order | 78 |
| Fe3O4 beta-cyclodextrin | 100% | Adsorption | Langmuir | 81 |
| Nano-Fe/Pd bimetallic | 100% | Adsorption | Pseudo-1 st order | 38 |
| Carbon-modifed titanium oxide nanoparticles (CMn-TiO2) | 93% | Photocatalytic degradation | Langmuir | 84 |
| Nanoscale zero-valent iron (NZVI) | 100% | Adsorption | - | 95 |
| Velvet-like magnetic carbon nitride nanocomposites (V-g-C3N4) | 100% | Adsorption | Langmuir and Freundlich | 85 |
| Nanoclays | 77% | Adsorption | Langmuir and Freundlich | 96 |

Conclusion and future prospects

The current review depicted the remediation strategies of PCBs. Use of chemical reagents, supercritical water oxidation, ultrasonic radiation, bimetallic systems, nZVI, and nZVI combination with a second metal have a high remediation efficiency (78-99%) with a rapid reaction time. Due to this fact, physicochemical approaches tend to be more effective than ecological remediation approaches. Activated carbon and the biofilm covered activated carbon approaches obtained the highest scores as compared to the technologies mentioned above. A low cost and relatively high remediation efficiency (more than 60%) allow them to be applied to either in-situ or ex-situ PCBs remediation. PCBs are complex chemicals, so knowledge of their chemical and physical properties is important to better understand their transport and fate thereby for selecting appropriate remediation approaches. The possibility of PCB remediation by using multiple technologies discussed in this paper need more data and pilot scale experiments in order to evaluate the effectiveness. The future vision of PCB remediation could be a comprehensive treatment solution. Because successful treatment of PCBs not only depends on the appreciated selection of the most effective remediation technology, it is also necessary to consider the public acceptance and environmental and human health impacts of the remediation technology, neither of which have been achieved.

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