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Occurrence, Fate and Treatment Methods of Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, Dioxins and Furans: A Mini Review.

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Review Article

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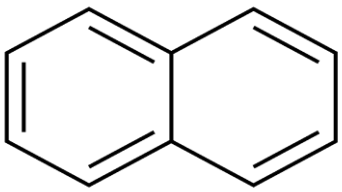
ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and furans are persistent organic pollutants with well-known toxicity and carcinogenic activity. These organic pollutants have the tendency to bioaccumulate, present little or no biodegradation and subsequently, could cause a menace to the ecosystems and human health. This review discusses the occurrence, fate and toxic effect of PAHs, PCBs, dioxins and furans. It also examines the most important advances in the treatment of water and wastewater pollution by PAHs, PCBs, dioxins and furans.

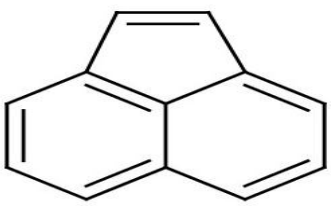
INTRODUCTION

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation. POPs are compounds of great concern due to their toxicity, persistence, long-range transport ability and bioaccumulation. Mining activities results to the contamination of the environment with potentially toxic compounds that change the ability of soil and water to sustainably develop its potential ecological functions and may seriously affect the ecosystems[1]. Oil refinery wastewater produced in crude oil mining and processing can cause serious water pollution and endanger physical health[2], while, domestic wastewater contains organic pollutants, nutrients, and other chemicals such as polycyclic aromatic hydrocarbons (PAHs)[3]. Polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dibenzofurans (Fs), PAHs, polychlorinated biphenyls (PCBs) etc. are examples of persistent organic pollutants (POPs)[4].

PAHs (Fig. 1) are group of chemicals that occur naturally in coal, crude oil and gasoline. PAHs are used in dyes, plastics, and pesticides while some are used in medicine. Therefore, they enter the surface water through wet and dry atmospheric deposition, hydrocarbon spillages, rainwater runoff into water bodies, and industrial effluent discharge, especially fromhydrocarbon processing industries.



Naphthalene



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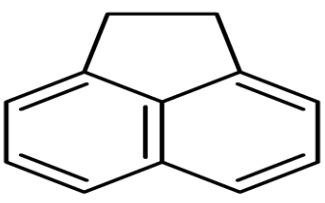

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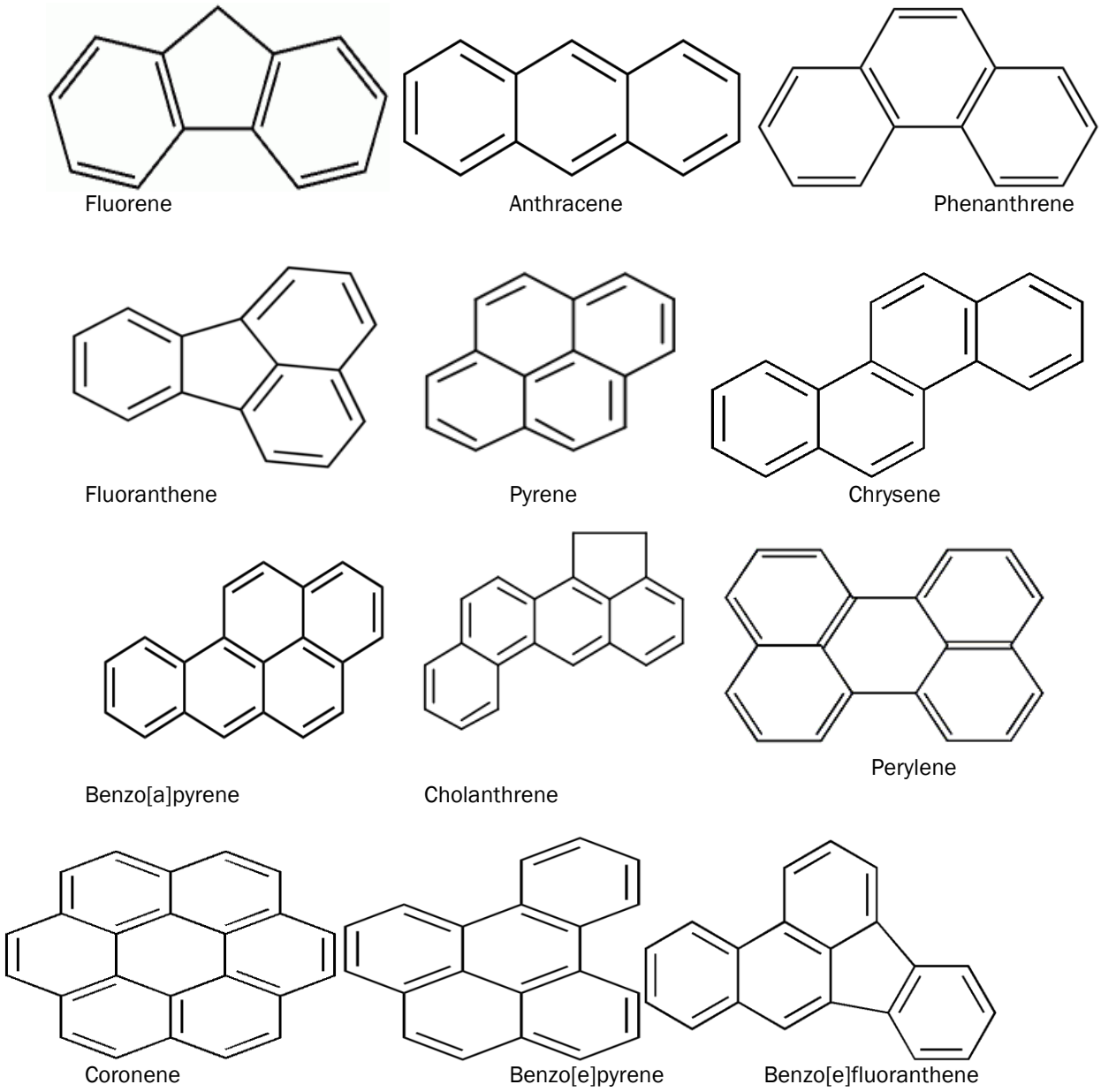


Fig. 1 - Selected polycyclic aromatic hydrocarbons

PCBs (Fig. 2) are organohalogen pollutant with 1–10 chlorine (Cl_2) atoms attached to a biphenyl molecule. They are widely used as dielectric and coolant fluids in electrical apparatus, cutting fluids for machining operations, carbon paper and in heat transfer fluids. PCBs have high hydrophobicity, stability, lipid solubility, and persistence, and these characteristics have resulted in their widespread permeation into the environmental medium[5]. PCBs and their metabolites can cause adverse health effects including carcinogenicity, endocrine disruption, neurotoxicity, dermatological and pulmonary diseases, developmental disorders of children and they interfere with calcium utilization in birds[5-7]. PCBs have been globally banned in accordance with the Stockholm Convention[8], however, PCBs are still being produced and used in many developing countries. PCBs also continue to be released from old equipment and waste sites, posing a threat to human health and the environment[9].

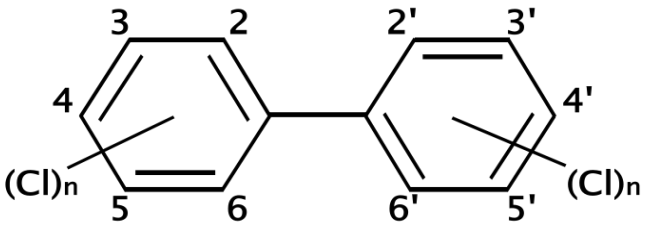
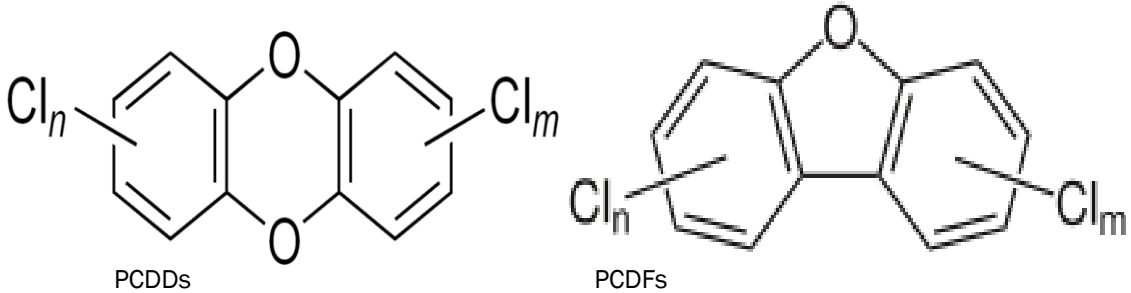


Fig. 2 - Chemical structure of PCBs

PCDDs, also known as dioxins and PCDFs, simply called furans are two series of almost planar tricyclic aromatic compounds with very similar chemical properties. PCDDs and PCDFs (Fig. 3) are not produced commercially but are byproducts in the manufacture of chlorinated phenols, chlorinated diphenyl ethers and PCBs. They are also formed in waste incineration, sewage sludge and from natural sources such as volcanoes and forest fires. Exposure to PCDDs and PCDFs may occur through inhalation, contact with the skin, and consumption of contaminated water and food (fish, meat, and dairy products). PCDDs and PCDFs are toxic, highly persistent with little or no degradation in the environment, bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and suspected human carcinogens.



PCDDs PCDFs

Fig. 3 - General structure of PCDDs and PCDFs

where *n* and *m* range from 0 to 4 for PCDDs, and $2 \leq n+m \leq 8$ in the case of PCDFs

The sources of PCDDs, FRs, PCBs, PAHs, phthalates etc. pollution is the treatment plants, which occur through the discharge of wastewater effluents and sludge, and contamination also results from manufacture, handling, use, and disposal of these chemicals. The presence of these EDCs in seawater could be as a result of the transport of contaminated wastewater effluent by rivers into oceans and seas[10]. The government policies on environmental management have therefore mandated all industries to properly manage their waste. These policies include the treatment of wastewater generated by these industries before it comes in contact with natural water streams.

Detection and quantification of PAHs, PCBs, dioxin and furan

The detection and quantification of PAHs,PCBs, dioxins and furans in environmental matrixes usually requires a pre-concentration or sample preparation step, prior to instrumental analysis by gas chromatography-mass spectrometer (GC-MS)or gas chromatography-flame ionization detector (GC-FID).

Bolzonella et al[11]measured PCBs, dioxin and furan groups in wastewater (influent), effluent (permeate), and waste activated sludge by means of high-resolution GC-MS (HRGC/HRMS) analyses. Deribe et al[12] carried out the determination of PCBs in fish species by the use of Agilent 6890 N gas chromatograph (GC) connected to an Agilent 5973 mass spectrometer (MS) after extraction of the fish tissue samples with acetonitrile, followed by dispersive solid phase extraction (dSPE) with a primary-secondary amino resin (PSA) to remove the fatty acids. Ozcan et al[6] developed an ultrasound-assisted emulsification-microextraction procedure for the determination of selected PCBs by GC-MS. The determination of PAHs, PCBs, and other organic pollutants in marine water samples has been developed by Perez-Carrera et al[13] by the use of stir bar sorptive extraction (SBSE) technique and thermal desorption coupled to capillary GC-MS (SBSE-TD-GC–MS). Polydimethyl siloxane (PDMS) was used for the extraction of the selected analytes and they reported that the method is easy, fast and presents low detection limits, good reproducibility and repeatability, and good sensitivity. The use of Soxhlet extraction followed by an automated cleanup system and gas chromatography-ion trap-mass spectrometry (GC-NCI-MS) was employed by Eljarrat et al[14] for the determination of PCDDs, PCDFs and dioxin-like PCBs. Quinete et al[8] reported the analysis of PCBs by GC-MS in electron capture negative ionization mode (GC/MS-ECNI). The determination was conducted after saponification of fat present in the biological tissues, extraction into organic solvent and clean-up. The use of GC-MS for the analysis of PAHs and other organic pollutants in coal gasification wastewater before and after treatment with anoxic moving bed biofilm reactor (ANMBBR)–biological aerated filter (BAF) system was reported by Zhuang et al[15]. The use of GC-FID for the quantification of PAHs has been widely reported also[16-18].

Removal of PAHs, PCBs, dioxin and furan from water and wastewater

Adsorption

The removal of inorganic and organic pollutants by the use of different materials (solid adsorbents) has been widely reported. The potential of chemically modified starch nanocrystals for the adsorption of 2-Naphthol, trichlorobenzene, xylene, quinoline, nitrobenzene, dichlorobenzene and chlorobenzene was reported by Alila et

al[19]. he Zhang et al[20] investigated the adsorption of organic pollutants from coking wastewater by activated coke, while,Xie et al[21] examined the adsorption capability and mechanism of hexadecyltrimethylammonium (HDTMA) modified zeolite (synthesized from coal fly ash) for the removal of aniline, nitrobenzene, and naphthalene.

Coagulation

Metal coagulants commonly use in water treatment falls into two general categories: those based on aluminum and those based on iron. The aluminum coagulants include aluminum sulfate (alum), aluminum chloride and sodium aluminate. The iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride ($FeCl_3$) and ferric sulfate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate. The use of aluminum and iron salts as coagulants, however, suffers from toxicity of the residual coagulant and sludge production, the ingestion of high concentrations of aluminum (present in treated water) causes Alzheimer's disease. The aim to find a substitute for aluminum and iron salts makes Zhao et al[22] to recently investigate the coagulation/flocculation performance of titanium tetrachloride ($TiCl_4$), $FeCl_3$, and aluminum sulfate ($Al_2(SO_4)_3$) for real water treatment. They indicated that the $TiCl_4$ showed superior coagulation performance compared to $FeCl_3$ and $Al_2(SO_4)_3$ in term of absorbance at 254 nm and dissolved organic carbon removal. The $TiCl_4$ flocculated sludge was also collected and recycled to produce TiO_2. The use of $FeCl_3$, polyaluminum chloride, and $Al_2(SO_4)_3$ coagulants for the removal of PCDDs and PCDFs from drinking water was investigated by Li et al[23]. The removal efficiency was > 99% for $FeCl_3$ and polyaluminum chloride, and 97–98% for $Al_2(SO_4)_3$. They also stated that coagulation with $FeCl_3$ preferentially removed tetra- and penta-substituted PCDD/ PCDFs from raw water.Electro-coagulation has also been effectively used to treat industrial wastewaters[24]. In electro-coagulation, flocs of metal hydroxides are formed within the effluent by electro-dissolution of soluble anodes. The coagulation method is simple and easy to operate, excessive amount of coagulants are evaded, short reaction time, low sludge production and it removes very small colloidal particles[25].

Biological wastewater treatment

The biological wastewater treatment is a natural wastewater treatment process in which microorganism such as bacteria, yeast, and fungi feed on complex materials present in wastewater and turn them into simpler substances. Biological treatment can be aerobic (in the presence of air, involves the use of aerobes, and assimilate organic contaminants into CO_2, water and biomass) or anaerobic (in the absence of air, employ the use of anaerobes and the final products of organic assimilation are methane, CO_2 gas and biomass). Biological wastewater treatment technologies include conventional activated sludge process (ASP), biological aerated filters (BAF), integrated and biological wastewater systems, membrane bioreactor (MBR), sequencing batch reactors (SBR), and package wastewater treatment plants. The ASP and MBR were selected and summarized.

ASP (Fig. 4) is a complex biological wastewater treatment system that is designed to remove carbon, phosphorus and/or nitrogen constituents in the wastewater and can be used for the treatment of sewage and industrial wastewaters. The different types of activated sludge plants are package plants, oxidation ditch, deep shaft and surface aerated basins/lagoons and the aeration methods are diffused aeration, surface aeration and pure oxygen aeration systems.The extension of ozone (O_3) to the ASP has been reported to improve the economics and performance of WWTPs. In this technique (O_3 sludge reduction method),O_3 is fed into a side stream of sludge that is been recycled back to the activated sludge tanks as shown in Fig. 5 (http://www.spartanwatertreatment.com/ozone-sludge-reduction.html).

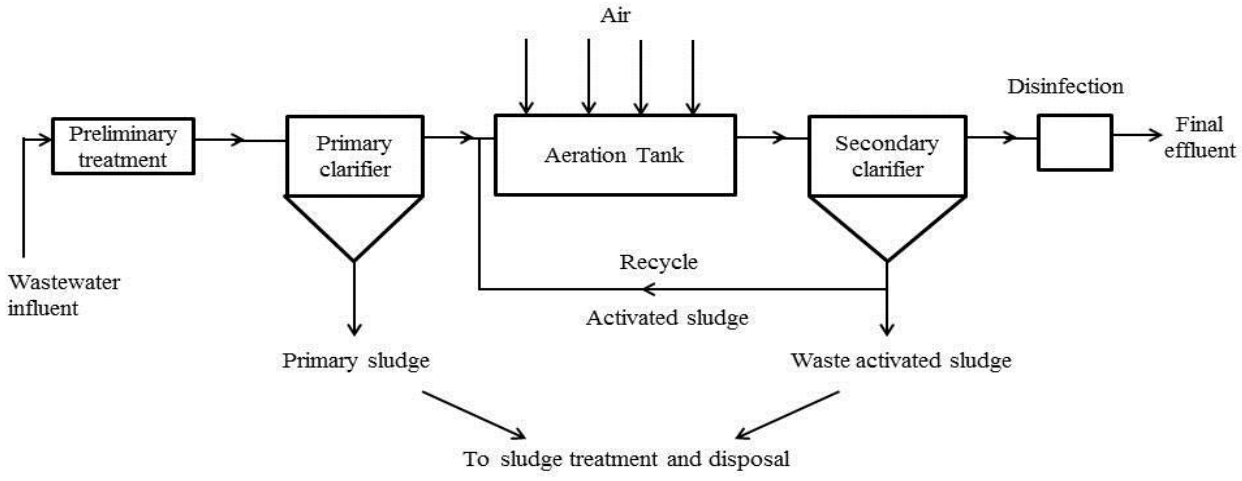


Fig. 4 - Flow diagram of activated sludge wastewater treatment system

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Microbial wastewater treatment

The microbial wastewater treatment is a biodecontamination technology that utilizes the metabolic potential of microbes to decrease the concentration of toxic compounds to undetectable, non-toxic or acceptable levels, however, elevated salinity, high temperature and high pH of wastewater might inhibit microbial growth and pose problems in the biological treatment systems. Yeast wastewater treatment processes have been used for the biodegradation of toxic substances such as PAHs present in industrial wastewater[26]. *Pichia anomala*[27] and *Sporidiobolus salmonicolor*[28]are the types of yeast used in the degradation of PAHs in literature

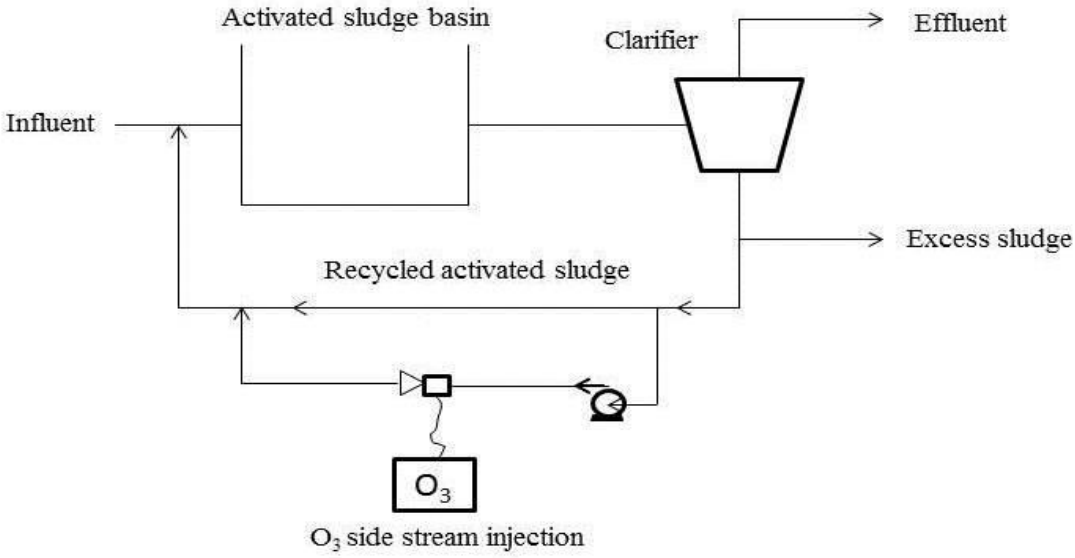

Fig. 5 - Activated sludge ozonation process

. *Phanerochaete chrysosporium*, a white rot fungus has been reported to have strong ability to degrade PAH and other toxic organic pollutants[29].

Advanced oxidation processes

Advanced oxidation processes (AOPs) are treatment techniques that utilize ozone (O_3), hydrogen peroxide (H_2O_2) and/or energy sources (UV light or catalyst) to produce hydroxyl radicals ($HO^{\bullet}$). The complete degradation and mineralization potential of AOPs are due to the generation of very reactive $HO^{\bullet}$ and other radicals. The radicals are non-selective and highly reactive to degrade a wide range of organic pollutants. The direct photolytic and photocatalytic degradation of mixed PCDDs and PCDFs have been reported by Wu et al[30]. They reported that the photocatalytic degradation declined as the number of chlorine atoms increased and that the photolytic rate of the UV/coupled catalyst was higher than that of UV/single catalyst system. It was also suggested that the primary degradation pathway for direct photolysis and photocatalysis of PCDDs/PCDFs was the C-Cl cleavage and C-O cleavage, respectively.

OzoneO_3 is produced when an electrical discharge occurs in a high-energy electric field between two conductors separated by a dielectric and a discharge gap, and with a gas of either pure oxygen or air flowing between them[31]. The electric discharge technique has been commonly used in the generation of O_3, however, corona discharge surface discharge, pulsed streamer discharge and atmospheric pressure glow discharge are now been considered[31]. Many researchers have therefore assessedthe applicability of ozonation in the treatment of water and wastewaters, however,it is sometimes difficult to degrade organic pollutants effectively by single ozonation process (SOP), hence, catalytic ozonation process (COP) with heterogeneous catalysts is often used for the removal of organic pollutants, which can overcome the slow reaction rate of the SOP[32]. Thus, Ma et al[33], Sánchez-Polo et al[34], Orge et al[35] and Chen et al[2] investigated the catalytic ozonation of nitrobenzene, ρ-chlorobenzoate, oxalic acid and heavy oil refinery wastewater, respectively, by integrated O_3 and activated carbon-supported manganese oxides (MnOx/GAC) system. Chen et al[2] suggested that the system first degrades big molecular pollutants with high toxicity and low biodegradability to small molecular oxidation products with low toxicity and high biodegradability, after which small molecular pollutants and oxidation products were further oxidized or mineralized.

The adsorption onto a cyclodextrin-based material as well as in combination with advanced oxidation using a UV-O_3 process as pretreatment was applied for the removal of PAHs, volatile organic compounds, and other toxic

organic pollutants from industrial effluents by Charles et al[36]. They reported that high levels of pollutant removal were attained with the combined use of oxidation and sorption when compared with single treatment process.

Several studies on oxides and nano oxides for water purification have been developed for the remediation of ground water, surface water and industrial wastewater. The limitation on the use of catalysts for photodegradation of wastewater is that catalysts are difficult to separate from solution, and catalyst loss may be large, with accompanying increase in costs. Catalyst loss can therefore be reduced by immobilization of the catalyst on suitable substrate[37]. TiO_2 and zinc oxide (ZnO) have been extensively used as photocatalyst because of their photostability, natural abundance, and non-toxicity[38-40], however, these photocatalysts are wide band-gap semiconductors (> 3.2 eV), and the photocatalytic efficiency remains very low because of the UV response. Hence, various efforts have been directed towards the development of visible-light responsive TiO_2 or ZnO materials.

Other reported AOP is the degradation of *p*-nitrotoluene in aqueous solution by ozonation combined with sonolysis by Song et al[41].

CONCLUSION

POPs have been found to persist in the environment, bioaccumulate in human and animal tissues and thus, have significant effect on human health and the environment. PAHs,PCBs, dioxins and furans contaminate the environment from the atmosphere, agrochemicals as well as direct discharge from industrial sources and sewage treatment plants. The analysis of PAHs,PCBs, dioxins and furans in environmental matrixes typically requires enrichment and clean-up procedure which are usually tedious and time consuming. Hence, it is important to develop sensitive, rapid, and robust analytical methods to quantify the trace levels of these organic pollutant present within the environment.Many treatment methods including adsorption, coagulation, biological, AOP*vis.* oxides and nano oxides, etc. treatments have been widely reported for the remediation of PAHs,PCBs, dioxins and furans from aqueous medium, however, the use of newer and/or combined treatment processes are required and additional data are needed to understand the relevance of PAHs,PCBs, dioxins and furans in water and wastewater systems.

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