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Recent Developments in the Application of Advanced Oxidative Processes for Remediation of Persistent Organic Pollutants from Water

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Abstract

Environmental pollution as a result of industrialization is a continuous menace. In our precious environment, Persistent organic pollutants (POPs) are constantly present and these pollutants are of great concern because of their high level of toxicity, persistency and bioaccumulation. Therefore, this chapter discusses different types and sources of POPs in the environment. The chapter also introduces Advanced oxidative processes (AOPs) and the classes of AOPs. Removal of selected POPs from aqueous solutions by AOPs, such as sulfate radical, ionizing radiation, heterogeneous photocatalysis, electrohydraulic discharge system, ozonation, and Fenton processes, were discussed. The major aim of the chapter is to make available to environmental scientists the recent developments in the removal of POPs by AOPs.

Keywords: advanced oxidation processes, persistent organic pollutants, degradation, removal, environment

1. Introduction

Today, global industrialization has resulted in the development of a variety of chemicals that, while useful, have attracted scientific attention because of their hazardous effects on humans and environment. Among these chemicals are Persistent organic pollutants (POPs) that are of serious concern because of their level of toxicity, long-persistent nature and bio-accumulation. The earth's ecology is currently being continuously contaminated by various pollutants. Pollutants of various forms are found in many locations. Some of these POPs are resistant to environmental deterioration (chemical, biological, and photolytic reactions) and exist for a lengthy period of time in our environment [1]. Persistent organic pollutants belong to a category of organic chemicals that are persistent, toxic, bioaccumulative, and are likely to have negative impacts on human health and the environment (persistent, bioaccumulative, and toxic substances) [2].

Persistent organic pollutants are defined by the Stockholm Convention as carbon-based chemicals that persist in the environment for a long period and are extensively disseminated. Persistent organic pollutants originate from man-made sources associated with the production, use, and disposal of some organic chemicals. Due to their persistence, ability to bioaccumulate in tissues, long-range transportability, and severe toxicity (even at low concentrations), POPs are a serious global hazard [3]. Persistent organic pollutants can also be produced unintentionally as by-products of combustion or chemical processing. Persistent organic pollutants are released into the environment on a regular basis, whether purposefully or unintentionally. The hydrophobicity of POPs is usually linked to halogenated compounds and these pollutants have low solubilities in water and high lipophilicities. They partition aggressively to solids, particularly organic matter, in aquatic systems and soils, avoiding the aqueous phase. These chemicals partition into lipids in organisms and are stored in fatty tissue instead of entering the aqueous milieu of cells. These chemicals exist persistently in plants and animals as a result of low metabolism [4]. Some of the POPs, such as polycyclic aromatic hydrocarbons (PAHs), can be produced from natural sources, however, POPs originate from the industries that are manufacturing a wide range of goods, such as agrochemicals, solvents, and flame-retardants [5].

2. Sources and fate of POPs in the environment

There are a number of POP chemicals, coming from certain series or 'families' of chemicals. Among the important classes of POP chemicals are many families of chlorinated (and brominated) aromatics, including polychlorinated dibenzo-p-dioxins and-furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and different organochlorine pesticides (for instance DDT and its metabolites, chlordane, toxaphene, among others). Some are accidental by-products of combustion or the industrial synthesis of other chemicals (e.g., the PCDD/Fs) not produced deliberately. Many POPs have been synthesized for industrial uses (e.g., PCBs, PBDEs, and chlorinated paraffins) or as agrochemicals (e.g., chlordane, Dichlorodiphenyl trichloroethane (DDT), and Lindane). Examples of more polar POPs are phenols (e.g., polyethoxylated alkylphenols which are non-ionic surfactants), and chlorinated phenols [6].

The three main causes of rising POP levels in ecosystems are industrial and agricultural activities as well as municipal populations. Sources of POPs are mainly from anthropogenic activities and can be introduced into the environment through many pathways. These pollutants can reach the environment through urban runoff, agricultural runoff, drainage system, industrial effluent, landfill leachate and deposition from atmosphere. Waste incineration, consumer goods production, transportation, energy generation, mineral and metal mining (ferrous and non-ferrous). Chemical synthesis also emits alarmingly large amounts of POPs into our precious environment [7].

It has been shown in literature that POPs can assimilate in the environment within weeks, but it will take years or decades for POPs to naturally decompose [8]. Persistent organic pollutants are known for their semi-volatility, which is a trait of their physicochemical properties that allows them to exist in the vapor phase or adsorbed on air particles, allowing for long-range movement in the atmosphere. Persistent organic pollutants are everywhere; they possess the ability to move through air, soil and water before being naturally decomposed [9]. They have been found in both industrialized and non-industrialized places, in urban and rural settings, in heavily populated and poorly populated areas, without significant

human aids. Persistent organic pollutants have been measured on every continent at locations that reflect every major climatic zone and geographic sector. These include places such as the Arctic, the open oceans, deserts, and the Antarctic, where there are no substantial local sources and long-distance movement from other areas of the world is the only conceivable explanation for their presence. Polychlorinated biphenyls have been found in the air in rates of up to 15 ng/m^3 in all parts of the world; in industrialized areas, concentrations can be several orders of magnitude higher. Rain and snow have also been found to contain PCBs [10].

Global cycling of POPs under the influence of climate change primarily demonstrates that global warming promotes secondary emission of POPs; for example, temperature rise will cause POPs to be re-released from soils and oceans while melting glaciers and permafrost will cause POPs to be re-released into freshwater ecosystems. Extreme weather events around the world, such as droughts and floods, cause POPs to be redistributed due to strong soil erosion. The global transport of POPs has been considerably influenced by changes in atmospheric circulation and ocean currents. Climate change has affected marine biological productivity, affecting the ocean's POP storage capacity. The patterns of aquatic and terrestrial food chains have changed dramatically, potentially amplifying POP toxicity in ecosystems. Generally, global warming speeds up the process of POP volatilization and increases the number of POPs in the environment, while also facilitating their breakdown. The future of environmental behaviors of POPs has been forecasted using models such as G-CIEMS (Grid-Catchment Integrated Environmental Modeling System), Berkeley-Trent Global Model (BETR-Global), and Globo-POP. Governments make use of these models to analyze the influence of global warming on the fate of POPs in the environmental and, as a result, properly control POPs [11, 12].

All human beings are being exposed to POPs at some point in their life, regardless of age, tribe or location. As proved by current epidemiological evidence, it has been suggested that early-life exposure to POPs can adversely affect the development of immune and respiratory systems [13]. Persistent organic pollutants infiltrate the human system as early as infancy, and these pollutants have been detected in variable amounts in baby meals, which are popular around the world for giving nutrients to infants [14]. According to studies, the proportion of POPs in the human body increases with age, with elderly population often having the greatest amount of POPs in the system, which is due to the fact that the metabolism of elderly people is normally slow [15]. Among the diseases associated with POPs are endocrine disturbance, obesity, diabetes, cardiovascular problems, cancer, reproductive and other health-related issues [1].

The toxicity and persistence of POPs to humans have created a need to develop effective POPs' cleanup methods. In the first instance, the production and use of POPs should be controlled. To address this, the United States joined forces with the European Community and 90 other countries to sign a groundbreaking United Nations treaty in Stockholm, Sweden on the 23 May 2001, and a convention on POPs known as the Stockholm Convention on POPs was signed. The Convention entered into force on the 17 May 2004 [16]. The major aim of the Convention is to protect the environment as well as human health from POPs by controlling the usage of POPs with the view to phasing them out. The Convention requires that each party should prohibit and/or take any administrative or legal action required for the reduction/elimination of POPs production and usage, export and import, as well as to take actions to prevent or minimize POPs' release into the environment. The Convention identified twelve POPs chemicals known as the "dirty dozen" for intervention, and new chemicals are considered for listing at each Conference of the parties. These chemicals are presented in **Table 1**. Nine of the initial POPs are pesticides, one is an industrial chemical and two are unintentionally produced

Chemical	Intentional production and use - Pesticide	Intentional production and use – industrial chemical	Unintentional production	Management Measure
Aldrin	X			Limited usage as local ectoparasiticide; and elimination for production
Endrin	X			Elimination
Heptachlor	X			Limited usage; and elimination for production
Mirex	X			Limited usage; and exemption for production in countries that registered for exemptions
Toxaphene	X			Elimination
DDT	X			Exemption for use in the production of dicofol; and restricted usage for malaria vector control
Chlordane	X			Limited usage; and exemption for production in countries that registered for exemptions.
Dieldrin	X			Reduction in the usage for agricultural activities; and elimination for production
Hexachlorobenzene	X	X	X	Limited usage; implementation of the measures to reduce or eliminate its release from unintentional production; and exemption for production in countries that registered for exemptions
Polychlorinated biphenyls		X	X	Elimination for usage by 2025; and elimination for production
Dioxins (polychlorinated dibenzo-p-dioxins)			X	Implementation of the measures to reduce or eliminate its release from unintentional production
Furans (polychlorinated dibenzofurans)			X	Implementation of the measures to reduce or eliminate the release from unintentional production

Table 1.
The twelve convention-identified POPs: The dirty dozen.

Chemical	Intentional production and use - pesticide	Intentional Production and use – industrial chemical	Unintentional production	Management measure
Chlordecone	X			Elimination
Lindane	X			Exemption for production in countries that registered for exemptions for usage as a human health pharmaceutical
Alpha hexachlorocyclohexane	X		X	Managing of unintentionally production; and elimination
Beta hexachlorocyclohexane	X		X	Managing of unintentionally production; and elimination
Pentachlorobenzene (PeCB)	X	X	X	Managing of unintentionally production; and elimination
Tetrabromodiphenyl ether and pentabromodiphenyl ether		X		Exemption for use as articles containing these chemicals for recycling; and elimination for production
Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctanesulfonyl fluoride (PFOS-F)		X		Phasing out with acceptable purpose and specific exemptions
Hexabromobiphenyl		X		Complete elimination
Hexabromodiphenyl ether and Heptabromodiphenyl ether		X		Exemption for use as articles containing these chemicals for recycling; and elimination for production

Table 2.
The POPs listed in May 2004.

through certain industrial processes. Nine new POPs (**Table 2**) were listed in May, 2004 which includes unintentionally produced and released POPs, which result from some industrial processes [17].

Another approach to prevent the proliferation of POPs is the development of novel advanced technologies for remediation of water pollution. Water for human and animal consumption must be adequately treated to ensure excellent health, thus pollutants must be removed. Freshwater resources are exposed to a number of organic pollutants, including dyes, medicines, industrial chemicals, pesticides, and personal care products, which are discharged directly into natural water systems on a daily basis. Treatment of industrial effluents before being released into natural water bodies is crucial for effective protection of natural water resources. Some of the successful water treatment procedures used in the service and provision of

industrial or municipal potable water include flocculation, coagulation, filtration, and chlorination. Conventional treatment, however, is ineffective against removal of POPs. Despite their established lipophilicity, POPs are unlikely to adsorb on organic matter, and application of treatment chemicals frequently produce undesirable intermediates, making conventional treatment methods unfruitful [18].

However, various advanced wastewater treatment technologies such as activated carbon adsorption, membrane bioreactor (MBR) and advanced oxidation processes (AOP) have been applied in the treatment of POPs to counter the difficulty in conventional methods [19].

3. Advanced oxidation processes (AOP)

Advanced oxidative processes are aqueous phase oxidation systems that produce highly efficient oxidizing agents, such as hydroxyl and sulfate radicals that are mainly generated as the dominating species, which have high ability to destroy POPs. The radicals ensure that soluble organic pollutants are effectively degraded into biodegradable and simple molecules. The solution pH, water turbidity, duration of reaction, the amount/volume of the organic component sensitive to degradation, and the presence of OH radical scavengers or activator chemicals can all have impacts on the OH radical's degradation activity. The distinctiveness of these processes is their diversified creation of extremely reactive OH radicals, which oxidize organic contaminants in wastewater non-specifically and quickly. Depending on the treatment goals and the features of the wastewater stream, AOPs can be used as a single procedure, in combination with other AOPs, or in combination with conventional treatment techniques [20]. The benefits, which include ease of operation, high performance, low selectivity, strong reproducibility, minimal by-products' generation, and total degradation of pollutants, make AOPs viable techniques for removal of POPs from aqueous effluents [21]. Classifications of AOPs for POPs removal are depicted in **Figure 1**.

Sulfate radical (SR, $\text{SO}_4^{\cdot -}$) based AOPs have recently shown promising potentials in the degradation of non-biodegradable chemicals, with peroxydisulfate

Figure 1.
Types of AOPs for POPs removal and degradation.

(PDS, $S_2O_8^{2-}$) or peroxymonosulfate (PMS, HSO_5^-) as oxidants. Sulfate radical has a half-life longer than $\cdot OH$ (hydroxyl radicals); $SO_4^{\cdot -}$ has a greater redox potential (2.5e3.1 V) than $\cdot OH$ that has a standard redox potential of 1.8e2.7 V; and SR is more selective for the oxidation of organic contaminants over a wide pH range. Sulfate radicals react with organic molecules by removing hydrogen, adding to double bonds, and transferring electrons. Electron-donating groups will have a faster reaction rate than electron-withdrawing groups with the SR because SR is electrophilic. Some organics will react immediately with persulfate, creating SRs that propagate secondary reactions or organic radicals that decompose the desired pollutants [22]. Peroxydisulfate is not costly, and has high aqueous solubility and stability at room temperature, that is why it is often utilized as a source of $SO_4^{\cdot -}$ [23, 24]. SBA-15 silica has been used as promising support for metal catalysts due to its outstanding hydrothermal and mechanical stabilities. Similarly, Fe- and Co-based catalysts supported on SBA-15 are widely used in catalytic degradation of non-biodegradable organic compounds [25]. Electro-activated persulfates could remove various POPs, such as pesticides, dyes, and pharmaceuticals, from simulated water at the laboratory scale. Wu and co-authors reported that the EC/ $Fe^{2+}/S_2O_8^{2-}$ process removed 65.8% of acid orange 7 from wastewater in 60 min [26]. It has been shown that the combination of Electrochemical (EC) and heterogeneous activation of PDS using Fe–Co/SBA-15 as catalyst is a satisfactory technique for POPs removal—excellent in real water treatment (e.g., groundwater and wastewater) [27]. Electrochemical technique has recently been used in various investigations for persulfate activation due to its advantages in creating less sludge and so reducing both reactor volume and investment costs. Some refractory organic pollutants can be completely removed from contaminated sites under ideal conditions [28].

One of the homogenous phase methods of AOPs, the application of ionizing radiation, is considered as one of the most favorable and effective AOPs in the removal of POPs. Water and wastewater treatment with ionizing radiation is favorable because both e_{aq}^- and $\cdot OH$ are generated in the process of water radiolysis when diluted aqueous solutions (natural waters/most types of wastewaters of various origins) are irradiated. Depending on the chemical reactivity of the target species, water radiolysis products may participate in oxidative reactions with organic contaminants [29]. The most common process is water radiolysis, which produces compounds that react with dissolved species. Physical (≈ 1 fs), physico-chemical (10^{-15} – 10^{-12} s), which involves numerous processes, and chemical stage (10^{-12} – 10^{-6} s) are the three primary stages that occur at distinct rates [30]. Ionization radiation such as electromagnetic and gamma ones, high energy electrons (electron beam, EB) and charged particles and neutrons, virtually only γ -rays, and EB irradiations are employed in water and wastewater treatment [31]. Untreated (standard blue) chemical effluent from dye manufactures treatment with EB irradiation was effective in significantly decreasing toxicity and color; $p < 0.0001$ was obtained for the sample treated by 2.5 kGy [32]. The hyphenation of established original AOPs with biological treatment for ordinary applications is one of the most recent advances [33]. A combination of electron-beam of radiation source 1 MeV EB accelerator, 400 kW and biological treatment was used for purification of dyeing complex wastewater under continuous flow conditions in South Korea by Han et al. [34].

Heterogeneous photocatalysis, one of the most AOPs for water purification, is an effective, cost-effective, and environmentally friendly method of eliminating organic pollutants. During the process, a semi-conductor irradiated with an appropriate wavelength of light produces active species, which oxidize organic compounds dissolved in water. The primary benefit of this approach is that it is inherently destructive; it does not require mass transfer; can be performed at ambient conditions (atmospheric oxygen is utilized as an oxidant); and can

result in complete mineralization of organic carbon into CO_2 [35]. The pollutant, catalyst, and source of illumination must all be in close proximity or in contact for photocatalysis to work efficiently and effectively. Advanced oxidation technology's ability to remove minimal concentrations of POPs from water has been thoroughly demonstrated, and the technology is gradually being implemented in many parts of the world, including developing countries [36]. Semiconductor photocatalysts commonly used include TiO_2 , CeO_2 , ZnO , Fe_2O_3 , CdS , and so on. Due to its strong photocatalytic capability, chemical and biological inertness, excellent photochemical stability, and inexpensive price, titanium dioxide (TiO_2) is a widely utilized photocatalyst in environmental degradation of organic molecules which led to complete mineralization into CO_2 , H_2O , and harmless inorganic anions [37]. After 180 min of irradiation ($\lambda > 400 \text{ nm}$), about 99% pentachlorophenol (PCP) was removed by Ag-deposited TiO_2 nanotubes (TNTs) under simulated solar light [38]. Several other photocatalysts have been utilized for removal of POPs in wastewater. Lopes da Silva et al. [39] investigated the degradation of perfluorooctanoic acid (PFOA) in water using Indium oxide and the results showed a good potential of nanosized In_2O_3 photocatalyst in degradation. Nanocrystalline ZnO particles doped with different concentrations of Fe impurity was able to degrade methylene blue (MB) dye in aqueous solution under UV/sunlight exposure [40]. Zn/TiO_2 catalyst synthesized from the hydrothermal method removed *ca.* 80% of paraquat from aqueous solution (using 4 g L^{-1} of catalyst) under UV and solar light irradiation [41].

Electrohydraulic discharge system is one of the most advanced oxidation methods for degrading hazardous organic contaminants in water and wastewater. Electrical plasma technology, as one of AOPs, has sparked a lot of interest in the removal of organic pollutants, owing to the absence of external chemicals, environmental compatibility, ability to kill microbes, non-generation of secondary pollution high removal efficiency, efficacy, and ease of operation at ambient temperature and pressure [42, 43]. Depending on the solution pH, conductivity, and discharge magnitude, an electrohydraulic discharge system can activate both the physical process and the chemical reaction mechanism, which subsequently generates free active species such as H_2O_2 , OH radical, O, O_3 , and $\text{O}_2^{\cdot-}$. This system could be combined with a number of AOPs including chemical, photolysis, ultrasonic irradiation, electrical, and supercritical water oxidation in water. Oxidative degradation of medicinal drug diclofenac (DCF) in water was investigated using a pulsed corona discharge generated above liquid. Efficient removal of DCF in water was achieved after 15 min of non-thermal plasma treatment as DCF in solution was totally removed [44]. Two different non-thermal plasma dielectric barrier discharge (DBD) reactors (planar and coaxial) at atmospheric pressure were assessed for the removal of organic micropollutants (Atrazine, Chlorfenvinfos, 2,4-Dibromophenol, and Lindane) from aqueous solutions ($1\text{--}5 \text{ mg L}^{-1}$) at laboratory scale. The parent compounds disappeared as the plasma treatment time increased, and the degradations in both DBD devices followed first-order kinetics (k) in distilled water. The highest k value was recorded for 2,4-dibromophenol in the planar reactor, whereas the lowest k value was obtained for atrazine in the coaxial reactor [45]. The degradation of 13 distinct textile colors in an experimental DBD plasma batch reactor was investigated, during a 600-second treatment in the batch reactor, between 90 and 99% of most dyes were degraded. The investigation revealed that the DBD approach could be utilized to remediate a range of synthetic dye polluted water at low concentrations (up to 50 mg L^{-1}) with success [46].

Ozonation is another AOP that aims to degrade a wide range of organic pollutants in water by targeting their unsaturated hydrocarbon bonds [47]. Ozonation is the most promising method for pollutant degradation, according to laboratory and pilot-scale research, because it successfully eliminates a variety of substrates

and by-products. Degradation, by ozonation, of 20 mg L^{-1} of sulfadimethoxine (SDM) at pH 7.0 in different water matrices was investigated. Water treatment *via* ozonation was proven to be effective as 100% removal of SDM was achieved within 10 min [48]. Dar et al. [49] used two different ozone generators (sources: water and air) to test the degradation of pentabromophenol (PBP) in an aqueous media. The water-source ozone generator achieved complete degradation of $50 \text{ } \mu\text{mol L}^{-1}$ PBP after 5 min, and the air-source ozone generator achieved complete degradation of $10 \text{ } \mu\text{mol L}^{-1}$ PBP after 45 min. The authors found out that ozonation is an effective and suitable procedure for PBP degradation in real water systems. The effectiveness of ozone treatment to eliminate the 16 priority Polycyclic aromatic hydrocarbons (PAHs) in waste activated sludge (WAS) was investigated by optimizing ozonation performance by varying key operating variables, including ozone gas flow rate, inlet concentration and dosage and then explore the pH dependent behavior of ozone-oxidation. The PAHs removal efficiency increased with ozone dosage and was strongly pH dependent. Even at ozone dosage of $40 \text{ mg O}_3\cdot\text{g}^{-1}$, the PAHs removal efficiency at pH 9.0 (44.5%) was significantly higher than the one observed at pH 5.0 and $200 \text{ mg O}_3\cdot\text{g}^{-1}$ (41.7%). The research indicates the need of WAS disintegration during ozonation to make PAHs more accessible to O_3 molecules and $\cdot\text{OH}$ to initiate oxidation reactions and recommended to adopt a sequential batch operation for ozonation to mitigate the negative effect of soluble organic compounds generated by sludge solubilization so as to practically use ozonation for elimination of PAHs in WAS [50]. Nanotechnology can also be incorporated into ozonation for more efficient removal. The elimination of five organochlorine pesticides {hexachlorobutadiene (HCHBD), pentachlorobenzene (PCHB), hexachlorobenzene (HCHB), lindane (LIN), and heptachlor (HCH)} using integrated O_3/nZVI procedures in water solution was explored. Except for LIN and HCHB, the ozonation method showed high removal efficiency of >90% after 60 min. The O_3/UV procedure yielded somewhat higher removal rate and efficiency. Within 5 min of starting the nZVI procedure, high removal efficiency for LIN, PCHB, and HCH were measured. The findings imply that the O_3/nZVI mechanisms have great potential for increasing organochlorine pollutants breakdown and elimination [51]. Ozone-based processes, i.e., single ozonation, O_3/UVA , $\text{O}_3/\text{UVA}/\text{Fe}^{3+}$ and $\text{O}_3/\text{UVA}/\text{magnetite}$ have been shown to be suitable technologies to deal with POPs [52].

Fenton oxidation is an AOP that is cost-effective and efficient method of removing POPs from water because of the low toxicity of the reagents, absence of mass transfer limitation due to its homogeneous catalytic nature (i.e., Fe^{2+} and H_2O_2), and the simplicity of the technology. The standard Fenton reaction, on the other hand, has a number of drawbacks, such as a narrow pH range, the formation of Fe-containing sludge, and a low hydrogen peroxide usage rate [53]. The Fenton system involves combining ferrous ions with hydrogen peroxide to produce hydroxyl radicals, which have a strong oxidizing ability and can breakdown organic pollutants. Ferric ions are generated during the reaction, which can be reacted to yield ferrous ions. A Fenton-like reaction is a reaction that occurs when hydrogen peroxide reacts with ferric ions. The main disadvantage of this method is the high cost of the reactants, H_2O_2 and Fe^{2+} . As a result, numerous methods have been developed to utilize Fe^{3+} salts rather than Fe^{2+} salts, resulting in the photo-Fenton and electro-Fenton approaches [54]. Amorphous FeOOH quantum dots (QDs) were coupled with polymeric photocatalysts $g\text{-C}_3\text{N}_4$ which was developed as a visible light driving photo-Fenton catalyst. Highly dispersed FeOOH QDs anchored on $g\text{-C}_3\text{N}_4$ showed enhanced visible light driving photo-Fenton degradation of methylene orange (MO) and phenol—an indication that the FeOOH QDs coupled with $g\text{-C}_3\text{N}_4$ is a promising visible light driving photo-Fenton catalyst for organic pollutants treatment. S-doped NiFe-based particles were prepared by a solvothermal method and used

POPs	AOPs	Remarks	References
Pharmaceuticals (clofibric acid, carbamazepine, iomeprol)	Heterogeneous photocatalysis	HPLC/DAD/FLD were used to measure the degradation of the persistent contaminants. When it comes to clofibric acid breakdown, TiO2 photocatalyst P25 outperformed the Hombikat UV100. A better choice than P25 for photocatalytic degradation of iomeprol was the Hombikat UV100. The photocatalysis of clofibric acid was generally slowed down by the presence of natural organic matter and carbamazepine. As a result of this research, it is clear that photocatalysis is an effective way to eliminate POPs, even when they are present at low concentrations or in a complex matrix.	[57]
Para-chlorophenol	Heterogeneous catalytic ozonation	In the investigation, para-chlorophenol (4-CP) was subjected to ozonation and hydrogen peroxide was produced simultaneously. When molecular ozone attacks the double bonds of 4-CP's aromatic ring, hydrogen peroxide is formed, which partially deprotonated to HO2 in the neutral pH range. The HO2 accelerated the breakdown of ozone to become ·OH radicals. The ·OH probe chemical succinic acid was created. As the probe chemical vanished, it confirmed the existence of the OH radical dot radical, and its dispersion across time. Ozone and the produced ·OH enabled the breakdown of 4-CP into small molecular weight organic compounds without scavengers inactivating the radicals.	[58]
20 organic contaminants (tetrahydrofuran, benzene, pyridine, ethylbenzene, 3-methylpyridyne, toluene, furfural, dibutyl sulfide, o-xylene, o-cresol, m-cresol, phenol, nitrophenol, tert-butyl disulfide, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 4-methylbenzaldehyde, 2,4-ethylphenol, naphthalene and p-nitrotoluene)	Hydrodynamic cavitation	A number of investigations were conducted using hydrodynamic cavitation to remediate a model effluent with 20 organic compounds representing various industrial contaminants. Three mineral acids were used to acidify the wastewater. For acidification, sulfuric acid was the only chemical that resulted in effective treatment without the production of secondary pollutants that could be observed in the field. When cavitation was used for 6 h, sulfuric acid gave the best treatment, with a total organic carbon (TOC) removal rate of 90% in the majority of cases. Nitric acid was less efficient (> 60% for most of the compounds). Hydrochloric acid had the lowest performance, with most compounds degrading at <50%.	[59]
Perfluorooctanesulfonate (PFOS)	Ionizing radiation	In aqueous solution using an electron beam, the work examined the effect of oxidants on radiolysis degradation of PFOS and the mechanism for decomposition of PFOS. In spite of the fact that the absorbed dose increased, PFOS breakdown efficiency dropped. It was shown that PFOS breakdown efficiency was roughly the same when using an electron beam plus 5.0 mM persulfate at a dose 100 kGy, as compared to using only electron beam at the same dosage.	[60]
Phenol	Fenton reaction	Thermal shrinkage polymerization was used to produce Fe-g-C3N4 <i>in situ</i> . Under visual irradiation, the photocatalysis-Fenton system with H2O2 showed excellent phenol removal rate. Fenton-photocatalysis eliminated 20 ppm of phenol in 50 min. The investigators investigated the most effective conditions to remove phenol: catalyst Fe-g-C3N4 with a 5% doping, an 8 mM H2O2 concentration, a pH of 3, and catalyst dose of 1.5 g L ⁻¹ .	[61]

POPs	AOPs	Remarks	References
Phenol	Ozonation	Studies were conducted on the effects of operating parameters such as pH and ozone dosage. The breakdown of contaminants increased with increasing pH (3–11). As the ozone dosage rate rose (from 5.5 to 36.17 mg L ⁻¹ min ⁻¹), so did the efficiency of pollutant removal. As a result of the ozonation process, the wastewater's ultraviolet absorbance (UV 254 nm) reduced, indicating the breakdown of complex organic molecules into low molecular weight organic compounds. Water's pH dipped from 11 to roughly 8.5 as a result of the formation of intermediate acidic species in the process.	[62]
Pentachlorophenol (PCP)	Photo-Fenton	It has been shown that PCP (1 mg L ⁻¹) undergoes photo-Fenton degradation in the presence of simulated and natural sun irradiation. In situations when PCP photolysis is important, the soluble bio-based substances (SBO) screen has a negative impact on PCP degradation. In contrast, the photo-Fenton process was significantly improved when SBO was introduced without PCP photolysis. As a result of SBO's capacity to complex iron and prevent its precipitation as oxides or hydroxides, photo-Fenton technique can be used at pH values that are close to neutral. A larger concentration of Fe(II) (4 mg L ⁻¹) showed a favorable effect on PCP degradation, while at 1 mg L ⁻¹ , PCP degradation rates were equivalent in the presence and absence of SBO.	[63]

Table 3.
POPs removal using various AOPs.

for degradation of methylene blue (MB) from aqueous solutions with visible light in photo Fenton reaction. Results showed that NiFe₂S₄ has a great performance of MB degradation in the photo-Fenton oxidation process; 100 mL of 30 mg L⁻¹ MB could be completely degraded (99.8%) within 6 min under optimal reaction conditions [55]. Xiang and co-authors employed yolk-shell ZnFe₂O₄ as photo-Fenton catalyst to investigate antibiotics degradation. The yolk-shell ZnFe₂O₄ not only exhibited excellent photocatalytic activity for the removal of popular pollutants, but also for the co-existing pollutants consisted of tetracycline (TC) and Ciprofloxacin (CIP). They reported a novel technique for preparing high efficiency of photo-Fenton catalysts for decontamination of refractory pollutants in aqueous solutions [56].

Various studies conducted on the usage of AOPs for elimination of POPs from water are summarized in **Table 3**.

4. Conclusion

Persistent organic pollutants get into the environment through municipal populations, industrial and agricultural activities. A number of chemicals have been identified as POPs, and these chemicals include, but not limited to, Aldrin, Endrin, Heptachlor, Mirex, Chlordane, Toxaphene, Dieldrin, Hexachlorobenzene, Furans (polychlorinated dibenzofurans), Polychlorinated biphenyls, Dioxins (polychlorinated dibenzo-p-dioxins) and DDT. Advanced oxidative processes (AOPs) are aqueous phase oxidation systems that have high ability to eliminate POPs from water systems. Although several advanced oxidation processes (AOPs)

have recently achieved success in the treatment of POPs in wastewater, the successes of POPs treatment using various advanced technologies are not without downsides, such as low degradation efficiency, toxic intermediate generation, massive sludge production, high energy expenditure and high operational cost. Combination of AOPs is recommended for effective elimination of POPs from water.

Conflict of interest

The authors declare no conflict of interest.

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