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Recent advances in the elimination of persistent organic pollutants by photocatalysis

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The non-ending needs of growing human population are being met by rapid industrialization and globalization, which have nowadays become an indispensable component of growth. Although these activities have led to phenomenal growth of the human civilization, at the same time, they have resulted in severe environmental pollution by discharge of highly toxic waste. This waste is severely detrimental not only for the environment but also for the health of the human population. Among different classes of pollutants, one being considered as one of the highly toxic ones is that of persistent organic pollutants (POPs). Advanced oxidation technologies (AOTs) play a major role in the degradation of pollutants by converting organic pollutants into CO₂, H₂O, and mineralized inorganic ions. AOTs include UV-based photocatalysis, ozonation, electrochemical oxidation, and Fenton and Fenton-like processes. There are some difficulties and challenges associated with AOT, such as being highly capital intensive and high consumption of energy. To overcome these bottlenecks, photocatalytic degradation is a promising method that uses solar energy for the degradation of such pollutants. Photocatalysis is further classified into homogenous and heterogenous photocatalysis. As a part of heterogenous photocatalysis, semiconductor photocatalysts have received great attention; but because of their drawbacks such as the recombination of the electron/hole pair, low adsorption rate, and low surface area coverage, nanotechnology was considered for bringing a novel and enhanced remediation photocatalysis process. To this end, the designing of a more efficient photocatalyst by modifying morphology, composition, and structure and reducing toxicity is the need of the hour for the abatement of environmental pollutants. This review focuses on the degradation and removal of highly toxic persistent organic pollutants by using photocatalytic degradation with a detailed account of the various pollutants, their degradation mechanism, process shortcomings, remedial measures, and future prospects.

KEYWORDS

advanced oxidation technologies(AOTs), persistent organic pollutants, remediation, heterogeneous photocatalysis, photocatalytic degradation

Introduction

Environmental pollutants are the major cause of adverse effects on the normal physical and biological environmental processes. The type of pollutants that needs global attention is persistent organic pollutants (POPs). POPs are toxic chemical compounds that remain very stable in the environment for a longer period, are geographically distributed all over the world, gets accumulated in the fatty tissue of the living organism, and are toxic to human health and wildlife. POPs are found around the globe, and some of them are listed and recognized by the United Nations Environment Programme (UNEP); Inter-governmental Negotiating Committee, Montreal, Canada; International POPs Elimination Network (IPEN); and Stockholm Convention (Fiedler et al., 2019). Initially, there were 12 POPs listed in the treaty. These 12 POPs are pesticides, industrial chemicals, and by-products. After that, 16 new POPs were included as of 2017 by 181 parties (Madaj et al., 2018). Anthropogenic sources of POPs play a major role in the harmful effects of pollutants.

There are different types of POPs in the environment, and their toxicity varies. POPs are generally of two types: intentional POPs and unintentional POPs (Gaur et al., 2018). Organochlorine insecticides and industrial chemicals such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAH), and polybrominated diphenyl ethers (PBDEs) are included in the range of POPs, which are used in a variety of products. Persistent organic pollutants are the silent killers, and they are present everywhere in our environment including in the tissues of the human, plants, and animals (Fry and Power, 2017). Exposure to POPs has chronic and acute effects on the organisms such as diabetes, obesity, reproductive impairment, neurological disorder, cancer, and damage to the liver, kidney, lung, and nervous system (Cao et al., 2020). Organisms can be exposed to natural and synthetically manufactured chemicals through diet, by accident, or in the environment, and this exposure is very detrimental because it can cause genotoxicity, ecotoxicity, immunotoxicity, reproductive toxicity, and chronic toxicity.

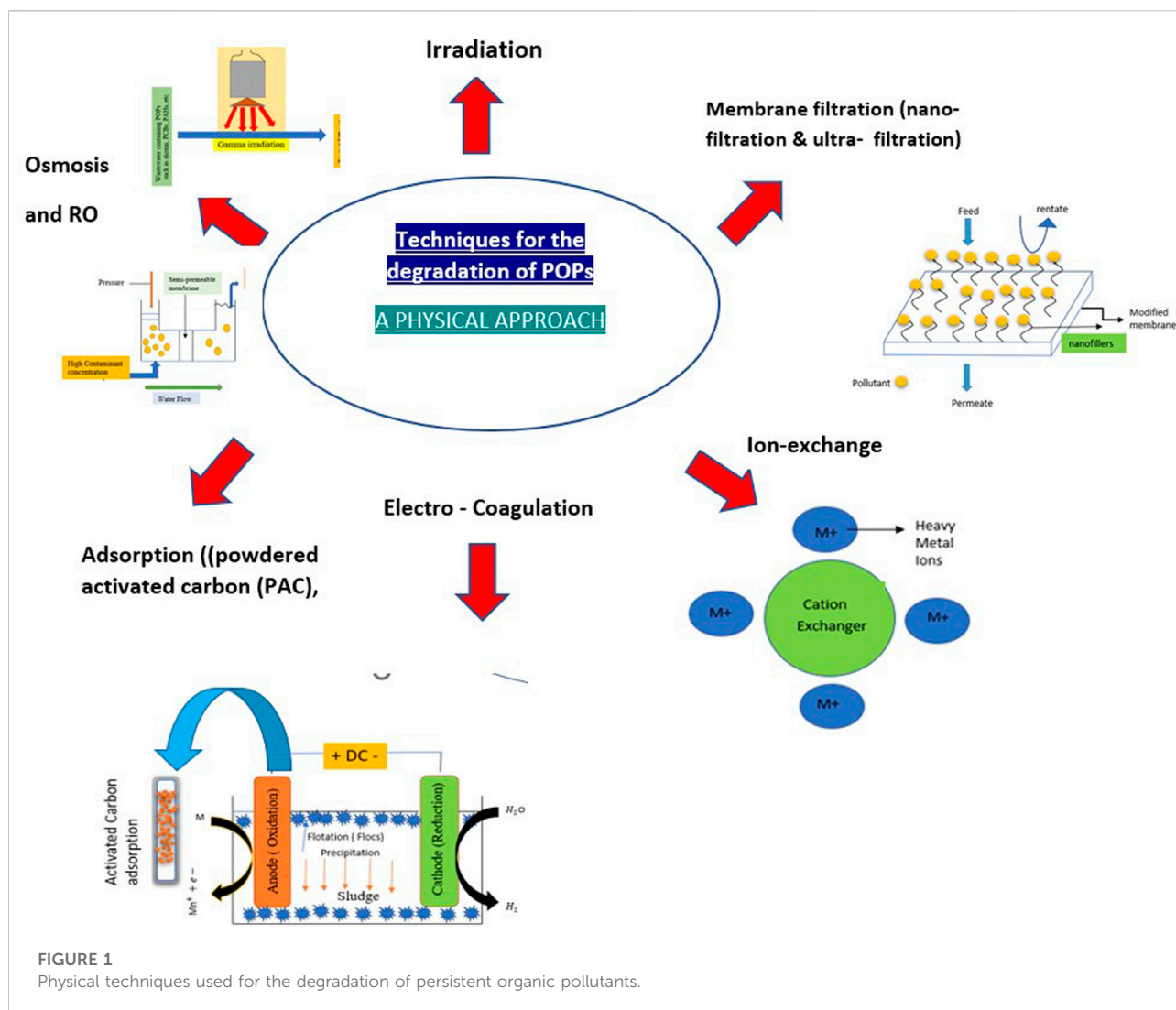
Various techniques to remove persistent organic pollutants need to be established. One of the chemical approaches well known for the degradation of POPs is the advanced oxidation technologies. AOTs are promising techniques for the removal of POPs, which are an emerging concern for the environment (Gmurek et al., 2017). The advanced oxidation methods that use light as a driving catalyst to create hydroxyl radicals include photolysis, photo-Fenton process, and photocatalysis. Photocatalysis is widely studied and used for the remediation of persistent organic pollutants. Photocatalysis is a process that combines photochemistry and catalysis and uses a synthetic substance as a catalyst. Photocatalysts can be classified into a variety of categories depending on their compositions, sizes,

diameters, electrical properties, and other characteristics. It includes typical semiconductors, molecular, plasmonic, 2D, quantum dots, metal organic frameworks, etc. (Jouyandeh et al., 2021). Some of the applications of photocatalysis include toxicity reduction of real wastewaters, abatement of air pollutants, disinfection, self-cleaning, green chemistry, degradation of natural organic matter, removal of inorganic compounds, medical applications, photodynamic therapy, hydrogen production, removal of contaminants in wastewater, and so on (Ibhadon and Fitzpatrick, 2013). The two types of photocatalysis processes that are well known are homogenous and heterogenous photocatalysis. The homogenous photocatalysis technique uses homogenous photocatalysts, in which the medium is in the same phase as the photocatalyst and the reaction. Heterogenous photocatalysis has become one of the most promising options for environmental remediation due to its capacity to produce highly reactive oxidizing species that can remove a wide spectrum of contaminants (Kar et al., 2021). In addition to several applications, there are challenges and disadvantages that are associated with the photocatalysis process. Advances in technology have opened new doors to overcome problems associated with photocatalytic degradation, but photocatalysis still faces challenges such as longer reaction times, lower efficiency, less recyclability of the photocatalyst for continuous use, high recombination rate, and less adsorption of the photocatalyst's active surface (Tahir et al., 2020).

Considering the detrimental effects of POPs and the urgent need for sustainable mitigation of persistent organic pollutants, this review, therefore, aims to summarize recent methods for removal of POPs through advanced oxidation technologies and photocatalysis. In addition, this review also dispenses data about POPs, their types, sources, and their effects on human health. The review mostly emphasizes on the photocatalysis-mediated remediation of POPs and the photocatalytic degradation mechanism, its types, and challenges faced during this process. Heterogenous photocatalysis has been described in detail with the challenges, future aspects, advantages, and the photocatalytic mechanism. While reviewing the literature, photocatalytic degradation was found to be effective as compared to the other organic pollutant-degradation techniques.

Techniques for the degradation of persistent organic pollutants

Persistent organic pollutants are environmental hazards that are resistant to degradation and may not be entirely eliminated by treatment techniques. Despite bans on some of them and their restricted use, we can still find their residues in the environment. POPs are known to have a toxic and deleterious effect on the health of the human population and environment, so it becomes very crucial to remove these substances from the environment.

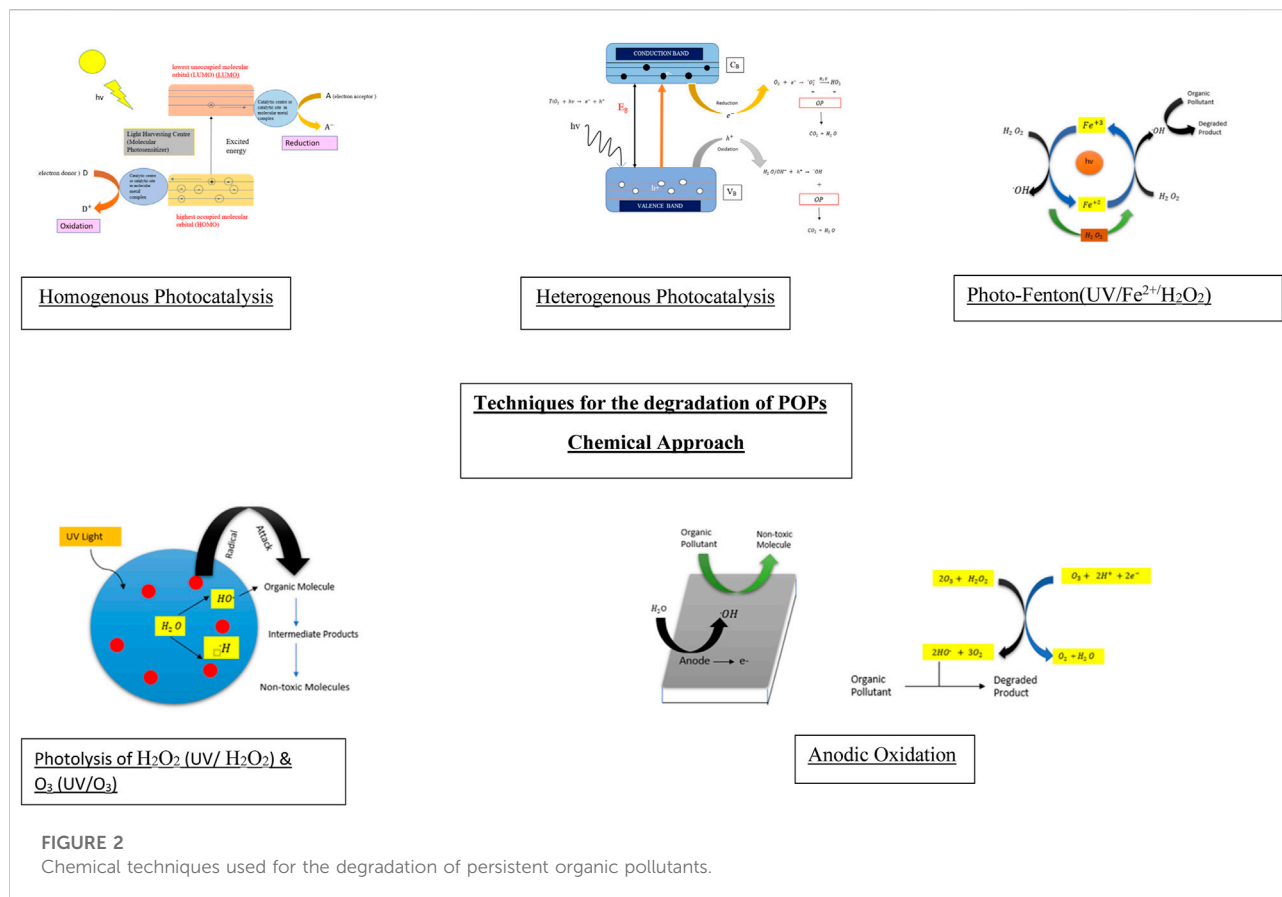


There are generally three types of approaches that are used to degrade organic pollutants: chemical approach, physical approach, and biological approach (Figures 1, 2, 3).

Advanced oxidation technologies are an important part of chemical approaches, which include electrochemical routes, sonolysis, photocatalysis, ozonation, photo-Fenton, and Fenton's reaction (Nguyen et al., 2020). The biological approach makes use of selected microorganisms for the degradation of unwanted substances present in the environment such as pesticides, textile dyes, hydrocarbons, and organic pollutants (Guo et al., 2019b). Methods that are generally included in the biological approach are bioparging, bioventing, land farming, composting, slurry reactors, biostimulation, bioaugmentation, and mycoremediation (Akhtar and Mannan 2020; Taoufik et al., 2021). Physical approaches are in the developing phase and incorporate techniques such as membrane filtration (nano-filtration and

ultrafiltration), coagulation, adsorption (powdered activated carbon (PAC), granular activated carbon (GAC), etc), ion exchange, irradiation, osmosis, and reverse osmosis.

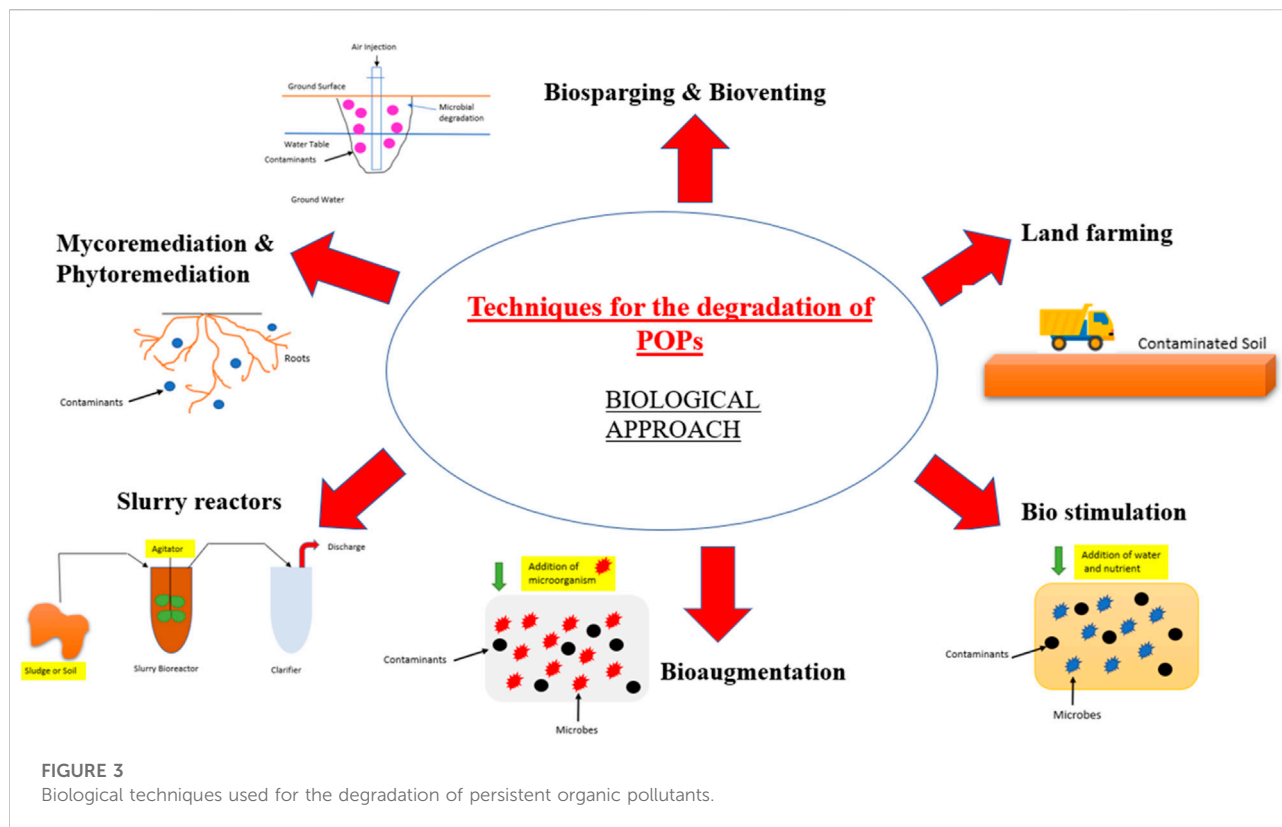
Conventional techniques include adsorption, incineration, solvent extraction, landfill stabilization/curing, composting, coagulation–flocculation–sedimentation, membrane filtration, ozonation, biological methods, phytoremediation, catalytic membrane reactors, and advanced oxidation technologies (AOTs). Table 2 presents the typical findings observed in the degradation of organic pollutants by using various remediation methods, which also include various conventional techniques. Biological processes generally involve living organisms such as bacteria, fungi, algae, and plants for the remediation of pollutants. Bioremediation is a useful technique with high throughput, cost-effectiveness, and eco-friendly properties. It uses microorganisms for the removal of organic pollutants under either aerobic or anaerobic conditions (Natarajan et al.,



2020). The presence of enzymes in the microbes make them useful for the remediation process of the pollutants because they attack the pollutant and convert them into less toxic substances (Mishra et al., 2020). Another technique used is phytoremediation, which is usually carried out by using the plants or through the involvement of bacteria in the system (Irga et al., 2018). This technique has been previously used in the removal of organochloride pesticides from the soil and water. Phytoremediation involves various processes, such as rhizoremediation, phytodegradation, phytovolatilization, phytoaccumulation, and phytoextraction. The biological methods are not convenient for the degradation of complex organic pollutants; in addition, physical and chemical methods are also not quite successful in the degradation because of the chemicals that remain untreated and the sludge treatment (Valizadeh et al., 2021). The physical methods have drawbacks while treating wastewater, such as the production of solid waste and secondary contamination. One of the techniques, coagulation–flocculation *via* chemicals, generates lots of sludge and chemicals, which are hazardous to the health of the environment and organisms. Adsorption is also costly because of the need for regular regeneration of the adsorbent as the contaminant gets adsorbed on its surface (Gusain et al., 2019).

Incineration is also used for the reduction of textile dyeing sludge, but the main drawback of this technique is that it produces harmful gases during the process, which are generally released into the environment (de Titto and Savino, 2019). Landfills are used to discard the textile dyeing sludge, but it is very toxic for the environment because it contains harmful aromatic amines which are absorbed in the soils (Vaverková, 2019). When techniques such as membrane filtration, osmosis, and reverse osmosis are used for large-scale remediation of wastewater, these techniques do not remain cost-effective in addition to operational difficulties.

One of the major drawbacks of physical methods is that it does not completely remove the pollutant from the environment. Aerobic and anaerobic biological treatments are also not suitable for the high concentration of the pollutant. The capacity of biodegradability becomes limited when this technology is used for the removal of pharmaceuticals and non-organic compounds from wastewater. Biodegradation is not effective for the removal of pollutants because some of the pollutants are non-biodegradable; in addition, the time required for the degradation is high along with use of sophisticated equipment (Akhtar and Mannan 2020). These conventional techniques have shortcomings, but by



understanding them and making improvements, overcoming these shortcomings is possible.

Wastewater, which is difficult to treat using biological treatment, is treated with advanced oxidation technologies because of their effectiveness in treating refractory pollutants present in the wastewater. Advanced oxidation technologies are more expensive in comparison to biological remediation techniques because of the additional energy and expensive chemicals used. In recent years, sulfate radical ($\text{SO}_4^{\cdot-}$)-based AOTs are used to degrade the refractory and recalcitrant organic pollutants present in the wastewater. Electrochemical technology is another technique that is effective for the complete degradation of the refractory pollutants present in industrial wastewater (Thakur and Chauhan, 2016). This technique has notable advantages, as it is compatible with the environment, is cost-effective, and has high efficiency.

AOTs are widely used for the remediation of toxic, complex, and bio-refractory contaminants because of several advantages, such as high efficiency, non-selectivity, great reproducibility, simplicity, and easy operation. In AOTs, many pollutants are oxidized by hydroxyl radicals and sulfate radicals to become less harmful compounds and later ultimately mineralized to the CO_2 and H_2O . Recent research studies show that the AOTs are effectively used for the degradation of common pollutants such as organic dyes, surfactants, hydrocarbons, phenols, pharmaceutical active ingredients,

PAHs, and pesticides (Baruah et al., 2016; Singh et al., 2020).

Table 1 provides a brief overview of some of the strategies used to remove persistent organic pollutants, including those that have been used in the past and present and those that are currently being developed. The discussion in the list significantly points to one direction: the present and future of mitigation of persistent organic pollutants are greener technologies, that is, photocatalytic degradation, which is briefly discussed in the upcoming section of this study. The photocatalytic treatment technique is an alternative that will soon be commercialized. The photocatalytic technique effectively eliminates contaminants ranging from traditional to emergent organic pollutants, including pathogens, viruses, detergents, and pesticides (Nguyen et al., 2020). In order to broaden the range of applications, it is also necessary to investigate the potential for combining various techniques with other technologies to increase the quantum yield and decrease the toxicity of the by-products and secondary pollutants that are produced. Many technological constraints must be overcome in the near future, from catalyst development to reactor design and process optimization, in order to make photocatalytic treatment technology more practical and feasible. In order to use semiconductor metal oxides and other nanoparticles for photocatalytic treatment in the future, it will be necessary to examine and assess the toxicity impact, cost analysis research,

TABLE 1 List of strategies used for the remediation of persistent organic pollutants, covering past, present, and future/emerging/innovative techniques.

POP	Past techniques	Present techniques	Future/emerging/innovative techniques	Remarks	References
1 Algal bloom (e.g., <i>Microcystis aeruginosa</i>)	<ul style="list-style-type: none"> Physical method (e.g., mechanical salvage and ultrasonic algal removal) Chemical methods (algaecides) Biological 	<ul style="list-style-type: none"> Heterogenous photocatalysis using $\text{BiOCl}_{0.6}\text{I}_{0.4}/\text{ZnO}$ floating photocatalyst Pre-oxidation Ultrasonic removal through a response surface methodology (RSM) and elitist non-dominated sorting genetic algorithm (NSGA-II)-integrated method 	<ul style="list-style-type: none"> Algal-bacterial consortia biotechnology is helpful in bloom control Identification of more marine algae-lysing bacterial strain will help in algal bloom regulation in marine ecosystem 	<ul style="list-style-type: none"> Algal-bacterial consortia technology is a promising technique for the treatment of cyanobacterial blooms in water Present and past techniques hardly achieve satisfactory removal of algal cells 	Qi et al. (2021)
2 Antibiotic and drugs	<ul style="list-style-type: none"> Adsorption by activated carbon Ozonation Biodegradation Electrochemical oxidation Sonocatalyst 	<ul style="list-style-type: none"> Photocatalysis/photolysis using heterostructure and nano-composite material photocatalyst such as TiO_2 and Bi 	<ul style="list-style-type: none"> Combination of techniques such as photocatalysis and ozonation, biodegradation and advanced oxidation technologies, and biological technique and ionizing radiations. Toxicity assessment will be conducted along with the remediation 	<ul style="list-style-type: none"> Photocatalysis using quantum dot nano photocatalyst is a great technology with efficiencies ranging between 84 and 90%, which outperforms previous techniques such as sonocatalyst and bioreactor 	Phoon et al. (2020)
<ul style="list-style-type: none"> Penicillin Paracetamol Ampicillin Tetracycline Amoxicillin 					
3 Polychlorinated Biphenyls (PCBs)	<ul style="list-style-type: none"> Biological remediation Dechlorination of PCBs by chemical reagent Phytoremediation Removal of PCBs by activated carbon 	<ul style="list-style-type: none"> Supercritical water oxidation Ultrasonic radiation Catalytic hydrodehalogenation of PCBs by bimetallic system Nanoscale zero valent ion (nZVI)-based reduced dehalogenation 	<ul style="list-style-type: none"> Multi technology Biofilm-covered activated carbon Electrokinetic remediation nZVI particles combination with a second metal 	<ul style="list-style-type: none"> A successful remediation depends on many factors Based on factors such as cost, time duration, environmental load, and efficiency, biofilm-coated activated carbon is a promising technology for the future with an efficiency range of 60–92% along with the no toxic by-products, low-cost material, and requirement of short time period 	Jing et al. (2018)
<ul style="list-style-type: none"> 2-chlorobiphenyl 2,2',3,4'-Tetrachlorobiphenyl 3-chlorobiphenyl 3,4-Dichlorobiphenyl 2,2',6 					

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TABLE 1 (Continued) List of strategies used for the remediation of persistent organic pollutants, covering past, present, and future/emerging/innovative techniques.

POP	Past techniques	Present techniques	Future/emerging/innovative techniques	Remarks	References
4 Chlorinated volatile organic compounds	<ul style="list-style-type: none"> Phytoremediation 	<ul style="list-style-type: none"> Ozonation 	<ul style="list-style-type: none"> Combination of nano-ZVI and semiconductor photocatalyst alone or in combination with a second metal 	<ul style="list-style-type: none"> Future technologies have a high remediation efficiency, but these technologies require further pilot and field-scale evaluation for the validation of their usefulness 	Ebrahimbabaie and Pichtel, (2021)
<ul style="list-style-type: none"> Chloromethane Dichloromethane Chloroethane Vinyl chloride Chloroform 	<ul style="list-style-type: none"> Chemical oxidation and reduction Bioremediation Bioaugmentation 	<ul style="list-style-type: none"> Photocatalytic oxidation with Ru/TiO₂, Ru-Ce/TiO, Ru/TiO₂, Ru-Ce/TiO, and nZVI photocatalyst Electrochemical oxidation Nanoscale zero valent ion (nZVI) 	<ul style="list-style-type: none"> Usage of nanomaterials to facilitate phytoremediation Biostimulation, bioaugmentation, and bioelectrochemical systems; technique with nanotechnology 		
5 Organochlorine pesticides	<ul style="list-style-type: none"> Phytoremediation 	Heterogenous photocatalysis with the following photocatalyst	<ul style="list-style-type: none"> Photocatalyst can be combined with other semiconductors to increase efficiency. Greater light absorption, a smaller bandgap, less charge carrier recombination, and better charge carrier separation could be factors in the increased efficiency 	<ul style="list-style-type: none"> In particular, heterogenous photocatalysis, (chemical remediation) has greater promising efficiency than biological and physical approaches with 57–97% efficiency for the degradation 	Ajiboye et al. (2020)
<ul style="list-style-type: none"> Aldrin, chlordecone Dieldrin, dicofol Endrin Dichlorodiphenyltrichloroethane (DDT) Chlordane Hexachlorobenzene (HCB) 	<ul style="list-style-type: none"> Bioremediation Incineration Low-temperature thermal desorption Adsorption Catalytic hydrogenation 	<ul style="list-style-type: none"> F- and N co-doped TiO₂ TiO₂ + HZSM-5 zeolite combine Nitrogen-doped anatase TiO₂ ZnS photocatalyst Graphitic carbon nitride (g-C₃N₄) Graphene oxide Thermal plasma for contaminated soil Electrokinetic—Fenton remediation Zero valent ion 	<ul style="list-style-type: none"> Future research must create photocatalysts that can utilize the solar system's visible light 		
6 Polycyclic aromatic hydrocarbon (PAHs)	Bioremediation	<ul style="list-style-type: none"> Oxidation process using ozone (O₃) and Fenton's reagent (Fe²⁺ + H₂O₂) 	<ul style="list-style-type: none"> Nanoparticle (NP)-based eco-engineered bioremediation strategy 	<ul style="list-style-type: none"> Site remediation of PAHs is still a difficult process because of the compact ring present in the structure, and there are still a lot of problems that need to be resolved at the laboratory, pilot, and reactor scales 	Patel et al. (2020)

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TABLE 1 (Continued) List of strategies used for the remediation of persistent organic pollutants, covering past, present, and future/emerging/innovative techniques.

POP	Past techniques	Present techniques	Future/emerging/innovative techniques	Remarks	References	
<ul style="list-style-type: none"> Acenaphthene Naphthalene Benz [a]anthracene Acenaphthylene 5-Methylchrysene Anthracene Fluorene 	<ul style="list-style-type: none"> Fungal remediation, phytoremediation, biosurfactant, rhizoremediation Electro remediation Membrane-based filtration <i>In situ</i> electrokinetic remediation Incineration 	<ul style="list-style-type: none"> Photocatalysis with photocatalytic materials such as titanium dioxide (TiO₂), zinc oxide (ZnO), silicon dioxide (SiO₂), etc., can be used with ultraviolet light 	<ul style="list-style-type: none"> Multiprocess/integrated methods Physical–biological coupled remediation Chemical–biological-coupled remediation (bio nanoparticles) Multi-biological remediation Combination of all three physical–chemical–biological-coupled remediation 			
7	<ul style="list-style-type: none"> Furans compounds and dioxins compounds Polychlorinated dibenzofurans Polychlorinated dibenzo-p-dioxins 	<ul style="list-style-type: none"> Rotary kiln incineration Landfill capping Deep well injection 	<ul style="list-style-type: none"> Electrokinetic treatment Thermal desorption Vitrification Supercritical water extraction Carbon adsorption technology Hydrothermal technology Photolysis/photocatalysis 	<ul style="list-style-type: none"> Bioremediation Plasma pyrolysis Phytoremediation Rhizodegradation Phytodegradation Phytoextraction Rhizofiltration Phytovolatilization Phyto hydraulics 	<ul style="list-style-type: none"> Recent remediation technologies, as opposed to traditional remediation methods, are quicker to process, chemical-free, ideal for real experiments, less space requirement, and environmentally friendly 	Rathna et al. (2018)
8	<ul style="list-style-type: none"> Emerging organic pollutant Dyes 	<ul style="list-style-type: none"> Sedimentation Filtration 	<ul style="list-style-type: none"> Bioremediation Photocatalytic degradation (NiFe₂O₄/ZnWO₄:g-C₃N₄/ZnV₂O₆ as a photocatalyst) 	<ul style="list-style-type: none"> Combined AOPs that will include AOPs with semiconductor nanomaterials or metal oxides Exploration of more nanoparticles or nano photocatalyst to increase the quantum yield and efficiency of the photocatalytic process 	<ul style="list-style-type: none"> According to the study, metal-oxide nanoparticles have more potential for dealing with all new organic contaminants than the photocatalytic technology that is now available 	Prakruthi et al. (2022)

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TABLE 1 (Continued) List of strategies used for the remediation of persistent organic pollutants, covering past, present, and future/emerging/innovative techniques.

POP	Past techniques	Present techniques	Future/emerging/innovative techniques	Remarks	References
<ul style="list-style-type: none"> • Personal care products • Pharmaceuticals • Phenolics • Herbicides and pesticides • Sulfonates • Pathogens and viruses • Detergents 	<ul style="list-style-type: none"> • Reverse osmosis • Flocculation • Coagulation • Membrane filtration • Adsorption by activated carbon 	<ul style="list-style-type: none"> • Metal organic frameworks • Biocomposites • Phytoremediation • Biodegradation/membrane filtration • Catalytic ozonation • Photo—Fenton • Ozonation/peroxone (O₃/H₂O₂) • TiO₂/UV/O₃ • UV/O₃–Na₂S₂O₈ 			
9 Polybrominated diphenyl ethers (PBDEs)	<ul style="list-style-type: none"> • Adsorption 	<ul style="list-style-type: none"> • Photocatalytic treatment 	Combined process of the recent technologies makes a wise choice	<ul style="list-style-type: none"> • Biodegradation is one of the most appealing strategies for PBDE treatment. However, the procedure is time-consuming and difficult 	Yao et al. (2021)
<ul style="list-style-type: none"> • Pentabromodiphenyl ethers (Penta-BDE) 	<ul style="list-style-type: none"> • Hydrothermal treatment 	<ul style="list-style-type: none"> • Nanoscale zero valent ion (nZVI) and their composites 	<ul style="list-style-type: none"> • Reductive debromination/microbial degradation 	<ul style="list-style-type: none"> • Combining several technologies is one method that may improve removal efficiency and speed up the degradation process. It could become the norm for PBDE treatment 	
<ul style="list-style-type: none"> • Octabromodiphenyl ethers (Octa-BDE) 	<ul style="list-style-type: none"> • Direct photolysis 	<ul style="list-style-type: none"> • Sulfate-based radical AOPs 	<ul style="list-style-type: none"> • Bimetallic reduction/oxidation/biodegradation treatment (nZVI/Pd reduction, nZVI/Pd-O₂ oxidation, and biodegradation by <i>Pseudomonas putida</i>) 		
<ul style="list-style-type: none"> • Decabromodiphenyl ethers (Deca-BDE) 		<ul style="list-style-type: none"> • Mechanochemical treatment • Microbial degradation • Phytoremediation • Compost • Reductive debromination 	<ul style="list-style-type: none"> • Electrokinetic and persulfate process 		

regeneration potential, and reusability potential. There is an identified gap between the commercialization of remediation techniques from the pilot scale. For a better understanding of the application at full scale, more research and investigation must be carried out at a pilot scale for usefulness so that the identified gap can be minimized (Daramola and Adebayo, 2021).

Techniques for the detection of pollutants

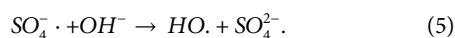
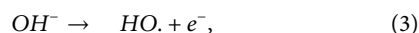
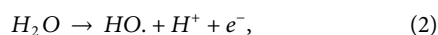
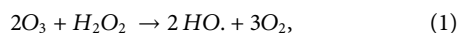
For effective remediation processes, there is a need for reliable, sensitive, and fast techniques for the screening and detection of pollutants (Moldovan et al., 2021). For detection of pollutants, electrochemical sensors, absorbance sensors, surface plasmon resonance (SPR), piezoelectric sensors, thermal sensors, enzyme/antibiotic sensors, MS (mass spectrometry), inductively coupled plasma mass spectrometry (ICPMS), OES (optical emission spectroscopy), Rayleigh scattering and post-sample fluorescence method, luminescence sensors, atomic absorption/emission spectroscopy, X-ray absorption spectroscopy, and surface-enhanced Raman scattering (SERS) are the techniques available (Singh et al., 2020). The available techniques require sophisticated ultra-modern instrumentation, which increases their cost price; therefore, these techniques are highly expensive and time-consuming. Sensors have received a great amount of attention for environmental pollutant detection in recent years. They are reliable, inexpensive, and accurate. Various functional materials are also used in environmental sensors, such as graphene, carbon nanotubes, graphitic carbon nitride, nano metals and their oxide materials, conductive polymer materials, nanoparticles, and mesoporous materials. The sensing method for the detection of environmental pollutants is still in the laboratory research stage, but they have good potential because of the attributes they have such as low cost, flexibility, portability, high selectivity, and high accuracy (Zhang et al., 2021).

Biosensors have been emerging over the past decade because they are easy, sensitive, fast, selective, and cost-effective. They can be classified into various types based on the type of analyte signal generated by the transducing element. Electrochemical and optical biosensors are the two types of biosensors that are used for pollutant detection (Yadav et al., 2021). There are still challenges to using the biosensor technique because of the low flexibility for the analyte and the low detection limit, but nanotechnology came as an alternative for increasing specificity and flexibility (Sposito et al., 2018). The introduction of nanomaterials with biosensors has reduced the disadvantages associated with them. The combination of nanomaterials with biosensors has been used for the detection of heavy metals, pathogens, pesticides, etc. The most recent emerging technique used for environmental pollutant detection is metal nanoclusters (MNCs). MNCs are made up of a few to hundreds of metal atoms with particle sizes that are close to the electron

Fermi wavelength. Because of their low toxicity, intense fluorescence, and great biocompatibility, MNCs have great potential as fluorescent probes. MNCs are used for the detection of inorganic, organic, and microbial pollutants (MU et al., 2021). Another promising tool used for the monitoring of hazardous chemicals in the environment is nanosensors. These nanosensors detect pollutants by detecting pollutants' surface markers or boosting the analytical signal. Compared to conventional approaches, nanosensors' unique characteristics make them dependable for sensitive detection of extremely low pollutant concentrations. Silver, zinc oxide, and silicon oxide nanoparticles are used in these nanosensors (Potes-Lesoinne et al., 2022). To address the toxicity hazards of chemically produced nanomaterials, green nanomaterials have received increased attention. As a result, nanotechnology has become a platform with several applications for creating a sustainable environment for current and upcoming generations.

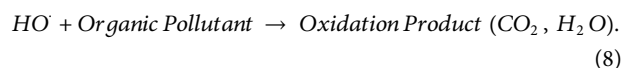
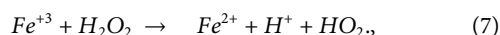
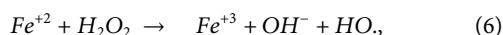
Advanced oxidation technologies

Advanced oxidation technologies (AOTs) are emergent, simple, cost-effective, and eco-friendly methods without secondary pollutant generation that effectively degrade recalcitrant organic pollutants such as aromatic amines and polycyclic aromatic hydrocarbons (PAHs). AOTs work on the *in situ* production of strong oxidizing agents including reactive oxygen species, such as singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($\text{OH}\cdot$), superoxide radicals ($\text{O}_2\cdot^-$), sulfate radicals ($\text{SO}_4\cdot^-$), and hole (h^+) (Mishra et al., 2020). These techniques are capable of oxidizing a bigger range of contaminants and, later, their mineralization to CO_2 , H_2O , and inorganic ions. AOTs are widely used in wastewater treatment plants to get organic contaminant-free water for the human population. A hydroxyl radical can be generated by using ozone, hydrogen peroxide (H_2O_2), oxidants, and in a combination of oxidizing agents such as ozone (O_3) and hydrogen peroxide (H_2O_2), irradiation (UV, ultrasound, microwave, gamma rays, etc), catalysts, or electrochemical reactions. Ozonation (Eq. 1), Fenton (Eq. 4), and photo-Fenton process-based AOTs generate hydroxyl radicals with the aforementioned combination. Hydroxyl radicals can also be generated *in situ* by the oxidation of water (Eq. 2) or hydroxide ions (Eq. 3) and through sulfate radicals (Eqs 4, 5). These free radicals with their high reactivity and oxidizing characteristics can attack most of the contaminants non-selectively. Hydroxyl radicals can be generated by three processes: photochemical process, non-photochemical process, and hybrid process. These processes are arranged into two groups: homogenous process and heterogenous process. The homogenous process generates hydroxyl radicals from ozone, hydrogen peroxide, and other oxidants in just a single phase, whereas the heterogenous process uses solid materials as catalysts such as semiconductors TiO_2 or ZnO .

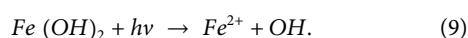


On the basis of photo-driven reactions, AOTs can be classified into two processes: 1) photochemical process and 2) non-photochemical process, as mentioned in Figure 4.

Fenton and Fenton system: The Fenton system includes Fenton, electro-Fenton, photo-Fenton, sono-photo-Fenton, sono-electro-Fenton, and photo-electro-Fenton, which are typical hydroxyl radical (OH) AOTs, as mentioned in Figure 5 (Rueda-Márquez et al., 2020). Fenton reagents are used when the activation of H_2O_2 is carried out by iron salts with the help of the oxidation process. Eq. 4 is a Fenton process that takes place at ambient temperature and pressure. It is a simple way to generate hydroxyl radicals that will destroy the organic compound by reacting with them. To produce the maximum amount of hydroxyl radicals, the process requires an acidic condition (pH 2–3). This method has wide applications because it requires easily available hydrogen peroxide and hydrogen salts.

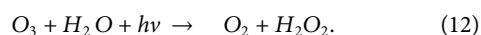
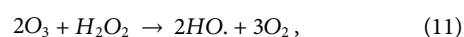
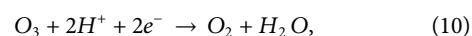


Easy availability of the iron salts and H_2O_2 makes this AOT cost-effective and practically viable. It shows high efficiency in the mineralization of organic pollutants into simpler compounds such as non-toxic carbon dioxide. Another attribute of this system is that it requires a shorter reaction time for the generation of hydroxyl radicals by the rapid reaction between the H_2O_2 and iron salts. Complicated reactor facilities are not required, and the system can work in ambient temperature and pressure. The Fenton process can be easily integrated with the pre-existing organic pollutant remediation processes such as coagulation and filtration because of the uncomplicated, flexible, and straightforward nature of the process. The Fenton system is popularly used for the remediation of wastewater and soil (Thakur and Chauhan, 2016). There are some drawbacks that have been identified such as a rigid pH range, excessive solid ferric sludge formation, ineffective utilization of hydrogen peroxide, and radical scavenging of H_2O_2 , which lead to the wastage of oxidants. The rate of degradation of pollutants can be increased by the combination of H_2O_2 and UV radiation with Fe^{+2} or Fe^{+3} oxalate ions. This photo-Fenton (PF) process increases the hydroxyl radical formation (Eq. 7).



Ozonation: Ozonation is one of the efficient methods of AOTs. In ozonation reactions, organic pollutants react directly or

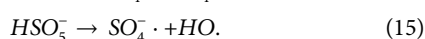
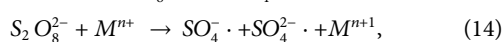
indirectly with the O_3 molecule. O_3 molecule decomposition leads to the generation of hydroxyl radicals. Ozone is also the strongest oxidant (Eq. 8) with high reactivity. There are two main mechanisms of ozonation: indirect and direct. In the direct mechanism, the molecular ozone directly does the electrophilic attack, and the indirect method involves an indirect attack by the hydroxyl radicals generated through the decomposition of ozone. The main ozonation reaction takes place in the alkaline medium because the disintegration of the ozone molecule with the water molecule is improved (de Titto and Savino, 2019). Ozone alone is not sufficient to cause complete degradation of the refractory organic pollutant that is why it is combined with H_2O_2 , UV light, catalyst, ultrasound, etc. to enhance the generation of hydroxyl radicals by the ozonation process. An appropriate catalyst or UV light irradiation can enhance the efficiency of the ozonation reaction (Eqs 10–12). The ozonation process can also be sped up with the help of homogenous and heterogenous catalysts (Vaverková, 2019). Transition metal ions such as Co(II), Mn(II), Ni(II), Fe(II), Mn(IV), Cu(II), Cr(II), Cd(II), Ag(II), and Zn(II) are involved in the homogenous catalytic ozonation, whereas in heterogenous catalytic ozonation, metal oxides such as MnO_2 , TiO_2 , or metals on metal oxide are present. Ozonation AOT includes O_3/UV , $O_3/Fe(II)$, $O_3/metal\ oxide\ catalyst$, $O_3/activated\ carbon$, $O_3/ultrasound$, $O_3/Fenton$, photocatalytic ozonation, and O_3/H_2O_2 (Eq. 9); additionally, a simple ozone molecule is insufficient because ozone alone does not facilitate complete oxidation due to a low reaction rate for the degradation of pollutant. pH, ozone dosage, ozone flow rate, catalyst loading, temperature, and reaction time are the influencing factors in the catalytic ozonation reaction.



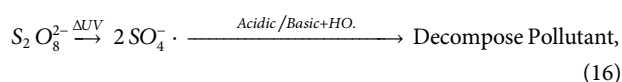
Ozonation is the most commonly used AOT for the degradation and oxidation of organic, inorganic, and micropollutants. Water disinfection or wastewater released from the petroleum refineries, textile industries, pharmaceutical industries, food industry, pulp, etc. is another area where ozonation-based AOT is most commonly employed (Singh and Borthakur, 2018). Ozonation is efficient in wastewater reclamation because of the reduced sludge formation during the process and the effective removal of the recalcitrant organic contaminants from the wastewater released from the various industries (Balachandran et al., 2016).

Sulfate radical-based advanced oxidation technologies (SR-AOTs): SR-AOTs have recently emerged as a promising alternative for the degradation of the organic contaminants and removal of the recalcitrant organic pollutant present in the air, soil, and water (Berkani et al., 2022). The reactive oxygen species generated in this type of AOT is sulfate radicals ($SO_4^{\cdot-}$). Sulfate

radicals are generated from the strongest oxidant such as peroxydisulfate (PDS) and peroxymonosulfate (PMS) (Eqs 15–16). The advantages of a sulfate radical include its strong oxidizing power ($E_0 = 2.60$ V), high efficiency, high stability, high selectivity in comparison to the hydroxyl radical, and relatively low cost. SR-AOT has a similarity to the hydroxyl AOT with respect to strong oxidative property and shorter life span. Sulfate radicals have different reaction patterns in comparison to the hydroxyl-based AOTs. The activation of radical promoters such as persulfate to generate sulfate radical can be carried out by using a thermal method (heat), metals (Eq. 14), metal oxides, alkaline, UV (Eq. 13) or visible light, microwave, ultrasound, etc. Thermal activation has an advantage over other activation methods because it does not produce the oxidation by-product during the process. PMS and PDS are activated by various transition metals such as Co, Fe, Mn, Cu, and Ag.



(peroxymonosulfate)



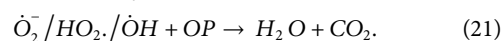
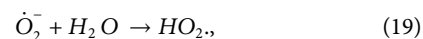
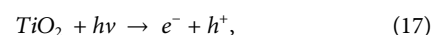
where PDS is peroxydisulfate.

In comparison to the hydroxyl radical, the sulfate radical selectively reacts with many refractory contaminants such as endocrine disruptor, pharmaceuticals, perfluorinated compounds, perfluorooctanoic acid (PFOA), and personal care products (Sun B. et al., 2020; Sun S. et al., 2020). The treatment of landfill leachate (LL) is mostly carried out by SR-AOTs. SR-AOTs have shown good performance across a wide pH range (3–9), especially in the alkaline and neutral media. SR-AOTs have been used for the treatment of petroleum wastewater, pharmaceutical wastewater, pulp and paper wastewater, textile wastewater, winery wastewater, coking wastewater, etc (Midassi et al., 2020). There are some disadvantages to using SR-AOTs: the presence of residual cation ions and sulfate ions in the effluent, costly expenses, higher amount of PMS/PDS is required for the elimination of contaminates, and the occasional formation of toxic by-products in the presence of Cl^- and Br^- .

Photocatalytic degradation

Photocatalysis can be described as the absorption of photons on the photocatalyst (solid material), which induces the chemical reaction that results in the decomposition of the adsorbed molecules on the photocatalyst (Hassan et al., 2019). The process of photocatalysis started with the transfer of the

pollutant to the photocatalyst surface, and this leads to the adsorption of the pollutants on the surface. When the photocatalytic material of the photocatalyst is exposed to the UV or visible light with equal or greater energy than that of the photocatalyst's bandgap, it results in the generation of strong reducing and oxidizing agents (electron-hole pair) that will eventually disassociate into electrons (e^-) and holes (h^+) in the conduction band and valence band, respectively. This photonic activation (e^- and h^+) causes the reduction and the oxidation of the adsorbed molecule present on the surface of the photocatalytic material. This is followed by desorption of the products that are obtained after the reaction and their removal from the photocatalyst surface. Oxidation and reduction reactions occur simultaneously in the photocatalytic reaction (equation 22–33). The crystal structure of the catalyst and the energy of the photons coming from the UV or visible light determine the reaction rate of the reaction. The specific mechanism of photocatalysis using TiO_2 photocatalyst is the reaction between the organic pollutants and the strong oxidizing and reducing agents (electron-hole pair) under irradiation of the UV or visible light (Aramyan 2017)(Eqs 17–21). Figure 6 illustrates the mechanism of photocatalysis degrading organic pollutants using the TiO_2 photocatalyst. Table 3 shows the degradation of different organic pollutants by photochemical degradation.



The detailed mechanism reaction of the fundamental process during photocatalysis is as follows:

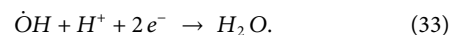
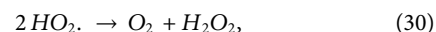
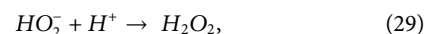
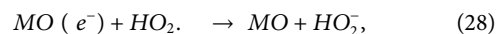
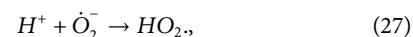
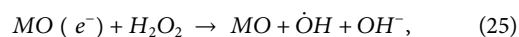
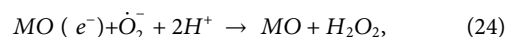
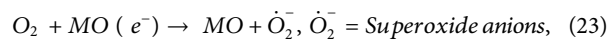
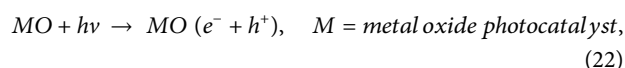


TABLE 2 Typical findings observed in the degradation of organic pollutants by using various remediation methods.

S. No	Remediation technique	Type of remediation technique	Pollutant degraded	Optimum condition/catalyst	Conclusions	References
1	Sonolysis	Chemical (AOT)	p-cresol	<ul style="list-style-type: none"> Operating frequencies (mega sonic system)—1 kHz Ultrasonic system—37 MHz Temperature—(30 ± 2°C) H₂O₂—10–60 mM 	<ul style="list-style-type: none"> p-cresol degradation (H₂O₂)—80% in 150 min Complete degradation of the p-cresol in 30 min (Fenton's reagent) Sonification (1MHz)—85% degradation in 150 min 	Chen et al. (2021)
2	Photocatalysis	Chemical (AOT)	Penicillin G	<ul style="list-style-type: none"> pH = 6.8 [ZnO]₀ = 0.8 g L⁻¹ [PG]₀ = 5 mg L⁻¹ Reaction time—150 min Stirring speed—500 rpm Temperature—22°C I (UV-A lamp) = 22 w m⁻² 	<ul style="list-style-type: none"> Degradation %—56.71% (ZnO nanoparticle) 26.21% (TiO₂ nanoparticle) in 90 min irradiation 	Hu et al. (2019)
3	Membrane filtrations (photo-Fenton ceramic membrane filtration)	Physical and chemical hybrid	Sulfadiazine (SDZ)	<ul style="list-style-type: none"> Photo-Fenton catalyst—goethite (α-FeOOH) H₂O₂ and UV irradiation I (UV-A lamp)—401 μW cm⁻² 	<ul style="list-style-type: none"> Degradation—100% within 60 min 70% (no H₂O₂ and UV irradiation) 99 % (with H₂O₂) Quantum yield—25% (UV₂₅₄ intensity—100 μW cm⁻² and H₂O₂—10 mmol L⁻¹) 	Liu et al. (2020)
4	Electro-Fenton oxidation	Electrochemical	Chloroquine (CLQ) drug	<ul style="list-style-type: none"> Na₂SO₄ = 0.05 M pH = 3.0 j = 60 mA/cm² O₂ flow rate = 80 ml/min T = 25°C Stirring = 300 rpm 	<ul style="list-style-type: none"> CLQ (Chloroquine) depletion—100% TOC—92% (Electro-Fenton-BDD (boron-doped diamond (BDD) anode.) oxidation) 	Hassan et al. (2019)
5	Ceramic membrane bioreactor (cMBR)	Physical + biological	Micropollutants in municipal wastewater	<ul style="list-style-type: none"> Airflow = 5 L/min Permeate flow = 42 L/h 	<ul style="list-style-type: none"> Removal range: 0%–43% (based on cMBR influent and effluent) in the cMBR system 	Aramyan, (2017)
6	Sulfate radical-AOT (SR-AOT)	Chemical (AOT)	Methylene blue	<ul style="list-style-type: none"> Activation of PMS—tourmaline/La_{1-x}Ce_xCoO₃ tourmaline–perovskite composite materials (CTL) 	<ul style="list-style-type: none"> Almost complete degradation of the MB within 13 min 	Adityosulindro et al. (2017)

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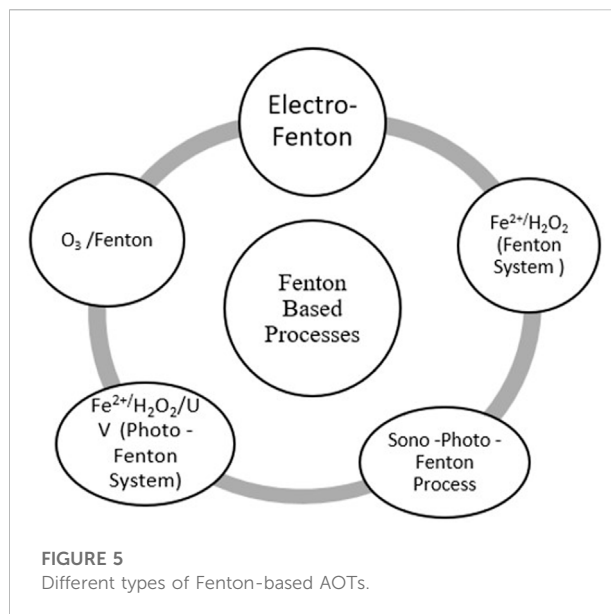
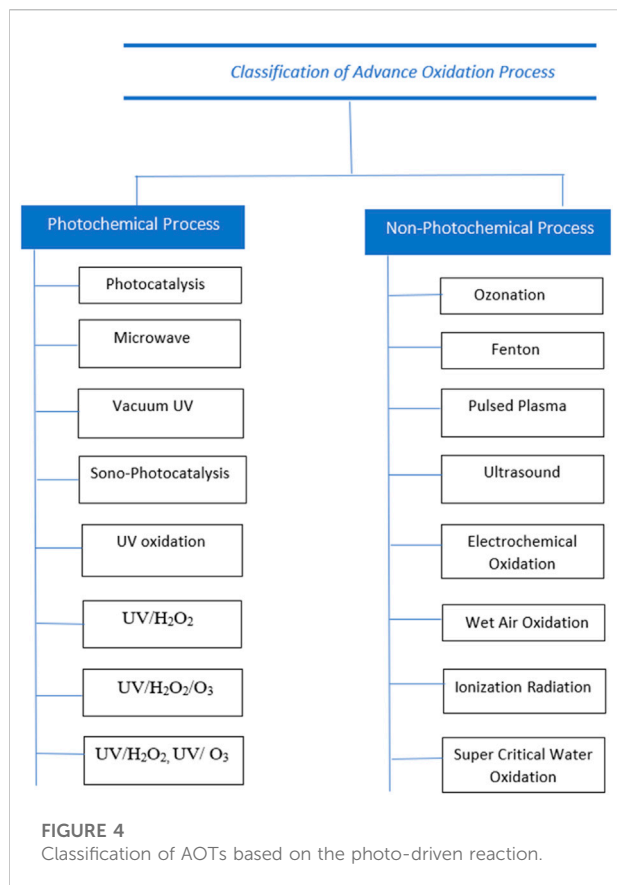
TABLE 2 (Continued) Typical findings observed in the degradation of organic pollutants by using various remediation methods.

S. No	Remediation technique	Type of remediation technique	Pollutant degraded	Optimum condition/catalyst	Conclusions	References
7	Biodegradation	Biological	Crude oil (Petroleum)	<ul style="list-style-type: none"> • Catalyst = 0.10 g/L • [PMS] = 0.2 g/L • Oil degrading bacteria: <i>B. velezensis</i>, <i>B. flexus</i>, <i>P. breneri</i>, and <i>P. azotofarmens</i> 	<ul style="list-style-type: none"> • 81% degradation (After 3 times recycling) • Out of 42, only one component (2, 6, 10, 14-tetramethylpentadecane) of crude oil is able to fully degrade • Other oil components got reduced 	Guo et al. (2020)
8	Coagulation–flocculation–sedimentation	Physical	Prototype norovirus (NV)	RT-PCR assay	<ul style="list-style-type: none"> • The removal of NV by this method was 1.5 log₁₀ based on RT-PCR assay 	Wang and Chen, (2020)
9	UV-based oxidation (UV/hydrogen peroxide (UV/H ₂ O ₂), UV/peroxydisulfate (UV/PDS), and UV/peroxymonosulfate (PMS))	Chemical (AOT)	Roxarsone (ROX)	<ul style="list-style-type: none"> • Denaturation = 95°C (15 min) • Annealing = 55°C (1.5 min) • Extension = 72°C (1.5 min) • Temp = 20 ±1°C 	<ul style="list-style-type: none"> • UV/H₂O₂ and UV/PDS are more effective than UV/PMS 	Rekhate and Srivastava, (2020)
10	Catalytic ozonation	Chemical	Reactive dyes	<ul style="list-style-type: none"> • UV Lamp = 10 W (254 nm) • Catalyst: MnFe₂O₄@CA • (CA, carbon aerogel (CA) materials) • Ozone gas flow rate –0.5 L/min • Concentration = 8 mg/L 	<ul style="list-style-type: none"> • Removal of TOC the UV/PDS exhibit best performance • 25% enhanced degradation in terms of COD (catalyst present) 	Wang et al. (2019)

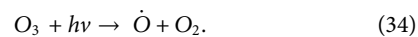
There are various advantages of the photocatalysis process which makes it a promising advanced oxidation technologies (AOT) to decompose and mineralize organic pollutants into harmless products, CO₂ and H₂O, while only utilizing the atmospheric oxygen under ambient operating temperature and pressure. Another reason that this AOT is environmentally friendly is that it does not cause secondary pollution. This technique saves a lot of energy because it utilizes solar energy for the degradation process (Adityosulindro et al., 2017).

Photocatalysts are the central element of the photocatalysis process that converts solar energy into a chemical process to degrade the organic pollutant (Guo et al., 2020). For the photocatalysis process, the semiconductor photocatalyst is widely used because semiconductors have a moderate bandgap

and oxidation and reduction can simultaneously occur on the surface of the photocatalyst (Wang and Chen 2020). Metal oxides are best suitable as photocatalysts because of their favorable light absorption, electronic structure, and bandgap, which is within the UV-visible range (Rekhate and Srivastava 2020). Among all of them, TiO₂ (titanium dioxide) gained the most attention because of its efficient and excellent performance under UV irradiation (Wang et al., 2019). Other semiconductor catalysts are used; some of them are ZnO (n-type semiconductor), WO_x (transition metal oxide and n-type semiconductor), SnO₂ (n-type semiconductor), CdS, graphene, graphite carbon nitride, etc. (Hou et al., 2021; Ma et al., 2021). Many photocatalysts were synthesized and used for the degradation of the organic pollutant, but some of the drawbacks of the semiconductor photocatalyst



oxides are most commonly used as a photocatalyst. Photocatalytic ozonation includes the presence of photocatalyst, UV-vis radiation, and ozone. In this process, the ozone molecule is adsorbed on the surface of the photocatalyst, which leads to the generation of active oxygen radicals and is followed by the reaction of water with active oxygen radicals to form hydroxyl radicals (Eq. 34).



Operational factors affect photocatalysis efficiency in addition to the intrinsic properties of the photocatalyst. Factors that affect photocatalytic activity are bandgap energy, surface area/structure of the catalyst, light intensity of the irradiated light, temperature, pH, recombination rate, and electron-hole pair separation (Shivaraju et al., 2016). Haque and Muneer (2007) briefly discuss the significance of pH. The pH value affects the surface charge properties of the photocatalyst, size of the photocatalytic aggregate, and even the sites of conductance, making it one of the significant operational elements in heterogenous photocatalysis. Gaya and Abdullah (2008) explained the directly proportional relationship between rate of photocatalysis reaction and photocatalyst dosage. However, the photocatalyst dosage should be used in the optimal level. Because of the light screening effect brought on by the extra photocatalytic particles, the response rate reduces when the dose exceeds the ideal amount. When there are too many photocatalytic particles in the system, less light illuminates the surface, which changes the photocatalytic efficacy. Temperature is another crucial parameter that directly affects the photocatalytic efficacy. Herrmann (2010) estimated that the ideal temperature is between 20°C and 80°C. The quantum

remain, such as rapid recombination of the electron/hole resulting from the low quantum yield of the process, low adsorption, and low surface coverage of the photocatalyst which decreases the efficiency of the process. Therefore, a novel photocatalyst gained attention for improving the photocatalysis process (Table 4).

The photocatalysis process has been used for the removal of toxic compounds from aqueous solutions such as dyes, phenolic compounds, and petroleum hydrocarbons (Yang et al., 2019). Microbes and toxic chemicals are also eliminated by the photocatalysis process (Mohammed and Ali 2019). Photocatalysis is also used for the production of hydrogen gas (Ismail and Bahnemann 2014). Wastewater treatment, air treatment, and disinfection are other applications of the photocatalysis process (Teodosiu et al., 2018; Escobedo and Lasa 2020; Kouchakpour et al., 2021). Depending on the catalyst phase, the AO mechanism can be divided into two categories: homogenous and heterogenous photocatalysis. In homogenous photocatalysis, the reactant and the photocatalyst are present in the same phase and include ozone and Fenton's reagent, which is a mixture of hydrogen peroxide and Fe^{+2} salts, to produce reactive species hydroxyl radicals under UV irradiation. In heterogenous photocatalysis, the catalyst and the reactant are not in the same phase and semiconductor

yield, radiant flux, and light intensity are also operational factors that affect the photocatalytic efficacy. To achieve a high photocatalytic degradation rate in wastewater treatment, strong light intensity is required to provide photocatalytic particles with enough photon energy. Saquib and Muneer (2003) also clarified that pollutant loading also causes variations in the photocatalytic efficiency. It has been demonstrated that significant concentrations of organic contaminants can saturate the photocatalytic surface, decreasing photonic efficiency and deactivating the photocatalyst in use.

Due to the distinct physical characteristics of materials at the nanoscale, nanotechnology has attracted a lot of attention in recent years. Nanotechnology also contributes to environmental remediation by the synthesis of the nanoparticles, nanowires, and nano-thin films, which are used in photocatalysis as nanocatalysts (Tang et al., 2020). Given that the nanoparticles have a high surface area-to-volume ratio and generally exhibit higher reactivity due to this, nanotechnology-based materials are especially suitable for environmental remediation operations due to their improved characteristics and efficacy. One of the many distinct types of materials that may be used effectively for a number of environmental remediation applications is inorganic, bio-fabricated, carbonaceous, and polymeric nanoparticles. Metal (Ag NPs/Ag ions, TiO₂ NPs, metal-doped TiO₂, and titanate nanotubes), metal oxide, and silica nanomaterials (amine-modified xerogels, amine-modified aluminosilicates and porous silica, and thiol-functionalized mesoporous silica) are included in the inorganic nanomaterials. Fullerene C₆₀, fullerene C₅₄₀, single-walled nanotubes, multi-walled nanotubes, and graphene are included in carbon-based nanomaterials because of their unique chemical, physical, and electronic properties of the carbonaceous material (Guerra et al., 2018). ZnO and CuO nanoparticles (metal nanoparticles), polymeric nanoparticles (organic nanoparticles with the shape of nanosphere or nano capsular), and carbon-based nanoparticles (graphene nanotubes, carbon nanotubes, and carbon fullerenes) are used as the photocatalyst for the solar-driven photodegradation process of persistent organic pollutants (Tang and Wang 2018; Kråkström et al., 2020).

The creation of diversely sized and shaped nanoparticles by a general synthesis involves the use of a variety of physical, chemical, and biological methods. A variety of techniques are included in the nanoparticle synthesis with the use of top-down method and the bottom-up approaches, employing the physical procedures such as crushing and grinding with many methods, including laser and sputtering obliteration and chemical reductions. Bottom-up strategies include laser pyrolysis, chemical vapor deposition (CVD), and modeling such as spinning and green synthesis (Bhavya et al., 2021). Nanotechnology increases the efficiency of the photocatalytic reaction (Shu et al., 2016). However, the occurrence of aggregation, non-specificity, and low stability might restrict

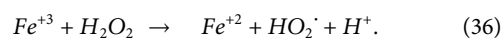
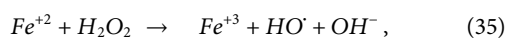
the usage of these nanotechnologies due to the lack of functionality, even if the large surface area-to-volume ratio of nanomaterials leads to increased reactivity with accompanying better performance. The application of solar photocatalysis for the degradation of organic pollutants at the industry-level scale is very costly. The implementation at a large scale is very high, but the nanotechnology ensures a cost-effective successful photothermal process for the wastewater treatment (Pandey et al., 2021). To fully utilize the potential of nanomaterials for environmental applications, these difficulties must be solved. However, there are additional strategies that can be used to mitigate environmental pollutants because of the nanotechnology.

Homogenous photocatalysis

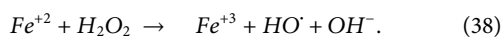
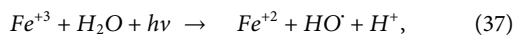
Homogenous photocatalysts are used for the homogenous photocatalysis process (Guo et al., 2017). In this photocatalyst and the reaction, the medium is in the same phase. For example, the degradation of aqueous organic dye is photo-assisted using water-soluble carbon dots. In homogenous photocatalysis, the separation of used catalysts is a tedious task in comparison to heterogenous photocatalysis, as we can easily separate the catalyst material after the work. Homogenous photocatalyst is generally formed through coordination chemistry that contains well-defined monoatomic metal centers in the molecular complexes. Homogenous photocatalyst has high photocatalytic activity and selectivity because of the easy changes that can be implemented in the coordination of the central metal atoms with various organic ligands. Homogeneous photocatalysis is more expensive than heterogeneous photocatalysis because the homogeneous photocatalyst is more costlier and more difficult to separate for product purification and reuse for a longer period of time (Cheng et al., 2022).

Light-harvesting centers and catalytically active sites are the two main components of the photocatalytic system. The light-harvesting center for homogenous photocatalysis is the light-absorbing system which is also called a molecular photosensitizer. The photosensitizer and catalytic units can also be homogenous molecules dissolved in an aqueous solution or any other medium. Under light irradiation, the electron gets excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) energy levels of the molecular photosensitizer. Figure 7 illustrates the photocatalytic process in a typical homogenous photocatalytic system. The large separation between HOMO and LUMO results in a very low percentage of absorption of the solar energy, so from the broad spectrum of solar energy, the photocatalyst absorbs very narrowly. The molecular photosensitizer is inherently very unstable by nature, which results in limited photocatalytic activity and stability of the homogenous photocatalyst.

Over the years, great effort and time have been devoted to obtaining the homogenous photocatalyst that can absorb a broad spectrum of solar energy and remain stable. $\text{Re}(\text{CO})_3(\text{bpy})^+$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ are the two examples of homogenous photocatalyst (Nippatlapalli et al., 2022; Song et al., 2022). The light-harvesting centers and catalytic active sites are ideal in homogenous photocatalysts in comparison to heterogenous photocatalysts. The coordination chemistry has been utilized to unite the merits of homogenous and heterogenous photocatalysts to upgrade the photocatalysis process (Zeng et al., 2018). The homogeneous photocatalyst frequently uses the ozone and photo-Fenton processes (Capodaglio 2020). Fenton process is one of the ways to generate the hydroxyl radical. In an acidic medium, the hydroxyl radicals are generated from the mixture of hydrogen peroxide and Fe^{+2} (Eq. 35). The acidic medium prevents iron precipitation. Due to the consumption of Fe^{+2} during the reaction, Fe^{+3} is generated which decreases the rate of reaction because of the HO_2 ($E^\circ = 1.65 \text{ V}$) generated after the reaction which is a weaker oxidant than the hydroxyl radical ($E^\circ = 2.80 \text{ V}$) (Eq. 36).



To accelerate the photoreduction of Fe^{+3} to Fe^{+2} , the photo-Fenton process is used in which the process is enhanced by UV-visible radiation. This photo-Fenton results in the extra generation of the hydroxyl radical (Eqs 37, 38).

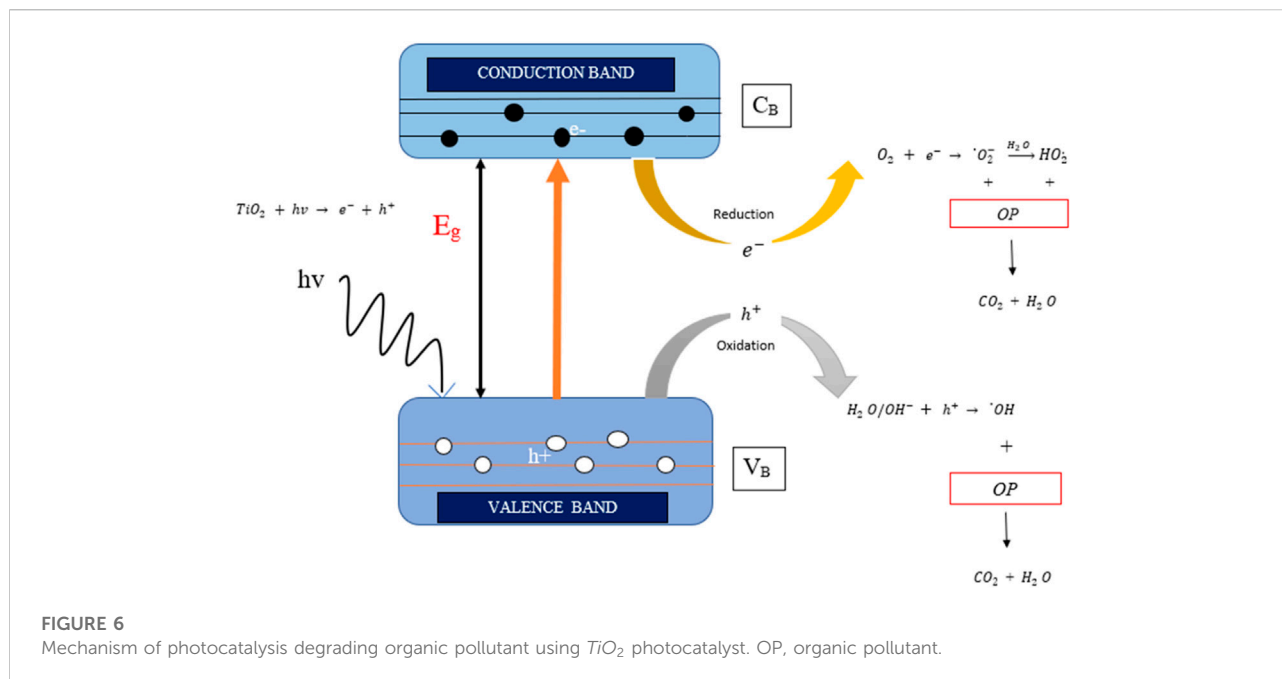


The photo-Fenton process is used for the remediation of the organic contaminants from the wastewater (Prete et al., 2021). Iron sludge formation after the reaction creates another task, which needs to be removed later. The homogenous Fenton process requires a high concentration of the ferrous catalyst, whereas in photo-Fenton, the amount of sludge produced and the concentration of the ferrous catalyst required is optimal. The concentration of ions dissolved in the wastewater significantly affects the photo-Fenton process. The low toxicity of Fe and its high abundance in the environment makes the photo-Fenton process highly environment friendly.

Solar-powered photocatalysis treatment of wastewater is a promising sustainable method for resolving the worldwide water crisis. For wastewater treatment, heterogenous and homogenous photocatalysis approaches were used. Homogenous photocatalysis was used by (Dükkanci et al., 2014) for the effective Orange II dye degradation. After 2 h, 80.8 percent decolorization was achieved using the homogenous Fenton device and a combination of ultrasound and ultraviolet light, indicating that UV promotes Orange II degradation. The use of ferric (Fe(III)) ions in homogenous photocatalysis appears to be an efficient and cost-effective approach of producing $\bullet\text{OH}$

radicals for dye degradation. Using ferric ions (Fe(III)) and visible light (VL) irradiation, the homogenous photocatalytic oxidation (PCO) of Reactive Black 5 (RB5) dye was investigated (SL) by Sadhu et al. (2020). Under artificial VL, more over 80% of the original 20 mg/L RB5 was decolorized in 60 min in the presence of 5 mM ferric ions at pH 2.6. The combination of both homogenous and heterogenous photocatalysis can be used for H_2 production. One such example is dye-sensitized photocatalysis. It is a relatively recent method for converting sunlight into a fuel such as H_2 . The self-assembly of a molecular dye and an electrocatalyst on a semiconductor nanoparticle is the basis of dye-sensitized photocatalysis (DSP) using molecular catalysts (Willkomm et al., 2016). Tributyltin (TBT) is one of the hazardous organotin compounds that have been introduced into the marine environment by mankind. Brosillon et al. (2016) showed that the homogenous photocatalysis (Photo-Fenton) is a viable solution for the decontaminating marine debris problem in comparison to the heterogenous photocatalysis ($\text{TiO}_2 + \text{UV}$). After 1 h of the photo-Fenton reaction, degradation yields for MBT (monobutyltin), DBT (dibutyltin), and TBT (tributyltin) varied from 52% to 76%, 27 %–73%, and 51%–79%, respectively. In homogenous photocatalytic processes, homogenous cocatalysts proved to be very effective electron-capturing species.

Using molecular cocatalysts in composite photocatalytic systems to capture more photogenerated electrons from photosensitizers might be a promising strategy. Irfan et al. (2021) showed that the homogenous cocatalysts (aminopyridine derived Co-complex) have led the way for increased electron capturing from photoexcited composite photocatalysts ($\text{CdS}/\text{Ni}_3\text{C}$), and they offer a lot of potential for improving photocatalytic performance for low-cost H_2 evolution under visible light. Nanoparticles have become popular as homogenous photocatalysts due to their enhanced features, such as a large surface-to-volume ratio, regulated uniform particle size and composition which enhances the degradation rate (Padmanaban et al., 2016). 3d complexes have been extensively researched as potential catalysts for solar fuel generation *via* water splitting and CO_2 reduction. One of the examples of 3d complexes used for CO_2 reduction is the Cu^{II} quarterpyridine complex $[\text{Cu}(\text{qpy})]^{2+}$. $[\text{Cu}(\text{qpy})]^{2+}$ was shown to be a highly efficient and selective catalyst for visible light-driven CO_2 reduction in CH_3CN , employing $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy:bipyridine) as a photosensitizer and BIH/TEOA (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo [d]imidazole/triethanolamine) as the sacrificial reductant. The inclusion of H_2O (1–4% v/v) considerably enhances the photocatalytic process, and a turnover number of >12,400 for CO generation can be attained with 97 percent selectivity, making it one of the most efficient molecular 3d CO_2 reduction catalysts (Guo et al., 2017). With atomically dispersed catalytic sites and tunable light absorption, homogenous photocatalysis is gaining a lot of attention because it offers higher activity and selectivity. As a



result, there is a growing trend to combine the advantages of both homogenous and heterogenous photocatalysts, with coordination chemistry serving as the connecting link (Gao et al., 2017)

Heterogenous photocatalysis

In heterogenous photocatalytic reactions, two or more phases are used in which the semiconductor photocatalyst such as TiO_2 gets excited by the UV or visible radiation coming from the solar spectrum in the presence of oxygen. For water and air treatment, heterogenous photocatalysis is a promising and rapidly advancing technology. The basic principle of heterogenous photocatalysis relies on the oxidative and reductive reaction that takes place on the surface of the semiconductor photocatalyst when the photocatalyst material gets exposed to the photon with energy equal to or greater than the semiconductor bandgap results in the generation of electron-hole pair. The electronic structure of the semiconductor consists of the valence band and the conduction band which plays a pivotal role in the photocatalytic process. Before excitation, the electrons and holes are present in the valence band, but when the photocatalyst is exposed to the photons with energies greater than the bandgap energy, this can result in the excitation of electrons in the valence band to the conduction band and the holes are there in the valence band. pH, photocatalyst concentration, substrate concentration, light intensity, wavelength, and the oxidizing

agent are the operational factors influencing the photocatalytic reaction.

The most studied semiconductor photocatalyst is titanium dioxide. TiO_2 is a naturally occurring mineral with excellent pigmentary properties, high ultraviolet (UV) absorption, and high stability which make it suitable for application in photocatalysis. TiO_2 is an effective and notable catalyst that is used for the photocatalytic degradation of chemicals, organic pollutants such as herbicides, dyes, pesticides, phenolic compounds, and inorganic materials and also helped in the inactivation of microorganisms such as bacteria, molds, and yeasts present in the air or water (Bui et al., 2016.) One of the noteworthy points of TiO_2 is that it operates only in the UV region. One of the advantages of TiO_2 is that it is inexpensive because its continuous re-use is possible as it can be supported on various substrates such as glass, fibers, stainless steel, and sand. TiO_2 photocatalyst has a lower quantum yield because of the fast recombination of the electron-hole pair which is generated during the reaction (Peiris et al., 2021). The visible light absorption is also low because of the larger bandgap which limits its utility, and absorption only takes place from the UV irradiation which makes the cost higher. To enhance the photoresponse activity of TiO_2 , the doping, formation of nanocomposites, surface modification, dye sensitization, noble metal, and non-noble metal deposition are tried out (Byrne et al., 2018; Cheng and Xu 2019; Vilar et al., 2019).

ZnO is an n-type semiconductor that has a bandgap similar (3.37 eV) to the TiO_2 photocatalyst. The degradation mechanism and the drawbacks are also the same as the TiO_2 photocatalyst, but the absorption

TABLE 3 Degradation of Environmental pollutants by photochemical degradation.

S. No.	Pollutant	Degradation mechanism	References
1	Organic pollutants present in the soil	Photoinduced transformation or degradation using the solid humic substances (HS) with the help of 2,4,6-trimethylphenol (TMP) and furfural	Trubetskoi et al. (2019)
2	Bisphenol A (BPA)	Photo-assisted electrochemical oxidation (PEC) which contains facet-tailored TiO ₂ single crystals (SC)	Liu et al. (2017a)
3	Methylparaben (emerging pollutant present in cosmetics and personal care products)	Photocatalytic degradation using Ag nanoparticle (NP)-loaded AgBr-mesoporous-WO ₃ composite photocatalyst (Ag/AgBr@m-WO ₃)	Suliman et al. (2019)
4	Methylene blue (organic pollutant)	Cu ₂ O nanoparticle (NP)-induced photocatalysis in the presence of UV light	Muthukumaran et al. (2020)
5	Methylene blue	Photocatalytic degradation by Ag-doped ZnO (Ag_ZnO) photocatalysts	Kwon and Kim (2020)
6	Methylene blue (water pollutant)	Photodegradation under sunlight response by using the 2D nano sheet of tin di/sulfide	Matmin et al. (2019)
7	2,4-Dichlorophenol (2,4-DCP)	Photocatalytic oxidation based on sulfate radical (photochemical activation of sulfate which results in the production of SO ₄ • ⁻ radicals with bismuth phosphate (BiPO ₄ , BPO) acting as photocatalyst)	Liu et al. (2017b)
8	Indole 3-butyric acid	Photochemical degradation by pure ZnO and MgO-doped ZnO nano catalysts under illumination of the ultraviolet (UV) light	Masoud et al. (2021)
9	Synthetic wastewater [D-glucose anhydrous, bacterial peptone, lab Lemco, ammonia hydrogen carbonate (CH ₃ NO ₃), potassium hydrogen carbonate (CHKO ₃), sodium hydrogen carbonate (CHNaO ₃)]	Photochemical treatment of a pollutant using UV light and H ₂ O ₂ (photo-Fenton-like process (UV/H ₂ O ₂ /Fe(III)))	Balbayeva et al. (2018)
10	Losartan (antihypertensive used in pharmaceuticals)	Advanced oxidation technologies: TiO ₂ —photocatalysis and UVC/persulfate (UVC/PS)	Guatque-Londoño et al. (2020)
11	4-Methoxy-2-nitrophenol (4Mx2Np) and 3-methyl-4-nitrophenol (3M4Np) [semi volatile organic compounds (SVOCs)]	UV-driven photocatalytic degradation of pollutants over the Nd ₂ CuO ₄ -Nd ₂ O ₃ heterostructured photoactive nanoparticles	Padervand et al. (2019)
12	Oxytetracycline (OTC)	H ₂ O ₂ /UVC and UVC process-based AOT	de Medeiros Lima et al. (2021)
13	Methyl orange	Photo electrocatalytic (PEC), and direct photolytic (DP) degradation on annealed TiO ₂ nanopore arrays (TNPs) and TiO ₂ nanotube arrays (TNAs)	Liu et al. (2009)
14	RB5 azo dye	Photolysis and Fenton reaction catalyzed with magnetite pellet under irradiation of UV light	Mahasti et al. (2020)
15	Rhodamine B (RhB) Dye	Photocatalytic degradation of RhB dye in wastewater by cauliflower-shaped ZnO nanoparticles	Rajendrachari et al. (2021)
16	Phenanthrene (polycyclic aromatic hydrocarbons (PAHs))	Photolysis of Fe(III)-oxalate complexes, Fenton-like reaction	Luo et al. (2021)
17	Paracetamol (pharmaceutical pollutant in water)	Fe(III)-Asp/UVA photolysis with the addition of Zn (II), Cu (II), and Mn (II)	Benssassi et al. (2021)

efficiency of the ZnO is greater than that of the TiO₂. ZnO is mostly suggested as the alternative photocatalyst to TiO₂. The mechanism of the photodegradation of the organic pollutant in the presence of solar radiation using ZnO photocatalyst is as follows (equation 39–43):

- 1) Transport of the electrons from the valence band to the conduction band when ZnO is photo-induced by the solar light with (photonic energy) $h\nu \geq E_g$ (excitation energy).
- 2). e^-/h^+ pair is generated, and they will migrate to the ZnO surface and be involved in the redox reaction.

3). In the redox reaction, hydroxyl radicals and superoxide radical anions are generated. The hydroxyl radicals will degrade the pollutants adsorbed on the surface of the ZnO. Intermediate compounds are rapidly produced during the reaction, which will be converted into carbon dioxide and water.

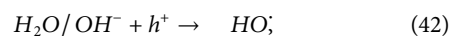
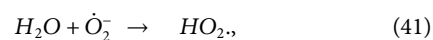
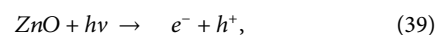


TABLE 4 Some of the reaction mechanisms for the degradation of persistent organic pollutants using advanced oxidation technologies, such as photocatalysis.

S. No	Pollutant degraded	Technique used	Reaction mechanism	References
1	Chlorinated organic compounds (COCs)	COC catalytic dechlorination by Pd-Fe bimetallic catalyst in acidic and basic solution	$Fe + 2H^+ \rightarrow Fe^{+2} + H_2 \text{ (in acidic solution)}$ $Fe + H_2O \rightarrow Fe^{+2} + H_2 + 2OH^- \text{ (in basic solution)}$ $Pd + RCl \rightarrow Pd - Cl - R$ $Pd - Cl - R + H_2 \rightarrow RH + H^+ + Pd + Cl^-$ RCl: Generalized chlorinated hydrocarbon	Quiton et al. (2021)
2	Polychlorinated biphenyls (PCBs) PCB 180—heptachlorobiphenyl	Degradation of PCB180 is achieved by porous core-shell β -cyclodextrin/graphitic carbon nitride (M β -CD/GCN) photocatalyst under solar light	$GCN \text{ nanosheet} + hv \rightarrow e^- + h^+$ $O_2 + (e^-) \rightarrow \dot{O}_2^-$ $\dot{O}_2^- + H^+ \rightarrow \dot{O}OH$ $2\dot{O}O_2 \rightarrow H_2O_2 + O_2$ $O_2 + e^- + 2H^+ \rightarrow H_2O_2$ $Fe^{+2} + H_2O_2 \rightarrow Fe(OH)^{+2} + OH^-$ $Fe(OH)^{+2} + hv \rightarrow Fe^{+2} + \dot{O}H$ $Fe^{+3} + hv + H_2O \rightarrow Fe^{+2} + \dot{O}H + h^+$ $Fe^{+2} + O_2 \rightarrow \dot{O}_2^- + Fe^{+3}$ $\dot{O}_2^- + h^+ + \dot{O}H + PCB180 \rightarrow PCB180 \text{ Intermediates}$	Wang et al. (2022a)
3	Orange G azo dye	Photo-Fenton: oxidation of orange G azo dye	$Fe(OH)^{+2} + hv \rightarrow Fe^{+2} + \dot{O}H$ $Fe^{+2} + H_2O_2 \rightarrow Fe(OH)^{+2} + \dot{O}H$ $H_2O_2 + hv \rightarrow 2\dot{O}H$ $84\dot{O}H + C_6H_{10}N_2O_7S_2Na_2 \rightarrow CO_2 + 45H_2O + 2NO_3^- + 2Na^+ + 2SO_4^{2-} + 4H^+$ $C_6H_{10}N_2O_7S_2Na_2 \text{ - Orange G azo dye}$	Tarkwa et al. (2019)
4	Synthetic organic dyes	Cobalt ferrite/Ag-fMWCNT hybrid nanocomposite catalyst for peroxymonosulfate-activated degradation of synthetic organic dyes	$(Catalyst)^{III} + HSO_5^- \rightarrow (Catalyst)^{II} + SO_5^- + H^+$ $(Catalyst)^{II} + HSO_5^- \rightarrow (Catalyst)^{III} + SO_4^- + OH^-$ $SO_4^- + H_2O \rightarrow \dot{O}H + SO_4^{2-} + H^+$ $SO_4^- + OH^- \rightarrow \dot{O}H + SO_4^{2-} / \dot{O}H + Dye \rightarrow CO_2 + H_2O + \text{Degradation product}$	Abdel-Salam and Yoon, (2022)
5	Dye, aromatic compounds, phenols, and phthalate esters	Sono-assisted photolysis methods for the mineralization of the POPs	$H_2O + \dot{H} \text{ (Irradiation with ultrasound)} \rightarrow \dot{H} + \dot{O}H \text{ (thermolysis)}$ $\dot{H} + \dot{H} \rightarrow H_2$ $\dot{H} + O_2 \rightarrow HO_2 \cdot$ $H_2O_2 + hv (<254) \text{ (Irradiation with UV)} \rightarrow \dot{O}H + \dot{O}H$ $HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$ $HO_2 \cdot + \dot{H} \rightarrow H_2O_2$ $\dot{O}H + \dot{O}H \rightarrow H_2O_2$ $\dot{O}H + \text{Pollutants} \rightarrow \text{Intermediate Products} + CO_2 + H_2O$ $\dot{O}H + H_2O_2 \rightarrow H_2O + HO_2 \cdot$ $\dot{H} + H_2O_2 \rightarrow H_2 + HO_2 \cdot$ $\dot{O}H + HO_2 \cdot \rightarrow H_2O + O_2$	Patidar and Srivastava, (2021)

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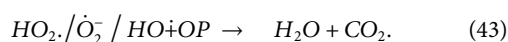
TABLE 4 (Continued) Some of the reaction mechanisms for the degradation of persistent organic pollutants using advanced oxidation technologies, such as photocatalysis.

S. No	Pollutant degraded	Technique used	Reaction mechanism	References
6	Perfluorooctanoic acid and perfluorooctane sulfonate (PFOX)	Photocatalytic degradation of PFOX in water (photooxidative and photo-reductive degradation)	$\dot{O}H + O_2 \rightarrow HO_2 \cdot + \dot{O}$ $S_2 O_8^{2-} + hv \rightarrow 2(SO_4^{\cdot -})$ $ClO^- + hv \rightarrow (Cl) \cdot + (O^-)$ $ClO^- + hv \rightarrow (Cl) \cdot + (O^-)$ <p>I⁺ degradation pathways</p> $C_7 F_{15} COOH (PFOX) + Photoexcited\ Species \rightarrow C_7 F_{15} CO O \cdot$ $C_7 F_{15} CO O \cdot + hv \xrightarrow{Direct\ Photolysis} C_7 F_{15} \cdot + CO_2$ $C_7 F_{15} \cdot + H_2O / OH/O_2 \rightarrow C_7 F_{15} OH$ $C_7 F_{15} OH \rightarrow C_6 F_{13} COF + HF$ $C_6 F_{13} COF + H_2O \rightarrow C_6 F_{13} COOH + HF$ $C_6 F_{13} COOH \xrightarrow{Photo\ Decomposition} C_5 F_{11} COOH$ <p>$C_5 F_{11} COOH$ is further degraded to $\dot{C}H_2OH$ by second degradation pathway</p>	Wang et al. (2017)
7	Tetracycline hydrochloride and 2,4-dichlorophenol	Visible light-driven degradation of tetracycline hydrochloride and 2,4-dichlorophenol by a film-like N-carbon@N-ZnO catalyst with a three-dimensional linked nanofibrous structure	$N \cdot ZnO + hv (Visible\ light) \rightarrow h_{VB}^+ + e_{CB}^- + O_2 \rightarrow \dot{O}_2 h_{VB}^+ + OH^- \rightarrow \dot{O}H$ $\dot{O}_2 + H_2O \rightarrow \dot{H}O_2 + OH^- \dot{H}O_2 + H_2O \rightarrow \dot{O}H + H_2O_2$ $H_2O_2 \rightarrow 2 \dot{O}H$ $\dot{O}H/h^+ + Organic\ Molecule \rightarrow CO_2 + H_2O$	Chen D.et al. (2020)
8	Tetracycline	Enhanced tetracycline degradation using OD/3D NiCo ₂ O ₄ /defected UiO-66 catalysts in peroxymonosulfate/simulated sunshine systems	$\gamma NiCo-DU50 + hv \rightarrow e^- + h^+$ $e^- + O_2 \rightarrow \dot{O}_2 e^- + HSO_5^- \rightarrow SO_4^{\cdot -} + OH^- 4SO_4^{\cdot -} + 2H_2O \rightarrow 4SO_4^{\cdot -} + ^1O_2$ $\dot{O}_2 + HSO_5^- \rightarrow SO_4^{\cdot -} + ^1O_2 + OH^- 2\dot{O}_2 + 2H_2O \rightarrow ^1O_2 + H_2O_2 + 2OH^- \dot{O}_2 + \dot{O}H \rightarrow OH^- + ^1O_2 h^+ + H_2O \rightarrow \dot{O}H + H^+$ $Ni^{3+}/Co^{3+} + HSO_5^- \rightarrow Ni^{2+}/Co^{2+} + SO_5^{\cdot -} + H^+$ $Ni^{3+}/Co^{3+} + e^- \rightarrow Ni^{2+}/Co^{2+}$ $Ni^{2+}/Co^{2+} + HSO_5^- \rightarrow Ni^{3+}/Co^{3+} + SO_4^{\cdot -} + OH^- SO_4^{\cdot -} + H_2O \rightarrow \dot{O}H + H^+ + SO_4^{\cdot -} O_2 / \dot{O}H / \dot{O}_2 / SO_4^{\cdot -} / h^+ + TC \rightarrow$ <p>Degradation Product</p>	Wang et al. (2022b)
9	Diclofenac	Degradation of diclofenac using mont-La (6%)-Cu _{0.6} Cd _{0.4} S as a photocatalyst when exposed to NUV-vis irradiation	$Mont-La (6\%) - Cu_{0.6}Cd_{0.4}S + hv \rightarrow h_{VB}^+ + e_{CB}^-$ $h_{VB}^+ + HO_{ads}^- \rightarrow HO_{ads} \cdot$ $h_{VB}^+ + H_2O_{ads} \rightarrow HO_{ads} \cdot + H^+$ $e^- + O_{2,ads} \rightarrow \dot{O}_2 \dot{O}_2^- + H^+ \rightarrow HO_2 \cdot$ $\dot{O}_2 + HO_2 \cdot + H^+ \rightarrow H_2O_2 + O_2$ $H_2O_2 + hv \rightarrow \dot{O}H$ $C_{14}H_{11}Cl_2NO_2 + 2 H \cdot \rightarrow Cl + C_{14}H_{12}O_2N$ $C_{14}H_{12}O_2N + \dot{O}H \rightarrow C_{13}H_{11}NO + CO_2 + 3H \cdot$ $C_{13}H_{11}NO + 2\dot{O}H \rightarrow C_7H_7NO_3 + H \cdot$	Boukhatem et al. (2017)

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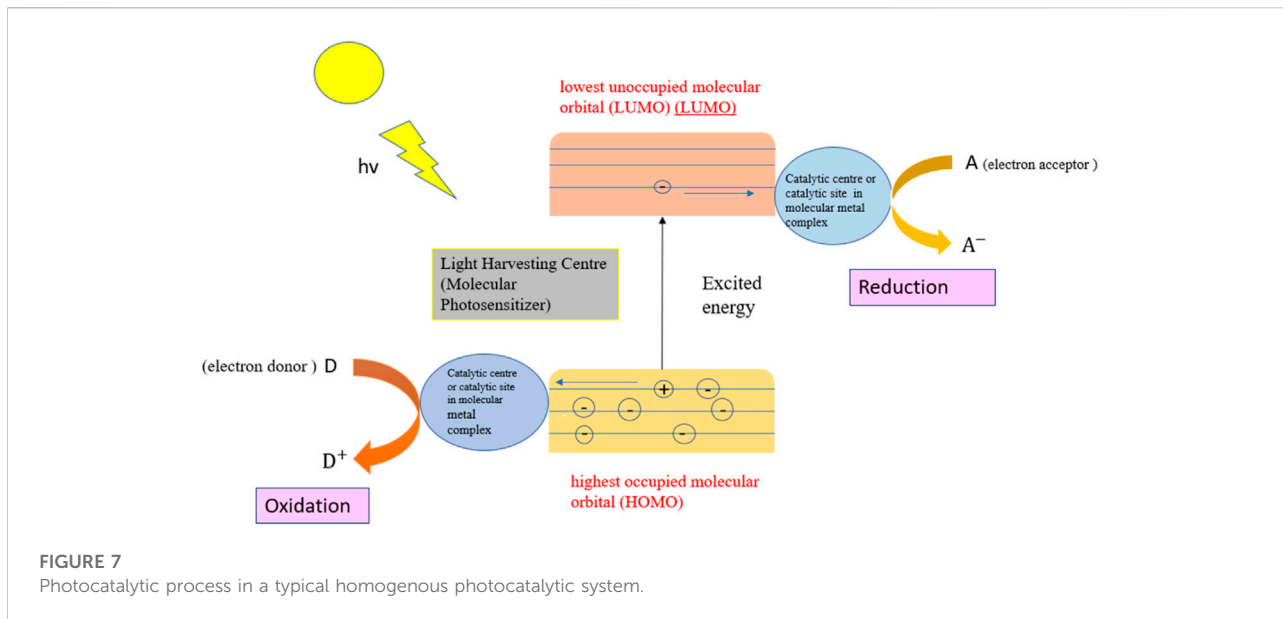
TABLE 4 (Continued) Some of the reaction mechanisms for the degradation of persistent organic pollutants using advanced oxidation technologies, such as photocatalysis.

S. No	Pollutant degraded	Technique used	Reaction mechanism	References
10	4-chlorophenol	Photocatalytic degradation of 4-chlorophenol by Gd-doped β -Bi ₂ O ₃ under visible light irradiation	$C_7H_7NO_3 + H. + \dot{O}H \rightarrow C_7H_7NO + NH_3$ $C_7H_7NO + 4H. \rightarrow C_7H_6O_4 + CH_3COOH$ $C_{14}H_{11}Cl_2NO_2 + H. \rightarrow C_3H_6O_2 + \dot{O}H$ $C_{14}H_{11}Cl_2NO_2 + 2O H. \rightarrow C_8H_9NO + HCl + 4 H. + CO_2$ $C_8H_9NO + H. \rightarrow C_{13}H_8NClO_2 + Cl$ $C_{13}H_8NClO_2 + H. \rightarrow C_{13}H_9NO_2 + Cl$ $C_{13}H_8NClO_2 \rightarrow C_{12}H_8NCl + Cl$ $h\nu \rightarrow \beta\text{-Bi}_2\text{O}_3 \quad h_{VB}^+ + e_{CB}^-$ $2 H_2O + h_{VB}^+ \rightarrow 2 \dot{O}H + H^+$ $\dot{O}H + 4 - CP \rightarrow \text{Degradation Products}$ $Gd^{3+} + e^- \rightarrow Gd^{2+}$ $Gd^{2+} + O_2 \rightarrow Gd^{3+} + \dot{O}_2^-$	Lin et al. (2019)
11	Tetracycline	Tetracycline degradation by enhanced UV-assisted Fenton performance of nanostructured biomimetic α -Fe ₂ O ₃	$\alpha\text{-Fe}_2\text{O}_3\text{-AI} + h\nu \rightarrow \alpha\text{-Fe}_2\text{O}_3\text{-AI} + e^- + h^+$ $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \dot{O}H + OH^- H_2O_2 + h\nu \rightarrow 2 \dot{O}H \quad h^+ + H_2O \rightarrow \dot{O}H + H^+$ $TC + \dot{O}H \rightarrow CO_2 + H_2O$ $O_2 + (e^-) \rightarrow \dot{O}_2^-$ $\dot{O}_2^- + TC \rightarrow CO_2 + H_2O$	Ari et al. (2022)
12	Methylene blue (MB)	Visible light-driven photodegradation of MB with the help of polyhedral magnetite nanoparticles modified with porous copper oxide as a catalyst	$CuO + h\nu \rightarrow e^- + h^+$ $O_2 + (e^-) \rightarrow \dot{O}_2^-$ $Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + \dot{O}H + OH^- Fe^{+3} + e^- \rightarrow Fe^{+2} \quad h^+ + H_2O \rightarrow \dot{O}H + H^+$ $\dot{O}H/\dot{O}_2^- + MB \rightarrow CO_2 + H_2O + \text{By products}$	(O. A. Alani et al., 2022)



ZnO has a higher efficiency because of the higher absorption of the light from the solar spectrum, which is UV/visible light. The photodegradation reaction of the ZnO is also perturbed by the rapid recombination of the electron/hole pair and its optical absorption because of its larger bandgap energy. To improve the ZnO efficiency, various attempts are done to reduce the recombination rate of the photogenerated electron-hole pair and decrease the energy bandgap. Transition metal oxide, SnO₂, CdS, graphene, graphene carbon nitride (g-C₃N₄), and Zn₂SnO₄ are the various semiconductor photocatalyst that is used (Védrine 2017; Zhu and Zhou 2019; Chen X. et al., 2020). To enhance the semiconductor photocatalysis, the metal doping of the semiconductor and photodegradation of the pollutant by the hybrid nanomaterial photocatalyst is attempted to increase the mobility of electron/

hole, improve the separation between the electron/hole pair, and enhance the visible light adsorption. Figure 8 illustrates the photodegradation mechanism of the pollutant by hybrid metal oxide photocatalyst nanomaterial. Non-metal doping and mix doping enhance photocatalytic activity by narrowing the bandgap and by the formation of the intra-bandgap energy states (Kuo et al., 2021). Coupling between the semiconductors with desirable matching electronic bandgap hinders the recombination of the photogenerated electron-hole pair. Ag-based semiconductor photocatalysis is an emerging method of photocatalysis. Nanomaterials (nanoparticles, nano-catalyst, nanofilms, nanofibers, nanomembranes, colloidal semiconductor nanocrystals, "quantum dots" (QDs), nanosheets, nanorods, etc.) are also used in the heterogenous photocatalysis as they possess the increased surface area-to-volume ratios and high surface reactivity compared to the other photocatalyst (Adhikari et al., 2018).



The ability to completely mineralize the organic pollutant in the environment makes the heterogeneous photocatalysis the effective AOT for the wastewater treatment, which cannot be done effectively using secondary water treatment (Parul et al., 2020). No consumable chemicals are required during the heterogeneous photocatalysis process, which makes this AOT inexpensive. The heterogeneous photocatalysis process is relatively safe in comparison to other processes because reactions mostly proceed in ordinary temperature and pressure, which are mild conditions (Rueda-Marquez

et al., 2020). One of the drawbacks of heterogeneous photocatalysis is that its large-scale synthesis is not suitable because of the problem of the electron-hole recombination and lower absorption because of the smaller surface areas (Pawar and Lee 2015). The large-scale utilization of the heterogeneous photocatalysis was successful only for the wastewater treatment with lower concentration of contaminants present in the wastewater.

The scientific community is interested in photocatalysis for POP degradation because it can generate hydroxyl radicals

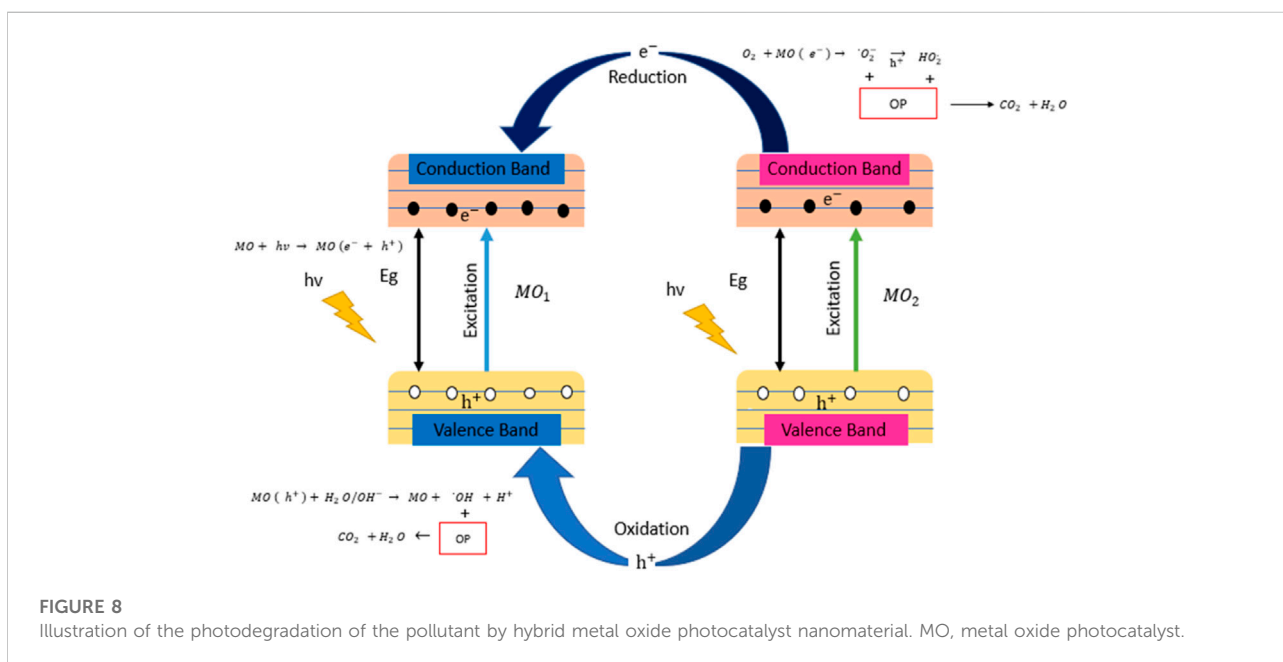


TABLE 5 Different challenges that come during the process of photocatalysis.

S. No	Challenges in the photocatalysis	Explanation	Solution	References
1	Engineering of photocatalyst	<ul style="list-style-type: none"> The photocatalytic efficacy of most current stable photocatalysts is limited by their broad bandgap, which indicates a narrow light absorption range Photogenerated electrons and holes recombine in the bulk phase of photocatalysts, preventing them from participating in photocatalytic reactions Instead of participating in the target reaction, certain photogenerated electrons or holes may corrode the photocatalyst 	Engineering in photocatalytic systems with various individual components to generate efficient interactions such as p–n junctions, heterojunctions, and Z-scheme systems, semiconductor coupling is thought to be a good way to improve overall photocatalytic efficiency	Humayun et al. (2018) Ohtani, (2017)
2	Industrial application	<ul style="list-style-type: none"> Due to a very complicated process, it is very difficult to scale up the photocatalysis process at a large scale There is a certain gap between laboratory and industrial application. Cost, catalyst recycling, energy consumption, environmental protection, and other factors are not considered in laboratory research Uncontrollable factors in the actual production process of the industrial application which are neglected during laboratory research 	<p>The key for accomplishing the commercial use of photocatalytic devices is the development of cost-effective, practical, and stable large-scale preparation procedures</p> <p>For the industrial use of photocatalytic technology, development of the reactors that can efficiently maximize the use of the heterogenous catalyst is crucial</p>	Mandade, (2021)
3	Catalyst toxicity	<ul style="list-style-type: none"> The catalyst toxicity associated with photocatalytic nanoparticles, which are commonly utilized in personal care products and are detrimental to human health and the environment, is a subject of concern Several negative consequences of nanomaterials have been discovered, and there are still significant gaps in our understanding of the nature and relationship of nanoparticles with the ecological system 	Develop environmentally friendly, clean, safe, and sustainable AOTs. There should be toxicity assessment of the nanomaterials which are used for the reaction because phototoxicity is reported on nanomaterials such as quantum dots when they were irradiated under the UV light	Roy et al. (2021)
4	Scavengers	<ul style="list-style-type: none"> The photocatalytic process gets impaired because of the interaction between the natural scavengers such as antioxidants with the photogenerated reactive oxygen species radicals Into the photocatalytic system, scavengers such as triethylamine, methanol, tetrachloromethane, lactic acid, triethanolamine, and different alcohols are used. Although the use of these scavengers can considerably improve photocatalytic performance, it also has the unintended consequence of product and environmental pollution 	When the scavengers are introduced to a heterogenous photocatalysis process, a careful interpretation and analysis is required	Schneider et al. (2020)

(•OH) for effective chemical oxidation of organic pollutants, including organic micropollutants (OMPs) ([Bertagna Silva et al., 2021](#)). UV-LED TiO₂ photocatalysis is used for the degradation of ibuprofen with 97% degradation after 25 min ([Ding and Hu, 2020](#)). Photocatalysts based on semiconductors are also used for the detoxification of emerging pharmaceutical contaminants in aquatic systems. In the presence of Zr, Belver et al. observed almost complete (90 percent) antipyrine degradation within 6 h using Zr-doped TiO₂ ([Belver et al., 2017](#)). Under UV illumination, acetaminophen photodegraded well when TiO₂ was supported on zeolite. Under optimum TiO₂ loading

(40 wt% and 1.0 g/L conc) on the surface of zeolite, 96.6% of the degradation was ascribed to enhanced charge separation ([Chang et al., 2015](#)). Bisphenol A and 2–4 dichlorophenol organic pollutants were effectively degraded by the catalytic ozonation and photocatalysis synergy system using a double-functional MgO/g-C₃N₄ catalyst. Within 2 min, the degradation efficiency was approximately 100%, which was 18 and 1.5 times greater than that of the individual photocatalytic and catalytic ozonation activity, respectively ([An et al., 2020](#)). [Hu et al., \(2020\)](#) used the FeOOH/Bi₂MoO₆-OVs (oxygen vacancies) photocatalyst for

effective degradation of phenol. The 10 % FeOOH/Bi₂MoO₆-OVs showed the best degrading activity when exposed to visible light. The elimination efficiency of phenol was 100% within 3 h, which was 1.54 times and 1.33 times faster than photocatalysis and Fenton alone, respectively.

Sonophotocatalytic processes are advanced integrated AOPs that combine sonolysis and photocatalysis to degrade organic pollutants effectively. To eliminate harmful wastewater impurities, these ecologically friendly technologies rely on ultrasound and the appropriate catalysts (Theerthagiri et al., 2021). Ghalamchi and Aber (2020) looked into the sonophotocatalytic activity of aminated silver phosphate/GCN (NH₂-Ag₃PO₄/GCN) in the degradation of methylene blue (MB) dye molecules, achieving an 82% removal efficiency. For the degradation of 2,4-dichlorophenol (2,4-DCP) and rhodamine B, Neena et al. produced ZnO nanorods with nitrogen-doped reduced graphene oxide (N-rGO). They evaluated the photocatalytic performance of ZnO, GO, N-rGO, ZnO/rGO, and ZnO/N-rGO and discovered that the ZnO/N-rGO composite had the highest photocatalytic activity in all of the model processes (Neena et al., 2019).

Challenges of the photocatalysis

One of the major research challenges is to overcome the limitations of the photocatalysis process. There are various challenges that arise while engineering the photocatalyst. In general, the efficiency and stability of today's heterogenous photocatalysts are still far from satisfactory because of the difficulties in controlling and balancing multiple competing processes, such as carrier generation, charge separation, and transportation, especially under the highly corrosive conditions of photochemical reactions (Guo et al., 2019a). When one component is introduced into photocatalysts to address one weakness, it frequently creates a new set of problems. Some of the examples of challenges in the photocatalysis are as follows: for the nanocomposite catalytic material, the attachment of the nanostructure to the substrate is a challenge; under solar irradiation, quantum efficiency reduces due to larger bandgap energy in the electronic structure of the semiconductor photocatalyst and photocatalytic activity and reactive oxygen species production reduce due to the electron/hole pair recombination on the active surface of the photocatalyst (Xu, 2021). Interaction with the intermediate products that are formed during the reaction results in the fast active surface site deactivation or poisoning, which will finally reduce the kinetic reaction rate. Due to a very complicated process, it is very difficult to scale up the photocatalysis process at a large scale. Integrating very dissimilar (e.g., metal and semiconductor) materials together at the nanoscale with well-defined size, shape, and interface, which are required for effective charge cascading in photocatalytic processes, continues to be a major issue (Saravanan et al., 2017). The research on

heterogenous photocatalysts is still in its early stages, and more systematic research studies are certainly needed. Some of these challenges are briefly discussed in the Table 5. One of the most urgent challenges is to develop environmentally friendly, clean, safe, and sustainable AOTs. The solution to these issues is to investigate model systems and gain a better understanding of the basic properties of various photocatalysts used in the photocatalysis process (Younis and Kim, 2020).

Conclusion

Conventional remediation methods such as biological, chemical, and physical methods are inadequate and insufficient to completely eradicate and degrade the persistent organic pollutants. Advanced oxidation processes have been widely used to completely mineralize refractory organic pollutants because it involves the generation of hydroxyl radical species in sufficient concentration under ambient temperature and pressure. Among all of the AOTs, the photocatalysis has proven to be very effective in the treatment of wastewater, air purification, and disinfection because of the ambient operating conditions, complete mineralization of the substrate into inorganic carbon dioxide and water, utilization of solar energy, and cost-effectiveness. Photocatalysis is a low-cost, ecologically friendly technique that may be used everywhere since it uses sunlight or UV rays. This technique has also been used to successfully destroy pathogens and algae blooms in fresh water sources. Photo disinfection sensitized by TiO₂ has been used to degrade green algae, treat humic substances that act as bacterial growth substrates, and inhibit bacterial degradation of impurities in natural water. Photocatalysis is suitable for the abatement of most air pollutants, including organic compounds, such as alkanes, alkenes, alkynes, aromatics, aldehydes, ketones, and inorganic molecules. Nanomaterials have gained significant attention for photocatalytic degradation. Advances in nanotechnology have opened new doors to overcome the problems related to the heterogenous photocatalytic degradation, but still, heterogenous photocatalysis faces challenges such as higher reaction time, lower efficiency, less recyclability of the photocatalyst for continuous use, high recombination rate, and less adsorption of the active surface of the photocatalyst. Therefore, efforts have been made to enhance the efficiency of the process by reactor design, putting efforts for more novel photocatalyst, modifications of the photocatalysis by doping and heterojunction, hybridizing the semiconductors, etc. To increase the efficiency, the photocatalysis process can be coupled with the other advanced oxidation process, which can be highly effective for both of them. For the detection of the intermediates qualitatively and quantitatively, various techniques can be used such as mass spectrometry with chromatography. The focus should be more on the detection of the intermediate products formed during the

reaction. The synthesis of the nanomaterial should be in an eco-friendly and sustainable way by collaborating with different researchers. But still, there are challenges ahead to enhance the advanced oxidation process for the better degradation of the environmental pollutants of wide variety at large scale. In the end, the main focus should be on the elimination and degradation of POPs from the environment in an eco-friendly way.

Author contributions

NG: final draft preparation. DD: framework of manuscript. AS: first draft preparation. RD: editing of manuscript. DVK: overall guidance and final editing.

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