



Review article

Advanced photocatalysis as a viable and sustainable wastewater treatment process: A comprehensive review

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ABSTRACT

In our era, water pollution not only poses a serious threat to human, animal, and biotic life but also causes serious damage to infrastructure and the ecosystem. A set of physical, chemical, and biological technologies have been exploited to decontaminate and/or disinfect water pollutants, toxins, microbes, and contaminants, but none of these could be ranked as sustainable and scalable wastewater technology. The photocatalytic process can harmonize the sunlight to degrade certain toxins, chemicals, microbes, and antibiotics, present in water. For example, transition metal oxides (ZnO, SnO₂, TiO₂, etc.), when integrated into an organic framework of graphene or nitrides, can bring about more than 90% removal of dyes, microbial load, pesticides, and antibiotics. Similarly, a modified network of graphitic carbon nitride can completely decontaminate petrochemicals. The present review will primarily highlight the mechanistic aspects for the removal and/or degradation of highly concerned contaminants, factors affecting photocatalysis, engineering designs of photoreactors, and pros and cons of various wastewater treatment technologies already in practice. The photocatalytic reactor can be a more viable and sustainable wastewater treatment opportunity. We hope the researcher will find a handful of information regarding the advanced oxidation process accomplished via photocatalysis and the benefits associated with the photocatalytic-type degradation of water pollutants and contaminants.

1. Introduction

Rapid industrialization, population growth, and protracted droughts warn of the shortfall of dwindling fresh water resources. To meet our growing water demands, we need a more sustainable and integrated water management system. The more alarming situation happens when wastewater pollutes the underground or freshwater, and unfortunately due to this dilemma, millions of people die each year solely because of waterborne infections (Ortiz-Prado et al., 2022). According to statistics

released by UNESCO in 2023, two billion individuals (26% of the worldwide population) lack access to clean water for drinking (Imminent risk of a global water crisis, 2023). Another study says that 4 billion people on a global scale don't have access to clean and sanitized water (Malato et al., 2009), and these statistics will become worse shortly because of the massive release of contaminants and micropollutants into the waterbeds. In a nutshell, fresh water has become a vulnerable resource and to sustain life on this planet, we are in urgent need of efficient, scalable, and viable water treatment or recycling techniques

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(Ren et al., 2021).

It has been speculated that about 2.01 billion tons of wastewater are produced annually, and unfortunately, 33 percent of this wastewater remains unchecked, which can destroy the water quality of a whole ocean or the underground water bed of a whole community. This simply means it can further contaminate the freshwater source and become a constant source of environmental pollution (Kaza et al., 2018). It is worth mentioning that many less efficient water treatment technologies like filtration, sedimentation, and flocculation become sources of secondary pollutants, and treated water when used for irrigation or other applications causes serious environmental and health issues. For example, Bagasse and bagasse bentonite, a byproduct of sugarcane processing (Kuncoro et al., 2018a), have been used as an adsorbent for the removal of dyes from wastewater (Darmokoeseoemo1 et al., 2016). Darmokoeseoemo et al. (2016) applied the telescope snail and Mangrove crab as adsorbents for the removal of Pb^{2+} from aqueous solutions. Neolaka et al. (2023a) applied activated carbon from various agricultural sources as a low-cost adsorbent for the removal of heavy metals and synthetic dyes. However, these techniques produce an even larger amount of waste and have been ruled out for many other reasons, like these adsorbents often do not adsorb all the contaminants. The physical adsorbents-based technologies are only considered efficient for primary treatment of wastewater. The AOP, on the other hand, provide a green and sustainable solution for wastewaters' treatment (Kuncoro et al., 2018b).

The effectiveness of a particular wastewater technology also depends upon the nature of pollutants the water contains, and it has been observed the composition of wastewater varies in the countries according to their income levels and geographical conditions. It is interesting to note that municipal wastewater of high-income countries contains 32 % of food items and more than 51 % of waste materials like plastic, clipboard, metal, and paper (Fig. 1). The wastewater of middle- and low-income countries contains more than 50 % of food items, wood, and plastic. On a global scale, food and organic matter can be declared as major constituents of municipal wastewater (Kaza et al., 2018).

The recycling of municipal wastewater for agricultural use needs less efficient but more economical and scalable technologies. This kind of recycling involves the removal of suspended particulates, plastics, and material objects. For this purpose, coagulation and/or sedimentation-

based technologies are often adopted and these treatment methodologies involve the accumulation of pollutants which are difficult to manage. Besides, chemical oxidation/sterilization may lead to the production of secondary pollutants and eventually challenge their eco-friendly nature of process (Fig. 2). Another commonly applied disinfection methodology involves the use of chlorine or other oxidizing agents and many of their by-products are carcinogenic and mutagenic in nature (Bradley et al., 2002). Researchers are nowadays attracted by photocatalysts which utilize benign reactive species produced via ultraviolet-visible light ($h\nu$), in particular due to arrangements for the degradation of organic contaminants. Photocatalytic degradation is thought to be a green technique that turns photonic energy into useable chemical energy.

The photo-catalytic process oxidizes the water pollutant in a series of steps more sustainable and efficient manner. The technique is equally applicable for the decontamination and sterilization of wastewater or sanitization of groundwater. The photocatalytic oxidation has the ability to treat the wastewaters containing heavy metals, drugs, chlorinated hydrocarbons, pesticides, dioxins, infections, and microbes. In contrast to conventional oxidation methods, the photo-catalytic process is chemical-free, more viable, and energy-saving. Further, photocatalytic degradation works on moderate pressure and temperature conditions and in the case of heterogeneous photocatalysts utilized, the process becomes more efficient (photocatalysts are easily separable).

Some photocatalysts capture sunlight energy to produce the electrons and holes from valence bands and/or conduction bands and initiate oxidation and reduction reactions. The most fascinating opportunity opens for the designability of the photocatalytic bandgaps. Several modifications are under consideration to improve the efficiency of photocatalysts and the majority of these studies focus on the separation of holes and photo-electrons (Wang et al., 2021).

Besides the modification of bandgap, photocatalytic immobilization has attained also a lot of fame for its improved light absorption capacity. The immobilization of photocatalysts also decreases the mass transfer of reacting species, and high energy photon backscattering. Table 1 compares the efficiency of various immobilized and free photocatalysts tested on laboratory scales. It must be kept in mind that several photocatalysts after successful laboratory trials require additional research for their stability, cost-effectiveness, safety, reuse, ease of recovery, and

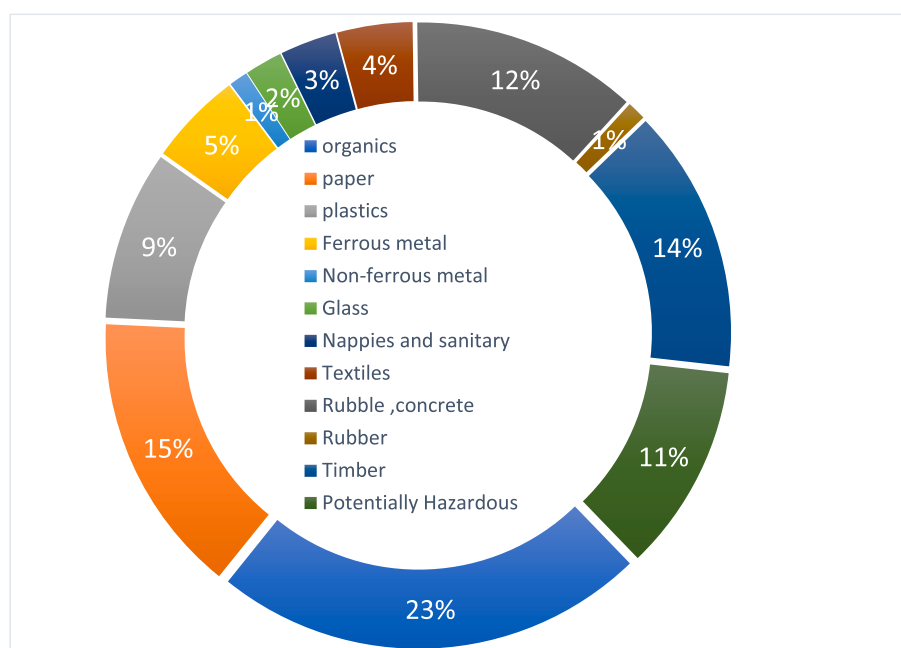


Fig. 1. Composition of the volume of typical municipal wastewater (Kaza et al., 2018).

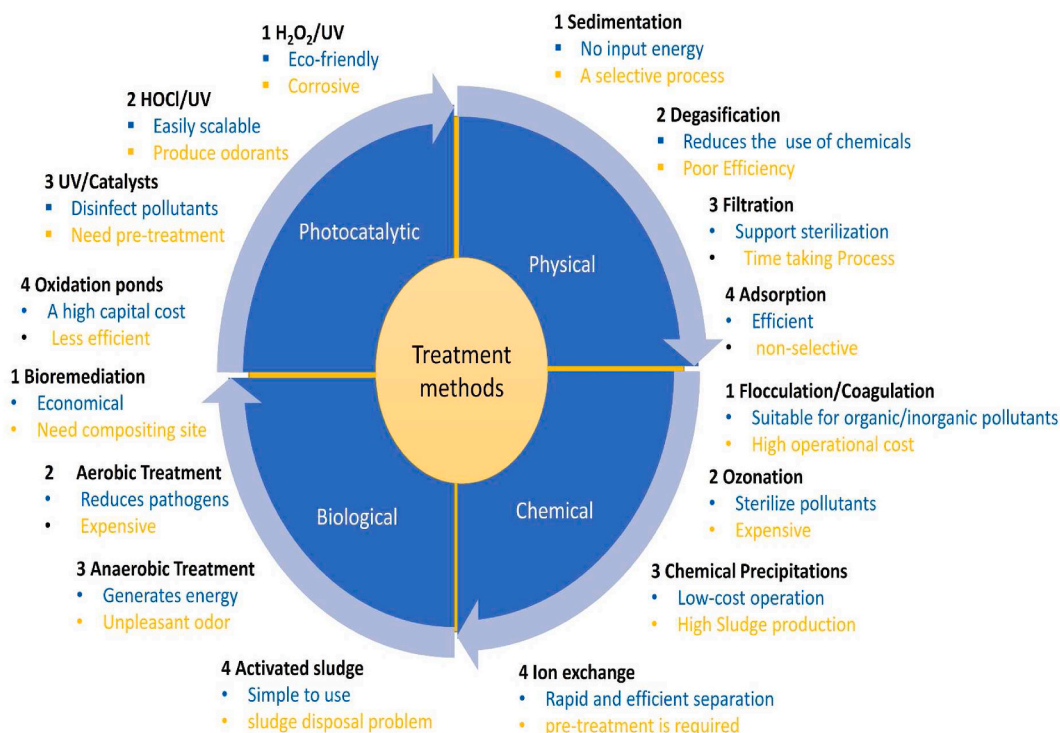


Fig. 2. Wastewater treatment opportunities with key pros (blue) and cons (orange).

upscaling. Likewise, the reduced particle size of the photocatalyst increases its catalytic efficiency but raises the cost (Loeb et al., 2018). The design of photocatalytic reactors is another crucially imperative factor in fulfilling the requirements of today's research and applications (Mauter et al., 2018; Nelson et al., 2018). The photocatalytic reactors have been categorized into various groups based on the elements of design and loading method of the photocatalysts in the reactor (Leb-bici et al., 2015) (see Table 2).

The photo-induced chemical events or transformations (the oxidation and reduction reactions) usually proceed on the surface of photocatalysts. The widely accepted photocatalysts are heterogeneous semiconductors and transition metal oxides (MO) (Linsebigler et al., 1995). The impurities that are added to the photocatalyst to increase its photocatalytic efficiency are dopants or doping agents. To prevent charge carrier recombination, dopants modify the photocatalyst's band gap. These materials often introduce impurity energy levels, trap electrons, create oxygen-deficient sites, and increase the number of active sites for the sorption of pollutant molecules. However, once the dopant concentration was raised even more, there was a noticeable drop in the photo-catalyst's degradation capacity (Bingham et al., 2011a). Recently, some good reviews have been published regarding the synthesis of photocatalysts, their immobilization, and their application for the removal of toxic dyes (Haleem et al., 2023; Sarkodie et al., 2023; Tran et al., 2023; Zango et al., 2023; Zhao et al., 2023; Malhotra et al., 2023). Malhotra et al. (2023) comprehensively reviewed the immobilization of photocatalysts and biopolymer (cellulose) and their applications for the removal of toxic dye. Another group of authors, Sharma et al. (2024), also reviewed the synthesis strategies and identification techniques regarding cadmium (Cd) based photocatalysts used for water splitting. Kumar et al. (2022) reviewed the reaction pathways for Bismuth-based photocatalysts when applied to reduce the CO_2 in fuel cells. There is a diversity of photocatalysts meant to reduce/oxidize a variety of pollutants. Henceforth, there is an ominous need for a review article that comprehensively covers the applications of photocatalysts to manage environmental pollutants.

In this review, we have assembled state-of-the-art information

regarding the mechanism, efficiency, key merits and limitations of various catalytic systems, and dopants. Moreover, the review article will provide updated data on factors affecting the efficiency of photocatalytic systems. The monograph also contains technical records for the use of the metal-organic framework, graphene oxide-based nanocomposite nitrides, and copolymers for the oxidation/reduction of metallic, organic, and biological pollutants.

2. Methodology

Before compiling the present review, we have searched the photocatalytic reactions exclusively from ScienceDirect, Google Scholar, and American Chemical Society Publications (pub.acs.org). The data regarding the pollutants and their risks was collected from the National Institute of Health (<https://www.nih.gov/>) and the National Library of Medicine (<https://pubmed.ncbi.nlm.nih.gov/>). In addition to the above repositories, the research articles on the subject area were also collected using Endnote online search while using the Pubmed connection filter. All the chemical structures were drawn using Chemschetch by Advanced Chemistry Development Inc. (ACD/Lab), Toronto, Canada, and Chemoffice 2020 by PerkinElmer Inc. (<https://www.perkinelmer.com/product/chemoffice-chemoffice>). All other types of graphs and drawings were made using Microsoft Excel and Microsoft PowerPoint.

3. The production of photocatalytic reactive species

The advanced oxidation processes (AOPs) in a broader sense cover the set of photocatalyzed chemical reactions that produce highly reactive species. These reactive species can rapidly react or degrade any organic species (contaminant/pollutant) present in water. The AOP has been declared the "water treatment process of the 21st century" (Munter, 2001). In AOP, a pair of electrons (e^-) and hole (h^+) having energies equal to or greater than the band gap (E_g) are produced as shown in Fig. 3 (Ortiz-Prado et al., 2022). Either electron or hole produced as above initiates a variety of chemical reactions in the medium (equations 1–11) (Imminent risk of a global water crisis, 2023; Malato

Table 1

A comparison of Efficiencies of various adsorbents when applied for photocatalyzed water treatment.

Pollutant Classification			Impact on ecosystem	Photolysis methodology		Annotations	Efficiency (%)	Ref	
Organic Compounds	Typical Examples			Adsorbent/Amount	Conditions (A_{max} ; time (min))				
	Dyes	MB	Toxic,	Ag@AgC@MIL100 (Fe)/CC	Vis light (500 W), 40	Natural dyes are ecologically friendly, biodegradable, and visually appealing, a few of these dyes are poisonous, carcinogenic, and can induce skin and eye irritation.	99.2	Lu et al. (2020)	
		MB, RhB, MO	Do	TiO ₂ /ZnO/RGO	Illumination (300 W), 120		99.6	Nguyen et al. (2020)	
							99.2		
							99.4		
		RhB	Do	BiFeWO ₆ /	Vis light (200 W), 180		90.4	Senthil et al. (2019)	
		Do	α -AgVO ₃	Vis light (300 W), 240	96.4	Ni et al. (2019)			
		MB, RhB	Do		SnO ₂ –MoS ₂		93.1		
		congo red	Phytotoxic		ZnO/PALFs f		Sunlight, 210	>95	
		Petroleum Hydrocarbons	Naphthalene	Toxic	K-doped g-C ₃ N ₄	Vis light (200 W), 180	Simple to extract, but it is a non-renewable and finite source of energy.	82.2	Deebansok et al. (2021)
	N-tetradecane		Harmful to Aquatic life	g-C ₃ N ₄ Hx ⁺	Vis light (300 W),240	87.3		Varjani (2017)	
	Phenolic Compounds		Phenols	Teratogen, ecotoxic	Au@	Sunlight, 210		Resistant to drying and heating, but it is hazardous to tissues and causes an unpleasant smell.	87.7
		Phenols	Teratogen, ecotoxic	Ni/rGO	UV–Vis (150 W), 150	85.7	Cinar et al. (2020)		
		–	Teratogen, ecotoxic	Cu–NiO	UV light (96 W), 60	100	Bui et al. (2020)		
				CuO–TiO ₂					
		BPA	Teratogen, ecotoxic	@ZIF-67	Vis light, 60		95.3	Tang et al. (2020)	
	Heavy metals	Cr	Cr(VI)	Ecotoxic, adversely affects aquatic life	TiO ₂ –ZrO ₂	UV light Simulated xenon, 5	Although vital enzymes are involved in several oxidation-reduction events, the creation of reactive oxygen species leads to oxidative damage and detrimental consequences on health.	100	Yan et al. (2020)
				PW12/CN@					
Cr(VI)			Ecotoxic, adversely affects aquatic life	Bi ₂ WO ₆	light (1000 W), 90	98.7		Yang et al. (2020b)	
Cr(VI)			Ecotoxic, adversely affects aquatic life	CdS	Vis light (300 W), 10	94.9		Zhang et al. (2018)	
				ZnIn ₂ S ₄ /					
Cr(VI)			Ecotoxic, adversely affects aquatic life	CdS	Vis light (300 W), 30	100.0		Li et al. (2017)	
Cr(VI)		Ecotoxic, adversely affects aquatic life	ZnO/Mn ₃ O	Sunlight (300 W), 70	94.0				
Pb		Pb(II)	Ecotoxic, causes neurological disorders	TiO ₂ /Alg/FeNPs	254 nm ultraviolet C (30 W), 72		99.6	Thomas et al. (2020)	
		Pb(II)	Ecotoxic, causes neurological disorders	Fe ₃ O ₄ @C@TiO ₂	UV–Vis (300 W), 180		92.0	Kanakaraju et al. (2019)	
		Pb(II)	Ecotoxic, causes neurological disorders	TiO ₂	300–450 nm (15 W), 240		–	Bi et al. (2019a)	
Hg		Hg(II)	Adversely affects aquatic life	α -Fe ₂ O ₃ /g-C ₃ N ₄	Vis light (400 W), 60		90	Kadi et al. (2020a)	
		Hg(II)	Adversely affects aquatic life	CuO/g-C ₃ N ₄	Vis light (150 W), 60		100.0	Kadi et al. (2020b)	
		Hg(II)	Adversely affects aquatic life	CoFe ₂ O ₄ /g-C ₃ N ₄	Vis light (300 W),60		100.0	Kadi et al. (2020c)	
Pharmaceutical		Anti-biotics	Sulfamethoxazole	Teratogen	MgO/ZnO/Graphene	UVA (30 W),210	Strong biological resistance, high polarity, water-soluble, hydrophilicity, and low yet acutely	94.4 COD	Moradi et al. (2020)
			Tetracycline	Cause ecological imbalance	TiO ₂ /CuO/MCM-41 MoS ₂ /	UV light (125 W), 60		70.5	Khanmohammadi et al. (2021)

(continued on next page)

Table 1 (continued)

Pollutant Classification		Typical Examples	Impact on ecosystem	Photolysis methodology		Annotations	Efficiency (%)	Ref
Organic Compounds				Adsorbent/Amount	Conditions (λ_{max} ; time (min))			
Organic Compounds	Anti-inflammatory	Levofloxacin	Adversely affects aquatic life	Ag ₂ Mo ₂ O ₇	Vis light (150 W),90	hazardous soil absorption coefficient	97.0	Adhikari et al. (2019)
		Norfloxacin	Ecotoxic, genotoxic	Ag ₃ PO ₄ /GO film	Vis light (250 W),100		83.6	Ji et al. (2020)
		Ibuprofen	Cytotoxic and genotoxic	TiO ₂	Simulated solar irradiation (500 W)		87.0	Khalaf et al. (2020)
		Metformin	Long-term exposure can cause cancer	TiO ₂ -ZrO ₂	UV light (125 W)		50.0	Carbuloni et al. (2020)
		Amoxicillin	Can degrade the aquatic environment	TiO ₂	V UV lamp (125 W)		90.0	Chinnaiyan et al. (2019)
	Lipid Regulator	metformin	Can degrade the aquatic environment	TiO ₂	V UV lamp (125 W)		98.0	Chinnaiyan et al. (2019)
		Imazapyr	non-toxic, causes ecological imbalance	Ag/Ag ₂ O-TiO ₂	Vis light (1 mW/cm ²)	Increases the risk of impacting human health and its effects on other life species like bees and butterflies while also assisting in the growth of more food by reducing pests and making food more affordable and accessible.	100	Shawky et al. (2020)
		Profenofos triazophos	Toxic, harmful towards birds and bee	TiO ₂ /Ce	Simulated xenon		98.7	Mkhalid et al. (2020)
		Phenoxyacetic acid	Ecotoxic, genotoxic	Au/TiO ₂	Vis light (300 W)		87.0	Liu et al. (2019b)
		Atrazine	Toxic, harmful towards birds and bee	Ag/LaTiO ₃	Vis light (300 W)		100	Lannoy et al. (2017)
Pesticides	-	Escherichia coli, Chlamydomonas pulsatilla	Causes ecological imbalance	Co-BiVO ₄	-	By absorbing oxygen from organic waste, microbes consume it, changing its chemical composition into something less harmful to the environment while Pathogens are gastrointestinal disease-causing agents.	81.3	Joven-Quintero et al. (2020)
		Escherichia coli	Causes ecological imbalance	g-C ₃ N ₄ @Co-TiO ₂	Vis light (300 W)		6 log Inactivation	Song et al. (2020)
Micro Organisms	-							

et al., 2009; Ren et al., 2021; Kaza et al., 2018; Kuncoro et al., 2018a; Darmokoeseomo1 et al., 2016; Darmokoeseomo et al., 2016)) (Liu et al., 2022). The fact that needs to be remembered is that the photocatalyst having a narrow band gap absorbs more photons of visible light. It is now equally important how the reactor design separates photogenerated electrons because the bulk recombination of charge carriers decreases the catalyst efficiency. Once separated successfully these charge carriers can directly reduce/oxidize the pollutants or form various reactive species which will subsequently accelerate the process of pollutant degradation. For example, the free electrons can directly produce hydroxyl radicals or oxygen can absorb free electrons to form superoxide radicals (O₂⁻) which eventually transform into hydroxyls (Koe et al., 2020).

The AOPs have the potential to eliminate organic contaminants more effectively as these pollutants are more susceptible to oxidation/reduction reactions (Sonu et al., 2023). However, the adsorption of gaseous pollutants like CO₂ is poor onto the photocatalyst surface which means, a high dissociation energy will be required to break thermodynamically stable O=C=O bond. This scenario challenges the utilization of photocatalysts for the reduction of gaseous organic contaminants (Kumar et al., 2022).

Fig. 3 elaborates on the production of various reactive species (equations (Ortiz-Prado et al., 2022; Imminent risk of a global water crisis, 2023; Malato et al., 2009; Ren et al., 2021; Kaza et al., 2018; Kuncoro et al., 2018a; Darmokoeseomo1 et al., 2016; Darmokoeseomo

et al., 2016)) involved in the photocatalyzed degradation (oxidation or reduction) of water pollutants (equation (Neolaka et al., 2023a)). Underneath UV-Vis illumination ($\lambda < 600$ nm), two additional reactions may take place in the presence of ferrous ions or ferric ions (Equation (10)) which also leads to the production of production of OH radicals (Equation (11)).

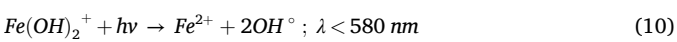
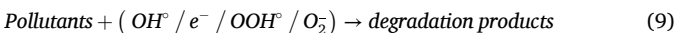


Table 2

The summary of challenges and opportunities that may arise during the photocatalytic waste water treatment.

Sr No	Photocatalysis Challenges	Description	Possible opportunities	References
1	Catalyst Toxicity	- Evidence is there to confirm the catalyst toxicity associated with photocatalyst especially quantum dots, MOFs, metal oxide, and nan photocatalysts, - Although several harmful effects of nanomaterials have been identified, there are still many unanswered questions regarding the nanoparticle's nature and how they interact with the entire system of the ecosystem.	More benign variants are under study. The toxicity of the photocatalyst needs to separately evaluated before their application in waste water treatment	Xie et al. (2020)
2	Photocatalytic Engineering	- The photocatalytic stability/efficacy is often challenged for the narrow bandgap, which demonstrates an increase in efficiency. - In the bulk phase of photocatalysts, photogenerated electrons, and holes unite once more, preventing them from taking part in photocatalytic activities. - The holes or photogenerated electrons may damage the photocatalyst instead of contributing to the intended reaction.	- The integrated photocatalytic systems are required which may include elements to interplay such as Z-scheme systems, heterojunction, and p-n junctions. - Modification in reactor design can keep the reactive species apart. - Surface fabrication of photocatalysts may improve the catalyst's turnover number	Nolan et al. (2016)
3	Scavengers	- The interaction of natural scavengers such as antioxidants with photogenerated reactive oxygen species impairs the photocatalytic process. - Scavengers such as methanol, lactic acid, triethylamine, triethanolamine, tetrachloromethane, and other alcohols are introduced into the photocatalytic system.	- Scavengers must be cautiously analyzed and interpreted when introduced into a heterogeneous photocatalysis process. - Although employing these scavengers can significantly boost photocatalytic efficacy, it also has the undesired side effect of polluting both the products and the surroundings.	Schneider et al. (2020)
4	Commercial application	- The photocatalysis method is extremely challenging to scale up at a large scale due to a very complex process. - Among laboratory and industry use, there's a certain gap. Laboratory research does not take into account costs, catalyst recycling, energy usage, environmental conservation, or other concerns. - Unmanageable elements that are ignored during laboratory research but are present in the commercial user's real manufacturing process.	- The creation of affordable, useful, and reliable large-scale preparation techniques is essential for achieving the industrial interest in photocatalytic equipment. - The progress of reactor designs that can effectively maximize the capacity of a heterogeneous catalyst is critical for the manufacturing and utilization of photocatalytic advanced technologies.	Saravanan et al. (2017)



Water pollutants already adsorbed on the surface of the catalytic substance are degraded by a series of chemical reactions which are initiated by reactive species produced on the surface of catalytic material, and an increase in the partitioning of charge carriers (electrons, holes, or free radicals) improves the efficiency of applied process (Liu et al., 2022).

4. Degradation of organic compounds

The water may get contaminated with organic compounds depending upon its use and contact with other pollutants/surfaces. The organic contaminants can be further divided into smaller categories like dyes, surfactants, hydrocarbons, halides, phenolics, plasticizers, insecticides, plastics, and many more (Ali et al., 2012). The majority of these pollutants are stable, toxic, and carcinogenic (Wang et al., 2014a; Li et al., 2019). However, the reactive species produced via photocatalyzed reactions can decompose many of these pollutants. For example, the cyanides present in water decompose by TiO_2 -containing photocatalysts (Frank et al., 1977). Likewise, Horikoshi and Serpone (Horikoshi et al., 2020) noted the photocatalytic degradation of polychlorinated biphenyl by using TiO_2 under ultraviolet light. Schneider et al. (2014) were able to decompose halogenated hydrocarbons like trichloroethylene and trichloro methane by applying TiO_2 based photocatalysts. The authors found that similar kinds of catalytic efficiencies can be expected by utilizing photocatalytic substances like ZnO , Fe_2O_3 , C_3N_4 , and Bi semiconductors.

The photocatalytic reaction becomes the most viable choice when the organic pollutants degrade (oxidize) into water (H_2O), carbon dioxide (CO_2), or any other generally regarded as safe inorganic substance (Huang et al., 2016). Equations (12) and (13) specifically manifest how a transition metal oxide when applied as a catalyst can be helpful for the production of conduction band electron (CB^-), and valence band hole (VB^+) which are subsequently engaged in the production of reactive species.



4.1. Dyes

Dyes are organic compounds frequently applied as colorants in textile, paper, polymer, and even food industries (Hunger, 2007). Interestingly, more than 1.0 million dyes are commercially available for different applications, and only textile industries contribute 17–20 % of

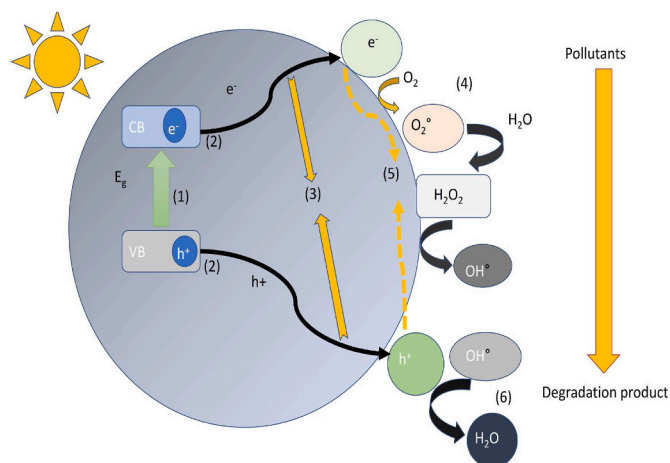
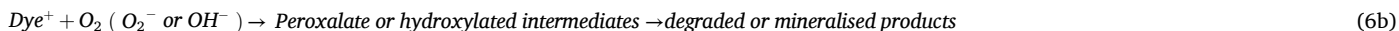


Fig. 3. The mechanism for the production of various reactive species (Ortiz-Prado et al., 2022; Imminent risk of a global water crisis, 2023; Malato et al., 2009; Ren et al., 2021; Kaza et al., 2018; Kuncoro et al., 2018a) involved in the photocatalyzed degradation (oxidation or reduction) of water pollutants (Liu et al., 2022).

industrial wastewater. Most of the existing dyes, like Rhodamine B (RhB), Methylene blue (MB), indigo red, rose Bengal, thymol blue, Methyl orange (MO), and many more are water-soluble, non-degradable, and cause certain known or concealed harmful effects to aquatic life or ecosystem (Robinson et al., 2001). An azo dye that is utilized to color textiles is methyl red (Neolaka et al., 2023b). Multiple approaches like adsorption, coagulation/flocculation, filtration, Ozonation, photo-



catalysis, and biosorption have been used to combat the pollution issues caused by dyes. A few of these techniques primarily separate or transform the water-soluble dye into another product. The AOP has emerged as a more viable and eco-friendly solution to degrade a variety of dyes and/or organic pollutants existing in waters. During the photocatalyzed AOP process, water transforms into reactive species like radicals (hydroxyl) and ions (superoxide) by the reaction of photo-generated electrons and O_2 . These reactive species can readily oxidize dyes or colorants, like methylene blue dyes (Lu et al., 2020).

The mass transfer rates, band gap, surface area, and light intensity control the degradation of water-soluble dyes. The surface area has been found to play a more significant role in the degradation of dyes by the process of photocatalysis: it increases the number of dye molecules that bind to the photocatalyst's surface and boosts its photocatalytic activity (Al-Tohamy et al., 2022). Nguyen et al. proposed the degradation pathway and mechanism under ultraviolet radiation by reporting TiO_2 , ZnO, and their GO composites' impacts on the degradation. Moreover, the heterojunction of these materials shows good photocatalytic stability, applicability, practicality, and recyclability as compared to single-component catalysts. Such outcomes can be assigned to the good separating efficiency of charged carriers, high surface areas, narrower band gaps, and the large absorptive capacities of the dyes. It was observed that $\text{TiO}_2/\text{ZnO}/\text{RGO}$ -based photocatalyst when applied for 120 min at an illumination of 300 W degraded more than 99 % of organic dyes like MB, RhB, and MO (Nguyen et al., 2020).

Senthil et al. (2019) reported that the BiFWO_6 and $\alpha\text{-AgVO}_3$ composite with 1 wt % of BiFWO_6 can remove more than 90 % RhB Dyes. Likewise, $\text{SnO}_2\text{-MoS}_2$ mono structure showed enhancement of RhB and MB degradation with absorption of visible light and the contribution of high surface area. Deebansok et al. (2021) explained the catalytic degradation of Congo red under ultraviolet and visible radiations. Absorption of photon energy from sources of irradiation like sunlight, UV, or light emitting diode (LED) that is greater than the band gaps may result in the production of holes and electrons because of the electronic excitation from the valence band to conduction band (Litter, 1999). The electrons once combined with oxygen can form anionic superoxide radicals (O_2^-) and valence band holes (Fig. 4) which absorb water molecules and produce hydroxyl radicals ($\text{OH}^\bullet$). These radicals can cause the oxidation of organic molecules that are adsorbed and intermediate compounds are oxidized by the molecular oxygen and $\text{OH}^\bullet$ radicals to produce CO_2 and H_2O . The utilization of oxygen and electrons in the conduction band produces the anionic superoxide radicals O_2^- . The protonation of superoxide radicals O_2^- produces hydroxyl radicals. The production of hydrogen peroxide and molecular oxygen occurs by these radicals. Hence, semiconductor photocatalysts enable both reactions (oxidation & reduction) to occur on the surface. The following equations provide the broad, in-depth mechanism of the degradation of dye in response to TiO_2 radiation (Natarajan et al., 2018).



4.2. Petroleum hydrocarbons

These pollutants contain alkanes, olefins, and polycyclic aromatic compounds (Douglas et al., 2012). Marine water consists of large quantities of petroleum hydrocarbon contaminants and they impose long lasting environmental impacts on human and aquatic life (Varjani, 2017). The municipal wastewater and ground water of certain regions may contain these pollutants. The biochar-supported k-doped graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) composite contributes to the good degradation of naphthalene utilizing photocatalysis by illumination of visible-light, because of the availability of a great number of functional moieties in the surfaces which are hydrophilic, enhancement of absorption of visible light and inhibition of recombination photogenerated species. It was observed that, even after five cycles, the photocatalytic degradation rate was not different from that of fresh photocatalysts (Li et al., 2020). Ghasemi et al. (2016) reported that the use of nano TiO_2 and Fe-ZSM-5 led for effective photocatalytic degradation of contaminants in wastewater. After 4 h of ultraviolet irradiation at a photocatalytic concentration of 2.1 g/L, pH of 4, and 45 °C temperature, the determination of COD (chemical oxygen demand) showed 80% efficiency in degradation process. Ultrathin graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) nanosheets with two-dimensions exhibit high surface area, short migrations distance of carrier, and controllability of electronic structures and bestow a desirable photocatalytic oxidation degradation capability for the petroleum hydrocarbon pollutants (Ghasemi et al., 2016). Yang et al. (2020a) suggested decatungstate charge transfer salt hybrid material, which was Visible/NIR Light – responsive, by the assembly $\text{g-C}_3\text{N}_4\text{Hx} + \text{cation}$ and decatungstate anion which exhibited distinctive isolation of charge carriers utilizing local surface plasmon resonance. It shows good performance of photocatalysis and is reusable for the removal of petroleum hydrocarbons.

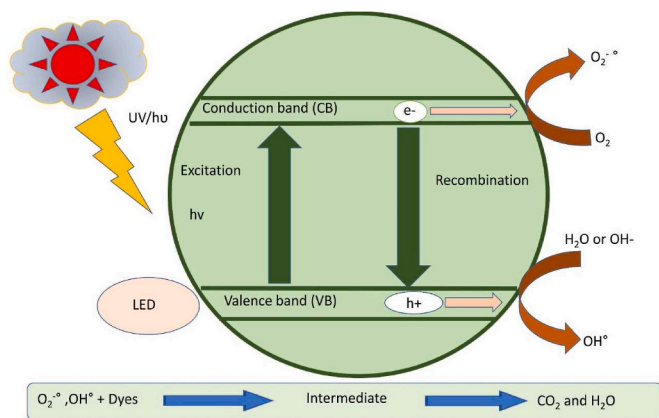


Fig. 4. The photocatalytic breakdown process for dyes in the presence of a Light-emitting diode (LED), ultraviolet (UV), and light ($h\nu$) (Natarajan et al., 2018).

4.3. Phenolic compound

Phenols are toxic, biologically reluctant, and highly soluble in water. The phenolics are produced by many industrial operations like refineries, paints, pharmaceuticals, and petroleum production facilities (Maszenan et al., 2011). Many scientists have explained the improvement of photocatalytic performance via preparing and modifying photocatalytic substances. The phenols, chlorophenols, and nitrophenols derivatives are broken into the bulk liquid in the photocatalytic reaction. A variety of intermediates are produced in the oxidation process by attacking OH radicals on the cyclic carbon (Fig. 5). The three major primary intermediates that are produced in the photocatalytic process are catechol, p-benzoquinone, and hydroquinone. Chloro-hydroquinone, 4-chlorocatechol, and resorcinol are the intermediates of the reaction that are transformed into acetylene, maleic acid, carbon dioxide, and carbon monoxide. Chlorophenols are mildly harmful and suspected to cause cancer. Its photocatalytic degradation results in the production of 4-nitrocatechol, hydroquinone, benzoquinone, and certain organic acids (Ahmed et al., 2010).

Darabdhara and Das (Darabdhara et al., 2019) explained the working of nanomaterials to degrade waste water contaminants and found that Au and Ni core-shell nanoparticles of the size of less than 8.0 nm composited on reduced graphene oxide (rGO) via solvothermal synthesis (Au/Ni/rGO nanocomposites) exhibited higher photocatalytic performances for the removal of 2-chlorophenol, phenol, and 2-nitrophenol in the presence of sunlight irradiation having more than 87% degradation rate. For the measurements of catalytic activity, the nanocomposite retained its integrity till the end of 6 cycles. The composite also exhibited distinctive magnetic features. The authors also observed that Cu-doped nickel oxide nanocatalysts show a phenol degradation in industrial waste water up to 85.7% during 2 h and 30 min exposure to sunlight (Darabdhara et al., 2019).

Doping of Cu can lead to the inducement of oxygen vacancy which is helpful for the NiO surface site for the water treatments. It can be responsible for the improvement of electron-hole isolation efficiency. Moreover, captured electrons at the copper ion Cu^{2+} site can lead to the generation of superoxide radical anion of oxygen $\text{O}_2^{\cdot-}$ via the oxidative process with the adsorbed oxygen, and the holes can lead to the production of hydroxyl radicals ($\text{OH}^{\cdot}$) (Ethiraj et al., 2020). The synergistic influence of superoxide and hydroxyl radicals can lead to phenol degradation. P-N hetrostructure of CuO-TiO_2 has been fabricated. The photocatalyst demonstrated a desirable photocatalytic degradation performance of methylene blue and 4-Nitrophenol underneath the radiation of visible light, which resulted from the charge separation and staggering band structure. The nanoparticles of Fe_3O_4 having magnetic properties exhibited a high value of photocatalysis for the phenolics by the defect engineered on Fe_3O_4 (Bui et al., 2020). Tang et al. (2020) found that the cobalt-based zeolitic imidazolate framework (ZIF)

complex by coordination with the defective TiO_2 illustrated good photocatalytic degradation performance against 1,4-bipheny derivatives. The phenomenon might be attributed to the redox potential of complex and improvement of charge carriers 'isolation.

In another study, Minella et al. (2019) prepared iron oxide magnetic nanoparticles and coated them with different concentrations of humic acid. The presence of iron on the surface of nanoparticles may lead to the promotion of Fenton and photo-Fenton-like processes, assessed by the utilization of a standard substrate, i.e., 4-chlorophenol. The molecular shape of the phenolics contributes to photocatalytic activity, revealed by investigating the effect of phenolics substituents positions on the degradation reaction activities of photocatalytic process. The same study has revealed that a phenol if substituted with electron donating and/or electron withdrawing group it declines the reaction rate and vice versa. In the case of 1,4-benzoquinone, $\text{O}_2^{\cdot-}$ radicals are the principal species in the photocatalytic degradation of phenolics (Minella et al., 2019). Likewise, Xiao et al. (2016) presented another rational approach to degrade phenolic compounds by applying MOF substances as photocatalysts (Xiao et al., 2016). This group of researchers also observed that the presence of electron withdrawing group on the surface of pollutants accelerate their degradation by nanocage-like MIL-125- NH_2 whereas the presence of electron-donating reduces the catalytic degradation (Shen et al., 2020).

5. Heavy metals detoxification

Heavy metals are indispensable for certain metabolic reactions taking place in human body, but their high concentration may elicit toxicity. The unchecked rise in metallurgy, mining, chemical manufacturing, and nuclear stations has increased the concentration of heavy metals in ocean, underground, and surface waters which is equally dangerous for human, animal, and aquatic life. Heavy metals tend to bind with proteins, nucleic acid, and other insignificant metabolites in existing organisms, and they destroy the cells of the body and cause fatal health issues. Because these heavy metals are difficult to be biodegraded and they can cause enrichment in animals and humans by the food chain passage or by drinking (Khan et al., 2015).

The food supply is one way that metals from wastewater may get into and accumulate in human bodies (Neolaka et al., 2023a). Due to their toxicity, cumulative nature, and incompatibility, heavy metal ions provide a major and dangerous risk to all living things when exposed over an extended period of time (Naat et al., 2021). Even at low quantities, the major industrial effluent metals Ni, Cu, and Zn are harmful to living things (Kheraa et al., 2020).

Wastewater contains a number of dangerous and hazardous pollutants, including heavy metals like mercury. Microalgae are renewable resources that can cleanse wastewater and create useful goods; they have thus been used recently as an alternative to conventional

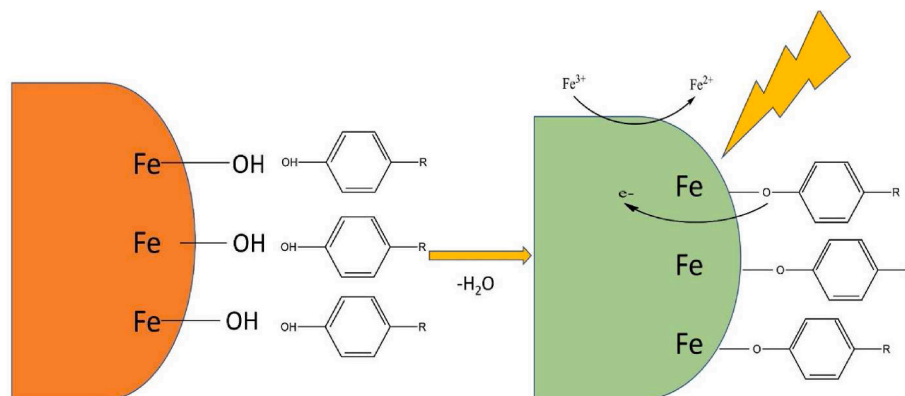


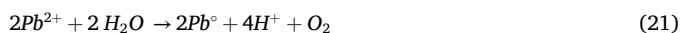
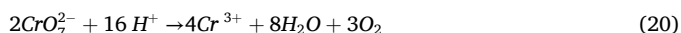
Fig. 5. Schematic illustration of the ligand-to-metal transfer of charge in the Fe_3O_4 nanoparticles to degrade phenolic compounds (Minella et al., 2019).

techniques for eliminating heavy metals. Furthermore, microalgae are very selective in their ability to bind metal ions and remove toxic compounds (Kusuma et al., 2024).

Besides, the majority of heavy metals binds with biomolecules to causes anemia, mutation, and impairment of human organs. The highly concerned heavy metals include but not limited to Zn, Hg, Ni, Cr, and Cd and these heavy metals must be eliminated before their discharge into environments. The photocatalysts have shown superior metal binding and detoxification characteristics as manifested in the subsequent sections.

5.1. Chromium (cr)

The chromium (Cr) exists in variable oxidation states, the most common states are zero (elemental form), +3, and +6 but it may also exist in other oxidation states. The toxicity and stability of Cr or its compounds definitely depend upon its oxidation state. Likewise, Cr binds with oxygen-containing anions such as CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, or HCrO_4^- , and, chromium ions and these compounds when become part of water bodies affect human skin and other organs. These compounds also causes mutation and toxicity (Wu et al., 2019; Wang et al., 2020a). Equation (Wang et al., 2021) describes the overall process of reducing Cr (VI) in acidic aqueous solutions:



Likewise, for neutral aqueous media (Equation (13)), chromium in water has been treated by some workers, using photocatalysis. TiO_2 - ZrO_2 has been utilized to remove heavy metal ions because of its good sorption properties and relatively high chemical stability. According to reports, this material has a high rate of removal after 4 cycles of Cu (II) that is (91%) and Cr(VI) that is (100%) (Yan et al., 2020). It can also effectively degrade both Cr (VI) and Cu (II) in a single phase. $\text{PW}_{12}/\text{CN}@\text{Bi}_2\text{WO}_6$ composite, an organic-inorganic hybrid, demonstrated improved photon absorbance and promoted charges, and Cr (VI) attained an exclusion rate that is about 98.7% (Yang et al., 2020b). Zhang et al. employed the nanocomposites that were made of carbon quantum dots in a freeze-dried state and nanosheets precursors of CdS, achieving an efficiency of 94% for the photocatalytic deduction of hexavalent Cr (VI). Fig. 6 describes the photocatalytic reduction of Cr (VI) accomplished by $\text{ZnIn}_2\text{S}_4/\text{CdS}$ hetero-structure (Zhang et al., 2018, 2020; Li et al., 2017).

5.2. Lead (pb)

The Lead has been considered as one of highly concerned pollutant of industrial wastewater (Kuncoro et al., 2018c) for its toxicity, migration, accumulation, and non-biodegradable nature (Darmokoeseomo1-Magdhalena et al., 2016). The chemical industries like mines and mineral, lead-acid batteries, and municipal sewage are the primary sources of anthropogenic lead (II) pollution. The toxicological consequences of lead on behavior and human health are numerous, and even the intoxication of lead can be lethal. The following are some potential photocatalysis reactions. The Pb(II) can be easily removed from aqueous solutions and can be accomplished using heterogeneous photocatalysis (Murrini et al., 2008). Alexander's group has successfully created the super paramagnetic NiFe_2O_4 -Pd nano-hybrid by NiFe_2O_4 -Pd had a 98% and 97% removal efficiency against Pb^{2+} and Cd^{2+} ions, respectively, demonstrating better photocatalytic activity than bare NiFe_2O_4 (Thomas et al., 2020). Kanakaraju et al. explained how the mixed heavy metal ions can be removed, specifically, Pb (II), Cu (II), and Cr(III) ions were practically eliminated (>98.40%) after 72 min by multi-functional $\text{TiO}_2/\text{Alg}/\text{Fe}$ NPs beads of the magnet (Kanakaraju et al., 2019). According to Hao et al. the magnetic $\text{Fe}_3\text{O}_4@\text{C}@\text{TiO}_2$ heterostructure (Fig. 7) could capture and remove Pb(II) (92% in 3 h). According to a four-step mechanism, iron oxides and e^- can form $\text{Fe}^{2+}/\text{Fe}^0$, and then Fe^0 and e^- subsequently diminish (eq (21)) the adsorbed Pb (II) and immobilize PbO. The researchers have extensively investigated the photocatalytic Pb (II) removal by titanium photocatalysts at different levels of Pb (II) intercalation. Different quantities of intercalated Pb(II) are used in the improved removal of photocatalytic Pb(II) (Bi et al., 2019a). It was observed that 0.10 mM Pb-improved Titanate's photocatalytic can Pb(II) removal efficacy was attributable to its improved specific surface area, higher adsorption affinity, and additional photo-generated carriers (Bi et al., 2020). Fig. 7 elaborates on the various type of reactions taking place during the photocatalytic removal of Pb(II) and Rhodamine B (Rh B) using a magnetic nanotube-based composite of $\text{Fe}_3\text{O}_4/\text{C}/\text{TiO}_2$.

5.3. Mercury (hg)

The principal sources of mercury (II) in industrial wastewater are discharges of electronics, plastics, chloro-alkali, batteries, and old medical equipment. It is the inhalation of mercury vapours or intake of organic mercuries by aquatic organisms, often referred to as Minamata's disease, that causes the greatest harm to human health [65]. Equation illustrates the global response to the deposition of metallic mercury.

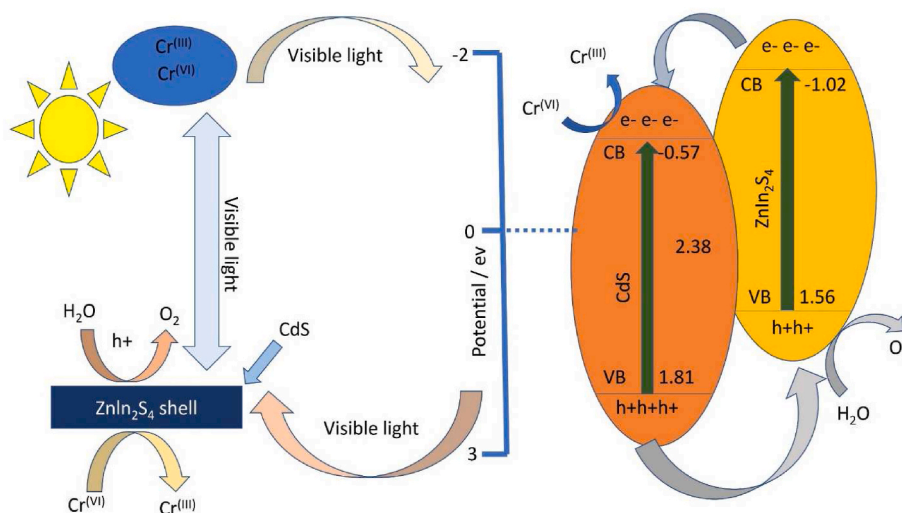


Fig. 6. Mechanism for the photocatalytic reduction of Chromium Cr (V) (Zhang et al., 2018).

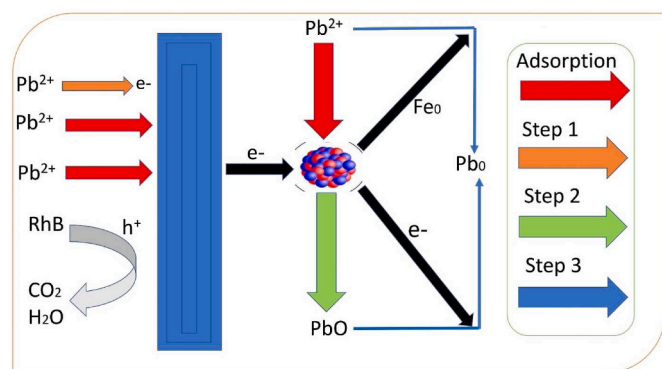
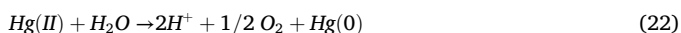


Fig.7. The simultaneous elimination of lead (Pb II) and Rhodamine B (Rh B) via $\text{Fe}_3\text{O}_4/\text{C}/\text{TiO}_2$ based photocatalyst (Bi et al., 2019b).



Mesoporous $\text{Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ nanocomposite, which demonstrated 4.6 and 6.8 fold greater photocatalysis activity than pristine $\alpha\text{-Fe}_2\text{O}_3$ NPs and $\text{g-C}_3\text{N}_4$ nanosheets, can find an intriguing application of Hg(II) photocatalysis (Kadi et al., 2020a). Sivasri et al. (2016) attempted dispersion of Fe_3O_4 nanoparticles in liquid crystals. Au-covered TiO_2 nanotubes have demonstrated the photocatalytic reduction of Hg(II) in aqueous media [67]. Mesoporous $\text{CuO}/\text{g-C}_3\text{N}_4$ heterostructure demonstrated a notable photoreduction rate of Hg(II) that is $628.74 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is another outstanding example (Kadi et al., 2020b). Kadi et al. have created a CoFe_2O_4 mesopore/ $\text{g-C}_3\text{N}_4$ by an outstanding photoreduction of Hg(II) in visible light and a narrow band (2.05 eV) until this energy [69].

5.4. Arsenic (as)

Although their concentrations are low, heavy metal ions like arsenic (As), which are hard to biodegrade, quickly accumulate in organisms, permeate into the atmosphere and are harmful. Ebrahimi and coworkers exploited the hydrothermal route to devise a $\text{BiVO}_4/\text{TiO}_2/\text{LED}$ system. It was found that, at pH 4.5, approximately 99.97% of the arsenic could be removed in perfect circumstances. Recently, a photocatalytic nanocomposite of $\text{nanoFe}_3\text{O}_4$ encapsulated in a carbon sphere has demonstrated a better ability to oxidize at pH 3.0 of As (III), with over 70% removal efficiency that is attained at 400 M concentration in 120 min (Teixeira et al., 2019).

5.5. Miscellaneous heavy metals

Some heavy metal ions, like cadmium (Cd) and uranium (U), are extremely dangerous despite having low quantities and being difficult to biodegrade. They also quickly aggregate in the environment and living things. To safeguard both humans and the environment, it is crucial to remove these hazardous heavy metal ions effectively (Wu et al., 2019). The protection of both people and the environment depends on these harmful heavy metal ions (Liu et al., 2019a). Xu and coworkers used an Ag-doped $\text{SnS}_2/\text{InVO}_4$ hybrid system to remove arsenic underneath visible light. The researchers claimed that the ideal InVO_4 content (2 wt %) at pH 6 with 97.6% elimination in under 120 min had produced the greatest results (He et al., 2020). Chowdhury et al. explained, a sensitized TiO_2 photocatalyst at pH 7.0 in 3 h that demonstrated 100% removal of Cd (II) (Chowdhury et al., 2017). Additionally, to guarantee optimum catalyst function, it is important to look into how environmental conditions may affect performance. For instance, the pH of the solution alters the heavy metal ions distribution, which in turn influences the surface charge of the material and causes an electrostatic interaction with the pollutant (Bhowmick et al., 2014).

6. Pharmaceuticals removal

Due to their detrimental effects on the ecosystem, new pollutants like pharmaceutical compounds (PCs) have become more of a worry in recent years, but the ability to treat such chemicals is restricted by traditional treatment techniques such as air stripping, flocculation, reverse osmosis, etc. Heterogeneous photocatalysis is determined to be one of the most effective ways to break down difficult-to-degrade contaminants like antibiotics, regulators and other drugs (Verma et al., 2020). Antibiotic usage has surged to 35 million tons worldwide in the previous ten years, raising the possibility that wastewater contains dangerous antibiotics. Recently, Soni et al. (2023) have fabricated cattle-derived-nitrogen-doped and biochar-supported oxygen-deficient metal oxide catalytic systems for the mitigation of doxycycline hydrochloride (DCHCl) and Cr (IV). The catalytic system offered an oxidation rate of 68.5 and 63.5 min^{-1} for DCHCl and Cr (IV), respectively, within first 60 min.

6.1. Antibiotics

Antibiotics have received increased focus from PCs since they harm the aquatic ecosystem and endanger the health of humans. Antibiotics and their by-products have a significant potential to interfere with the environment, have high toxicity, and have good stability. Severe issues with the aquatic environment are brought on by the enormous quantity of antibiotics that are released into the atmosphere via animal faeces and sewage. Therefore, it is crucial to research the most efficient processes for removing these chemicals from wastewater (Meng et al., 2017).

Isari and coworkers triumphantly fabricated N-Cu co-doped TiO_2/CNTs to treat sewage effectively and used them in conjunction with ultrasonic radiography and visible light. COD, Sulfamethoxazole, and TOC each had 93%, 89%, and 100% elimination efficiencies under ideal circumstances (Isari et al., 2020a). Moradi and coworkers exploited MZG ($\text{MgO}/\text{ZnO}/\text{Graphene}$), in comparison to single and binary systems, as a ternary nanocomposite to explore the refractory sulfamethoxazole antibiotics in synthesized wastewater. Using an MZG dose of 0.8 g/L at pH 9.0, the full degradation of the Sulfamethoxazole antibiotic (at 55-mg/L level) could be achieved by sono-photocatalytic treatment at US power of 250 W and LED power of 90 W, after 2 h. After six successive cycles of recycling, the nanocomposite's degrading efficiency dropped by up to 9.8% (Moradi et al., 2020). Tetracycline (TC) is the single most significant antibiotic and common substance among chemical substances that are found in ground-waters, soil, and even drinking waters, and surface waters (Wang et al., 2020b).

It can cause the development of antibiotic-resistant genes and ecotoxicity in aquatic systems. It is seen as a possible threat to aquatic ecosystems and human health. Morteza et al. created numerous $\text{CuO(x)}/\text{TiO}_2/\text{MCM-41}$ nanocomposite by using the hydrothermal/impregnation process, with various CuO contents. Under ultraviolet light, they degraded TC using these catalysts. It was noted that while h^+ can directly oxidize TC, TC was also successfully oxidized by O_2^- and OH (Khanmohammadi et al., 2021).

Isari et al. used sono-photocatalysis to prepare WO_3/CNT nanocomposite for the elimination of TC. It was suggested that ultrasonic energy enhanced the splitting of water and dissolved oxygen into free radicals, like OH and O_2 , and that these oxidation radicals then reacted with TC molecules to form intermediate intermediates. The pharmaceutical sector produces the ubiquitous fluoroquinolone antibiotic levofloxacin, which has the potential to pollute wastewater (Isari et al., 2020b). Adhikari et al. created the $\text{MoS}_2/\text{Ag}_2\text{Mo}_2\text{O}_7$ photocatalyst under visible light to oxidize the drug levofloxacin. With 30 wt percent $\text{MoS}_2/\text{Ag}_2\text{Mo}_2\text{O}_7$, an increased catalytic performance (97% efficiency) and good stability were noted. This is due to the heterojunction structure's ability to significantly enhance light absorption, electron-hole separation, and charge transfer efficacy across interfaces to the sorbed substrate (Adhikari et al., 2019).

Using the hot water approach, Wang and coworkers prepared the magnetic $\text{NiFe}_2\text{O}_4/\text{CS}$ composite for the levofloxacin elimination process to activate persulfate. Levofloxacin was degraded in 1 h when the optimal conditions for its degradation were followed: $\text{NiFe}_2\text{O}_4/\text{CS}$ composite 0.6 g/L, persulfate 1.8 g/L, and 5, 67% of an initial pH adjustment (Wang et al., 2019).

Yang's research team by creating various graphene oxide-loaded $\text{Ag}_3\text{PO}_4/\text{GO}$ film catalysts discovered a solution to the recycling problem. The Norfloxacin degradation rate was approximately 100 min is about 83.68%, and the rate constant of reaction (k) for Ag_3PO_4 was 1.9 folds greater than that of pure Ag_3PO_4 (Ji et al., 2020).

6.2. Anti-inflammatories

Vast usage of anti-inflammatory drugs, which have strong hydrophilicity and high polarity but low absorption coefficient in soil, has made it simple for them to survive surface water, underground water, and even resources of drinking water. This results in significant water resource pollution. In treatment plants of drinking water, the freshwater supply is frequently treated with anti-inflammatory medications including ibuprofen, naproxen, diclofenac, ketoprofen, etc. It has a considerable negative influence on a variety of marine organisms, including fish, freshwater algae, and daphnia, when it is unrestricted by the aquatic atmosphere and breaks down by the human body (Günel et al., 2020). According to Achilleos et al. diclofenac in an aqueous solution can be destroyed and mineralized constructed on titanium dioxide, via semiconductor photocatalysis (Achilleos et al., 2010). One of the most widely used anti-inflammatory medications that are non-steroidal, ibuprofen can be used to treat chronic pain and rheumatism (Lu et al., 2019). Khalaf et al. investigated ibuprofen removal from the aquatic environment using photocatalysis and titanium dioxide. They verified that, on glass, the active thin layer of immobilized TiO_2 can act as a useful tool to degrade pollutants like ibuprofen and its derivatives (Khalaf et al., 2020). Zhang et al. employed a magnetic $\text{Fe}_3\text{O}_4/\text{MIL-53}(\text{Fe})$ composite for the photocatalytic elimination of antibiotics and achieved a removal percentage of 99% in the existence of H_2O_2 during a 60-min visible light irradiation time (Liu et al., 2020).

6.3. Lipid regulators

The most popular hypoglycemic medication for the treatment of non-insulin-dependent diabetes or type 2 diabetes among lipid regulators is metformin. After consumption, metformin is eliminated from the body and is not digested by the body. These substances pollute marine resources by entering aquatic resources through a variety of sources. Carbuloni et al. demonstrated the efficiency of photocatalysis in the metformin removal from water using TiO_2 and a synthetic $\text{TiO}_2\text{-ZrO}_2$ catalyst (Carbuloni et al., 2020). Chinnaiyan et al. investigated a photocatalyst of Titanium dioxide to degrade metformin and amoxicillin. The investigational study discovered that amoxicillin (90%) and metformin were effective when the pH was 7.6, 10 mg/L was the initial pollutant concentration, 563 mg/L was the TiO_2 concentration, and the duration of the reaction was 150 min (Chinnaiyan et al., 2019).

7. Removal of pesticides

Pesticides and other chemicals used as fruit thinner, defoliant, growth regulator, desiccant, and ripening agents, are often become part of the water stream to cause an unknown number of environmental and health complications. Pesticides are among the highly concerned chemicals involved in water pollution (Hamza et al., 2016). These all have dangerous effects and are carcinogenic. These pesticides have biological resistance and high toxicity. The small concentration of pesticides can lead to massive human health impacts and also affect the ecosystem. The semiconductor photocatalytic technology is very helpful in pesticide degradation since it has anti-biodegradation and chemical

stability (AbuKhadra et al., 2020; Shawky et al., 2020). For pesticide degradation, materials of the semiconductor by the photocatalytic process are concentrated in the metal oxides of ZnO and TiO_2 (Taghizade Firozjaee et al., 2018). In the presence of visible light, the degradation of herbicide dimethanamid-p with the help of mesoporous $\text{Ag}/\text{Ag}_2\text{O}-\text{TiO}_2$ p-n hetero-junction was appraised. The complete removal in the photocatalytic process showed the destruction of imazapyr after 3 h (Mkhalid et al., 2020). The photocatalytic degradation of tria-zophos and profenofos residue in Chinese cabbage was examined by exploiting co-doped TiO_2 (Liu et al., 2019b). It has resulted in the degradation percents of triazophos and profenofos reaching 32.1% and 53.3%, respectively, after 24 h. The Au- modified photocatalytic performances of TiO_2 and bare TiO_2 alone were studied underneath visible light and UV for the degradation of phenoxy acetic acid (Lannoy et al., 2017). Shaky examined the photocatalytic degradation of herbicide atrazine by utilizing Ag/LaTiO_3 nanowire. It led to complete photo-degradation of the herbicide with the photocatalytic process by using Ag of 2.5 wt% under visible light 40 min after loading (Sisi et al., 2020).

The photocatalytic treatments remove α -endosulfan, 3, 4-dichloroaniline, 4-isopropylamine, chlorpyrifos, dicofol, and parathion methyl from pesticides with efficiencies greater than 80%. Likewise, 4,4-dichloro benzophenone, HCHs, epoxide of heptachlor, and endosulfan-sulphate, are the least degraded with degradation rates under 30% (Miguel et al., 2012). A 48% partial elimination of the investigated pesticides is achieved with photocatalytic treatment using TiO_2/r -radiation. The average percentage rises to 57% when hydrogen peroxide is applied. Some pesticides under study, primarily aldrin, isodrin, 4,4 dichlorobenzophenone, DDTs certain endosulfan, moline, triazines, and anilides, and the trifluralin degrade more quickly when hydrogen peroxide is added (Vaya et al., 2020).

8. Inactivation of microorganisms

Microorganisms pose a significant threat to both the environment and health of human beings. These tiny organisms, such as fungi, viruses, bacteria, and parasites, can cause a range of diseases and infections. They are found in various settings, including contaminated water sources, polluted air, and unsanitary conditions. Hazardous microorganisms can spread through direct contact, contaminated food or water, or airborne transmission. Some notorious examples include *Salmonella*, *Escherichia coli* (*E. coli*), influenza viruses, and the human immunodeficiency virus (HIV). These microorganisms have the potential to cause widespread outbreaks and epidemics, making it crucial to implement proper hygiene practices, sanitation measures, and vaccination programs to prevent their proliferation and protect public health. The common wastewater microorganisms are *Salmonella*, *Escherichia coli* (*E. coli*), and influenza viruses which are involved in diarrhea, respiratory diseases, dysentery, colitis, pneumonia, tracheitis, and meningitis. Matsunaga et al. put forward that the usage of TiO_2 photocatalyst could be helpful in the killing of bacterial water. He was provided with an innovative pathway by the photocatalytic process for the inactivation of micrograms. Additionally, many inorganic and organic compounds can be degraded and can reduce microorganisms by reactive oxygen species (ROS). Water treatment was one of the recorded effective methods. The ROS can destroy Coenzyme- An on the cell membrane which disturbs respiration, and/or even causes cell death by the oxidation of nucleic acid, proteins, and other macromolecules (Wu et al., 2010).

Moreover, the studies explain that ROS oxidize the cell membranes in a way that destroys the outer layer and can trigger the proteins, cations, and nucleic acids leakage which leads to the death of bacterial cells (Wang et al., 2012). Kim et al. utilized CO- the doped BiVO_4 scheme for the pretreatment of wastewater. The photocatalyst efficiently absorbed uv visible light (Fig. 8) to cause more than 80 % mortality *Escherichia coli* and 65.6 % of *Chlamydomonas pulsatilla* (Regmi et al., 2017). Song et al. also appraised the inactivation of *Escherichia coli* (*E. coli*) with the photocatalytic process by using $\text{g-C}_3\text{N}_4/\text{Co-TiO}_2$

Nanofibers in the presence of visible light. It was inferred that this catalyst can reduce 6 logs of bacterial cells within 1.5 h (Song et al., 2020). Wong et al. currently studied the different effects of physico-chemical factors which include photocatalytic concentration, temperature, PH, and inorganic ions of Fe_2O_3 -AgBr by inactivation of gram-positive and bacteria gram-negative under an LED lamp. Moreover, the oxidative of H_2O_2 from the CB of Fe_2O_3 and h^+ oxidation of AgBr can lead to the deactivation of bacterial cell wall (Ng et al., 2016). Abd Elkodous et al. put forward an effective photocatalytic Nanocomposite ($\text{Co}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$; $x = 0.9/\text{SiO}_2/\text{TiO}_2/\text{C-dots}$) complete layer-by layer process and the composite showed about 80.47% inhibition of *E. coli* and 78.54% decline in *candida* species (Abd Elkodous et al., 2020).

Bacterial cells are destroyed as a result of a sequence of events in the mechanism of photocatalysis-induced bacterial inactivation. The separation of electron-hole is brought about when a photocatalyst is exposed to light, which causes the generation of reactive oxygen species (ROS) such as hydrogen peroxide (H_2O_2), superoxide radicals ($\bullet\text{O}_2^-$), and hydroxyl radicals ($\bullet\text{OH}$). The bacterial cells are actually damaged by the reactive oxygen species (ROS) generated during photocatalysis. Rapidly increasing intracellular ROS exceed bacteria's ability to defend themselves, which results in the breakdown of proteins, the release of ions, and the production of protein carbonyl derivatives. The bacterial cell envelope, which includes the cell wall and membrane, is usually the first target of the photocatalytic oxidation process, which then moves on to other internal elements. Studies using transmission electron microscopy have demonstrated how photocatalytic inactivation gradually weakens the structure of the cell wall. The main reactive agents engaged in the photocatalytic bacterial inactivation process may be identified using various scavengers. Scavengers that can halt the process and assist in identifying important reactive species include sodium oxalate, isopropanol, and Cr (VI). Different bacteria have distinct photocatalytic inactivation mechanisms, and conduction band electrons and diffusible H_2O_2 function as disinfectants (Wang et al., 2015a).

9. Types of photocatalysts used for water treatment

Numerous photocatalysts are used in wastewater treatment to eliminate impurities, disinfect water, and break down organic pollutants. These photocatalysts fall into a number of classes, such as polymers, metal-free compounds, chalcogenides, sulphides, and halides. Elements from group 16 of the periodic table, such as sulphur, selenium, and tellurium, are found in compounds known as chalcogenide photocatalysts. Cadmium sulphide (CdS) and copper indium diselenide (CuInSe_2) are two examples. It can be useful in breaking down organic contaminants in water and has strong photocatalytic activity when exposed to visible light. These substances are more effective in

photocatalytic processes because they have a shorter bandgap than metal oxides, which enables them to absorb visible light.

Ag_2S is a sulfide photocatalyst that has shown promise in wastewater treatment applications. It can be used for the degradation of organic pollutants and the disinfection of water under light irradiation. These materials work well for photocatalytic processes because of their low bandgap and ability to absorb visible light. The photocatalytic qualities of silver halides have been studied in the context of wastewater treatment. When exposed to light, they can produce reactive species, which can break down organic pollutants. Materials containing halogen elements, such as chlorine, bromine, and iodine, are known as halide photocatalysts. These materials are effective for photocatalytic processes because they have a small bandgap and can absorb visible light. Materials devoid of any metal components are known as metal-free photocatalysts. Due to its superior photocatalytic activity, $\text{g-C}_3\text{N}_4$, a metal-free polymer photocatalyst, has drawn a lot of interest (Kumar et al., 2023). In addition to its strong chemical stability and appropriate bandgap for visible light absorption, it possesses good photocatalytic abilities for CO_2 reduction, pollutant degradation, and water splitting.

Materials made of organic polymers, such as polythiophene and polyaniline, are known as polymer photocatalysts. These materials are effective for photocatalytic processes because they have a small bandgap and can absorb visible light. The conducting polymer polythiophene has been investigated for photocatalytic uses because of its capacity to produce charge carriers and absorb visible light. It is simple to synthesis and modify to increase its photocatalytic activity for use in the generation of hydrogen and the breakdown of pollutants. Another conducting polymer that has been researched for photocatalysis is polyaniline. Because of its strong stability, electrical conductivity, and redox characteristics, it may be used in processes like water splitting and the breakdown of organic pollutants when exposed to visible light (Khan et al., 2020). The subsequent section covers the details of photocatalysts frequently applied in an aqueous medium or practiced to decontaminate wastewater.

9.1. Metal oxide photocatalysts

9.1.1. Zinc oxide (ZnO)

Zinc oxide (ZnO) have the characteristics which makes it suitable as catalysts particularly for the reactions taking place in light. The ZnO photocatalyst is effective to degrade organic materials as in heterogeneous photocatalysis. Zinc oxide photocatalyst has maximum photon absorption and minimum electron loss during excitation. The improvement of immigration of photon-induced charger carriers in the excitation state resulted in heterogeneous photocatalysis under visible, UV, or solar light. Further, binary oxide photocatalyst has many unique features that gained much attention from researchers. The binary oxide photocatalyst properties are dependent on the role of the content of the dopant and the preparation method incorporated in the binary oxide photocatalyst. ZnO photocatalyst has emerged as one of the efficient ways in the green environmental management system because of its exceptional features. It has a wide band gap that is direct and located near the UV spectral regions, good ability of photocatalysis, strong capability of oxidation, and great free excitation binding energy. ZnO exists as a white powder (zinc white), odorless, having a bitter taste with insolubility in water. There are numerous approaches accepted to improve the zinc oxide efficiency of photo-degradation. Many strategies are adopted to synthesize a high active surface area of zinc oxide and sunlight-driven photocatalytic activity by zinc oxide photocatalyst. The addition of an electron donor or electron mediator with a zinc oxide catalyst further improved the photocatalytic ability of the reaction with the positive holes. The zinc oxide photocatalyst has a lot of industrial applications due to its non-toxicity, high activity of photocatalysis, and photostability. Further, there are approaches adopted to increase the photocatalytic ability under direct sunlight radiation by band gap energy reduction and minimizing the losses of recombination. The

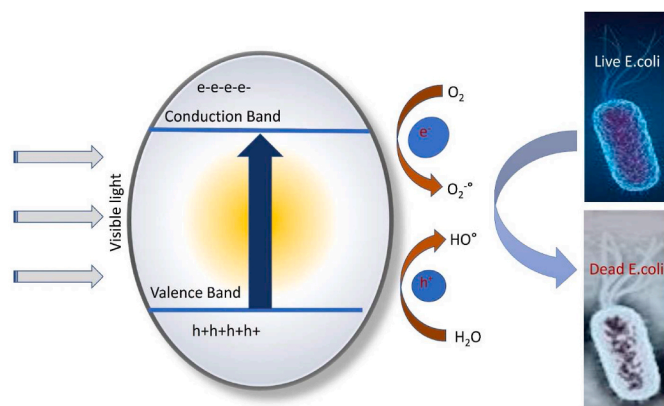


Fig. 8. The suggested Fe_2O_3 -AgBr method for pathogen inactivation is shown schematically (Ng et al., 2016; Wu et al., 2010).

approaches are adopted to rise the degradation activity of photocatalysis in the degradation of dye, removal of phenolic, and persistent organic pollutants (Lee et al., 2016).

9.1.2. Titanium dioxide (TiO₂) photocatalyst

TiO₂ photocatalyst (Fig. 9) is the most frequently used metal oxide for the purification of wastewater because of its great stability, inexpensive cost, low toxicity, high oxidizing power, and long-term photostability (Zheng et al., 2010). The degradation of municipal pollutants by the accumulation of UV/H₂O₂ was inspected in this study using a commercial powder TiO₂ catalyst (Ali et al., 2022). By using two non-similar categories of TiO₂ catalysts, the photocatalysis method was used to investigate the organic chemicals removal and detoxification from wastewater. The major goal was to determine how much the catalyst concentration and the length of the procedure affected the degradation of organic contaminants. According to research, under 6 h of photocatalytic activity, wastewater treated with 3–4 mm TiO₂ particles showed little degradation of organic components. TiO₂ nanoparticles have proven to be particularly effective at treating organically contaminated wastewater by photocatalysis. The use of observable light illumination and a good system of air contact increases the effectiveness of the degradation of photocatalytic organic molecules. According to the findings, using a TiO₂ nanocatalyst may remove 99% of organic contaminants in just 120 min. Removal of organic contaminants from textile wastewater while applying photocatalyst has significant advantages from environmental and financial points of view, over conventional approaches in the application of long-term, notwithstanding certain costs associated with illumination (Khalilova et al., 2016, 2018). The following equations show how the TiO₂ photocatalyst works as a photocatalyst (Islas Garcia, 2021).

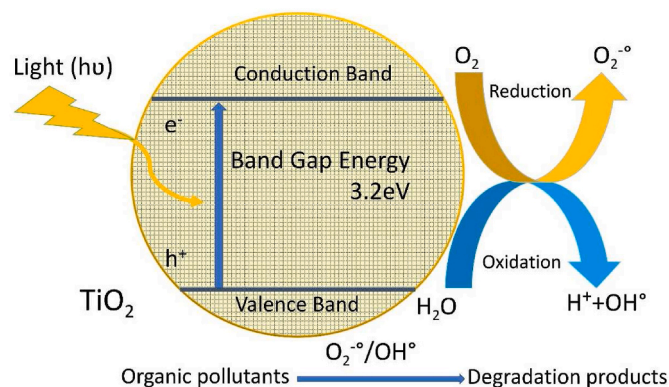
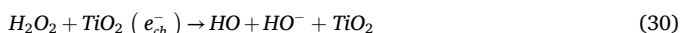
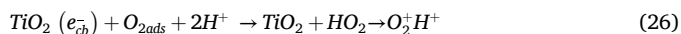
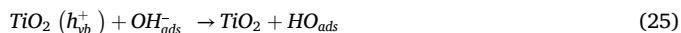
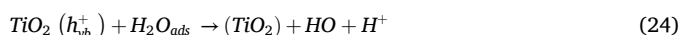
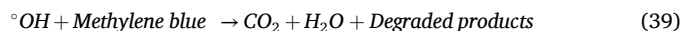
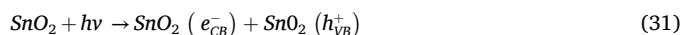


Fig. 9. Diagram of the TiO₂ photocatalysis mechanism adopted from (Schneider et al., 2014).

9.1.3. Tin oxide photocatalyst (SnO₂)

In the SnO₂ photocatalytic process, the movement of electrons from the valence band (VB) to the conduction band (CB), produces both reductive conduction electrons (e⁻) and oxidative valence holes (h⁺) at the same time (Fig. 10) when the light irradiation energy is equivalent to or greater than the catalyst band gap energy (Eq. (31)). The conduction band electrons (e_{CB}⁻) are selected by the molecules of oxygen to create reactive peroxide radical (O₂⁻) (Eq. (32)) that is then transformed into radicals of hydroxyl by a sequence of electron reduction processes. Electrons and holes both contribute to the redox reaction in equations (Li et al., 2019) and (Frank et al., 1977). The hydroxyl radical (OH) is created when the valence band holes (h⁺ VB) interact with H₂O molecules in (Eq. (35)). Under ultrasounds (US), ultrasonic cavitation causes the molecules of water to pyrolyze into (H) and (OH) radicals, creating hot spots with high temperatures and pressures in Eq (Schneider et al., 2014). According to Eq. (Huang et al., 2016), a small number of (OH) radicals recombine to produce H₂O₂, which then dissociates into (OH) radicals as shown in (Eq. (38)). Lastly, as shown in (Eq. (39)), the degeneration of the organic contaminants is brought about by the radicals of hydroxyl produced by both sono-catalysis and photocatalysis processes (Bezzerrouk et al., 2021).



9.2. Cadmium sulfide photocatalyst

Cadmium is usually a toxic heavy metal and produces a serious risk to human beings and the ecosystem. It is similarly very significant for many industrial applications. To avoid the contamination of the environment by cadmium, the strategy is known as the recovery or recycling of Cd in high-value products. Phytoextraction and hyper accumulators strategy is adopted for the remediation strategy. The cadmium-enriched

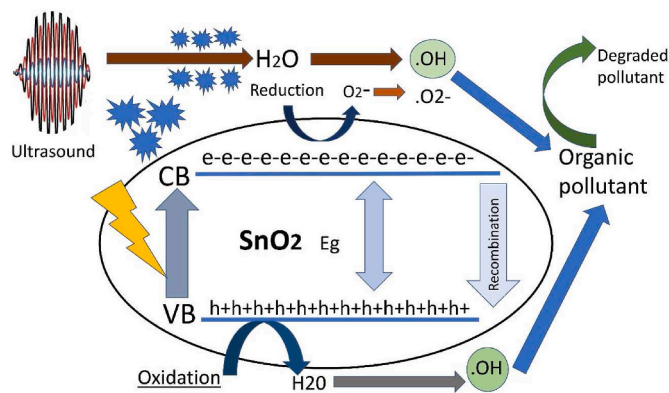


Fig. 10. Using a thin layer of SnO₂, a representation of the mechanism of sono-photocatalytic for the breakdown of the methylene blue dye (Ray et al., 2021).

hyper accumulators biomass recycling in the formula of CdS@C nanocomposite by the pyrolysis carbonization in addition to the hydrothermal reaction. This nanocomposite is represented as the catalyst for the photodegradation of wastewater treatment. In comparison to pure CdS, the preparation of nanocomposites of Cds@C showed the enhanced light capacity of harvesting and good efficiency of photocatalytic because of the lower energy of band gap and highly effective isolation of electrons from holes. The Cd enriched into the nanocomposite of CdS supported with carbon exhibited high performance. It showed good photocatalytic extraction from the slightly and moderately contaminated wastewater. The nanocomposite exhibited a good collection of light and quick separating and transportation ability of photo-generated carriers of charge because of the nearby connection between mesoporous carbon and CdS. Further, the construction of free radicals (OH and O₂ free radicals) showed great promotion of photo-degradation of organic pollutants by the utilization of Cds@C nanocomposite (Li et al., 2021). The fact that CdS is visible light sensitive and thermally stable makes it considered as one of the most attractive transition metal sulfides for use as a photocatalyst (Sharma et al., 2024).

9.3. Graphene oxide photocatalysts (rGO)

To increase electronic conductivity and enhance the capacity to separate and transmit the efficacy of the photo-carriers, GO serves as an electron acceptor or sink in photocatalysis. Moreover, a large surface area encourages the adsorption of pollutants, increasing the photocatalytic activity of the catalysts. Electrons (e⁻) are moved from the valence band of reduced graphene oxide (rGO) when exposed to visible photons with equivalent energy or larger than the energy of band gap (VB). The photocatalyst surface (Fig. 11) or dissolved O₂ can easily capture the electrons produced as a result of irradiation to produce superoxide radicals or O₂^{•-}. As an outcome, O₂^{•-} can be associated with H₂O to form the potent oxidizing radicals, hydroxyl radical (OH•) and hydroperoxy radical (H₂O•), which degrade organic molecules. In addition, surface hydroxyl groups (H₂O) on the photocatalyst surface may trap photo-generated holes to make hydroxyl radicals (OH•). Organic molecules will eventually undergo oxidation to produce CO₂ and H₂O as described in the given equations (Ikram et al., 2020):

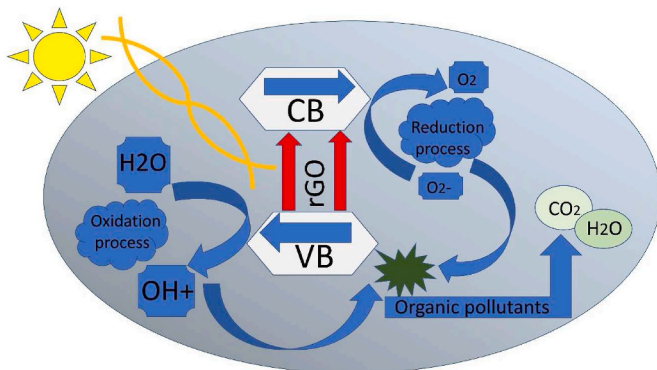
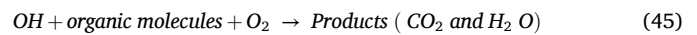


Fig. 11. Photocatalytic Reactions of Reduced Graphene Oxide applicable to the dye degradation (Ikram et al., 2020) as explained in reactions of Eqs. (40)–(45).



9.4. Ferric oxide photocatalyst (Fe₂O₃)

The distress of environmental pollution and water contamination by the dyes is one of the major concerns this time. The advancement in semiconductor and oxide-based magnetic nanomaterial has great potential remediation for water pollution. The production of the nanocomposite was approved by a facile hydrothermal methodology. The ZnSe and ZnO nanoparticles were designed on alpha-Fe₂O₃ layers and led to the formation of hetero-junction. The alpha-Fe₂O₃/ZnSe nanocomposite exhibited 98.9 percent degradation for Congo red (100 ppm) in aqueous media. Nanocomposite of alpha-Fe₂O₃/ZnO exhibited 26.0 percent degradation of the 100-ppm solution of dye, showing poor performance of photocatalytic degradation. This is recognized as the development of configuration type-I heterostructure in recombination. Further, alpha-Fe₂O₃/ZnSe nanocomposite exhibited a greater and increased photocatalytic response. This enhancement of photocatalytic degradation response is assignable to the formation of free configuration (type - II heterostructure) recombination. The alpha-Fe₂O₃/ZnSe nanocomposite is recognized as one of the best photocatalytic degraders for the dye synthesized under mild conditions. Synthesis of hematite NPs-ZnO nanoflakes i. e alpha-Fe₂O₃/ZnO and hematite NPs- ZnSe nanocomposite by facile hydrothermal method showed altered photocatalytic response. The efficiency was investigated by the Congo red dye degradation. Because of the high recombination charge carrier's alpha-Fe₂O₃/ZnO, nanocomposite exhibited lower photocatalytic activity toward dye in comparison to the bare photocatalyst. The poor performance is due to type-I heterostructure which is recognized as a recombination-enhanced configuration. The alpha-Fe₂O₃/ZnSe is a robust photocatalyst that exhibited superior photocatalytic activity. This robustness of nanocomposite is due to its type-II heterostructure and recombination-free configuration. New approaches are adopted for the synthesis of high-performance nanocomposite by the utilization of green materials which showed tremendous application for the degradation of wastewater (Khurram et al., 2021).

9.5. Nano-photocatalyst

The term photocatalysis itself has been derived from the Greek words “photo” and “catalysis,” both of which mean decomposition under the presence of light. The term is applied by sunlight/UV/Visible photons to stimulate the substance (Ong et al., 2018). Photocatalyst changes the reaction rate without being involved in the transformation process. The thermal catalyst and photocatalysts have the key difference of activation by light in the latter (Chen et al., 2019). However, the term nano-catalyst implies to using nanomaterials as the photocatalyst which has a shape-dependent feature and a better surface ratio and, recently, they are commonly utilized for the purification of water. The nanomaterials show many responses as compared to bulk material because they have distinctive surface properties and quantum effects. It helps to increase mechanical, chemical, electric, and magnetic reactivity along with optical properties (Gómez-Pastora et al., 2017). The nano-photocatalysts increases the rate of oxidation/reduction for larger area of contact or surface area (Gomes et al., 2019).

Nanoparticles, for instance, zero valence-based metals, semiconductors, and bimetallic categories are most frequently used for the treatment of water and diverse types of pollutants like organochlorine pesticides, azo dyes, chlorpyrifos and nitroaromatics (Umar et al., 2015). Various studies have shown that TiO₂-based nanotubes are utilized effectively for removing pollutants, for example, azo dyes like Congo red, phenolic aromatics like dichlorophenols, toluene, chlorinated ethene and trichlorobenzene, from the wastewater (Samanta et al., 2016). SiO₂, ZnO, TiO₂, Al₂O₃, etc. Are the most important nano-photocatalysts. The supreme among them all is Titanium dioxide

(TiO₂), having the excellent photocatalytic ability, toxic-free nature, low cost, easy availability on earth, and chemical stability. TiO₂ exists in brookite, rutile, and anatase three natural states. Anatase is a good nanophotocatalyst. 3.2 eV is the bandgap and under 387 nm it absorbs UV light. The photocatalyst ZnO is utilized for degradation having an effective reusable ability (Sadeh et al., 2017). The composite materials and reference substances degradation like dimethyl sulfoxide for the evaluation of wastewater treatments by utilizing nanocomposite of CdS/TiO₂ as a photocatalyst underneath the light in visible spectrum has been inspected. The iron-doped material having ferromagnetism supports reprocessing and reuse easily (Raliya et al., 2017). The features of Pd-incorporated zinc oxide nanomaterial, like high photocatalytic reactivities, are utilized for *Escherichia coli* (*E. coli*) removal from wastewater. Innovative efforts are made on metal oxide to raise its efficacy underneath visible light by modifying it with metals or metal ions. Carbonaceous-based substances, sensitizers of dyes, and many more have been exploited. Nevertheless, there are many methods for additional modification in the nanophotocatalysts (Ali et al., 2019).

Nanophotocatalysts occur in both heterogeneous and homogeneous form, however the formers are preferred nowadays to decompose pollutants and be used in other environment-related applications (Bhanvase et al., 2017). The interface between fluid is applied in prior development and solid photocatalysts like metal or semiconductor. The heterogeneous photocatalysts are working where semiconductor photocatalysts that are light-based utilized an interaction with liquid and gas phases (Yamakata et al., 2019). The heterogeneous photocatalyst is dependent on the scaled-up reactor constructed on the advanced designs with the improvement of performance (Di Mauro et al., 2017). The critical task is to design effective nano-catalyst illumination and mass-transferring optimization, especially in the liquid phase. The photons transferring are upgraded by recruiting light remittent diode and optical fibers but there is lacking productive revolution. Extensive efforts are made for the progress of solar photoreactor (Hassan et al., 2019). The optimistic role of nano-photocatalyst is recognized in the research laboratory for water treatment. Minimizing the problem at the commercial level is not an acceptable approach. The absence of influential photoreactor configuration and lesser photocatalytic competence causes the potential lack in commercial applications. Despite this, heterogeneous photocatalyst has fascinating advantages because they are inexpensive, additive-free, have low concentration work efficiency, and have chemical stability (TiO₂ is stable in aqueous media) (Serrà et al., 2020). The heterogeneous photocatalyst is currently achieving pre-industrial scale (Lekshmi et al., 2020).

9.5.1. Pros and cons of nano photocatalyst

Nano photocatalyst has a vital part in the mineralization of hazardous substances of organic nature at a temperature of 25 °C and is proven very effective for the detoxification of water. The pros of photocatalyst involve less toxicity, low cost, chemical stability, easy accessibility, and excellent photoactive properties with a range of 1–100 nm (Tahir et al., 2019). The Nano photocatalyst exhibit various advantages like chemical and physical stability, low price, and eco-friendly nature. Amongst all, TiO₂ has good photo stability, and numerous photocatalysts like metal sulphide, zinc oxide, and copper-based materials display comparatively low stability because of photo-corrosion (Ciambelli et al., 2020). The shining of light on them causes oxidation or reduction depending on the materials and their oxidation state is changed by the generation of electrons or holes which can lead to the decomposition of the photocatalysts and decrease the photocatalytic process performance (Weng et al., 2019). There needs synthesis of nanocomposites for getting stable photocatalysts for elongated-term performances.

The main pros of nano-sized particles are the quantum size effect, which is helpful to improve the bandgap energy and reduction of particle size. Further, the photodegradation process has many advantages like low cost, reusability, and complete degradation of values. Despite this, the nanophotocatalysts are facing some problems of toxicity and

recovery of catalyst from the mixture. These problems limit the application and possibility of photocatalysts at a higher level (Rajabi et al., 2016). The scientific community is concentrating on the nanocomposite of diverse materials to decrease the toxicity of waste water. So, it is important to be aware the scientific community synthesizes novel photocatalyst which are workable in the visible span for the sustainability and promotion of doped photocatalysts with different materials like graphene and derivatives of it to decrease toxicity. The drawback can be overcome by catalyst recovery; a major method could be utilized like magnetic nanophotocatalysts in the treatment of wastewater. When these magnetic photocatalysts are exploited, the catalyst recovery is achieved through the external magnetic field to permit the recycling of the nano-catalyst and to achieve the effective and naturally responsive decontamination of wastewater (Mahmoodi et al., 2009).

A wide range of investigations are going on in the nano-photocatalysts field which is resulted in progress in designing a reactor and development regarding the nano-photocatalysts. Many developments in the nano-photocatalysts materials occurred but there are still many inquiries relevant to the nano-photocatalysts substances. The principal challenge in intensification is existing limitations in mass transferring and the high consumption of photons. The nano-composite concept is ideal for resolving the problem of recombination ability of electron pair, which can be advanced by nanocomposites combination with nano-photocatalytic reactors constructions (Van Gerven et al., 2007). The most recent and advanced reactors are microfluidic reactors, which allow for intensive research into the reaction and synthesis phases. The microfluidic reactors interact with the reactants on a micro-scale (Lin et al., 2009). The important features are a large surface-to-volume ratio, improvement in the diffusions, the greatness of mass transfer coefficients factor, less Reynold's flow, high stability in hydrodynamics, and informal handling which help to make them ideal more than conventional reactors. Moreover, it is still problematic to apply photocatalysts on the large scale in actual waste-water.

Furthermore, significant structure syntheses like nanorods, nanosphere, nanoflakes, nanoflowers, and nanocones having greater structural and functional properties could open extensive study areas. Several nanomaterials structures with many potential features can be synthesized through a measured synthesis approach (Wang et al., 2014b). Future research should need exploration of new nanophotocatalysts. Preparation of the innovative photocatalyst materials with good performance, inexpensiveness, eco-friendliness, and good stability is needed significantly. Furthermore, for the exploitation of pollutants treatment, several approaches, such as thermodynamics, photocatalysis, electrocatalysis, and adsorption, should be combined with careful matching. In the early decade, the fabrication of nanocomposites in the presence of TiO₂ and ZnO was well explained for water treatment. The preparation methods of nanocomposites by utilizing carbonaceous material, ceramic and polymer materials are still in the early stage. It helps to produce nanocomposite with the improvement of properties. The heterogeneous photocatalyst is prohibited by several technical problems that are required to investigate successfully. Finally, in the future, the significant photocatalytic treatments with the betterment of solar-driven, excellence in efficiency, and lesser site area needs can be comprehended and should be of concern (Umar et al., 2012).

10. Factors affecting photocatalytic performance in wastewater treatment

10.1. pH

The pH value of water/medium defines the fate and chemistry of organic compounds as it affects charge, ionization, solubility, and partitioning coefficient and (Sacco et al., 2012). The pH also control of surface charge of the photocatalysts and the isoelectric point (Chong et al., 2009). Numerous approaches have been utilized to calculate the zero point charges for studies of photocatalytic oxidation performance

(Chanu et al., 2019). The zero point charge denotes a point where the surface charge of the photocatalyst becomes zero and it usually happens in the 4.5–7.0 pH range (Gnanaprakasam et al., 2015; Ochuma et al., 2007). The photodegradation of organic pollutants significantly ($p \leq 0.05$) affected by the pH of the reaction medium. The pH of the solution also controls the oxidizing potential of the valence band of photocatalyst (Reza et al., 2017). The exact mechanism for how the pH can control photodegradation is complex but as a whole photodegradation depends on (i) rate of oxidation of pollutants, (ii) attack of hydroxyl radicals, and (iii) the pollutant reduction by the conduction band electrons [152]. The increase in pH beyond the isoelectric point of the photocatalysts leads to the incorporation of the negative charges onto the surface of the photocatalysts (Venkatachalam et al., 2007). The electrostatic interaction may take place as the negatively charged photocatalyst attracts/absorbs the cationic pollutants and adsorb which eventually leads to electron transferring between the pollutants and photocatalysts for photodegradation (Li et al., 2008). As pH shifts below the isoelectric point of the photocatalyst, the functional group in the protonated photocatalyst and on the surface induces the positive charge which helps to attract the anionic pollutants (Karunakaran et al., 2008). Thu et al. found that methyl orange at or below pH 3 get adsorbed on TiO_2 in the presence of doped by Cu only under acidic conditions while at or above pH 9 it adsorbs in alkaline conditions. Adsorption is primarily responsible for efficient photocatalyst degradation. In the alkaline condition, hydroxyl radicals are majorly involved, while in the acidic environment, the holes having larger oxidation potential are majorly involved in the photo-degradation (Nguyen Thi Thu et al., 2016).

With the increase of pH values, the OH radicals increase in the solution and the reaction between hydroxyl ions and positive holes enhances degradation efficiency. The high basic pH value ($\text{pH} > 11$) produces additional hydroxyl ions which initiate free radical reactions to neutralize contaminants (Konstantinou et al., 2004). The lowering in media pH value is essential for the anionic pollutants to be photodegraded (Pouretedal et al., 2009). At lower pH, owing to the photocatalyst surface protonation, the sorption of the cation species decreases which can lead to photodegradation decline. At the too-low value of pH, the anionic species cause protonation which can lead to avoiding the sorption by electrostatic repulsion on the photocatalyst surface (Rajabi et al., 2013). The unavailable OH ions at low pH suppress the degradation ability. So, because of the change in the form of many pollutants at different pH, and the effect point zero charges of the adsorption abilities of sorbents, optimization of pH is a major step (Prado et al., 2009). For instance, the photodegradation of malachite green is very favorable at a low value of pH and that of methyl blue is favorable at a high value of pH with TiO_2 -based photocatalyst (Ling et al., 2004).

10.2. Catalytic loading

The catalyst amount utilized also has significant effects on photocatalytic degradation. The rise in the quantity of the catalyst increases the quantity of OH radicals' formation which can lead to the participation in the organic compounds' degradation. Beyond the limited catalyst quantity, the turbidity of solution also shows increases and the prevention of UV rays continues, that is resulting in are reduction in the degradation percentage (Coleman et al., 2007). The rate of degradation up rises with the rise of catalyst loading until 0.7 g/L after that occurs on reduction in the degradation. The decrease in the activity of photocatalysis is ascribed to the effect of scattering of light and shielding by the suspended photocatalyst (Jamali et al., 2013).

With the increased amount of the photocatalytic dosage, the amount of photo-mineralization of water pollutants also rises. This is because of greater numbers of the active site on the photocatalysts which results in the adsorption of more photons and the manufacture of OH radicals and positive holes in the existence of radiation. These hydroxyl radicals and positive holes take part in the photocatalytic reaction and boost the percentage of pollutants' degradation. At a low dose of catalysts, solar

light in a maximum value is involved in transmission from the solutions directly, and consumption of a part occurs for the performance of the catalysts. Beyond a certain limit, the high dose of catalyst can be a reason for a decline in the photo degradation rate for the pollutants. The major reason is the solution turbidity which increases catalyst amount and block UV/Vis illumination from entering solutions and, helps to enhance the scattering of light. This causes a smaller quantity of photoactive species and results in the reduction of the percentage of degradations. Moreover, high dosage causes nanoparticles' agglomeration which involves in reduction of active sites numbering that are accessible for exposure (Sohrabnezhad et al., 2009).

10.3. Light wavelength

Based on the photocatalyst used for the reaction, the light source with different ranges of wavelength emission has an important influence on the photocatalytic method. The ultraviolet light utilized in the procedure must have enough energy to promote the formation of an electron hole. There are various categories of the electromagnetic spectrum of UV irradiation, like UV- A, UV-B, and UV- C, depending upon the emission of the wavelength of light. UV- A has wavelength (315–400 nm), UV- B (280–315 nm), and UV- C (100–280 nm). The investigation has shown that UV ranges from 254 nm to 315 nm provide sufficient photons for the photonic activation of photocatalysts like ZnO and TiO_2 . The band gap energy of TiO_2 is 310–400 wavelength region. Moreover, CeO_2 consists of wavelength of 388 nm. ZnO has a wavelength of 387 nm with unique optical properties and efficiency of UV absorption (Janssens et al., 2019; Ghamsari et al., 2017).

10.4. Concentration of pollutants

The different concentrations of pollutants result in the variation in the irradiation period to accomplish the mineralization fully. The rise in the early concentration of organic compounds affects the degradation performance of photocatalysis. The increase in the initial concentrations of the organic pollutants will result in adsorption on the photocatalyst surface. This can be attributed to the deficiency of the surface of photocatalyst for the formation of hydroxyl radicals and the lowering of the activity of photocatalysis of the catalyst. Further, the increase in the early concentration of organic pollutants will lower the number of photons arriving at the photocatalytic surface. It results in a decrease in the electrons' excitation from the valence band to the conduction band. Resultantly, the photocatalytic activity of the photocatalyst is reduced (Gaya et al., 2008).

The degradation percentage in the process of photocatalysis principally depends upon the quantity of the organic contaminants sorbed on the photocatalyst surface. It is independent of the quantity existing in bulk aqueous media. Moreover, it is dependent on the reaction and formation of OH radicals with the pollutants' molecules to contribute to the degradation rate. The adsorption of photocatalysts is dependent on the initial concentration of the pollutants and it rises with a growth in the pollutants concentrations (Kiriakidou et al., 1999). The high adsorption value of pollutants with the more initiated concentration of pollutants contributes to the pollutants getting excited upon light illumination. This is ascribed to the increase in the efficiency of photo degradation. Beyond the concentration limit, photo degradation is declined by raising the early concentration of pollutants. This is because of the covering of the photocatalytic surface with pollutants. There occurs reduction in the number of photons which approach the surface of catalyst and a reduction in the positive holes and hydroxyl ions radicals because the pollutants molecules occupy the active sites (Daneshvar et al., 2004).

10.5. Temperature

The increase in the photocatalytic reaction temperature by more

than 80 °C caused the promotion of the recombination of electron-hole charges. The temperature below 80 °C contributes to the sorption of the impurities on the surface of TiO₂ and operation at this temperature can help to decrease the heating capacity of water. It has been described that a temperature range of 20–80 °C is very effective for the organic reaction under UV light (Herrmann, 2005; Li Puma et al., 2002).

10.6. Light intensity

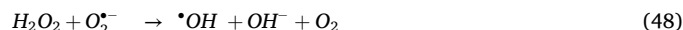
The rise in light intensity leads to a much larger waste of energy during the degradation. The light intensity rise leads to a rise in the cost (Guozheng et al., 2010). When the light intensity is not controlled then a high amount of light intensity is lost. Light energy loss happens when the photon having lesser energy than the threshold photon energy is incapable to ignite the electron-hole pair and results in loss of energy (Yang et al., 2007). The larger light intensities can result in much more waste of energy instead of the degradation of organic pollutants. It is very serious to develop desirable light intensities to deduce the energy loss which can be caused by electron-hole recombination (Dillert et al., 2013).

10.7. Effect of oxidants

Delaying the generation of produced electrons and holes under solar light irradiation can enhance photocatalytic activity (Mukwevho et al., 2019). To increase the photocatalytic oxidation of organic pollutants, oxidants—irreversible electron acceptors such as H₂O₂, KBrO₃, NO₃, (NH₄)₂S₂O₈, Na₂S₂O₈, and K₂S₂O₈—are added to the reactions as foreign agents to quench the conduction band electrons and form intermediate radicals. To increase the photocatalytic efficiency, each of these electron acceptors acts as a powerful oxidizing agent and electron scavenger in the following ways: (a) decreasing the time needed for recombination of electron-hole pair; (b) producing higher •OH amounts for degradation; and (c) production oxidant species to increase the oxidation rate (Wang et al., 1999). However, based on the experimental circumstances, the result of adding oxidizing agents must be carefully studied since they might also have a detrimental influence on the photocatalytic oxidizing of pollutants (Weavers et al., 1997).

10.8. Influence of H₂O₂

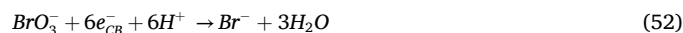
The most researched oxidizing agent to improve the photocatalytic breakdown of organic pollutants in water is H₂O₂. The addition of H₂O₂ boosts the activity of the photocatalyst by raising the concentration of radicals and radical anions. As exposed in equations (Douglas et al., 2012) through (Varjani, 2017), the mechanistic way of radical and radical anion formation by H₂O₂ addition is as follows. H₂O₂ can produce hydroxyl radicals and anions by either directly photolyzing it (Eq. (48)) or reacting with photo-electrons from the conduction band (Eq. (49)). As soon as oxygen is present in the medium, it combines with the conduction band photo-electrons to create oxygen radical anions, which then interact with H₂O₂ to create hydroxyl radicals, anions, and oxygen molecules (Eq. (50)) (Muruganandham et al., 2004). Furthermore, hydroxyl anion and positive hole can interact to form hydroxyl radicals. The photo degradation of the organic contaminants existing in waters is considerably aided by these photogenerated hydroxyl radicals. As a result, as H₂O₂ concentration rises, H₂O₂ molecules trap electrons and generate more hydroxyl radicals, which accelerate the degradation of pollutants in waters when illuminated by sunlight and inhibit the recombining of charge carriers. Nevertheless, if the H₂O₂ amount is increased above the optimal concentration, it begins to function as a scavenger for hydroxyl radicals and h_{VB}⁺, which can be stated as equations (Ghasemi et al., 2016)–(53), which reduce the effectiveness of photocatalysis (Poulios et al., 1999).



At high H₂O₂ concentrations, the amounts of hydroxyl radical and positive hole, which are respectively responsible for the oxidation and breakdown of contaminants, start to decline, which inhibits photocatalytic degradation. Consequently, tuning of the H₂O₂ concentration must be carried out before large-scale applications to ensure an efficient photo-degradation rate (Sobana et al., 2008).

10.9. Effect of KBrO₃

Moreover, KBrO₃ is frequently utilized as an oxidizing agent to boost a photocatalyst is reaction's ability to degrade materials by acting as an effective electron acceptor. For the prevention of photoelectrons and holes from recombination, BrO₃[−] reacts with conduction band electrons to form water molecules and bromide anion. Making photo-generated holes accessible for the oxidizing organic pollutants in the aqueous medium extends their lifetime.

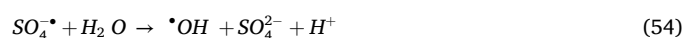


On adding more BrO₃[−] than the optimal concentration, a reduction in the breakdown of organic pollutants was seen. Due to competition to adsorb onto the photo catalyst's surface caused by the formation of additional Br anion, the photocatalytic destruction of organic materials is impacted (San et al., 2001).

10.10. Effect of K₂S₂O₈ and (NH₄)₂S₂O₈

The production of the sulphate radical anion SO₄^{•−} is what causes the photo degradation of pollutants in dirty water to improve when S₂O₈^{2−} is added. From S₂O₈^{2−}, SO₄^{•−} can be created as shown below (equation (55)). To form sulphate anion and hydroxyl radical, SO₄^{•−} may either interact with the water or trap electrons (equations (Ethiraj et al., 2020) and (Bui et al., 2020)). Furthermore, SO₄^{•−} and organic contaminants can directly interact to form intermediates and sulphate anions, which can then interact with SO₄^{•−} to form mineralized products that have been degraded.

Reduction in the photocatalytic degradation of contaminants was seen as S₂O₈^{2−} concentration increased. The excess SO₄^{2−} produced combines with the hydroxyl radicals and positive holes to form SO₄^{•−}, which has a lower degradation potential than hydroxyl radicals. As a result, the degradation of pollutants also reduces with arise in S₂O₈^{2−} concentration along with a decrease in the concentration of the hydroxyl radical and positive holes (equations (Ethiraj et al., 2020) and (Bui et al., 2020)). Thus, for effective degradation of organic pollutants, oxidant concentration must be optimized (Sobana et al., 2007).



10.11. Effect of doping

The doping refers to the manipulation or modification of the valence states of atoms or ions in a material and alters the number of electrons that an atom can donate or accept in chemical reactions, which can have significant effects on the material's properties and reactivity. In the context of photocatalytic efficiencies, doping can be used to enhance the efficiency of the process by optimizing the redox potentials involved in the reduction reactions. By adjusting the valence states of the catalyst material, it is possible to achieve a better match between the redox potentials required for the reduction of pollutants. This can help overcome the limitations posed by the high redox potential required for certain organic compounds like bisphenol and improve the overall photocatalytic efficacy (Kumar et al., 2022).

The impurities that are added to the photocatalyst to increase its photocatalytic efficiency are known as dopants or doping agents. To prevent charge carrier recombination, dopants modify the photocatalyst's band gap. These materials often introduce impurity energy levels, trap electrons, create oxygen-deficient sites, and increase the number of active sites for the sorption of pollutant molecules (Bingham et al., 2011b). By capturing photo induced electrons or holes, the addition of extra energy levels aids in delaying the separation of charge carriers and changes the semiconductor material's band gaps. The sorption of photons underneath the visible area is encouraged by higher energy levels, narrow bandgap, and oxygen vacancies, which increase the rate of photocatalytic events by increasing the space charge region's narrowing to promote photo-induced charge carrier recombination (Eustis et al., 2006; Tong et al., 2018). For the photocatalytic degradation of antibiotics, Eswar and coworkers adjusted the levels of nitrogen and vanadium as dopants in titania catalysts. They found that by reducing the bandgaps and serving as charge trapping center, raising dopant concentrations of 0.1–2 atom% in the titania increased its degrading performance compared to un-doped titania. However, a considerable decrease in the photocatalyst's ability to degrade was seen as the dopant concentration was increased further.

10.11.1. Noble metal doping

A group of metals known with inert nature, anti-corrosive, and anti-oxidizing character includes gold (Au), silver (Ag), mercury (Hg), ruthenium (Ru), platinum (Pt), etc. (Wu et al., 2017). These metals are usually incorporated into the photocatalysts to decrease corrosion on the photocatalyst surface, improve efficiency, and extending the lifetime of the photocatalysts. Noble metals function as effective dopants for a photocatalyst because (a) they increase the photocatalyst's activity underneath visible light, (b) they introduce fermi levels below the conduction band, (c) they rise the active sites number for organic pollutants 'sorption, and (d) they trap photoelectrons to lessen carrier charge pair recombination (Eustis et al., 2006; Tong et al., 2018). The photo-degradation Congo red (CR) and Acid orange (AO) were compared, by Yu et al. and Ozacar et al. respectively, doping of several noble metals on ZnO nanoparticles, and they discovered that Pd-doped ZnO exhibits perfect efficiency amongst all (Güy et al., 2016; Yu et al., 2013). According to Yu et al. Pd performs the best at degrading pollutants out of all the noble metals doped on ZnO because it effectively facilitates electron-hole charge pair dissociation. A higher charge pair separation rate promotes the interaction between hydroxyl groups, which produces more positive holes and hydroxyl radicals, which aid in the mineralization of the dye. When employing a diverse noble metal doped on ZnO, the reducing order of electron-hole pair separation was thought to be Rh < Pt < Ag < Pd, which was also the order of dye degradation when exploiting various noble metal doped photocatalysts. The cost of utilizing noble metal dopants is a drawback because they are pretty expensive (Liu et al., 2011).

10.11.2. Metal doping

Transitional metals dopants, like Mn, Ni, Cr, Fe, and Zn, among

others, decrease the band gap of photocatalysts similar to noble metal doping by adding intra-bandgap phases and activating the catalyst in the presence of visible light irradiation and expanding the time of recombination created electron-hole charge pairs (Liu et al., 2011). Doping with transitional metals (Fig. 12) is also advantageous, especially because these metals are less expensive than noble metals; nevertheless, they are not corrosion-resistant. The shape, size, photocatalyst active surface area, and crystal structure could potentially be altered by the doping of metal ions, which influences greatly on the photocatalytic properties (Ma et al., 2010). Ghasemi et al. investigated the photo-mineralization of Acid blue 92 (AB92) dye contained water appraising the effect of several transition metal dopants (Fe, Cr, Co, Mn, Zn Cu, and Ni) on TiO₂. In comparison to pure titania, metal-doped TiO₂ nanocomposites offer reduced crystalline sizes and greater specific surface areas. Moreover, adding a small number of dopants are involved in the absorption edge movement toward the visible spectrum by introducing an energy level between the conduction bands and the valence of TiO₂ (Ghasemi et al., 2009). Order in which dyes degrade when various metal dopants are used in TiO₂. In comparison to pure titania, metal-doped TiO₂ nanocomposite displays reduction in crystalline size and involves in upraise in specific surface area. Moreover, adding a small number of dopants causes the absorption edge to move toward the visible spectrum by introducing an energy level between the valence and conduction bands of TiO₂. Also, because it brings oxygen vacancies into the lattice spaces and onto the surface of the photocatalysts, Fe is one of the most advantageous transitional metals which are used as dopant agents. This stimulates the production of •OH radicals, which rises the photocatalytic efficiency (Wu et al., 2012).

10.11.3. Rare earth metal doping

The earth's crust is rich in rare-earth metals, which are also preferred for doping because they are less expensive than noble metals. F-orbital can form complexes with semiconductor materials since it is present in rare earth metals, which increases the photocatalytic effectiveness of photocatalysis (Bingham et al., 2011b). Because of the partly filled 4f-orbitals, the incorporation of rare-earth metals, particularly lanthanides, produces infra-4f optical transitions (Myilsamy et al., 2016). Likewise, the addition of rare-earth metals to photocatalysts up to a certain limit inhibits charge carriers from recombining and makes them accessible to take part in photocatalysis (Sarkar et al., 2015). Rare-earth elements typically display more radii than photocatalysts and are more readily disseminated on the surface than interstitial lattice dopants (Ravichandran et al., 2017). Such an element is responsible for the upraise in the active surface area and are involve in the limitation of the photocatalyst's Nano crystalline size (Ahmad, 2019). Moreover, Zhang et al. showed that the usage of TiO₂ nanocomposite as photocatalysts for the degradation of RhB reduced the anatase to rutile phase transformation about Ln ion radius (La³⁺ > Gd³⁺ > Yb³⁺) (Shi et al., 2009). TiO₂

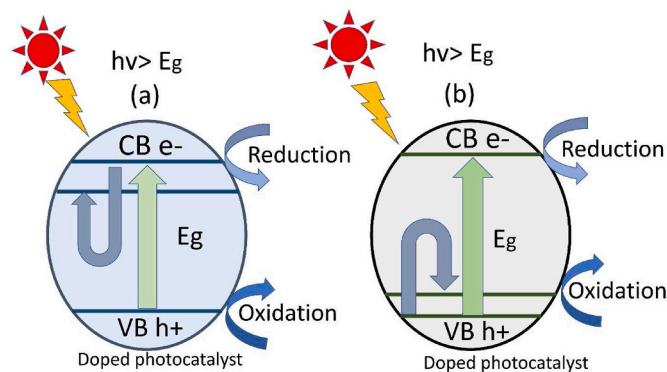


Fig. 12. For photocatalytic improvement, doping has two effects: (a) electron trapping in CB and (b) hole trapping in VB (Ray et al., 2021).

nanoparticles were produced by Xu et al. and doped with various rare earth elements (Ce^{3+} , La^{3+} , Nd^{3+} , Pr^{3+} , Gd^{3+} , Sm^{3+} , and Er^{3+}), and their photocatalytic properties were assessed. Using lanthanide-doped TiO_2 nanocomposite, a noticeable red shift was seen towards the longer wavelength (Zhang et al., 2004).

10.11.4. Non-metallic doping

Due to their superior stability, high photocatalytic effectiveness, and simplicity of the doping method, non-metallic doping and anionic doping are reportedly superior to transition metal doping and cationic doping in photocatalysts (Alam et al., 2018). Several non-metallic doping agents, including phosphorus, nitrogen, sulphur, fluorine, and carbon, have been examined and found to increase photodegradation efficiency by adding additional impurity energy levels show proximity to the valence band and facilitating the absorption of light in visible range (Zhou et al., 2016). One of the maximum effective non-metallic dopants for boosting photocatalyst activity in the visible light spectrum is nitrogen (N). It is simple to incorporate such non-metallic dopants into the structure of the photocatalysts, either at interstitial sites (where N–O bonds form) or substitutional sites (where N atoms take the place of O). Under visible light, interstitial N-doped photocatalysts are found to have greater activity of photocatalysis than substitutional N-doped ones (Devi et al., 2013). By boosting the absorption of visible light and increasing the generation of photoelectrons and holes for photocatalysis, nitrogen can readily lower the band energy gaps of the photocatalysts on the shifting of the valence bands in upward direction. Valentin et al. has investigated, in theoretical research, the influence of doping non-metals (N, B, F, and C) on the electronic structure of anatase TiO_2 in interstitial and substitutional sites. Except for F, one energy level is generated above the valence band. The electronegativity of the dopants, which declines as the dopant concentration rises, determines these energy levels (Atchudan et al., 2018). These energy levels are stimulated by the dopants' electronegativity, which decreases as electronegativity increases. Although fluorine, which has the maximum electronegativity, is involved in states introduction below the O 2p valence band, boron, which is less electronegative, introduced states at 2.18 eV above the valence band. In contrast, it supplies electrons and energy levels below and above the valence band of O 2p for B and C interstitial doping (Varley et al., 2011). Nevertheless, nitrogen atoms join lattice O and produce NO-like species as a result. Non-metal dopants alter the bandgap in order to boost the photo degradations of pollutants in aqueous media and to upraise the stability of the photocatalysts (Peng et al., 2008).

10.11.5. Co-doping

Non-metallic/mono-metallic doping has the potential to dramatically increase the photocatalytic effectiveness of the photocatalysts, but it is responsible for the recombination of charge carriers produced by the photo process. By reducing the solubility of the doping agents, which lowers the production of recombination centers, the inclusion of overseas atoms as co-dopant can make these impurity bands passive (Zhu et al., 2009). Co-doping or incorporation of compensating dopants elicits strong interactions with defect of charge and aids in charge transferring between the donor and acceptor, which upsurge the dopant solubility and aids in lowering of the bandgap energy level. Additionally, the co-doping procedure is utilized to broaden the absorption light spectrum and quicken carrier mobility, decrease the ionization energy of acceptors and donors, and boost activation energy. Co-doped nanocomposite materials have smaller crystallite diameters than doped nanocomposite materials (Avilés-García et al., 2018).

Moreover, compared to doped nanomaterials, co-doped nanocomposite materials have smaller crystallite sizes, providing more adsorption sites and promoting improved photocatalytic efficacy. The synergetic effect of two or more than two elements, like metal-non-metal atoms (Mo and C doped, Mo and N doped), non-metal-non-metal atoms (N and S doped, C and N doped), and metal-metal atoms (V and Zn

doped, Sn and Fe doped) on the optical and electrical structures, were merged into the photocatalyst lattice. By lowering the recombining of charges (electron-hole pairs), such co-dopants augment the photo degradation efficiency. For instance, co-doping N (non-metal) and C (non-metal) on TiO_2 enhances TiO_2 's photo-degradation capacity when illuminated by visible light. The introduction of impurity levels near TiO_2 is caused by the co-doping of C (Wang et al., 2015b).

For instance, co-doping N (non-metal) and C (non-metal) on TiO_2 enhances TiO_2 's photo-degrading capacity when illuminated by visible light. Co-doping of C introduces impurity levels close to the valence band of TiO_2 . Electrons energy level from the co-dopants surface state were also involved in the TiO_2 conduction band and also the electrons from the valence band, making them available for the capture and photo-degradation process. Further contributing to the oxidation of the organic component or being consumed to produce hydroxyl radicals are photogenerated holes at the surface states and impurity level. TiO_2 's photo-degradation activity is therefore enhanced by co-doping (Kanakaraju et al., 2022).

10.11.6. Self-doping

The intriguing methods for changing the band gaps of large value of semiconductors is self-doping, which broadens the photo response of substances from the UV area of sunlight spectrum to visible light span and also maintains the photocatalyst's redox reaction ability at the highest level (Liu et al., 2023). Self-doping increases photocatalytic efficiency by introducing oxygen vacancies into metal oxide semiconductors without the addition of any additional impurities. Self-doping in TiO_2 produced Ti^{3+} species and oxygen vacancies, which caused the narrowing of gap and encouraged the photocatalytic performance of TiO_2 in the presence of visible light, according to both experimental and theoretical calculations (Li et al., 2015). The photocatalytic activities of pristine TiO_2 and TiO_2 doped by self-doping treated at 27 h, 24 h, and 20 h (Ti-27, Ti-24, and Ti-20 respectively) were compared by Liu et al. Ti-27 with excellent recyclability greatly increased the photo degradation effectiveness of TiO_2 by nine times (Pan et al., 2022).

10.12. Inorganic ion impact

The existence of inorganic ions dissolved in wastewater, like Zn, Mg, Cu, Fe, phosphate, nitrate, chloride, etc., can have a big impact on how well a photocatalyst degrades organic pollutants. Pollutant molecules may compete with inorganic ions to adsorb on the photocatalyst surface and involve in the obstruction of the active sites (Temam et al., 2022). Crittenden et al. (1996) showed that the photocatalytic reaction was subjected to deactivation by utilizing a photocatalyst for water treatment in the presence of inorganic ions, either in a fixed bed or slurry configuration. The research concluded that while Ca^{2+} , Zn^{2+} , and Mg^{2+} exposed minor impacts, a select few inorganic cations, like Cu^{2+} , Fe^{2+} , and, Al^{3+} significantly reduced the pollutants photo mineralization underneath reaction of photocatalysis. This is a result of the maximal oxidation states that these cations (Ca^{2+} , Zn^{2+} , and Mg^{2+}) show, which prevents them from having any inhibitory effects on photocatalysis. Similar to this, the presence of many kinds of inorganic anions, such as Cl^- , ClO_4^- , NO_3^- , etc., significantly decreases the photocatalyst ability of photocatalysis, while a small number of inorganic anions, such as ClO_3^- , BrO_3^- , $\text{S}_2\text{O}_8^{2-}$, IO_4^- , etc., act as oxidizing agent in the medium and increase photo-mineralization up to a certain concentration limit (Crittenden et al., 1996).

To better understand how inorganic ions affect heterogeneous photocatalysis, several mechanisms have been described. These include UV screening, radical and hole scavenging, competitive sorption on the active site, competition for photons, precipitation on the surface, and catalyst reaction (Pabel et al., 2023). Inorganic anions Cl^- , SO_4^{2-} , HCO_3^- , and PO_4^{3-} were found to be holes and radical scavengers that slow down photocatalysis. Equations (Tang et al., 2020) and (Minella et al., 2019)

can be used to represent of scavenging mechanisms of radicals and holes when Cl^- is present in the medium.



The preferred adsorption displacement mechanism, which causes the chloride ion to have an inhibitory impact, lowers the number of hydroxyl anions needed for photocatalysis. Pre-water treatment with ion exchange resins to remove inorganic ions is one of the best ways to avoid the inorganic ions drawbacks in wastewater during the photocatalytic decomposition of organic pollutants (Chen et al., 2022).

10.13. Effects of surface area, size, and morphology

The critical component affecting the rate of degradation for water pollutants by photocatalysis is the photocatalyst's surface morphology, such as size and area of contact. The size and morphology of photocatalytic materials significantly affect their efficiency in decontamination processes. The smaller particle sizes provide a larger surface area, leading to enhanced photocatalytic activity. The nanoscale photocatalysts exhibit higher efficiency due to their increased surface area-to-volume ratio, which promotes more active sites for pollutant degradation. The morphology of photocatalytic materials, such as nanoparticles, nanorods, or nanosheets, also influences their photocatalytic performance. Different morphologies offer varying degrees of light absorption, charge separation, and pollutant adsorption, affecting the overall efficiency of the photocatalytic process. For example, nanorods with a high aspect ratio have shown improved photocatalytic activity compared to nanoparticles due to their enhanced light absorption and charge transfer properties (Zango et al., 2023).

The pollutant's adsorption onto the surface of the photocatalyst, which is taken into account for photo mineralization, has a direct relationship with surface shape (Guillard et al., 2003). For a similar reason, nano-engineered materials have greater electrical, optical, and photocatalytic capabilities than bulk semiconductor materials, they are always regarded as improved photocatalysts. In general, smaller nanoparticles have greater surface area and are responsible for the generation of more active sites, which contribute to better mineralization through the contaminant's direct adsorption onto surfaces or by efficient photon adsorption (Kumar et al., 2018). Ameen et al. explained the photocatalyst area of contact (PANI/Graphene nanocomposite) growth and the rate at which Rose bengal dye is photodegraded. However, due to a higher recombination rate beyond the limit, the photocatalytic activity starts to decline for nano-catalysts of the ideal size. The efficacy of photocatalysts in pollutant degradation can be influenced by the shape of the nanomaterial (Ameen et al., 2012). For example, Kumar et al. inspected the photodegradation of the anionic dye MO using several ZnO morphologies (nanorods, nanoflower, and nano spindle). The results showed that, because ZnO nanorods generate a significant number of species of reactions in the direction of the longitudinal surface, structures consisting of rod-like arrangements have better photocatalytic performance than flowers and spindle structures (Kumar et al., 2015).

11. Design of photocatalytic reactors

There have been many improvements in the realm of heterogeneous photocatalysts. The industrial applications and their success are based on the rational design of the Photocatalyst. The design of photocatalyst plays an important role in the degradation of toxins in wastewater. The selection of a suitable reactor is very important because it speeds up the rate of reaction and not only help to save energy but also important in terms of working of photocatalysts. The light energy utilized by the photocatalytic reactors, the light utilization performance of the source, and the mass-transferring efficacy of the reactors should be taken into

consideration. The photocatalyst positioning into the reactors helps to raise the contact area, and performance of the catalyst, accelerate the reaction rate, and optimize the photocatalyst reaction procedure (Sacco et al., 2020).

It is also noteworthy to mention here that the level of toxins/contaminants/biological species must be below the tolerable/recommended levels of recovery of these pollutants. Likewise, it should be kept in observation that light energy coming from the source reaches the photoreactor/penetrates and is absorbed by the reactor. The mass transfer rates of wastewater need to be optimized for maximum interaction between pollutants and photocatalysts. The suitable flow rate/mass transfer rates also ensure high oxygen uptake at the gas-liquid interface. The wastewater must be screened for the dissolved oxygen and be switched to aeration to improve the efficiency of photocatalytic reactors. The dissolved oxygen works as an electron scavenger and traps the conduction band electrons which prevents their recombination (Nayak, 2022). Finally, pH of the wastewater should be adjusted to required level to optimize the efficiency of treatment process and life of reactor compartments and photocatalyst. The wastewater should be free from any substances that may interfere with the photocatalytic process or cause fouling of the reactors. Proper mineralization, aeration of photocatalyst chamber, and the maintenance of suitable flow rate can degrade organic contaminants found in water matrices. With an increase in dissolved oxygen, dye photodegradation accelerates, because the oxygen-free radicals produced causes more photodegradation (Pal et al., 2016).

There are various categories of photocatalytic reactors (Figs. 13–19). The photocatalyst particles that are suspended and reactors consisting of continuous inert immobilized carriers are utilized. The photocatalytic reactors can also operate in batches with recirculating or usage of continuous modes and exploiting adequate geometries can optimize the light collection from specific source (Cassano et al., 2000). The most critical parameter is the whole surface area of the photocatalyst that come under the source of radiation in a unit volume and dispersion of light inside the reactors (Pareek et al., 2008). If the proper photocatalytic design is not utilized, it can significantly increase energy consumption, improper distribution of photons, and poor working of catalyst (Enesca, 2021). The key challenge in photocatalytic wastewater treatment is developing an effective photocatalytic reactor design for large-scale applications like industrial as well as commercial purposes (Abhang et al., 2011; Chong et al., 2010). The large-scale photocatalytic degradation processes with higher efficiency can be launched through the quick evaluation of the diverse kinds of pilot plant configurations. It is reported that compact photocatalytic reactors will be highly efficient in the organic pollutants degradation and the incorporation of flexible and dispersive light capacity (Hossain, 2018).

The photocatalytic reactor can be categorized into fixed bed reactors

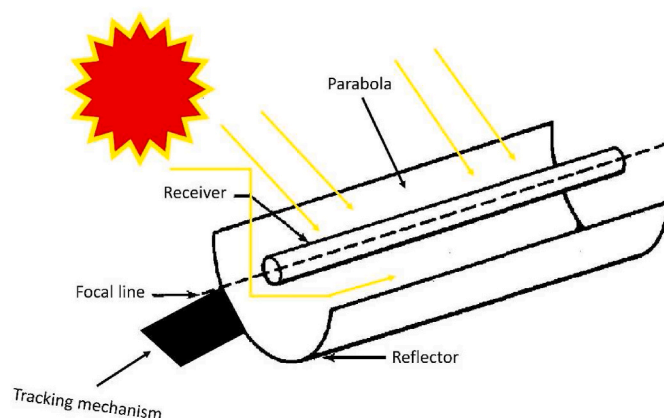


Fig. 13. A parabolic trough-based solar concentrator is depicted in a diagram (Alpert et al., 1991).

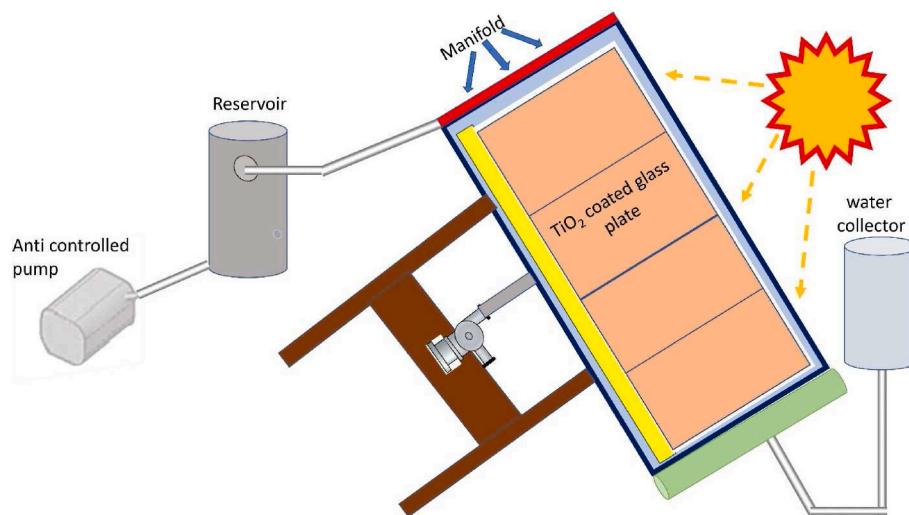


Fig. 14. The Thin Film Fixed Bed (TFFBR) Reactor's schematic design (Sundar et al., 2020).

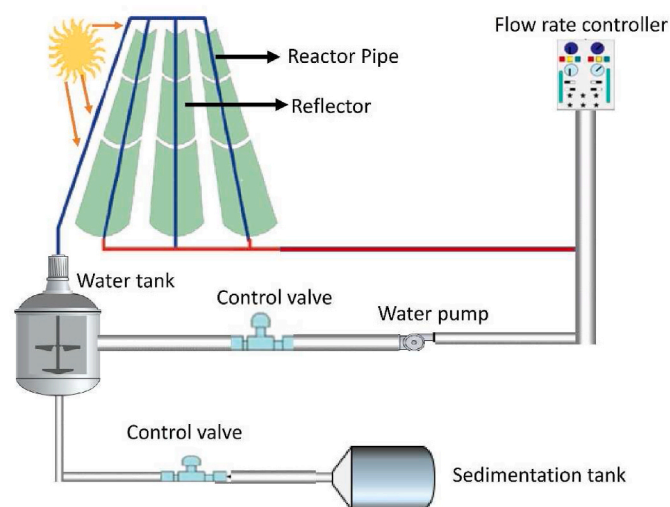


Fig. 15. Schematic diagram of Compound parabolic collecting reactor (Alpert et al., 1991).

and fluidized bed reactors. In fluidized bed reactors, the granulated carriers suspended in the treatment solution are directly loaded with the catalyst. They have a lot of surface area, little restriction on mass transfer, and a quick rate of reaction, but the catalyst is hard to recover and easily clumps together, causing a blockage. It suggests that commercial amplification is difficult (Bello et al., 2017). The fixed bed reactors show surface area very small in comparison to the fluidized bed reactors, so it is a very difficult to separate the catalyst from the aqueous phase. However, in this type of configuration, recycling of the photocatalyst becomes more feasible. Right now, it cannot be claimed with sufficient evidence that which type of design can work for industrial amplification of fixed bed catalysts (Phan et al., 2017).

In addition to it, the up scaling of the reactor needs mathematical model development, inclusive of different sub-models. By utilizing CFD (computational fluid dynamics) the photocatalytic reactors have been modeled for liquid phases and gaseous. Different CFD models have been designed for the up scaling of photoreactors and wastewater treatment for the pollutants like oxalic acid, polyvinyl alcohol, phenol, Rhodamine B, methyl blue, tri (2-chloroethyl) phosphate, and tributyl phosphate. The CFD modeling utilizes the emission of source of light characterized by the model of linear source which is best for numerous reactors

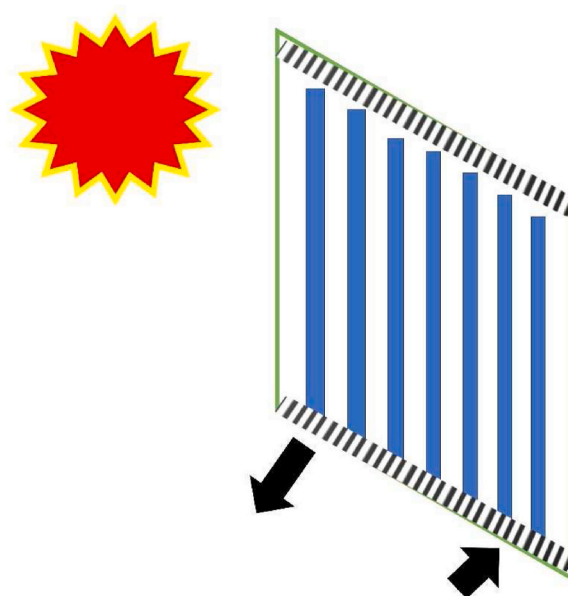


Fig. 16. The schematic diagram showing a Double Skin Sheet Reactor (DSSR) (Malato et al., 2009).

configuration with some restrictions (Joven-Quintero et al., 2020).

The photons generation that is necessary for wastewater degradation is a major expense. It is demonstrated that the sun has low cost and ecological benefits as a light source. These photons when employed in photocatalytic reactors are beneficial for the degradation of wastewater. There have been a lot of studies on the creation and testing of various types of photoreactors for the past 15 years (Fattahi et al., 2021). The most prevalent reactor designs are described in the following section.

11.1. Parabolic trough reactor

The parabolic trough reactor is also known as plug flow reactor. These type of detoxification loops had been initially introduced in the laboratories of United States. As illustrated in Fig. 13, the reactor constitutes a parabolic trough collector (PTC), tank for SO₂ gas, mass flow controller (MFC), tank of carrier gas for N₂ gas, tank for gas mixing, and analyzer of flow gas. PTC is made up of a receiver tube, collector support, and a single stainless steel mirror. This PTC design was made by

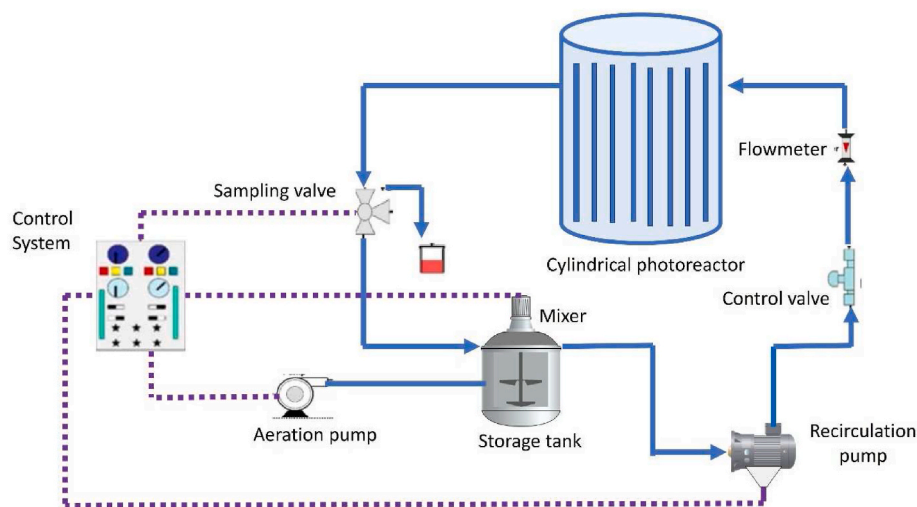


Fig. 17. Cylindrical photoreactor using TiO_2/WO_3 heterostructured catalyst (Neolaka et al., 2019).

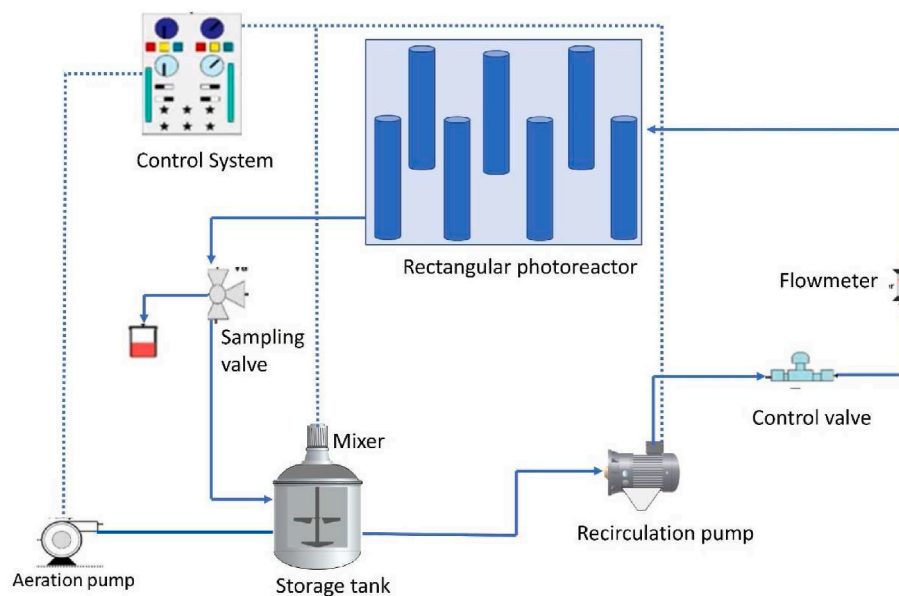


Fig. 18. Rectangular Photoreactor making a thin film of wastewater over Schottky junction catalyst as documented by Bahmani et al. (Bahmani et al., 2020) and (Feng et al., 2021).

using a parabola. The concentration helps the sun to focus on the parabola trough reactor (PTR) focal point. It is routed by using Dewar pipe equal to a parabola travelling by the pipe of solar focusing. From European nations this PTR was analyzed by various investigation organizations (Alsarayreh et al., 2022).

11.2. Thin film fixed bed reactor (FFBFR)

Fig. 14 shows the typical diaphragm of film fixed bed reactor. This reactor is an essential variety utilized without the concentration of equipment. It utilizes both diffused and direct radiation from the sun. A slanted plate having a very thin coating of photocatalyst embraces wastewater (Fig. 14). This design is effective as compared to the PTR in the elimination of the same pollutants in wastewater received from various sources. The FFBFR is a sort of pilot-scale solar photocatalytic reactor having a single pass-through in the entire procedure (Kong et al., 2019). The preservation of reactor tilt at 20° to horizontal and was held north to face the offering of a post-potent effect from the light of sun. In this operation, a model Pyra-monitor (SP1110, Skype instrument, UK)

was utilized to measure solar radiation in W/m^2 in full sunlight conditions. The surface area of light was 0.4 m broad (0.47 m^2) and 1.17 m in depth. The volume under irradiation had an irradiation size of 200 mL, a residence time of 2.5 min, and rate of flow of 4.8 L/h. The experiment did not involve coating the photocatalytic layer, and the TiO_2 photocatalyst showed density of 20.50 g/m^2 (Sundar et al., 2020).

11.3. Compound parabolic collecting reactor (CPCR)

The solar compound collector (10 L) with an intake tank offers continuous aeration and stirring. The large area of the light collector (area of 0.24 m^2) as in the design (Fig. 15) improves the catalytic efficiency. The reactor consists of six pipes of borosilicate connected to a frame of aluminum on a panel at a 30-degree angle. To connect the glass tube packed with the beads with catalyst coating, pipes, and coupling of plastic was employed. The pyra-monitor was utilized to quantify the light intensity. The intensity of light ranged from 800 to 900 W/m^2 . The wastewater whirling happens for 30 min at the rate of mixing for the homogenization of the reaction. The reaction initiates the composite

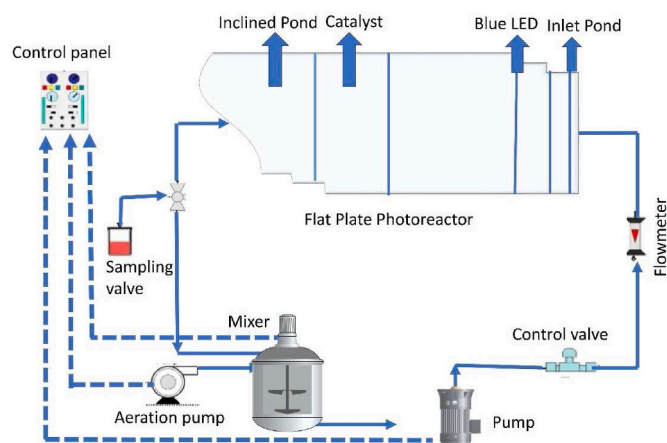


Fig. 19. Schematic representation of slurry flat plate photo reactor (Neolaka et al., 2019).

beads of CPC using the radiations of sun. The reflecting mirror curvature on the PTR and CPC is very dissimilar. The pipe in the PTR reflector is parallel to the focal line and has a shape of parabolic. As a result, the pipe receives a sharp focus from parallel light that enters the parabolic trough. Two half-cycle profiles that are placed next to one another make up the CPC's reflector, which helps to direct light directly above the two circle's linkages. Focusing on the angle at which striking of the sun's rays occurs at the surface, the compound parabolic contractors might assist in collecting the radiation at different angles. The light beam of angles that take entry into the aperture will be absorbed by the surface of absorber at the collector bottom area. The surface's low reflection value will help prevent optical loss (Blanco et al., 2017).

11.4. Double skin sheet reactor (DSSR)

Fig. 16 illustrates the design of a Double skin sheet reactor (DSSR) which comprises a transparent structural and flat box made of PLEXIGLAS®. The PLEXIGLAS® transmission starts below 400 nm that is in solar spectrum part which is the wavelength of Ultraviolet-A. The interior construction of the reactor displays the channels that allow the flow of suspension and pollutants. The reactor of this double skin sheet can benefit from both direct and diffused sun lights. As discussed, each reactor design has a potential impact on the scale-up consideration of wastewater degradation. So, there are greater prospects for the utilization of TFFBR which has been proven very effective compared to the PTR in the elimination of the pollutants which are dissolved in the pure wastewater received from various industrial units. Moreover, the advancement in research and progress has helped in the improvement of the design of CPC which could help revolutionize the scaling up of photocatalytic treatment of waste water (Malato et al., 2009).

11.5. Cylindrical photoreactors

The irradiation in the cylindrical photoreactor (Fig. 17) is done by the central lamp or the lamps with circular pattern positioning. The photocatalyst is dispersed in a liquid, or it can be fixed on numerous surfaces together with the covering of lamp. The tank of storage with mixture and aeration, flow meter, valves, pumps, and system of control that is capable of managing the whole system is the major arrangement of the components. The aeration of the storage tank is a must because it is necessary to keep the saturation level of oxygen in the formation of oxidative radicals. The radial flow distribution is beneficial for the radial flow distribution that helps to increase the diffusion homogeneity of mobile photocatalysts. The phenolics, pharmaceuticals, and colours are eliminated by this sort of reactor. The optimization of geometry with the irradiation, characteristics of pollutants, and technological aspects, and

the cylindrical photoreactor can be combined into the system of large-scale waste-water treatment. The cost-effective plan for increasing the capacity of the reactor is helpful in energy consumption considerably. The major issue is to anticipate the Photocatalytic performance built on the pollutants type and chemistry of the catalyst interface. (Neolaka et al., 2019; Manjunath et al., 2020). Fig. 17 explains the design of a cylindrical photo reactor.

11.6. Rectangle photoreactor

The source of radiation is positioned on the interior lateral side, vertically, horizontally, or in the middle in this reactor. The photocatalyst that is immobilized is placed on the wall of photoreactors, lamp covers, or substrates (glass, textile, or composites). The rate of flow is adjusted to the reactor shape for the provision of equivalent diffusion across the volume when using the mobile photocatalysts. Resultantly, the setup components of photoreactors are selected to maximize the oxidative species formation that is necessary for the organic pollutants' elimination. The rectangular reactor that is based on the modular design may be scaled up readily to allow the increase of the treated solution volume in every cycle. The rectangular reactors, due to their geometrical variety and simplicity, are utilized for large outdoor and small indoor applications. The major problem is the minimization of excessive velocities and provision of homogeneous photocatalyst irradiation by the setting of radiation and managing of flow rate (Manjunath et al., 2020; Azam et al., 2019).

Bahmani et al. manufactured rectangular Photoreactor making a thin film of wastewater over Schottky junction catalyst (BiOI/BiFeO₃/UiO-66 (Zr/Ti)-MOF complex) as shown in Fig. 18. The ternary innovative photocatalyst can separate and absorb visible light. The BiOI on the UiO-66(Zr/Ti) surface and BiFeO₃ perovskite helps to improve the separating ability and the rate of migration of the charges by a photon inducing which in turn increases the efficiency of photocatalyst in the thin film slurry flat photoreactor with continues flow loop which shows irradiation by a blue Light emitting diode (LED). The inclined cell shows a length size of 22.5 cm, width size of 2.5 cm, height of 5 cm, and a hole of 2 cm diameter implanted at the edge of the reactor for the betterment in separation and allowing the drainage of solution. The setting of photoreactor was done at a slope of about 5 on the horizontal axis. Nano-scale roughness is formed on the surface of the catalyst which results in an even liquid film on the surface of the reactor. The reactor has long durability, good stability, the highest photocatalytic ability, reusability, regeneration, and efficient separation (Bahmani et al., 2020).

A palladium-vanadium tetroxide type photoreactor filled with glass beads was designed by Meng et al. which is quicker by about 132 percent in comparison to the flat plate type reactor. This is additional efficient energy in the phenol degradation by the process of photocatalysis. The good activity of photocatalysis is usually caused by the surface area of the photocatalyst which is highly exposed, the high value of the coefficient of mass transformation, and photon transferring affectivity. The reactor shows high value of cost in comparison to the TiO₂ (Meng et al., 2019).

Qin et al. organized the TiO₂ nanotubes showing orientation on the foil of titanium by one-stage hydrothermal production. The photocatalytic degradation and adsorption of TiO₂ foil catalyst were studied in the formaldehyde degradation by an experimental device that was a self-supporting ring reactor for the degradation of formaldehyde twice as efficiently in comparison to commercial TiO₂- dioxide-based catalyst. Consistently morphological and orientation-based TiO₂ nanowires on the Ti substrate were prepared by hydrothermal production exhibiting one step which can be beneficial to be recycled without secondary pollutants (Qin et al., 2020).

Rahmani et al. prepared TiO₂/SiO₂ thin films by the methodology of sol-gel which was covered on outer shell inner wall of the annular reactor and at 400 °C heat treatment. The photoreactor with tubular type is utilized in the oil pollution degradation. The optimum condition

for the performing ability of the photocatalytic ring reactor was investigated. The best consequences come at the starting *n*-alkane 500 ppm concentration and pH 5 with a conversion rate of *n*-alkane 85 %.

Several parameters like Temperature, pH, the concentration of the ion's scavenger, and oxygen concentration, are needed in the consideration of the design of a good photocatalyst. The progress of a reactor with an optimistic model and excellent performance is very worth mentioning (Rahmani et al., 2020).

11.7. Challenges and opportunities regarding photocatalytic water treatment

An estimation of the required amount of catalyst and reactor volume is essential if we consider a continuous and simple mixed-flow reactor for the treatment of wastewater. Several parameters create hurdles in the efficient design of photocatalytic reactor. The scaling up of photocatalytic reactors often become more complicated than the chemical reactors scaling. For example, in the case of heterogenous catalysis, besides the contact requirements between the catalyst and reactants, it is compulsory to achieve good way exposing of the catalyst to light. Besides the conventional reactors complications like the contact of reactant-catalyst, mass transfer, flow pattern, mixing, catalyst installation, temperature control, reaction kinetics, etc., other factors of engineering for catalyst illumination show more relevancy. In the absence of an appropriate energy photon, no activity is shown by the catalyst (Mukherjee et al., 1999). The problem of energy absorption of a photon is considered regardless of the mechanism of reaction kinetics. The illumination factor is most important because the catalyst amount activated regulates the water handling capacity of water. The high interaction between transportation, absorption of light, kinetics of reaction can lead to coupling of solid in the physicochemical procedure and it is not uncertain that it is the major problem in the of photocatalytic reactors progress (Periyathamby et al., 1999).

The major hurdle in the photocatalytic reactor is related to the even light distribution over a vast surface area. For a specific geometry of photocatalytic reactor, the axial and radial directions up-scaling is limited by the opacity, local volumetric light absorption, light scattering and penetration depth of light. The configuration of the light source/reactor system has a strong influence on the reactor design, making independent consideration appear impractical (Ray et al., 1998). Further, the reactor wall requires transparent materials like glass for reactor construction and exhibit many difficulties like breaking and sealing issues and size limitations (Chen et al., 1998).

As associated with conventional chemical reaction rates, the rate of the process of photosynthesis is generally slow due to the lower-level concentration of the pollutants and the requirements to deliver a large quantity of catalyst inside reactor that is active. The porous anatase catalyst coating has an effective surface area of about 1 mm thick when applied to the surface. The reactor's catalyst supply shows limitation and individual degrading process can be more effective, overall efficiency of conversion will be slow. This issue disables the reactor's capability of processing, and the time required to complete the conversion is measured in hours rather than days. The photocatalytic process is aided by solid photocatalyst particles, which are composed of discrete phases that are divided within the reactor's continuous fluid phases. The reactor contains two phases: liquid and solid. Within the reactor, the solid phase could be dispersed phase or stationary phase (SPS). The catalyst particles are used in a stationary phase dispersed (SPD) system, and the agitation of fluid phase is done mechanically or by other means. The photoreactor is similar to the slurry and fluidized bed reactors in terms of agitation. The Aqueous suspension of the particles of catalyst is annular type or immersion photoreactors in various studies. The suspension's use necessitates the recycling and separating the catalyst that ultrafine from the liquid treated, which is, costly, time-consuming and inconvenient. Furthermore, penetration depth of ultra-violet light is reduced because of good absorption by dissolved organic

species of pollutants and catalyst particles (Ray, 1999).

The above issues can be reduced in the SPS photoreactor by photocatalyst particles immobilization on the surface that is fixed and transparent, such as the fiber mesh, reactor wall or by supporting them on particles of ceramic beads or glass held in a fixed position in the photoreactor. On other side the catalyst that is immobilized on the support, causes issues. The reaction usually takes place at the solid-liquid interaction, with a portion of the contact of catalyst with the reactant. The overall rate may be limited by the pollutants mass transportation to the surface of photocatalyst. Furthermore, because of the low concentration of pollutants, the reaction is usually slow, necessitating the use of a reactor with a high ratio of illuminated immobilized particles. Furthermore, because of the low concentration of pollutants, the reaction is usually slow, necessitating the use of a reactor with a high ratio of illuminated catalyst having immobility to the surface showing illumination as well as the possibility of total illumination of reactor (Anjum et al., 2023).

11.8. Challenges of the photocatalytic process

The supreme challenge for wastewater degradation by using photocatalytic process is to overcome the restrictions of the procedure. While engineering the photocatalysts various challenges arise. Generally, the stability and the photocatalytic process efficiency are very far from satisfaction due to the problems in balancing and controlling the many competing phenomenon like transportation, separation of charge, and carrier generation, especially in the difficult conditions of the photocatalysis (Gaur et al., 2022).

A wide range of research has been done to introducing photo-active materials in the catalysts which often encounter another set of difficulties. Likewise, understanding and modulating the exact mechanism of interaction between a particular photocatalyst and pollutant is another area of major concern and importance. The efficiency of quantum is reduced by solar radiation due to the large bandgap energy in the semiconductor photocatalyst electronic structure, and the activity of the photocatalytic process and production of reactive oxygen species are reduced due to electron/hole pair joining on the photocatalyst active surface. The interaction of the intermediate product of reaction resulted in fast active surface site poisoning or deactivation, resulting in a decrease in the rate of reaction kinetics (Younis et al., 2020). Due to the complexity of the process, scaling up the photocatalytic process is very difficult at a large scale. Mixing dissimilar materials (semiconductors and metals) at the nanoscale with betterment in size and shape, and the interface mandatory for the effective charge cascading the photocatalytic degradation process is looking like a major issue. The reaction on the heterogeneous photocatalyst is in the early stage and requires systematic studies in the research. The major problem is the growth of environmentally friendly, safe, clean, and sustainable advanced oxidation technologies (AOTs). The solution to the problem consists of the investigation of the model system and understand the major properties of the various kinds of photocatalyst utilized in the photocatalyst process (Xu, 2021).

12. Conclusions and future prospects

The massive and unchecked release of pollutants and contaminants in natural water bodies has triggered the importance of viable and scalable waste-water treatment technologies. The conventional waste-water treatment methods like filtration, sedimentation, adsorption, and coagulation and few advanced membranes, chemical, and biotechnology-based techniques either face higher running costs and/or associated with the risk of the introduction of harmful secondary contaminants into the environment. The photocatalysts provide a large number of new opportunities and perspectives and certainly come with many challenges. The photocatalyzed advanced oxidation process has been found more effective and scalable to deal with water pollutants

comprising heavy metals, drugs, pesticides, dyes, petroleum hydrocarbons, phenolic, pharmaceuticals, antibiotics, anti-inflammatories, and microbes. Although the biological wastewater treatment methods are more economical, these methods produce secondary pollutants which often become difficult to handle.

So far, the photocatalysts have shown exceptional performance in the degradation of organic compounds and microbial contaminants but there is a prompt need to make the process adaptable, eco-friendly, and cost-effective. Recently, nano photocatalysts are proved very effective for waste-water degradation. There are some limitations of nano-photocatalysts but a good deal of research is going on for the designing of reactors and development regarding the nano-photocatalysts. Besides, doping of the photocatalyst improves the photocatalytic efficiency, stability, immobilization potential, ease of catalyst recovery, and reuse. Likewise, the research reports indicate that heterogeneous photocatalysis carried out via using integrated semiconductors, metal-organic framework, nanocomposite, and certain transition metals oxides offered higher efficiencies. The majority of studies reported during the last couple of decades have discussed water treatment by zinc oxide, Titanium-dioxide, Tin-Oxide, Cadmium sulfide, graphene oxide, Reduced graphene oxide (RGO), and Ferric oxide. Besides, nanophotocatalysts, for their distinctive surface properties and quantum effects, were helpful in increasing in catalytic efficiency.

The photocatalytic reactor design can affect the efficiency, process cost, and nature of degradation products. To improve the efficiency of photocatalysts various factors like pH, catalytic loading, light wavelength, the concentration of pollutants, temperature, light intensity, reactor design, the effect of oxidants and hydrogen peroxide, the effect of potassium bromate, the effect of potassium persulfate and ammonium persulfate, the effect of doping and dissolved oxygen are. Further, the shape and design of photocatalytic reactors play a central role in wastewater degradation. The selection of a suitable reactor is very significant for the efficiency of photocatalytic treatment and saving of energy. Various types of photoreactors are available but the most prevalent reactor designs are thin film fixed bed reactor, compound parabolic collecting reactor, double skin sheet reactor, cylindrical photoreactor, parabolic trough reactor, and rectangular photoreactor.

The microfluidic reactors interact with the reactants on a micro-scale and offer a large surface-to-volume ratio, higher diffusions, large mass transfer coefficients, less Reynold's flow, high stability in hydrodynamics, and informal handling which help make them ideal more than conventional reactors. Moreover, it is still problematic to apply photocatalysts on the large scale in actual waste-water. Besides, the nanocomposite preparation methods utilize carbonaceous material, ceramic, and polymer materials which cause several technical problems that are required to be dispelled. Finally, in the future, the significant photocatalytic treatments with the betterment of solar-drivenness, excellence in efficiency, and lesser site area needs can be comprehended and should be of concern.

The challenges in designing the large-scale reactor have been unaddressed. Likewise, more research is need to improve the stability of photocatalysts, engineer their valancies, charge separation at the solid-liquid interphase, and recycling. There is need for effective separation and migration of photoinduced carriers in the photoinduced conversion of organic pollutants using semiconductor photocatalysts. More research should be focused on efficient harnessing of sunlight for sustainable utilization of photocatalysts. Besides, there is dire need of standardization and regulation (Ogundele et al., 2023; Iyyappan et al., 2023).

CRediT authorship contribution statement

Muhammad Ahtasham Iqbal: Investigation, Data curation, Conceptualization. **Sumia Akram:** Software, Methodology. **Shahreen khaliid:** Software, Methodology. **Basant Lal:** Writing – review & editing. **Sohaib Ul Hassan:** Resources, Project administration. **Rizwan Ashraf:** Investigation, Data curation. **Gulmira Kezembayeva:** Software, Data

curation. **Muhammad Mushtaq:** Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition. **Nurzhana Chinibayeva:** Writing – review & editing. **Ahmad Hosseini-Bandegharai:** Methodology, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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