


## A comparative study of advanced oxidation processes for wastewater treatment

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### ABSTRACT

This research emphasized the importance of removing organic pollutants from wastewater discharges. In this review, different advanced oxidation processes are discussed. A broad classification of advanced oxidation processes was used for wastewater treatment. An overview of TiO<sub>2</sub>-based photocatalysis, the Fenton process, and photocatalytic ozonation has been done. The mechanism of different methods has been studied. The advantages and limitations of these processes are also discussed. Various kinds of catalyzed were used in TiO<sub>2</sub>-based photocatalysis for various categories of organic contaminants, and several factors with crucial effects on TiO<sub>2</sub>-based photocatalytic degradation were examined. The typical treatment scheme of Fenton's method was reviewed. Also similarly, a review of photocatalytic ozonation: mechanism of the reaction, its applications with different catalysts, and economic aspects of photocatalytic ozonation were done.

**Key words:** advanced oxidation process, Fenton's process, photocatalytic ozonation, TiO<sub>2</sub>-based photocatalysis, wastewater treatment

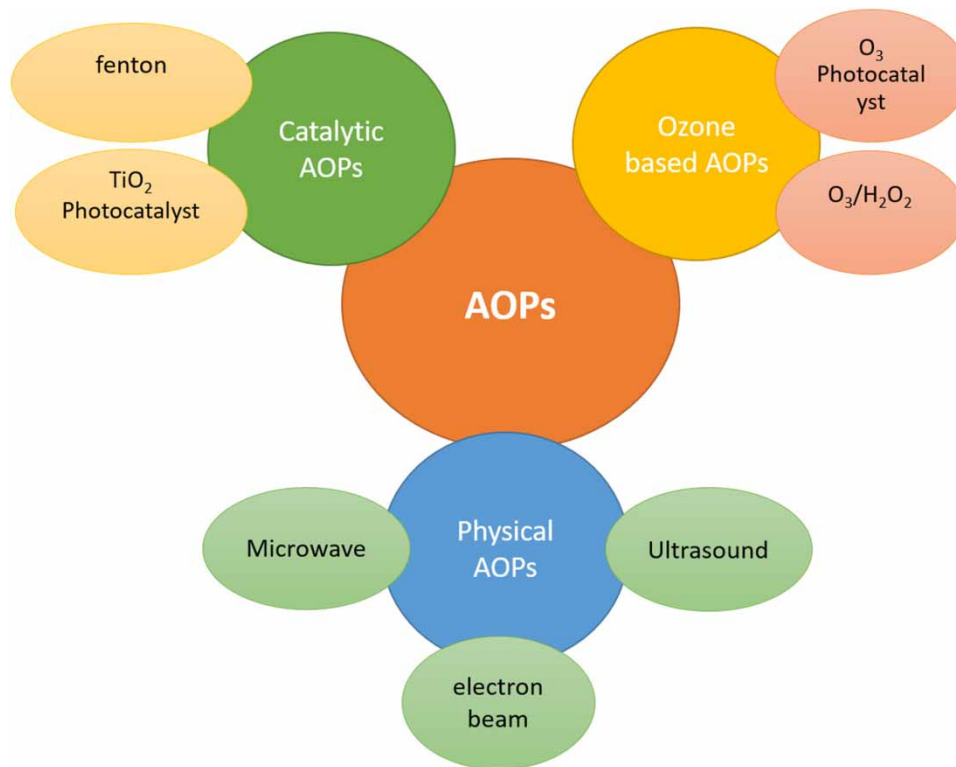
### HIGHLIGHTS

- Overview of advanced oxidation processes (AOPs) and their potential for wastewater treatment.
- Photocatalysis: using catalysts and light to produce reactive oxygen species (ROS) for oxidation.
- Ozonation: using ozone to generate ROS for oxidation.
- AOPs effective at removing organic compounds that are resistant to biological treatment.

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## GRAPHICAL ABSTRACT



## INTRODUCTION

In today's world, finding freshwater is a major problem. As industries grow, they produce a huge amount of untreated or partially treated discharge in freshwater reservoirs (Akar & Uysal 2010). Synthetic colours were released from industrial effluents such as fabric, paper, dyeing, printing, food, and others, posing serious risks to both human health and the environment. Drinking water of poor quality that is contaminated with pathogens and chemical contaminants is related to several adverse short- and long-term health effects, for example, diarrhea. On the other hand, the need for freshwater is increasing day by day as the population is growing in the world. There are so many traditional techniques available for wastewater treatment such as filtration, coagulation, and precipitation but these techniques are not sufficient for the removal of organic and inorganic impurities. Therefore, advanced oxidation processes (AOPs) have caught the interest of academics and industry experts, and they have been recommended for use in wastewater remediation. AOPs are generally understood to be water phase oxidation techniques that rely on the intermediary action of extremely reactive species like hydroxyl radicals (OH) (Tsydenova *et al.* 2015), the potent oxidant species known as the hydroxyl radical (OH) can oxidize and mineralize almost any molecular substance, producing the ecologically friendly gases CO<sub>2</sub> and inorganic ions (Malato *et al.* 2009). Rate constants (kOH, r = kOH [OH] C) for most reactions involving hydroxyl radicals in an aqueous solution are usually in the order of 10<sup>6</sup>–10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. By targeting intracellular structures, cytoplasmic membranes, and cell walls, free radicals can also harm microbial organisms.

According to Tsydenova *et al.* (2015), one major area of research is water treatment using AOPs.

- Treatment of industrial effluents, such as those from distilleries, agrochemical plants, kraft-bleaching plants, pulp and paper plants, textile dyehouses, oil fields, and metal-plating plants;
- Treatment of harmful effluents, such as waste from hospitals and slaughterhouses; removing pathogens and pharmaceutical residues that persist and disrupt the endocrine system from municipal wastewater treatment plant (WWTP) effluents (after secondary treatment) removing heavy metals like arsenic and chromium from water and organic micropollutants like pesticides;
- Maintenance and acclimatization of biological sludge from WWTPs.

Clearly, when properly developed, chemical destruction methods provide a complete solution to the pollutant abatement issue in contrast to phase separation methods, which pose the issue of final disposal.

The hydroxyl radical is the most highly oxidizing species that is available, as shown in Table 1. According to Carey (1992), the generation of  $\cdot\text{OH}$  to initiate oxidations is the foundation of the majority of AOPs for the treatment of waste water.

**Table 1** | The oxidation potential of various chemical reactants

Oxidant	Oxidation potential (V)
OH	2.8
O <sub>3</sub>	2.070
H <sub>2</sub> O <sub>2</sub>	1.770
MnO <sub>4</sub> <sup>-</sup>	1.670
ClO <sub>2</sub>	1.5
Cl <sub>2</sub>	1.360

Reactive organic radicals are formed when hydroxyl radicals react in a variety of ways to produce reactive organic radicals. These reactive organic radicals undergo additional reactions that typically lead to the oxidation of the organic substrate.



The most common reaction is the radical chain reaction that begins with the abstraction of a hydrogen atom (1–4). There are numerous ways to make hydroxyl radicals ( $\cdot\text{OH}$ ) that could be used in AOPs. In this overview article, the chemical foundation and constraints of some of the key processes proposed for the oxidation of organic contaminants are reviewed. Figure 1 (Miklos *et al.* 2018) provides an overview of various established and emerging AOPs, which are categorized as ozone-based,

- (1) catalytic advanced oxidation process (c-AOP) and
- (2) physical advanced oxidation process (p-AOP) AOPs.

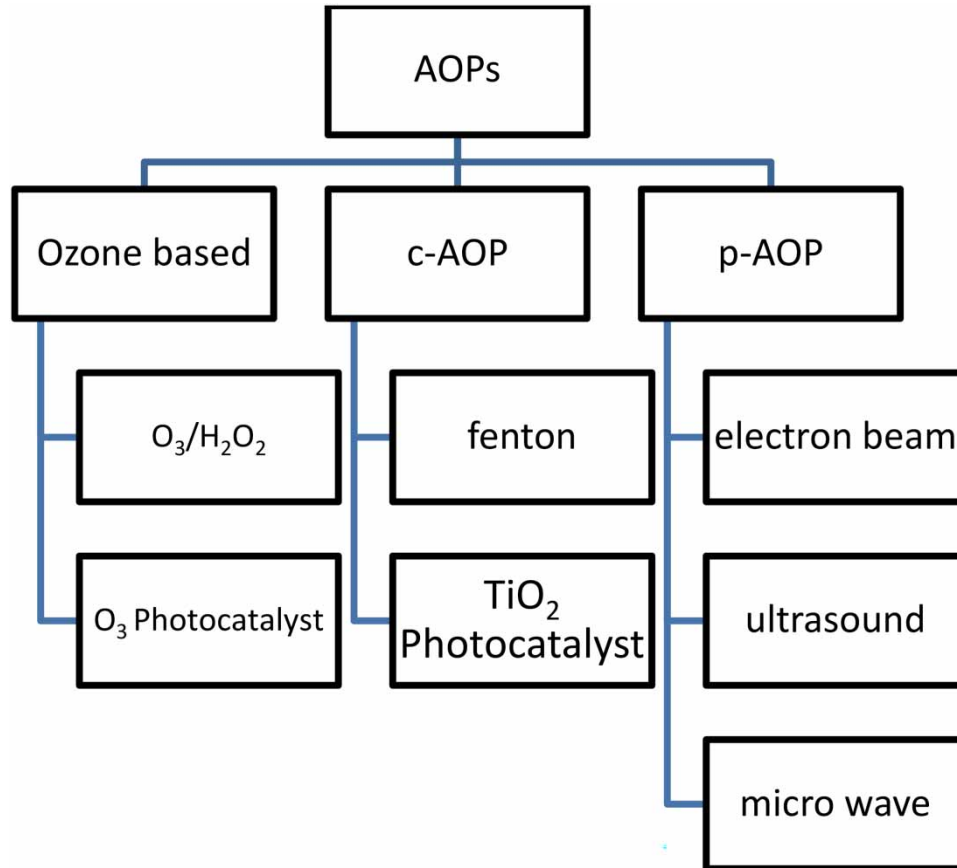
However, it is important to note that this classification system should not be taken too seriously because a number of processes involve various technologies and could therefore be placed in a variety of categories. But all these AOPs are not frequently used. So in this review study, we mainly focused on ozone-based photocatalytic ozonation, the Fenton process, and TiO<sub>2</sub> photocatalyst because these are used frequently for the degradation of organic contaminants from wastewater on industrial as well as at the laboratory scale.

## AOPs based on ozone

### O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>

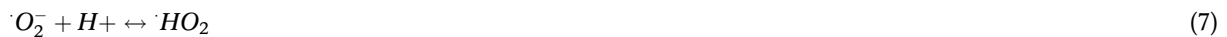
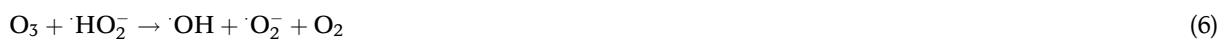
O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>-based AOPs are methods that use the combination of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> as a means of removing contaminants from water. These methods rely on the production of hydroxyl radicals, that are extremely volatile ( $\cdot\text{OH}$ ), which are very effective at purifying water by eliminating a variety of organic contaminants, viruses, and other toxins.

The formation of  $\cdot\text{OH}$  is the result of a complicated set of reactions involving O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (Schulte *et al.* 1995; Wang *et al.* 2003), these reactions ultimately result in the creation of two hydroxyl radicals from one molecule of



**Figure 1** | Broad overview and classification of different AOPs.

hydrogen peroxide and two molecules of ozone.



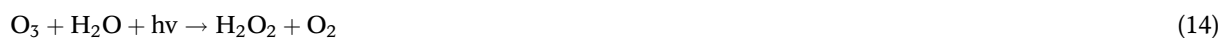
A combination of hydrogen peroxide and ozone is used in this kind of ozone-based process, and the hydrogen peroxide serves as a reagent and speeds up the breakdown of the ozone into the hydroxyl radical. According to research by [Staehlin \*et al.\* \(1982\)](#),  $\text{H}_2\text{O}_2$  interacts with ozone very slowly at an acidic pH but quickly dissociates into  $\text{HO}_2$  at a high pH. This demonstrated that ozone decomposition is an efficient process both in potable water purification and reuse of water and is more efficient than  $\text{OH-O}_3/\text{H}_2\text{O}_2$ . When manufactured dyehouses were treated with peroxide ( $\text{H}_2\text{O}_2/\text{O}_3$ ) at 10 mM  $\text{H}_2\text{O}_2$ , 74% of the ozone was absorbed at pH 11.5 while only 11% was absorbed at pH 2.5. [Acar \(2004\)](#)'s studies on ozone decomposition in the presence of  $\text{H}_2\text{O}_2$  also showed that the decomposition of ozone is increased at the following pH values investigated: pH = 2.5, pH = 7, and pH = 10; however, it is more evident at pH levels of 7 and 10. Additionally, statistical analysis revealed that original dissolved ozone content and pH are key factors that have a big impact on how much COD and color are removed. Studies have shown that the advantages for its utilization in wastewater are constrained because of strong competitive reactions and already effective radical formation with  $\text{O}_3$  alone ([Hübner \*et al.\* 2015](#)).

*Photocatalytic ozonation.* Ozone (O<sub>3</sub>) has very high oxidation potential as shown in Table 1; so, it is considered as a strong oxidant that can interact with a variety of inorganic and organic compounds (Preis *et al.* 1995; Mehrjouei *et al.* 2014a, 2014b). With no sludge and residual ozone, ozonation methods are a hopeful technique for disposing of effluent because the ozone breaks down into oxygen and water.

Organic pollutants are reacted with ozone in water either directly using molecular O<sub>3</sub> or indirectly using <sup>•</sup>OH. The use of photocatalytic ozonation to remove biodegradable contaminants from water is not monetarily feasible because it is still one of the highly expensive treatment methods. In a two-step process (Equations (12) and (13)), the light involved which initiated the homolysis of O<sub>3</sub> and the following generation of <sup>•</sup>OH by the reaction of O(<sup>•</sup>D) with H<sub>2</sub>O has been suggested by Rajeswari & Kanmani (2009).



However, it has been found that the ozone immersed in water and subjected to photolysis produces hydrogen peroxide (Equation (14)) in a series of processes where the hydroxyl radicals generated facilitate oxidation.



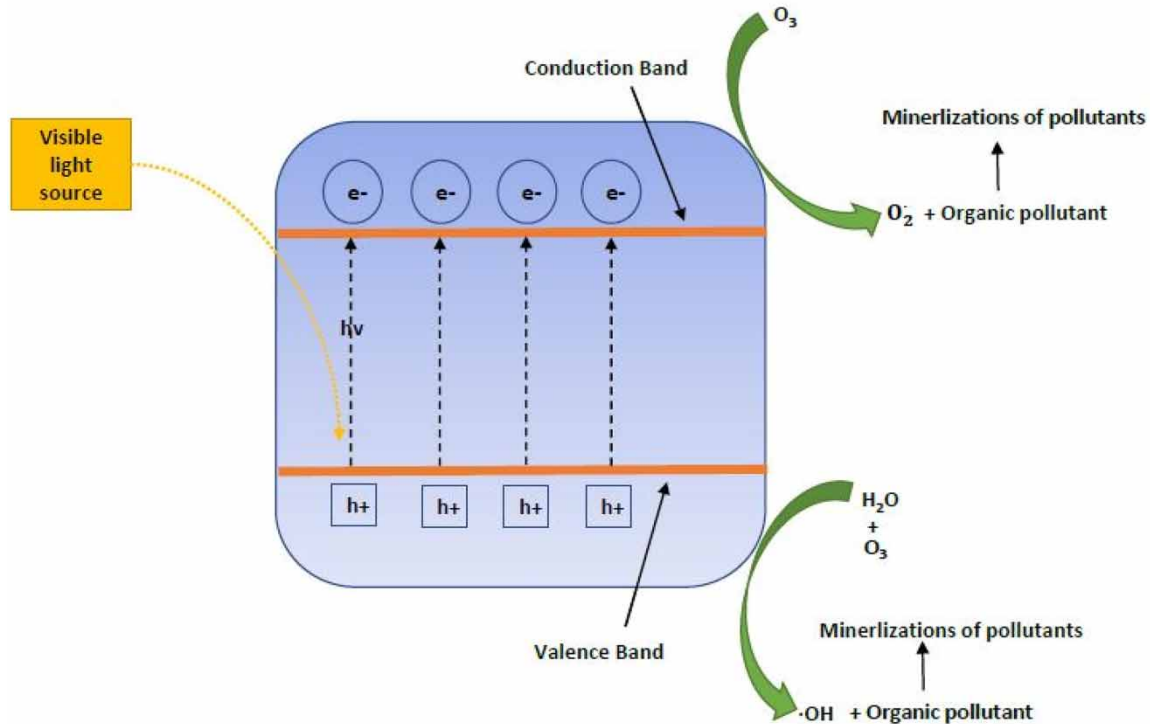
The high expense of O<sub>3</sub> generation and incomplete degradation of organic waste found in water are two drawbacks of ozonation in water purification. According to Legube & Karpel Vel Leitner (1999) and Agustina *et al.* (2005), many scholars use alternative methods to ozonation to increase the generation of <sup>•</sup>OH, such as the use of a catalytic system of O<sub>3</sub> and boosting <sup>•</sup>OH formation by using photo-Fenton or TiO<sub>2</sub> (Mehrjouei *et al.* 2012). Since organic compounds are anticipated to breakdown more rapidly and completely in the presence of ozone to CO<sub>2</sub>, water, a mixture of photocatalysis and ozone (O<sub>3</sub>), a powerful oxidizer, is sensible for the treatment for degradation of organic compounds. Photocatalytic ozonation was found to be the most efficient technique for completely mineralizing 4-chloronitrobenzene, degrading aniline (Ochiai *et al.* 2013), dibutyl phthalate (Huang *et al.* 2015; Wang *et al.* 2018), and acid (Hammad Khan *et al.* 2013).

In the beginning of a photocatalytic process, UV-Vis light is used to excite the electrons from the surface of the photocatalyst, which can supply the necessary band gap energy to produce photoactivated electron at CB and hole pairs at VB. Physical adsorption, weak hydrogen bond formation with surface hydroxyl groups, and molecular or dissociative adsorption into Lewis acid sites are three different interactions that ozone molecules can engage concurrently to adsorb on the surface of the photocatalyst. Each interaction results in the generation of active oxygen radicals (O<sub>2</sub><sup>•</sup>). These active oxygen radicals interact with water molecules to create (OH), which are essential for photocatalytic ozonation reactions.

Figure 2 depicts the process of photocatalytic ozonation, in which electrons and holes are produced when visible light strikes the photocatalyst surface (Mecha & Chollom 2020). Where ozone is photogenerated, hydroxyl radicals and superoxide radicals are produced, and this causes the organic contaminants to become calcified.

*Application of photocatalysts to photocatalytic ozonation reactors.* Mare *et al.* (1999) and used the photocatalysts in different-different hydroxyls. Some of them mixed the photocatalysts with wastewater. Also, Araña *et al.* (2002; Addamo *et al.* (2005); Hur *et al.* (2005) used immobilized photocatalysts on an inert support material. When 2-chlorophenol is photocatalytically oxidized, immobilized TiO<sub>2</sub> particles have a 50% lower mineralization and dichlorination rate than suspended TiO<sub>2</sub> particles under the same testing circumstances. In suspension systems, the recycling of photocatalysts is very expensive so it is not used on an industrial scale and is limited to laboratory use alone.

Hur *et al.* (2005); Černigoj *et al.* (2007); Zou & Zhu (2008) immobilized photocatalysts and used them in photocatalytic ozonation processes. A lot of study has been done on them. As a result, different designs have been documented. For example, the use of an annular flow reactor with a Pyrex glass tube's interior side coated with an immobilized TiO<sub>2</sub> layer as the reactor wall; immobilized TiO<sub>2</sub> on alumina balls and they were placed in four reaction tubes inside the batch photoreactor (Ochiai *et al.* 2013); for their photocatalytic study, TiO<sub>2</sub> nanoparticles were used as adapted Ti-mesh sheets. However, these photocatalytic ozonation designs have some drawbacks, so some scholars come up with the best designs where the photocatalysts are fixed to the surface plates and used in a multiphase falling film reactor (Mehrjouei *et al.* 2013, 2014a, 2014b). In this



**Figure 2** | Photocatalytic ozonation mechanism.

arrangement, under carefully controlled circumstances, wastewater samples (i.e., liquid phase) pass over immobilized  $TiO_2$  particles (i.e., solid phase) near the movement of  $O_3/O_2$  molecules (gaseous phase). The key benefit of using falling film reactors is that these designs offer a large wastewater volume-to-active photocatalyst surface ratio, resulting in improved oxidation system mass transfer properties.

Reduced toxicity in wastewater is achieved by photocatalytic ozonation in addition to the breakdown and mineralization of organic contaminants in wastewater. A lot of research scholars studied this and got success in reducing the toxicity of wastewater with the help of photocatalytic ozonation. Ochiai *et al.* (2013) demonstrated that the removal rate of pathogens in effluent will nearly double if they merely switch from ozonation to photocatalytic ozonation. Similarly, Beltrán *et al.*, (2008) performed *Daphnia* experiments and discovered that photocatalytic ozonation reduced the toxicity of sulfamethoxazole solutions from 60 to 10%. The removal of Galaxolide and Tonalide (as pollutants) from wastewater using oxidative and photochemical methods is one of the most successful and provides the greatest oxidation effectiveness. The creation and buildup of toxic transformation products in wastewater in this instance caused the toxicity readings to first indicate a small decline (within the first 10 min) before increasing.

*Economic benefits of photocatalytic ozonation.* The cost of photocatalytic ozonation devices is higher than that of simple photocatalysis, and they might not be commercially viable. However, determining the exact energy usage for each oxidation system, where the energy expended during the oxidation process is assigned to the amount of decomposed materials, could lead to a more accurate cost assessment of these oxidation techniques for water filtration. Oxalic acid decomposition by photocatalytic oxidation and catalytic ozonation was about 2 and 9 times less cost-effective than that by photocatalytic ozonation, respectively, according to research by Mehrjouei *et al.* (2014a, 2014b), which looked at using three distinct kinds of AOPs to degrade oxalic acid and dichloroacetic acid. In comparison to photocatalytic ozonation systems, catalytic ozonation and photocatalytic oxidation were 2 and 15 times more costly for the removal of dichloroacetic acid, another molecule.

Similar to this, research by Kopf *et al.* (2000) has demonstrated the precise energy requirements for mineralizing monochloroacetic acid through photocatalytic ozonation. The findings of this research demonstrate that ozonation without photocatalyst and well-known photocatalytic oxidation with  $O_2$  are two qualitatively and

numerically distinct processes. The photocatalytic decay of ozone brought on by the interaction of TiO<sub>2</sub> and UV-A rays is most likely the cause of the greater oxidation rate. Photocatalytic ozonation consumes considerably less specific energy than the other processes when taking into account the overall mineralization of the compounds, according to a comparison of the electric energy usage during the tests. Gilbert (2002) compared four different AOPs with four different pollutant compounds and found that photocatalytic ozonation has high energy consumption than simple ozonation.

Based on these studies, it appears that photocatalytic ozonation may be more economically beneficial than photocatalysis and ozonation in the removal of some organic pollutants under ideal operating conditions, depending on factors like the concentration of O<sub>3</sub> and pollutant, experimental variables, pollutant properties, etc. However, this conclusion cannot be applied universally. Table 2 summarizes recent work on photocatalytic ozonation.

**Table 2** | An overview of current work in the field of photocatalytic ozonation

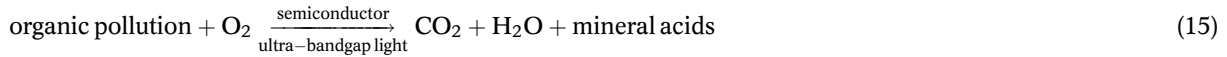
S. No.	Removing compound	Experimental conditions	Outcomes	References
1	Metoprolol	TiFec + TiO <sub>2</sub> + Fe and solar light	Its showed maximum 85% mineralization in 5 h	Quiñones <i>et al.</i> (2014)
2	Reactive red 198 (RR198) and Direct green 6 (DG6)	UV/O <sub>3</sub> , O <sub>3</sub> /MWCNT and UV/O <sub>3</sub> /MWCNT	UV/O <sub>3</sub> /MWCNT showed the highest efficiency of the removal of dye.	Mahmoodi .(2013)
3	1-amino-4-bromoanthraquinone-2-sulfonic acid (ABAS)	Use of TiO <sub>2</sub> thin film on a glass and UV-A 39w lamp	TiO <sub>2</sub> /UV/O <sub>3</sub> showed <90% TOC removal and it is more efficient method for the treatment of ABAS wastewater	Wang <i>et al.</i> (2013)
4	Reactive red 198 (RR198) and Reactive red 120 (RR120)	Use of copper ferrite nanoparticle catalyst	Copper ferrites nanoparticle enhanced the photocatalytic ozonation and its removed dyes without O <sub>2</sub> and heating.	Mahmoodi .(2011)
5	Pentachlorophenol, atrazine, chlorfenvinfos, diuron, alachlor, and isoproturon	Use of Degussa P25 catalyst	It showed strong TOC removal except for atrazine	Farré <i>et al.</i> (2005)
6	Tetracycline	UV/TiO <sub>2</sub> /O <sub>3</sub> Conc.: 1–100 mg/L	Removal of 90% TOC	Wang <i>et al.</i> (2003)
7	Acetamiprid and atrazine	UV-A/TiO <sub>2</sub> /O <sub>3</sub> Conc.: 100 ug/L	photocatalytic ozonation enhanced containment removal by 105–127%	Silva <i>et al.</i> (2019)
8	1,4-dioxane	O <sub>3</sub> /UV/TiO <sub>2</sub> /ZnO/Mg(OH) <sub>2</sub> = 100 mg/L, V = 400 ml, gas = 200 ml <sup>-min</sup> , photocatalyst = 0.3 g/L and pH = 3	It help to degrade it by 100% and remove TOC by 84.37%	Wang <i>et al.</i> (2020a, 2020b)
9	Terephthalic acid	vanadium oxide (V <sub>x</sub> O <sub>y</sub> ) with ZnO	Photocatalytic ozonation enhanced its by 310%	Fuentes <i>et al.</i> (2020)
10	Aqueous micropollutants	Magnetite and titania with graphene	Photocatalytic ozonation enhanced degradation efficiency	Chávez <i>et al.</i> (2020)
11	Primidone	GO/TiO <sub>2</sub>	GO enhanced mineralization upto 82% compared to alone TiO <sub>2</sub>	Checa <i>et al.</i> (2019)
12	Methylene blue	UV/Fe-PSA/O <sub>3</sub> peanut shell ash (PSA)	94% decolorization and 72.7% COD removal	Ikhlaqa <i>et al.</i> (2020)

### Catalyst-based AOPs

A 'photocatalyst' is a 'catalyst that accelerates the solar photo reaction,' and the following are the minimum requirements for a catalyst to qualify for photocatalyst: The photocatalyst should (i) not be immediately

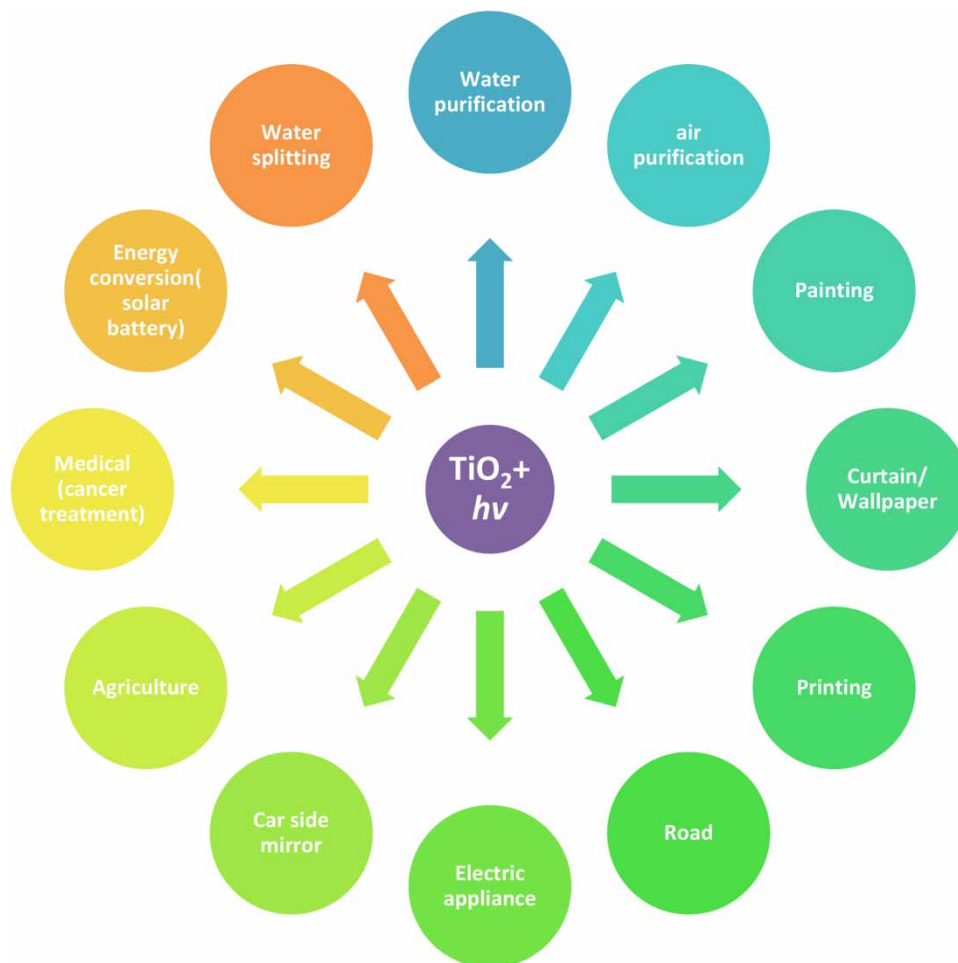
consumed or involved in the reaction and (ii) other mechanisms from already-existing photoreactions must be provided, as well as an increased reaction rate.

According to Ollis & Al-Ekabi (1993), photocatalytic reactions use oxygen as the oxidizing substance and a semiconductor metal oxide as the catalyst. The use of semiconductors as photosensitizers for the full oxidative mineralization of contaminants by oxygen has garnered more attention in recent years. The entire procedure in semiconductor photo catalysis for water filtration can be summarized by the following reaction because the pollutants are typically organic (Mills *et al.* 1993)



### TiO<sub>2</sub> photocatalysis

TiO<sub>2</sub> photocatalysis is a highly effective advanced oxidation method. It uses reactive oxygen species (i.e., superoxide radical, hydroxyl radicals) to oxidize almost all organic pollutants without producing any harmful byproducts. Under UV light, commercial TiO<sub>2</sub> is one of the best photocatalysts. Because of its physicochemical properties, such as the generation of charge carriers (electrons and holes) upon UV light absorption corresponding to the band gap and higher refractive index, TiO<sub>2</sub> is regarded as a material with multiple uses (Daghrir *et al.* 2013; Noman *et al.* 2019). Potential applications include photocatalytic decay, solar water splitting, electrochemical devices, hydrogen storage, photovoltaic cells, monitoring equipment, and biocidal applications. The application of TiO<sub>2</sub> photocatalysis in various environmental fields is summarized in Figure 3.

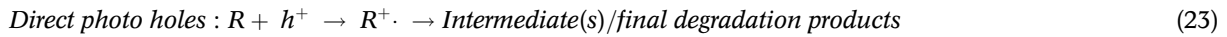
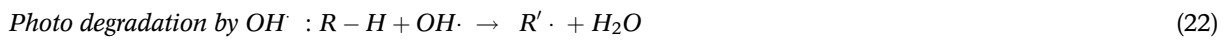
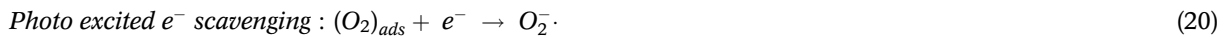
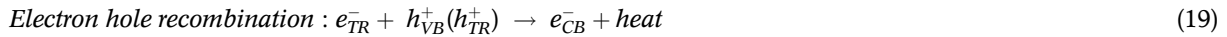


**Figure 3** | TiO<sub>2</sub> photocatalysis used in numerous environmental and energy-related applications.

TiO<sub>2</sub> has also gained attention for its applications in H<sub>2</sub> production (Tanaka *et al.* 2014), water splitting (Maeda & Domen 2010), and CO<sub>2</sub> reduction (Mori *et al.* 2012). When the TiO<sub>2</sub> catalysts suspended in water are exposed



to UV light, the photo-induced electrons in the conduction band (CB) take part in the reduction processes, which usually create superoxide radical anions ( $O_2^{\cdot-}$ ) when they combine with the dissolved oxygen in the air. The VB's photo-induced holes spread to the  $TiO_2$  surface where they interact with the water molecules that have been absorbed to create OH (Ishibashi *et al.* 2000). Actually, a key active molecule in the photocatalytic oxidation process, the  $\cdot OH$ , is very significant (Lee & Park 2013), it is generally believed that the following equation represents the photo-induced formation process of the electron-hole pair in the  $TiO_2$  photocatalyst.

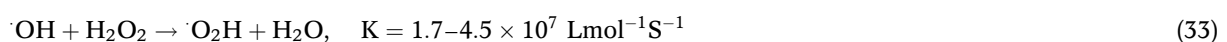
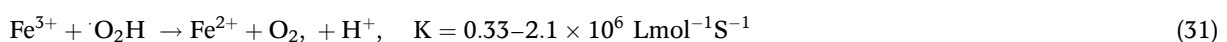
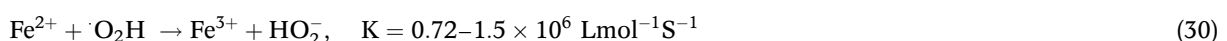
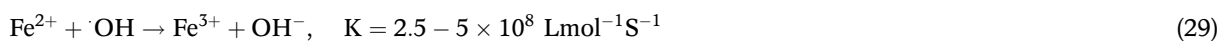
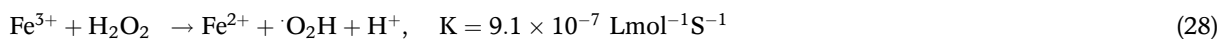


where, respectively,  $e_{TR}^-$  and  $h_{TR}^+$  stand for the surface-trapped VB electron and CB hole.

To improve  $TiO_2$ -based photocatalysts for wastewater organic compounds, various parameters were controlled. These key boundaries including intensity of light (Blake *et al.* 1991; Nasirian & Mehrvar 2016),  $TiO_2$  design and structure (Bagbi *et al.* 2017; Saquib & Muneer 2003), substrate type (Akhavan *et al.* 2011; Fernandez-Ibanez *et al.* 2015), pH value (Chiang *et al.* 2004; Huang *et al.* 2008), and doping type impacted the productivity of the photocatalysis interaction. Due to its strong oxidation power it decomposes recalcitrant substances and it is significantly more cost-effective and friendly to the environment than chlorine that is in the water purification process. The proper techniques are being used to certify the  $TiO_2$  photocatalytic device. A overview of recent studies on  $TiO_2$  photocatalysis can be found in Table 3.

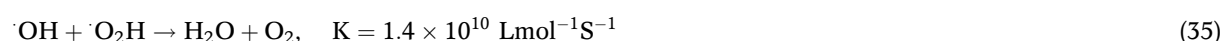
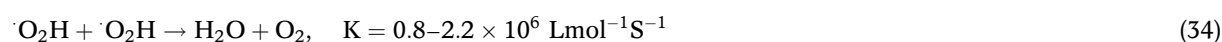
### Fenton process

Fenton (1894) discovered the Fenton process in 1894. The oxidant  $H_2O_2$  is broken down into OH by the Fe<sup>2+</sup>-catalyzed Fenton reaction, which eliminates organic molecules, and oxidizes tartaric acid in the presence of iron ( $Fe^{2+}$ ) (Neyens & Baeyens 2003). In recent times, the Fenton method was successfully used in the wastewater treatment process to purge effluent of a variety of dangerous organic substances (Moradi *et al.* 2020a 2020b). The Fenton process works better when combined with other methods like UV or sonification (Babuponnusami & Muthukumar 2014), and reactions have been taken into account in order to comprehend the entire Fenton mechanism



**Table 3** | A summary of current research in the field of TiO<sub>2</sub> photocatalysis

S. No.	Removing compound	Experimental conditions	Outcomes	Reference
1	2-chlorophenol (CP)	Graphene oxide based TiO <sub>2</sub> catalysed was used and Solar light, catalyst = 25 mg/L, time = 4 h,	This Ni(OH) <sub>2</sub> /GO/TiO <sub>2</sub> enhanced removal efficiency of CP to 80%	Barakat <i>et al.</i> (2020)
2	Rhodamine B	Graphene oxide + TiO <sub>2</sub> +UV, H <sub>2</sub> O <sub>2</sub> , pH 3–11	Rhodamine B degraded to 100%	Munikrishnappa <i>et al.</i> (2019)
3	Congo red	rGO + TiO <sub>2</sub> + Visible light, 2.5,5,7.5,and 10% concentration of rGO based TiO <sub>2</sub> , at 120 min	Congo red degraded to 92%	Brindha & Sivakumar .(2017)
4	Methyl orange (MO) and Methylene blue (MB)	TiO <sub>2</sub> + visible light, time = 120 min, Pd-TiO <sub>2</sub> concentration = 0.25, 0.5, 0.75, and 1.0 wt.%	The removal efficiency of MB and MO was 94.4 and 92.6%, respectively.	Nguyen <i>et al.</i> (2018)
5	Azo dye	ZnO + TiO <sub>2</sub> + UV-Vis light; time = 180 min; TiO <sub>2</sub> = 0.5–1.5 gL <sup>-1</sup>	Almost 99% azo dye removal was reported	Çalışkan <i>et al.</i> (2017)
6	Crystal violet dye (CV)	N-TiO <sub>2</sub> + UV, time = 180 min	Almost 100% dye removal was reported	Vaiano <i>et al.</i> (2019)
7	Reactive red 76 (RR76) and Reactive blue 19 (RB19)	TiO <sub>2</sub> , C-TiO <sub>2</sub> , S-TiO <sub>2</sub> under Visible light, time = 120 min	C-TiO <sub>2</sub> reported 100% dye removal after 60 min, S-TiO <sub>2</sub> reported 100% dye removal after 120 min, TiO <sub>2</sub> reported only 20% dye removal after 120 min.	Hsing <i>et al.</i> (2007)
8	Opaque dye	Pr-Co co-doped TiO <sub>2</sub> catalysed was used. 300–1,100 nm light; 120 min	The removal efficiency of opaque dye was reported more than 90%	Yu <i>et al.</i> (2020)
9	Remazol dye	Photo-Fenton Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub> + UV light, time = 180 min	Remazol dye degraded to 90.57%	Singh <i>et al.</i> (2019)
10	Methyl orange	Photo-Fenton-TiO <sub>2</sub> catalysed was used. visible light; 2 h	Methyl orange degraded to 98%	Zhang <i>et al.</i> (2019)
11	RhB, bMO, MB, Cr (VI)ions	Bi <sub>2</sub> WO <sub>6</sub> particles + TiO <sub>2</sub> Photocatalysis	The removal efficiency of rhodamine B, methyl orange, methylene blue and Cr <sup>4+</sup> ions was 80.58, 77, 99 and 94%, respectively.	Wang <i>et al.</i> (2020a, 2020b)
12	Ofloxacin	MnFe <sub>2</sub> O <sub>4</sub> @rGO@TiO <sub>2</sub> pH = 5.4	Best degradation at neutral pH 5.4	Abdel-Wahed <i>et al.</i> (2020)
13	Copper and tetracycline (TC)	formic acid-assisted photocatalysis process with TiO <sub>2</sub>	Formic acid with TiO <sub>2</sub> enhanced degradation properties	Nguyen <i>et al.</i> (2021a, 2021b)
14	Methylene red and Methylene blue	TiO <sub>2</sub> @ZnO heterojunction + sunlight	The removal efficiency of methylene blue and Methylene red was 25 and 13%, respectively.	Mousa <i>et al.</i> (2021)

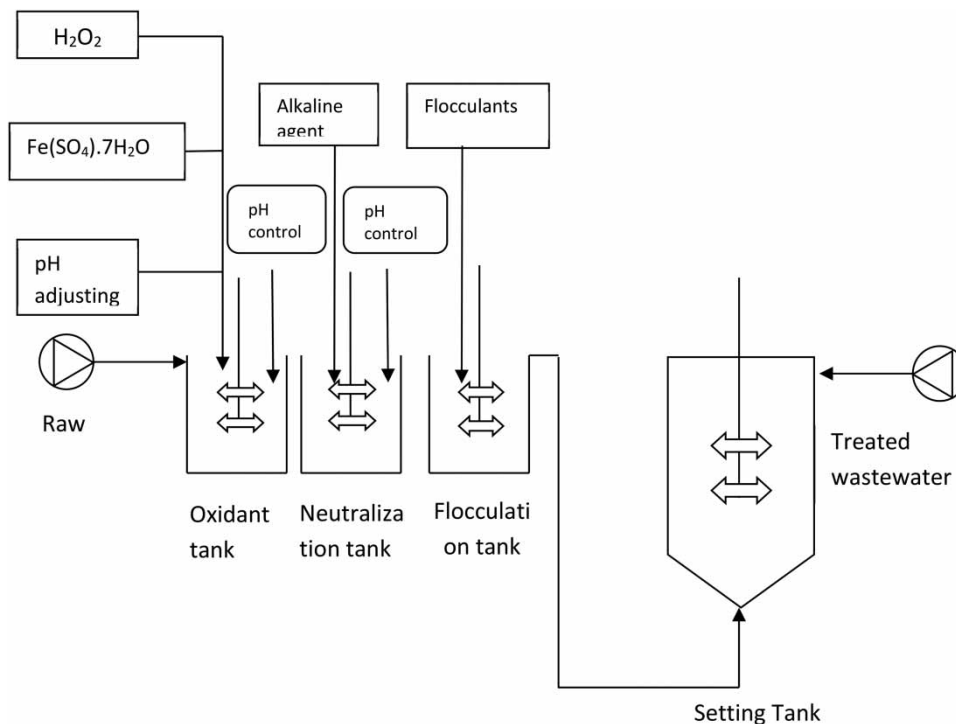


In Equations (27)–(31), the ferrous iron produced from ferric particle and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) consumed are the rate-limiting stages in the Fenton process. H<sub>2</sub>O<sub>2</sub> radicle reactions are discussed in Equations (32)–(35). According to Bautista *et al.* (2008), the breakdown of H<sub>2</sub>O<sub>2</sub> into O<sub>2</sub> and H<sub>2</sub>O as shown in Equation (34) requires the use of mass oxidants, which increases treatment expenses unnecessarily (Pignatello *et al.* 2006). Equations (36)–(39) illustrate how ·OH may combine with alkyl radicals generated by wastewater organics to form

dimers or reactions with ferrous and ferric ions (Bautista *et al.* 2008).



Figure 4 depicts a plan for the Fenton oxidation treatment. A bunch reactor is utilized where the pH is typically kept within the range of 3–3.5.  $\text{H}_2\text{O}_2$  is usually handled as a 35% fluid arrangement, and  $\text{Fe}^{2+}$  is typically introduced as ferrous sulfate. Most of the time, the process works under normal pressure and temperature. Corrosion can be a serious issue, consequently, an acid-resistant substance must be coated onto the reactor tank. The reactants are introduced in the following order: wastewater followed by dilute sulfuric acid (to keep the atmosphere acidic). The final ingredients are hydrogen peroxide, a base or acid to modify pH, and the catalyst ( $\text{Fe}^{2+}$  salt in an acidic solution). The  $\text{Fe}(\text{OH})_3$  and other accompanying solids are separated by settling after flocculants expand in a balance tank where the discharge from the Fenton reactor is sent. If required, a third sand-filtration step can be applied.



**Figure 4** | Schematic representation for Fenton treatment.

The homogenous Fenton processes are widely applied because they are based on the iron catalysis that breaks the oxidant  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$ , which nonselectively degrade organic pollutants. The effectiveness of these procedures may be increased when combined with other techniques, like UV light or ultrasound, that enhanced the conversion of the  $\text{Fe}^{2+}$  catalyst from  $\text{Fe}^{3+}$  and produce more  $\cdot\text{OH}$ .

Depletion of iron ions over time and creation of solid sediment, both of which necessitate additional management, are the main issues with the Fenton process (Kishimoto *et al.* 2013; Ochando-Pulido *et al.* 2017). Second is the high cost of chemicals like  $\text{H}_2\text{O}_2$  (Cañizares *et al.* 2009; Babuponnusami & Muthukumar 2014). The cost of homogeneous Fenton process ranges from 0.2 to 17.7 €/m<sup>3</sup> that affects the overall effectiveness of the method. Fenton sludge has been linked to a number of negative effects on the economy and the environment.

Several recent advancements to address some of these issues have been made such as the availability of the iron catalyst in the solid form: zero-valent Fe has been shown to be very effective in acidic conditions, where the catalyst particle's top layer is oxidized by the Fenton process to produce  $\text{Fe}^{2+}$  *in situ*. The production of Fe-supporting catalysts, where the Fe of the catalyst is usually embedded or enclosed in a solid support and originates from Fe minerals or Fe salts, and has also attracted attention recently. Iron can also be found naturally in the form of minerals. Hydroxides may change in size, orientation, dimensions, and shape when dehydroxylated into their oxide products under specific circumstances. Utilizing waste is a hopeful option. Relatively inexpensive leftovers can be used to support catalysts or as a source of iron, decreasing the need for Fe ores and upholding the circular economy's guiding principles. Additionally, because of their abundant active sites, low diffusion resistance, high surface area, and proximity to reactants, nanomaterials are ideal for use as Fenton catalysts (Wang *et al.* 2012, 2016). Table 4 outlines some of the Fenton process types. The wastewater treatment by Fenton oxidation is summarized in Table 5.

**Table 4** | Classification of the Fenton process

S. No.		
1	Homogenous	Photo-Fenton (PF) Sono-Fenton (SF) Electro-Fenton (EF) Photo-electro-Fenton (PEF) Sono-electro-Fenton (SEF)
2	Heterogeneous	Nanomaterials Synthesized Fe-supporting catalyst Fe minerals and waste-derived catalysts Zero-valent state metal catalyst

**Table 5** | A summary of current studies in the field of Fenton oxidation

S. No.	Removing compound	Experimental conditions	Outcome	Reference
1	Pulp-bleaching wastewater	$[\text{Fe}^{2+}] = 8.5 \text{ mM}$ , $[\text{H}_2\text{O}_2] = 177 \text{ mM}$ ; pH = 2; time = 10 min; Temp. = 60 °C	Maximum removal efficiency in this conditions was 85%	Ribeiro <i>et al.</i> (2019)
2	Benzene dye	Condition: pH of 4.13, $[\text{H}_2\text{O}_2] = 1.0 \text{ M}$ , $[\text{Fe}^{2+}] = 0.36 \text{ M}$ .	Removal efficiency of COD, TOC and color was 85, 75 and 99.9%, respectively.	Guo <i>et al.</i> (2018)
3	Leachate	Conditions: $\text{H}_2\text{O}_2/\text{COD}$ ratio (w/w) = 0.5/1–4, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ w/w ratio of 5/1 and pH = 9	BOD removal 99% and COD removal 94%	Trapido <i>et al.</i> (2017)
4	Sawmill	$[\text{Fe}^{3+}] = 0.45 \text{ mM}$ , $[\text{H}_2\text{O}_2] = 188.2 \text{ mM}$ , pH = 3 time = 60 min, and Temp. = 120 °C	COD and TOC removal efficiency reported was 80 and 70%, respectively.	Ribeiro & Nunes (2021)
5	Reverse osmosis concentrate from the graphical industry	1.2 mol $\text{Fe}^{2+}/\text{mol H}_2\text{O}_2$ , 0.2 g $\text{H}_2\text{O}_2/\text{gCOD}$ and, pH = 3, time = 20 min.	This optimum conditions showed best degradation of organic pollutants.	Van Aken <i>et al.</i> (2013)
6	Containers and drum cleaning	$\text{H}_2\text{O}_2 = 45 \text{ g/L}$ , $\text{FeCl}_3 = 0.8 \text{ g/L}$ , pH = 3	COD was measured as about 1,500 mg/L which was highest	Güneş <i>et al.</i> (2019)
7	Petroleum refinery	$[\text{H}_2\text{O}_2] = 1,008.4 \text{ mM}$ and $[\text{Fe}^{3+}] = 686.0 \text{ mg}$ , pH = 3	The maximum TOC removal efficiency was reported 70% and COD was 98%	Hasan <i>et al.</i> (2012)

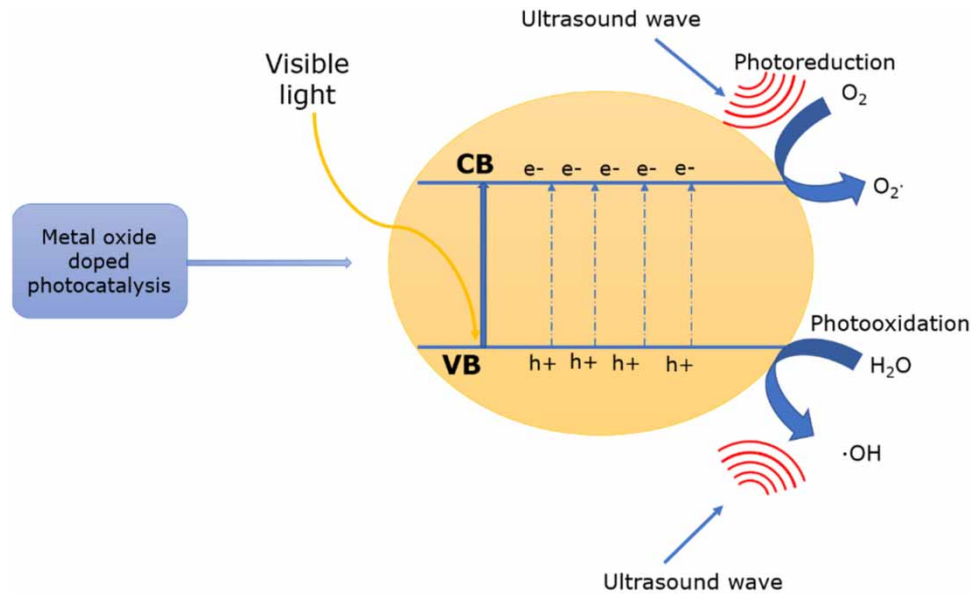
## Physical AOPs

### Electron beam

In the electron beam AOP, an accelerated electron penetrates the water's surface, resulting in the formation of electronically excited species both reducing and oxidizing species ( $\cdot\text{OH}$ , and  $\cdot\text{H}$ ) in the water that could facilitate highly efficient pollutant decomposition and water disinfection (Ponomarev & Ershov 2020). Nickelsen *et al.* (1994) recognized that the incoming energy immediately correlates with the accelerated electron which have greatest penetration depth. However, due to the high cost of an electron accelerator and the high danger of exposure to X-rays, this method has drawbacks. Table 6 shows the outline of ongoing work done in the space of electron beam AOP.

**Table 6** | An overview of recent research in the field of electron beam

S. No.	Removing compound	Experimental conditions	Outcomes	References
1.	Polyvinyl alcohol	Electron beam (EB) + MBR treatment	The removal of COD achieved to 10%	Sun <i>et al.</i> (2016)
2.	Textile wastewater	Electron beam + activated sludge	COD removal was enhanced by upto 79% after introducing activated sludge.	Mohd Nasir <i>et al.</i> (2010)
3.	Antidepressant drug fluoxetine (FLX)	Electron beam irradiation + acidic condition	FLX degradation efficiency was achieved by 100%	Shao <i>et al.</i> (2018)
4.	Iopromide	Electron beam/ $\text{H}_2\text{O}_2$ system	This system enhanced removal efficiency of iopromide.	Kwon <i>et al.</i> (2012)
5.	Clopyralid	Electron beam/ $\text{H}_2\text{O}_2$ system + basic medium	The removal efficiency reported was 99%.	Andreozzi <i>et al.</i> (1999)
6.	1,4-Dioxane	Electron beam	The maximum removal efficiency of 1,4-dioxane was reported 94–99%.	Pearce <i>et al.</i> (2022)
7.	Dyeing wastewater	Electron beam + wastewater (30,000 $\text{m}^3/\text{d}$ )	The colour of dye present in water was decreased upto 10 times.	Wang <i>et al.</i> (2022)
8.	Tricyclazole (TC)	Electron beam, pH = 7.0, and TC = 4 mg/L and $\text{H}_2\text{O}_2$ = 4 mM, absorbed dose = 3.5 kGy	This reported 96% degradation of tricyclazole	Nguyen <i>et al.</i> (2021a, 2021b)
9.	Leucomalachite green (LMG)	pH = 6, absorbed = 4 kGy, an LMG = 4 mg/L and an $\text{H}_2\text{O}_2$ = 8 mM	The maximum degradation efficiency of LMG was 98.2% at these optimal conditions	Nickelsen <i>et al.</i> (1994)
10.	Benzothiazole (BTH)	BTH conc. 20, 40, 50, 60, and 80 $\text{mg L}^{-1}$ and adsorbed conc. 0.5, 1.0, 1.5, 2.0, and 5.0 kGy, respectively	Benzothiazole degraded efficiency upto 90%	Chen <i>et al.</i> (2022)
11.	Atrazine	Atrazine concentrations = 2 mg/L, electron beam irradiation = 6 kGy, pH = 5, $\text{H}_2\text{O}_2$ = 3 mM	100.1% degradation of atrazine	Van Luu <i>et al.</i> (2021)
12.	1,4-Dioxane	Adsorbed conc. = 2.3kGy	90–94% degradation were observed	Pearce <i>et al.</i> (2022)
13.	Tricyclazole (TC)	Absorbed dose = 3.5 kGy, pH = 7.0, TC = 4 mg/L and a $\text{H}_2\text{O}_2$ = 4 mM	96.5% degradation were observed	Nguyen <i>et al.</i> (2021a, 2021b)
14.	Salbutamol (SAL)	SAL conc. = 100 $\text{mg L}^{-1}$ Absorbed conc. = 10 kGy	95.1% removal were observed	Shao <i>et al.</i> (2023)
15.	Reactive blue 21 (RB21)	RB21 conc. = 0.61 $\text{g.L}^{-1}$ Absorbed conc. = 5 kGy	63.51% removal were observed	Melo <i>et al.</i> (2021)
16.	Pyrazinamide (PZA)	PZA conc. = 0.2 mM, Absorbed conc.: 5 kGy	99% removal were observed	Zou <i>et al.</i> (2021)



**Figure 5** | Mechanism of TiO<sub>2</sub>-doped material with ultrasound waves.

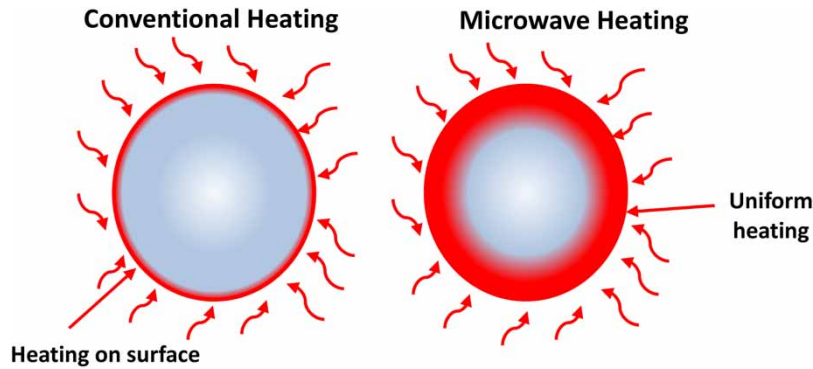
### Ultrasound

In 1927, Richards *et al.* first used ultrasound to accelerate chemical reactions, produce cavitation, and degas water. Currently, for the most used advanced oxidation method for treating effluent, ultrasound is used. During the ultrasound process, aqueous solutions produce hydroxyl radicals, which oxidize contaminants in the presence of ultrasound.



**Table 7** | A summary of the latest ultrasonic research that has been done

S.No.	Removing compound	Experimental conditions	Outcomes	References
1	Paracetamol	Sonophotocatalysis and TiO <sub>2</sub> is a photocatalyst	The maximum degradation rate was observed	Miklos <i>et al.</i> (2018)
2	Acid red 88 (AR88)	Ultrasound + TiO <sub>2</sub> , AR88 = 0.09 mM and photocatalyst = 1 g/L	Enhanced degradation activity	Madhavan <i>et al.</i> (2010a, 2010b)
3	Orange-G (OG)	Ultrasound (213KHz) + TiO <sub>2</sub> pH = 5.8	At these optimum conditions degradation rate of OG reported maximum	Madhavan <i>et al.</i> (2010a, 2010b)
4	Dye-contaminated wastewater	Probe-type sonicator (sonolysis with dipping), Optimal pH = 6, time = 90 min.	In sonolysis with dipping, 82.18% of COD removal was obtained	Nair & Patel (2014)
5	Coomassie brilliant blue (CBB)	Ultrasonic irradiation (350KHz) and time = 30 min	The degradation of CBB was reported 90%	Rayaroth <i>et al.</i> (2017)
6	Ulfamethoxazole (SUX) antibiotic	MgO + ZnO + graphene (MZG) + UV light + US, SUX conc. = 55 mg/L, MZG conc. = 0.8 g/L, time = 120 min, pH = 9	complete degradation of SUX can be attained	Moradi <i>et al.</i> (2020a, 2020b)
7	C.I. Acid Orange 7	Ultrasound + goethite + H <sub>2</sub> O <sub>2</sub> , pH = 3, time = 30min	90% decolorization efficiency was obtained	Zhang <i>et al.</i> (2019)
8	<i>p</i> -nitrophenol	Sonophotocatalysis (25KHz) + H <sub>2</sub> O <sub>2</sub> + UV	Degradation efficiency of 94% was obtained	Mishra & Gogate (2011)



**Figure 6** | Heating illustration of conventional and microwave heating.



According to Mahamuni & Adewuyi (2010), when the cavity collapses in the presence of ultrasound, the pyrolysis process occurs inside the cavity and close to the contact between the cavity and the adjacent fluids. This results in the formation of  $\cdot\text{OH}$ . Pyrolysis is done by the incredibly high temperatures attained during cavitation (Miklos *et al.* 2018), but the use of ultrasound requires a lot of energy and has a low electrical efficiency compared to other AOPs. Therefore, catalysts and oxidants have been linked to ultrasound in recent years. There may be additional advantages from these hybrid processes. Compared to UV radiation, sonication (20–500 kHz) is more effective and produces less heat. Sonolysis, sono-Fenton systems, sonophotocatalysis, and sono-ozone methods are examples of ultrasound techniques used in conjunction with wastewater treatment (Panda & Manickam 2017). Figure 5 shows the mechanism of metal oxide-doped material with the help of ultrasound. Ultrasound enhanced the degradation capability of organic contaminants. The most recent research in the field of ultrasound AOP is summarized in Table 7.

### Microwave

According to Xia *et al.* (2002), the advantages of microwave technology over conventional methods in terms of energy efficiency, fast and uniform heating, hot spots effect, and non-thermal effect have sparked an interest in

**Table 8** | Overview of work done in the area of microwave in recent years

S.No.	Removing compound	Experimental Conditions	Outcomes	References
1	Pentachlorophenol (PCP)	Microwave (700W), adsorbents FeO and $\text{CoFe}_2\text{O}_4$ , PCP conc. = 1,000 mg/L,	The removal efficiency of PCP at these optimum conditions was reported more than 99%	Jou (2008)
2	Cypermethrin	Microwave + Photo-Fenton, time = 4 min	Degraded efficiently more than 98% in just 4 min	Gromboni <i>et al.</i> (2007)
3	Cutting-oil in water emulsions (COWE)	Microwave (800W)-assisted Catalytic Wet Peroxide Oxidation (MW-CWPO), catalyst: graphite (10 g/L), COWE 0.5% w, pH: 9, $\text{H}_2\text{O}_2$ : 15.7 g/L,	At these optimum conditions 82% TOC removal was reported	Garcia-Costa <i>et al.</i> (2021)
4	Antibiotic metacycline (MTC)	Microwave + Fenton reaction (MAFR) + $\text{CuCO}_2\text{O}_4$ (10 mg), $\text{H}_2\text{O}_2$ : = 500 $\mu\text{L}$ , MTC = 50 mg/L, Temp. = 90 °C	This showed 86.4% removal efficiency even after 5th cycle	Qi <i>et al.</i> (2019)
5	Sodium dodecyl benzene sulfonate (SDBS)	Microwave (280 W)+ potassium persulfate (KPS), Concentration: SDBS = 25–100 mg/L, KPS = 2 g/L	The degradation of SDBS was reported to be 98.3%	Bhandari & Gogate (2019)

**Table 9** | Merits and demerits of different AOPs

Method	Merits	Demerits
Ozone-based AOPs	<ul style="list-style-type: none"> <li>• High oxidation power: Ozone is a strong oxidant that can effectively degrade a wide range of organic and inorganic pollutants in water and wastewater. This makes it an effective method for the treatment of complex wastewater with recalcitrant pollutants.</li> <li>• Versatile: Ozone can be used as a standalone treatment method or can be combined with other AOPs like UV, hydrogen peroxide, or catalysts to enhance the treatment efficiency.</li> <li>• Fast reaction time: Ozone has a short reaction time, typically in seconds, which makes it suitable for treating large volumes of water or wastewater in a short amount of time.</li> <li>• No residuals: Unlike some other oxidants, ozone does not leave any harmful residual byproducts after treatment, which makes it environmentally friendly.</li> </ul>	<ul style="list-style-type: none"> <li>• High cost: Ozone production requires a significant amount of energy, making it an expensive treatment option compared to other methods.</li> <li>• Complex system: Ozone-based AOPs require specialized equipment and control systems that can be complex to operate and maintain.</li> <li>• Risk of ozone exposure: Ozone is a respiratory irritant and can be harmful to human health at high concentrations. This makes it important to ensure proper safety measures are in place to protect workers and the environment.</li> <li>• Limited efficiency: While ozone can be effective at degrading many pollutants, it may not be as effective against certain pollutants or wastewater types, and may require the use of additional treatment methods.</li> </ul>
Fenton process	<ul style="list-style-type: none"> <li>• High efficiency: Fenton's reagent has been shown to effectively remove a wide range of organic and inorganic pollutants in water and wastewater. This is due to the high oxidative power of the hydroxyl radicals generated by the reaction of <math>\text{Fe}^{2+}</math> and <math>\text{H}_2\text{O}_2</math>.</li> <li>• Low cost: The reagents used in Fenton's process, including <math>\text{Fe}^{2+}</math> and <math>\text{H}_2\text{O}_2</math>, are relatively inexpensive, making it a cost-effective treatment option.</li> <li>• Simple operation: Fenton's process is relatively easy to operate and can be implemented on a small or large scale.</li> <li>• Can operate at neutral pH: Fenton's reaction can occur at neutral pH, unlike other AOPs that require an acidic pH.</li> </ul>	<ul style="list-style-type: none"> <li>• Sludge generation: Fenton's reaction can produce sludge which requires proper disposal.</li> <li>• pH limitation: Fenton's process requires low pH (&lt;3), which can cause corrosion of equipment that can increase the cost of treatment.</li> <li>• Iron impurities: Fenton's reagent is sensitive to iron impurities, which can decrease its effectiveness.</li> </ul>
TiO <sub>2</sub> photocatalyst	<ul style="list-style-type: none"> <li>• Effective at low concentrations: TiO<sub>2</sub> photocatalysts are effective at low concentrations and can efficiently degrade a wide range of organic and inorganic pollutants.</li> <li>• Versatility: TiO<sub>2</sub> photocatalysts can be used in a variety of treatment processes such as batch or continuous flow processes.</li> <li>• No toxic byproducts: TiO<sub>2</sub> photocatalysis does not produce any toxic byproducts during the reaction, which makes it an environmentally friendly treatment method.</li> <li>• High stability: TiO<sub>2</sub> photocatalysts are stable and can be reused multiple times, making it a cost-effective treatment option.</li> </ul>	<ul style="list-style-type: none"> <li>• UV light requirement: TiO<sub>2</sub> photocatalysts require UV light to activate the photocatalytic process, which increases the cost of treatment.</li> <li>• Surface fouling: The surface of the TiO<sub>2</sub> photocatalysts can become fouled with pollutants over time, which can decrease the effectiveness of the catalyst.</li> <li>• Narrow wavelength range: The effectiveness of TiO<sub>2</sub> photocatalysis is limited to a narrow range of UV wavelengths, which can limit its applicability in certain situations.</li> </ul>
Electron beam	<ul style="list-style-type: none"> <li>• High oxidation power: Electron beam irradiation generates reactive species, such as hydroxyl radicals, which can effectively degrade a wide range of pollutants in water and wastewater.</li> <li>• Fast reaction time: Electron beam irradiation has a short reaction time, typically in milliseconds, which makes it suitable for treating large volumes of water or wastewater in a short amount of time.</li> <li>• No Chemicals Required: Unlike some other AOPs, electron beam irradiation does not require the addition of any chemicals, which makes it an environmentally friendly treatment method.</li> <li>• Low Residuals: Electron beam irradiation does not leave any significant residual byproducts after treatment, which reduces the need for further treatment and disposal costs.</li> </ul>	<ul style="list-style-type: none"> <li>• High cost: Electron beam irradiation requires specialized equipment and high energy consumption, making it an expensive treatment option compared to other methods.</li> <li>• Complex system: Electron beam-based AOPs require specialized equipment and control systems that can be complex to operate and maintain.</li> <li>• Possible Radiolytic Byproducts: The irradiation process can produce radiolytic byproducts, which can pose a risk to the environment and human health if not handled properly.</li> <li>• Limited Efficiency: While electron beam irradiation can be effective at degrading many pollutants, it may not be as effective against certain pollutants or wastewater types, and may require the use of additional treatment methods.</li> </ul>
Ultrasound	<ul style="list-style-type: none"> <li>• Low cost: Compared to other physical AOPs such as electron beam, ultrasound is a relatively low-cost treatment option.</li> </ul>	<ul style="list-style-type: none"> <li>• Limited penetration depth: Ultrasound has a limited penetration depth, which can restrict the treatment of deep-seated contaminants in water and wastewater.</li> </ul>

*(Continued.)*



Table 9 | Continued

Method	Merits	Demerits
	<ul style="list-style-type: none"> <li>• Environmental friendly: Ultrasound does not generate any chemicals or byproducts during treatment, which makes it an environmentally friendly treatment method.</li> <li>• High efficiency: Ultrasound can effectively degrade a wide range of pollutants in water and wastewater, and can be used in combination with other treatment methods to enhance the degradation efficiency.</li> <li>• Easy to scale up: Ultrasound can be easily scaled up for large-scale applications, and can be used in both batch and continuous flow processes.</li> </ul>	<ul style="list-style-type: none"> <li>• Energy consumption: Ultrasound requires energy to generate the sound waves, and the energy consumption can be high depending on the frequency and power used.</li> <li>• Possible formation of toxic byproducts: Under certain conditions, such as the presence of bromide ions in water, ultrasound can form toxic byproducts, such as bromate, which can be harmful to human health.</li> <li>• Equipment limitations: Ultrasound equipment can be sensitive to temperature and pressure variations, and can require regular maintenance to ensure proper operation.</li> </ul>
Microwave	<ul style="list-style-type: none"> <li>• High efficiency: Microwave irradiation generates heat rapidly and uniformly, which can effectively degrade a wide range of pollutants in water and wastewater.</li> <li>• Fast reaction time: Microwave irradiation has a short reaction time, typically in seconds to minutes, which makes it suitable for treating large volumes of water or wastewater in a short amount of time.</li> <li>• Easy to operate: Microwave-based AOPs are relatively easy to operate, and can be controlled by adjusting the microwave power and irradiation time.</li> <li>• Scalable: Microwave-based AOPs can be easily scaled up for large-scale applications, and can be used in both batch and continuous flow processes.</li> </ul>	<ul style="list-style-type: none"> <li>• High energy consumption: Microwave irradiation requires high energy consumption, and can be expensive compared to other physical AOPs such as ultrasound.</li> <li>• Equipment limitations: Microwave equipment can be sensitive to temperature and pressure variations, and can require regular maintenance to ensure proper operation.</li> <li>• Safety concerns: Microwave irradiation can pose a safety risk to operators if not handled properly, due to the potential for electromagnetic radiation exposure.</li> <li>• Formation of byproducts: Microwave irradiation can generate byproducts, such as carbon dioxide and nitrogen oxides, which can contribute to environmental problems if not properly handled.</li> </ul>

wastewater treatment. The microwave increases the generation of active radicals like  $\text{OH}^\bullet$  and  $\text{SO}_4^{\bullet-}$ , which have a greater integrated treatment impact, when coupled with AOPs. Microwave-assisted advanced oxidation processes (MW-AOPs) have quickly evolved as innovative treatment approaches to degrade pollutants. The advanced microwave/UV/TiO<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> technology for treating non-biodegradable water contaminants proved to be a hybrid technology that combined photocatalysis with ozonation with assistance from microwave. Figure 6 shows that microwave heating of a solution involved numerous steps. Microwave radiations pass through the material, altering the electric field and polar molecules, such as H<sub>2</sub>O, and continually attempt to align with the microwave's electric field, thus resulting in the movement of dipoles producing molecular friction, which ultimately produces heat. This generation of heat is uniform throughout the solution as shown in Figure 6 (Verma & Samanta 2018). This results in the improvement of microwave heating performance over traditional heating or surface heating techniques. A summary of recent research in the field of microwave-assisted AOP can be found in Table 8.

*Merits and demerits of AOPs.* After reviewing various AOPs, it could be visualized that all the processes are associated with one or the other limitation so these findings are summarized in Table 9.

## CONCLUSION

Present review compiles the salient features of AOPs used for wastewater treatment. In all these processes, hydroxyl radical plays a major role due to its oxidation potential. Among all the methods, photo catalysis is found to be most efficient and most popular method for wastewater treatment. All the AOPs have limitations, and efforts are being made so that these limitations could be overcome. For instance, some doping in the materials brings the light source from UV to visible region. There is also a need to stop or reduce electron-hole recombination, this is being done by trapping of an electron or utilization of a hole. There is also a requirement to increase the stability of the material used in these auto oxidation processes. AOPs can be commercialized and used on an industrial scale with some modifications in the materials used for various oxidation reactions.

## ACKNOWLEDGEMENTS

The authors are grateful for the support of Lovely Professional University for providing the basic infrastructure for this review.

## FINANCIAL SUPPORT

No funding assistance is available.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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First received 12 January 2023; accepted in revised form 5 April 2023. Available online 18 April 2023