

A Review on Advanced Oxidation Processes for Effective Water Treatment

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Abstract

Advanced oxidation processes (AOPs) such as fenton, ozonation, sonolysis, photocatalysis, UV photolysis, and wet air oxidation are one amongst the most suitable techniques for water and wastewater treatment. These, AOPs have also been chosen for the complete degradation of various categories of emerging pollutants that could not be managed by any conventional technologies. The mineralization is achieved by chemical reactions between the various reacting species generated and the pollutants. The present article provides a view of the mechanistic features of various AOPs and its possible synergisation for process enhancement to achieve better treatment efficiency.



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Introduction

The availability of the earth's fresh water resources has drastically depleted or contaminated due to improper water management, leading to the vulnerable situation. On the other hand the demand for safe potable water is increasing day-by-day due to the exponential growth of population and inability of the traditional treatment¹. There are many traditional and contemporary purification techniques available or practiced for delivering safe water as per the local standards and these spans from basic filtration, adsorption to most advanced techniques; membrane separation and advanced oxidation processes (AOPs). Amongst the contemporary, the

latter one is recognized as highly effective in delivery of safe drinking water free of organics, inorganics, and microbes²⁻³. Owing to strong reactive oxygen species generation ability of AOPs it was considered for treating different types of water and wastewaters containing the various classification of pollutants including endocrine disrupting chemicals (EDCs), persistent organic pollutants (POPs), total organic carbon (TOC) and micropollutants⁴⁻⁵. This AOPs is a broad classification wherein consists of various techniques for the generation of reactive oxygen species and is shown in Figure 1. In general, the realistic aim of any water purification techniques is to render water that is free of toxic matters (organic,

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inorganic and biological). In this regard, AOPs are characterized as best water treatment/purification processes that involve generation of hydroxyl radical (*OH) in sufficient quantity to affect water purification at standard temperature and pressure⁶. The significant advantage of AOPs over all existing chemical and biological processes is that they are totally “environmental-friendly” as they neither transfer pollutants from one phase to the other

(as in chemical precipitation and adsorption) nor produce massive amounts of hazardous sludge⁷⁻¹⁰. The first AOP based water purification/treatment in full scale was proposed in early 1980s and followed by considerable achievements have been reported^{11,12}. Thus, the present review will emphasize on the various aspects of AOPs for efficient water management.

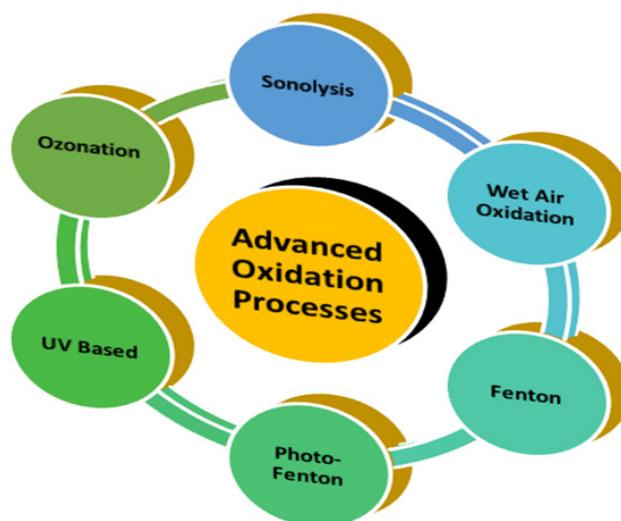


Fig. 1: Classifications of Advanced Oxidation Process

The enhanced degradation of various categories of pollutants by different AOPs has drawn attention from various research communities. The AOP allows the in-situ generation of various reactive oxygen species (ROS) via different process such as sonolysis, ozonation, UV, Fenton processes, etc. These ROS are subsequently utilized towards the degradation of the various categories of pollutants. The insights on the process parameters and degradation of different AOPs have been conferred. Thus, the present article consolidates the significant works that was reported by the various researchers for efficient water management.

Sonolysis

It involves efficient utilization of ultrasonic sound with a frequency range of 20 KHz -10 MHz^{13, 14}. It does not utilize any hazardous chemicals as mediator's and hence regarded as eco friendly process. The organic molecules are degraded as a result of explosions of the cavitation bubbles formed as a result of ultrasonic/hydrodynamics. The generated

cavitation bubbles tend to fluctuate in their size until get collapsed at their resonance size, leads to dissipation of the stored energy causing the explosions¹³. The formation of these cavitation bubbles highly depends on the ultrasound frequency¹⁵. In general, lower frequencies leads to formation of lesser concentration of active bubbles due to presence of high water vapor content in the collapsing bubbles¹⁵. However, high frequency leads to collision among the active bubbles which generates smaller number of reactive species leading to lesser efficiency¹⁵. The schematic of working principle of Sonolysis is depicted in figure 2.

The explosion of these bubbles leads to degradation of the pollutants via pyrolysis at extreme pressure and temperature (500–10,000 atm & 3,000– 5000 K respectively)^{16,17} subsequently leading to the generation of *OH by the dissociation of water molecules. Thus formed *OH further reacts with the pollutants leading to their simplest form^{18,19}. The degradation at the bubble-liquid interface is

dominated by the $\cdot\text{OH}$. Also, the migration of free radicals from the bubble–liquid interface into the bulk liquid leads to secondary reactions in it. It is facile sludge free process with no additional generation of secondary pollutants, promoting it as one of the most preferred techniques over photolysis, photo-Fenton and Fenton process, etc.¹⁴. Moreover, it has inherent ability to treat cloudy water and leads to the efficient

degradation of volatile and sparingly soluble organic matters causing high turbidity¹⁹. Nevertheless, its lower viability due to higher energy consumption and lesser mineralization efficiency limitations directs towards intensifying with various other AOPs like photocatalysis (sono-photocatalysis), photo-fenton (sono-fenton), ozonolysis (sono-ozonation), sonophotolysis, etc.

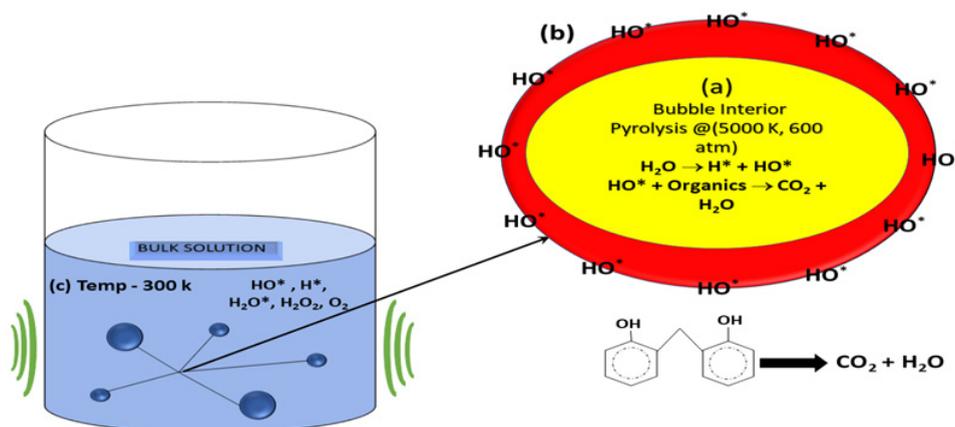


Fig. 2: Schematics of working principle of Sonolysis (a) Bubble interior (b) Liquid-bubble interface (c) Bulk solution

The mineralization efficiency can also be enhanced by varying the operational parameters such as initial substrate concentration, pH, catalyst loading and ultrasonic power²⁰. Among the intensified, sono-photolysis involves the synergistic effects of UV irradiation and ultrasound waves towards the mineralization of the pollutants in the absence of catalysts. Whereas, sono-photocatalysis involves the use of UV irradiation and ultrasound waves in the presence of a semiconductor photocatalyst. The synergistic effect of UV/ultrasonic waves leads to enhanced generation of the reactive radicals leading to improved mineralization efficiency. The enhanced generation was attributed to the formation of electron-hole pair as a result of excitation in the semiconductor photocatalyst²¹. Additionally, presence of photocatalyst improves the bubble cavitation phenomenon resulting in enhanced migration of the reactive species towards the liquid bulk region²¹. Thus, intensification of the above process leads to increased concentration of the free radicals as a result of ultrasound on the peroxide species²². In case of sono-ozonolysis, the mass transfer of the $\cdot\text{OH}$ and ozone are enhanced leading

to in-situ generation of $\text{H}_2\text{O}_2/\text{HO}^*$ (each O_3 molecules degrades generating $2\cdot\text{OH}$)²² resulting effective mineralization of the pollutants. The reactive species are generated as a consequence of cavitation phenomenon in water and thermolysis of ozone. The mineralization can be further enhanced either by increasing the pressure or adding peroxide²³. The combination helps in achieving efficiency levels > 80 % within a pH range of 5.5 – 6.5²⁴.

Ozonation

Ozone is categorized as strong oxidant and a powerful disinfectant²⁵ after fluorine. Theoretically ozone has been reported to oxidize both inorganic and organic pollutants but practically ozone is highly selective towards pollutant²⁵. Hence ozone is considered as an electrophile with high selectivity in its reaction²⁶. Ozonation for water treatment is highly applicable for degrading microbes²⁶, decolorization^{27,28}, micropollutants removal^{29,30}, non-protonated amines²⁶ and taste and odor removal^{26,31}. This technique is commercially implemented in European countries like Switzerland, Germany and etc as an oxidizer and in wastewater

treatment plants³². Ozone generator, cooling system for ozone generator, pre-treatment unit for dehydrating the air added into the Ozonator and post-treatment reactor for removing excess ozone in

the off-gas are the units required for implementation of ozonation³³. The schematic of a typical ozone reactor is shown in figure 3.

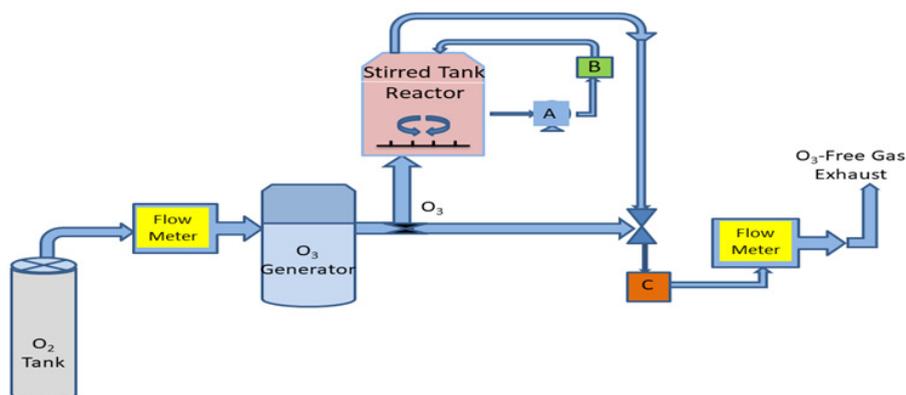


Fig. 3: A typical reactor assembly for ozonation. (A=Liquid circulation pump; B=Ozone liquid analyzer; C=Ozone gas analyzer)³⁴

Aquatic Phase Reaction of Ozone

In water, ozone is wobbly and hence undertakes reaction with the elements of water components²⁵. The ozone decomposition mechanism in water entangle complex sequence of atoms and single electron transport with intermediate *OH formation and further involves the formation of OH⁻, HO₂⁻, O₂⁻, O₃⁻, HO₃⁻, OH, O₂ and HO₄⁻ entities as shown in figure 4. This ozone decomposition process can be accelerated by escalating the pH or hydrogen peroxide concentration²⁶. It is well known that

Ozone is the predominant disinfectant in water while OH and O₃ both act as oxidants in the oxidation process in water with O₃ being highly selective and *OH is being highly reactive²⁶. Hence ozonation can simultaneously be used for disinfection and oxidation. In the inception ozone concentration in water decreases rapidly and then follows first-order kinetics while in the second phase of ozone decrease through oxidation following second-order kinetics^{26,35,36}.

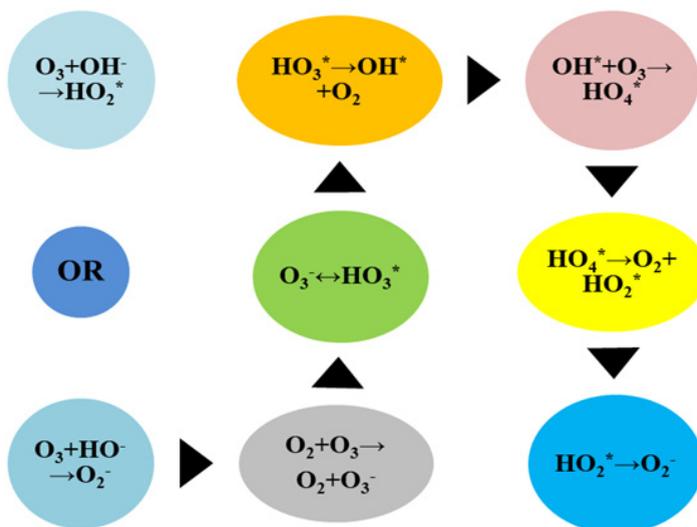


Fig. 4: Ozonation reaction in water matrix²⁵

The half-life of dissolved ozone varies from seconds to hours depending upon the water^{26,28,37} pH, alkalinity, natural organic matter content^{26,28}. Among the three the natural organic matter can react with ozone or scavenge *OH i.e. directly or indirectly affecting ozone stability²⁶. It has been reported that ozone is potent to react with substances directly or indirectly with *OH even at neutral pH as hydrogen peroxide, superoxide ions²⁵. Ozone, *OH or the blend of the two and subsumed throughout the ozonation of organic and inorganic compounds. Ozone oxidation is enhanced by electron donating groups like -CH₃, O⁻, -OCH₃^{26,32} and is reduced by electron

withdrawing groups like -Cl, -NO₂²⁶. Sulfidic groups and compounds containing amino groups and double bond also exhibit high ozone reactivity while the reactivity with the saturated compounds is low being accumulated during the ozonation process²⁶. Low reactivity is also observed in the reaction of ozone with methyl and ethyl ether. Two electron oxidation liberating oxygen atom from ozone is followed in ozonation for oxidizing inorganic compounds^{26,38,39}. The oxidation potential decreases with protonation of species due to decrease in nucleophilicity²⁶. Hence the Ozonation can be effectively applied to varieties of pollutants as shown in the Table 1.

Table 1: Various categories of pollutants degraded by ozonation

S.No.	Category	Pollutant	Ref.
1)	Microbial (cyanobacteria) product	Microcystin-LR	[40]
2)	Pesticide	Carbofuran	[41]
3)	Solvent	Dinoseb	[26, 42]
		Vinyl chloride	
		Dichloroethenes	
4)	Ligands	Nitrilotriacetate (NTA)	[43]
		Ethylenediaminetetraacetate (EDTA)	
		Dichlorofenac	
		Carbamazepine	
5)	Pharmaceutical	Benzafibrate	[44]
		Diclofenac	
		Ibuprofen	
		Sulfamethoxazole	
		Roxithromycin	
		Iopromide	
6)	Olefins	17 α - ethinyl estradiol	[42]
7)	Deproteinized amines		[45]
8)	Inorganic micropollutants	Fe(II)	[46]
		CN ⁻	
		Mn(II)	
		H ₂ S	
		NO ₂ ⁻	

Influence of Process Conditions

Higher dosage of ozone at elevated pH with low bromide concentration increases the abatement efficiency of micro-pollutants²⁹. While low alkalinity and low dissolved oxygen concentrations decrease the oxidation capacity of the system²⁶. For active compounds like diclofenac, sulfamethoxazole, carbamazepine, trimethoprim, hydrochlorothiazide, phenazone, tramadol, metoprolol etc. with ozone

and *OH are independent of pH change without variation in degradation efficiency; however elevated pH readily converts O₃ resulting in the abatement of ozone-resistant²⁹.

Limitation of Ozonation

Low oxidation by ozone is reported for chlorinated benzenes, geosmin, and methylisoborneol (MIB), trihalomethanes (THMs) etc²⁵. *Cryptosporidium*

paravumoo cyst are a resistant microbe against disinfection requiring higher amount ozone exposure and hence forms undesirable by-products in drinking water^{26,47}. Ammonia removal by ozone is slow as it possesses weak oxidation potential²⁶. It has been seen that the oxidation products produced by ozonation can have unknown toxic matters however these are in low concentration as compared to parental compounds having negligible antimicrobial and estrogenic activities. The toxic matter includes formaldehyde, ketones, phenols, nitromethanes and carcinogens like bromates, N-nitrodimethylamine (NDMA)^{32,48}. Bromate a potential carcinogen formation occurs when ozone and $\cdot\text{OH}$ react with bromide in the liquid phase. Apart from all the high costs of ozone as a reagent is a major limiting factor in implementing ozonation.

$\text{O}_3/\text{H}_2\text{O}_2$

Ozone combined with hydrogen peroxide has emerged as a new dimension in water treatment which can oxidize both inorganic and organic substances more effectively than standalone process. The first studies for wastewater treatment by using $\text{O}_3/\text{H}_2\text{O}_2$ were performed by simultaneous by Nakayama *et al.*, and Hango *et al.*, While, Brunet *et al.*, and Duguet *et al.*, performed for treating drinking water⁵¹. Studies showed that H_2O_2 application in ozonation enhanced the organic substance and Trihalomethanes (THM) precursor oxidation. Its addition increases the ozone transfer rate^{51,52-56}, follows a single electron transfer forming HO_2^- which initiates the ozone decomposition cycle forming $\cdot\text{OH}$. The H_2O_2 incorporation in ozonation especially increases the color removing efficiency but treating drinking water, the oxidation of pesticides, aromatic compounds, and chlorinated solvents mainly applies $\text{O}_3/\text{H}_2\text{O}_2$ ^{50,61}. Benefits of $\text{O}_3/\text{H}_2\text{O}_2$ usage include shorter reaction time, allowing higher application of ozone doses and low agglomeration of ozone at the reactor outlet. Process conditions like reaction time increment after ozone addition, intensifying pH and applying hydrogen peroxide can enhance the oxidation property of ozone. However, increase in reaction time and pH is not economically viable however H_2O_2 being a low-cost reagent most commonly applied in drinking water treatment for achieving higher efficiency. Ozone decomposition by H_2O_2 incorporation is initiated by $\cdot\text{OH}$ and superoxide formation²⁶. In case of treating surface waters using

conventional ozonation and $\text{O}_3/\text{H}_2\text{O}_2$ much difference was not observed in the transformation of ozone to HO^* . But in case of groundwater, containing para-chlorobenzoic acid (pCBA) the oxidation of it by conventional ozone is 20 % and was increased to 50 % by incorporating H_2O_2 along with O_3 ²⁶. Compounds like geosmin and 2-methylisoborneol (MIB) produced by algae are also difficult to oxidize by ozone as they contain saturated ring system. However, they are well suited to be treated by $\text{O}_3/\text{H}_2\text{O}_2$ having high oxidation rate constant²⁶. The Bromate formation is low in $\text{O}_3/\text{H}_2\text{O}_2$ process than the conventional ozonation⁵¹.

$\text{O}_3/\text{Catalyst}$

Homogeneous and heterogeneous catalyst addition in ozonation process also plays a key role in enhancing the oxidation reaction⁵⁷. Metal oxides like Fe_2O_3 , Al_2O_3 -Me, TiO_2 -Me, MnO_2 , Ru/CeO_2 and metal ions like Fe^{2+} , Fe^{3+} , Mn^{2+} , etc. have been used as catalysts⁵⁷. Successful removal of chemical oxygen demand, organochlorides, and total organic carbon had been achieved by combining iron and manganese^{57,58}. Combinations like O_3/TiO_2 , $\text{Ru}/\text{CeO}_2/\text{O}_3$ ³³, $\text{Al}_2\text{O}_3/\text{O}_3$ showed better efficacy in removing total organic matters⁵⁷. Granular activated carbon is also considered as a catalyst for the destruction of bio-refractory compounds^{57,60}.

UV bases AOP

The UV treatment is generally applied as a tertiary for killing the microbes and degradation of those aquatic organic compounds which can absorb UV light. On the absorption of UV light, the electrons in the pollutant excite from the ground state to the excited state, (equation. 1) from where the electrons are transferred to an oxygen molecule which converts both O_2 and the pollutant molecule into a radical (equation. 2). The radical being a highly reactive species oxidizes other molecules to acquire a stable form.



UV light can also result in the homolytic cleavage of the chemical bond of the pollutants resulting in the formation of two radicals (equation. 3). UV light with a wavelength less than 190 nm can effectively break highly stable C-F bond whereas wavelength in the

range 210-230 nm can break C-Cl bond. The radicals formed can then react with oxygen (equation. 4) or may take part in the further oxidation-reduction reactions with the other dissolve molecules.



High energy UV lights with a wavelength smaller than 190 nm can photolyze water molecule to form *OH (equation. 5), that subsequently oxidize other organic substrates⁶¹.



Lamps like Mercury arc with different UV light emitting intensities are used for generation of the UV radiation. These are generally of three types: Low pressure, medium and high-pressure lamp. The former is monochromatic in nature and emit light of wavelength 253.7 nm. Medium and high pressure lamps emit a wide range of wavelengths in the UV region and penetrate deeper because of their higher intensity and take less time for the completion of the treatment. The limitation with the application of them is that they are energy intensive⁶². Lamps like Pulse radiation lamps and Excimer lamps were also utilized for generation of UV irradiation⁶³. The main component of UV treatment system includes lamps, ballast and a reactor. Mercury arc lamps are generally used as the UV lamps. Ballast is a support device, which mainly performs two functions: first, they provide appropriate voltage for the reliable starting of the lamp; secondly, they maintain a

continuous current flow to the lamp, to prevent the lamps from short-circuiting. Finally, the Reactor, they are of two types: contact and non-contact reactor. The contact reactors are the one in which the UV lamps remain in submerged condition. The lamps are generally enclosed within quartz sleeves in order to prevent them from damages. Non-contact reactors are the one in which a transparent material is placed between the water sample and the lamps. The lamps can be positioned either in perpendicular or parallel to the wastewater flow direction^{62,64}. The major strength of this process is eco-friendly and shorter treatment time. It also does not require the use of chemicals; therefore, no residual products are left after the treatment⁶². This technique has been applied for the degradation of numerous organic compounds, including EDCs (Endocrine disrupting chemicals) and various industrial solvents. It is an effective method for degrading NDMA (N-nitrosodimethylamine) a well-known potent carcinogen and mostly found in wastewater in trace amounts⁶⁵⁻⁶⁷. Sakai *et al.*, (2012) found 222 nm Kr- Excimer - UV lamps to be a better option for NDMA degradation in the place of low pressure (LP) and filtered medium pressure lamps (FMP)⁶⁸. Sanches *et al.*, 2010 utilized low-pressure UV lamps to check the degradation of five pesticides viz: Alachlor, Atrazine, Diuron, Pentachlorophenol, Chlorphenvinphos and Isoproturon. More than 50 % of all the pesticides were completely degraded by the conventional low-pressure mercury lamp except Isoproturon. The low quantum yield of Isoproturon, in spite of having high molar absorption coefficient, can be a reason behind its less degradation⁶⁹. Various categories of pollutants treated by UV photolysis are summarized in Table 2.

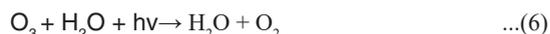
Table 2: Various categories of pollutants treated by UV photolysis

Category	Specific Pollutant	Ref.
Trace Organic Chemical Pharmaceuticals	NDMA(N-nitrosodimethylamine)	[68]
	Diclofenac, Antipyrine, Chlorotetracycline, Norfloxacin, Caffeine, Dipyridamole, Diltiazem, Clofibric acid, Acetamidrid sulfamethoxazole (SMX), oxytetracycline (OTC) and ciprofloxacin (CIP)	[70] [71]
Pesticides	Ditrizoate	[72]
	Atrazine, Diuron, Alachlor, Pentachlorophenol, Chlorphenvinphos	[69]
Anabolic-androgenic steroid	Boldenone	[73]
EDC	Butylparaben	[74]

The limitations of the technique are the $\cdot\text{OH}$ formed by the action of UV, sometimes leads to the partial degradation of the organic contaminants, leaving behind the intermediates concentration in a higher level at the place of CO_2 and H_2O . The higher concentration of Total Suspended Solids (TSS) and particulate material (e.g. humic compounds and iron) lags the treatment. Further, it is energy intensive and expensive as compared to the other tertiary processes like chlorination⁶².

UV/O₃ Process

Treatment by combining UV and O₃ is a well-established advanced oxidation technology. This technique is more advantageous than the individual UV and O₃ technologies since it combines the advantages of both. The ultraviolet light coming in contact with the ozone (O₃) breaks it to form $\cdot\text{OH}$, through the following reaction steps⁷⁵:



The $\cdot\text{OH}$ formed, then either completely mineralizes the organic substances to form CO_2 or H_2O or form some easily degradable intermediate substances. Being an unstable and reactive molecule, O₃ gas is generated in-situ in the experiment. Thus, the generated O₃ is then sparged into the reactor in which UV lamps are installed^{75,76}. These UV lamps are enclosed within Quartz sleeves in the contact reactors, which ensure better transmission of UV. In the non-contact type UV lamp and wastewater are separated by a transparent separator. Schematics of a UV reactor configuration are shown in figure 5.

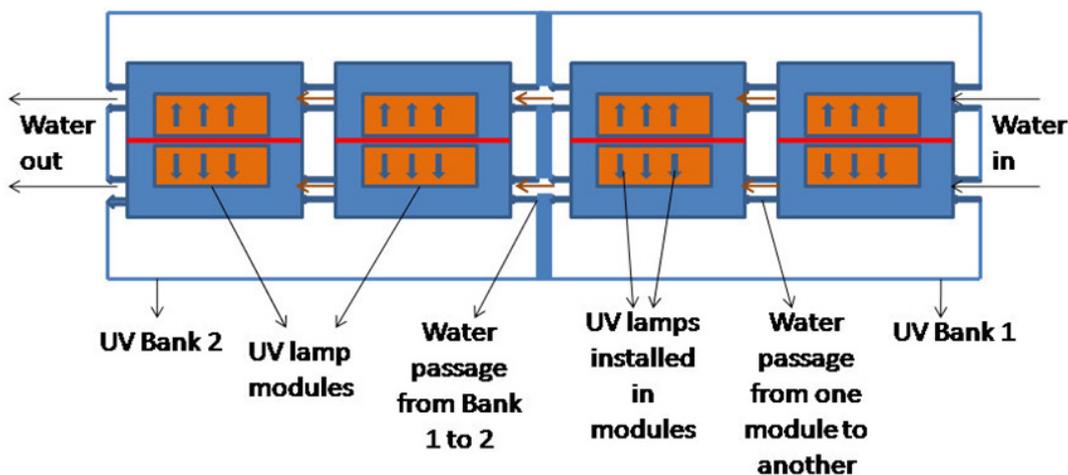


Fig. 5: Schematic representation of a UV reactor consisting of two UV Banks⁷⁷

In most of the studies, it was found that the UV/O₃ treatment was successful in TOC and COD reduction besides its pollutant degradation capacity^{75,78-80}. In a study performed by Hassan *et al.*, (2017), it was found that the color removal was higher for UV/O₃ in comparison to individual treatment with O₃⁸⁰. Tehrani *et al.*, (2010) studied the removal of Reactive Blue 19 dye through the UV/O₃ and O₃ treatment. In their study, it was found that the UV/O₃ treatment was more effective in COD removal than the O₃. It

was also found that decolorization decreased as the initial concentration of dye was increased⁷⁸. The factors which can affect the treatment includes: pH, initial pollutant concentration, the turbidity of the solution, amount of O₃ dose, amount of UV dose, types of UV lamps used for the process, reaction time, scavengers present in the water⁸⁰⁻⁸². Table 4 enlists some selected pollutants removed effectively by UV/O₃ treatment.

Table 3: Selected Pollutants Removed By UV/O3 Treatment

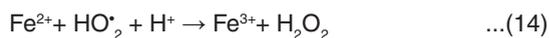
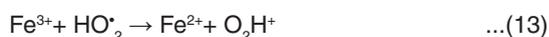
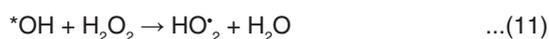
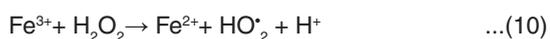
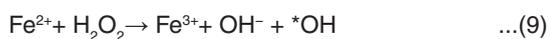
Category	Specific pollutant	Reference
Dyes	RB-19	[79]
	DB-86	[80]
	MV-40	[81]
	Direct Yellow 50	[82]
Phenols	4-Chlorophenol	[83]
Pharmaceuticals	Ketoprofen	[84]
	Caffeine	[85]
Pesticides	Linuron	[86]
Other organic chemicals	Nitrosopyrrolidine	[87]
	Bisphenol A	[88]

Fenton Processes

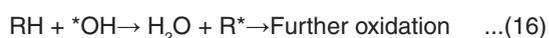
The Fenton is one of the prominent AOP and the chemistry of reactions related to this includes reactions of peroxides (H_2O_2) with Fe^{2+} to generate reactive oxygen species that can degrade the organic as well as inorganic matter in aqueous phase. Fenton chemistry dates back to 1894 when the activation of H_2O_2 by ferrous salts was reported for oxidizing tartaric acid by Henry J. Fenton⁸⁹. In 1934 it was proposed by Haber and Weiss⁹⁰ that there is a formation of $\cdot OH$ due to the Fenton reaction. This $\cdot OH$ has an oxidation potential of 2.73 V. Hence it is one of the most active and powerful oxidants, which can be used in the degradation of most organic compounds including emerging⁹¹.

Homogeneous Fenton Reactions

The Fenton process is an easy and economical method to generate highly reactive oxygen species for degrading contaminants. H_2O_2 is safe and easy to handle, comparatively cheap and easily decomposes into water and oxygen. Similarly, iron is also cheaper and safe to use. This mechanism of decomposition of H_2O_2 was later revised by Barb *et al.*,⁹²⁻⁹⁴ to introduce the chain reactions of the Fenton process. The proposed mechanism which involves the breaking down of H_2O_2 to produce $\cdot OH$ /free radical is a sequence of seven reactions in an acidic medium under dark conditions⁹⁵. The reactions are as follows:



$\cdot OH$, which is the required oxidant for degradation of the contaminants is produced by reaction 9. Reaction 10, therefore, becomes the rate-limiting reaction because it is slower than proceeding by several orders of magnitude. The organic compounds (RH/R) can be oxidized by any one or combinations of the following: (1) $\cdot OH$, (2) abstraction of hydrogen ($R\cdot$), (3) addition of hydroxyl ($\cdot ROH$)⁹⁶.



$\cdot OH$, can be scavenged by either Fe^{2+} or H_2O_2 as shown in equation 10 and 11. Hence optimization of Fe^{2+} / H_2O_2 is to be carried for reducing the scavenging of $\cdot OH$. Whereas, the produced Fe^{3+} precipitates to form ferric oxy-hydroxides as the pH increases from its optimum generating an undesirable sludge giving problems in practical applications^{97,98}. Additionally, the drawbacks of application of Fenton process for large-scale wastewater treatment include pH dependency (effective only in the range of pH 2 to 5), generation of iron-based sludge, the necessity of its expensive post-treatment and finally

neutralizing the treated water before disposal⁹⁹. Therefore, further research is required on modified Fenton processes such as photo Fenton which can increase the reaction rate by light irradiation. Sometimes the use of chelating agents provides optimum pH for Fenton reactions. Chelating ligands compete favorably with hydroxide ion; hence increase the pH range over which compounds are soluble. The reaction kinetics is as similar to Fenton oxidation at the optimum pH. Various chelators include Fe³⁺-CIP chelate, deferioxamine, cyclodextrin, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA)¹⁰⁰⁻¹⁰³ were adopted. However, additional research is required to identify chelating agents that can increase the rate of oxidation, stability, and eco-friendliness.

Photo – Fenton Process

Irradiating Fenton reaction solutions with ultraviolet and visible light increases its reaction rate and the efficiency towards waste degradation⁹⁹. The increase in efficiency is correlated to the photochemistry of Fe³⁺ complexes [Fe³⁺(OH)]⁺ and [Fe³⁺(RCO₂)]²⁺ to dissociate into Fe²⁺. The photochemistry of Fe³⁺ gives an advantage to Fenton processes because the reduced Fe²⁺ reacts with H₂O₂ forming ^{*}OH as per reaction 9¹⁰⁴. The photo-Fenton reaction reaches its optimum around pH 2.8 and as the pH increases above this the Fe³⁺ precipitates as oxyhydroxides and as pH decreases below the optimum, the concentration of Fe(OH)²⁺ will decline¹⁰⁵. The Photolysis of hydrogen peroxide takes place under UV light irradiation as shown (equation 18):



Although the quantum yield by photolysis of hydrogen peroxide shown in reaction 10 is good, due to the weak absorption of light irradiation by H₂O₂, its activity in photo Fenton reactions is not significant. Similar to Fenton, photo-Fenton has the drawbacks of high cost for sludge processing and the requirement of narrow pH range, limits its application in waste/wastewater treatment^{97,106}.

Heterogenous Photocatalysts

Heterogeneous photocatalysis is different compared to other treatment methods involving oxidation and reduction simultaneously, with the use of light irradiation and a light absorbing photocatalyst. Various compounds can utilize light irradiation to catalytically undergo photolysis to produce redox reactions. These compounds usually have a band structure with empty conduction and a filled valence band⁸⁹. Once light irradiation is incident on a semiconductor and if the energy of photons exceeds the energy gap of the semiconductor, electrons are excited from valence band to the conduction band leaving behind the holes^{90,91}. The activated electrons in the valence band and holes in the conduction band react with water generating ^{*}OH, superoxide (^{*}O₂⁻) and peroxide radicals (^{*}OOH). These radicals further degrade various pollutants to obtain products such as CO₂ and H₂O⁹²⁻⁹⁴. The mechanism of photocatalysis and degradation of contaminants is illustrated in figure 6.

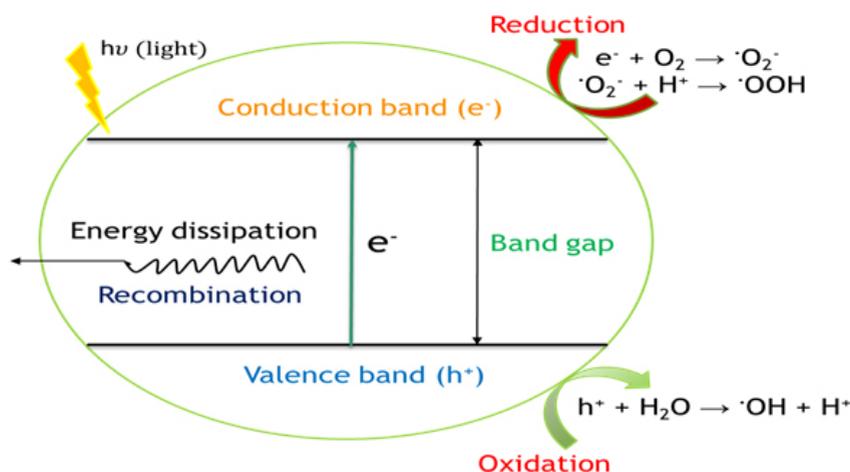


Fig. 6: Schematic representation Photocatalysis of mechanism

The heterogenous photocatalyst materials consist of TiO_2 , ZnO , Fe_2O_3 , WO_3 , SnO_2 , ZrO_2 , CdSZnS , etc. Among them, TiO_2 is the most extensively used heterogenous photocatalyst due to its easy availability, cheapness and high chemical stability. The other classification of photocatalyst also

experimented for its applicability. Owing to the limitation of utilizing the visible light the conventional photocatalyst materials were hybridized with suitable cocatalyst. Table 4 shows the various hybridized heterogeneous photocatalysts utilized for waste degradation.

Table 4: Various photocatalysts studied for degrading different pollutants

Sl. No.	Photocatalyst	Pollutant	Removal efficiency	Ref.
1.	Graphene oxide/ WS_2 /Mg doped ZnO nanocomposite.	Rhodamine B (RhB)	90% in 5 min	[98]
2.	Pd- TiO_2 photocatalyst	Amoxicillin (AMX)	97.5% in 5h	[107]
3.	Hexagonal WS_2 platelets	Rhodamine B	98% in 105min	[99]
4.	Ag^+ , Fe^{3+} and Zn^{2+} intercalated cadmium(II) metal organic frameworks	2-chlorophenol (2CP)	93% in 5h	[104]
5.	Reduced graphene oxide and Ag wrapped TiO_2	Bisphenol A (BPA)	69.1% in 5h	[105]
6.	Graphene bridged $\text{Ag}_3\text{PO}_4/\text{Ag}/\text{BiVO}_4$ photocatalyst	Tetracycline	94.96% removal in 60min	[106]
7.	Magnetic biochar supported g-C $3\text{N}_4/\text{FeVO}_4$	methyl paraben (MeP) and 2-chlorophenol (2-CP)	98.4% MeP removal and 90.7% 2-CP removal	[100]
8.	In-based MOF/graphene oxide	Amoxicillin (AMX)	93% AMX removal, 80% TOC removal	[101]
9.	Magnetic RGO/ $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite	Methylene Blue (MB)	98.64% in 60min	[102]
11.	Fe_3O_4 nanoparticles and oxalate complex	Phenol	97.61% in 3h	[103]
12.	Copper zinc tin sulfide (CZTS) nanoparticles	Methylene blue (MB) dye	50% in 45min	[108]
13.	Reticulated ZnO	Acid Red 88 dye	79% in 180min	[109]
14.	$\alpha\text{-Fe}_2\text{O}_3$ nanosheets	Bisphenol S	91% in 120min	[110]
15.	Ag/ TiO_2 photocatalyst dichlorophenol (DCP)	Amoxicillin (AMX), 2,4-	63.48% AMX & 60.23% 2,4-DCP in 5h	[111]

Fenton Reactions Using Heterogeneous Catalysts

In conventional Fenton process removal of dissolved iron from the treated water is one of the biggest challenges which prompted the use of heterogeneous catalysts along with Fenton process. The investigation has been carried out on the use of supported iron catalysts to decrease sludge

formation and to increase the pH range over which the Fenton reaction is effective. In Heterogeneous catalysts supported Fenton process reactant molecules get adsorbed on the active sites present on the surface of the catalyst. The products get desorbed after the reaction takes place¹¹². The use of goethite ($\alpha\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), $\text{FeS}_2/\text{SiO}_2$, Ilmenite (FeTiO_3) and Titanomagnetite (Fe_3TiO_4) as

heterogeneous Fenton catalysts has been studied by various researchers¹¹³⁻¹¹⁶. The advantage of an ideal heterogeneous catalyst is its ability to separate

from water and function in wide range of pH. Various pollutants degraded using Fenton/Heterogeneous catalysts are tabulated in table 5.

Table 5: Pollutants degraded using Fenton/ Heterogeneous catalysts

Sl. No	Fenton/ Heterogeneous catalysts	Pollutant	Removal Efficiency	Ref.
1.	Photo-Fenton/ magnetite and EDDS	Bisphenol A (BPA)	BPA = 70% in 11h	[117]
2.	Bioelectro-Fenton /carbon felt cathode /boron-doped diamond anode	Pharmaceutical wastewater	COD = 60%, 5-fluorouracil = 88%, caffeine = 43% in 3days	[118]
3.	Fenton/ FeS ₂ /SiO ₂	Ciproflaxacin	Ciproflaxacin = 99% in 60 min	[113]
4.	Fenton/ ferric sludge	Landfill leachate	BOD7 = 99%, COD = 86%	[119]
5.	Photo-Fenton	Micropollutants from municipal wastewater	Micropollutants = 40%	[120]
6.	Fenton with graphene modified iron sludge as catalyst	Rhodamine B (RhB), acid red G (ARG), metronidazole	RhB = 99%, ARG = 98.5%, metronidazole = 91.8%	[121]
7.	Photo Fenton oxidation with zeolite as catalyst	Paracetamol	Paracetamol removal = ~99%, TOC removal = 60% in 5h	[122]

Other AOPs

The above discussed processes are the most prominence among the AOPs with practical applicability. Apart there are few like wet air oxidation (WAO), super critical wet oxidation process (SWOP) process and electron beam radiation. Off this WAO utilizes the molecular oxygen or air as oxidizer in high pressure and temperature environment.

This extreme condition allows the generation of free radicals that decomposes the waste¹²³. Thus temperature and pressure are the controlling factor for WAO process. Most of the organic acids excluding acetic and propionic acid¹²⁴ are converted to CO₂ at high temperature. Figure 7 depicts the simple functionalities of wet oxidation.

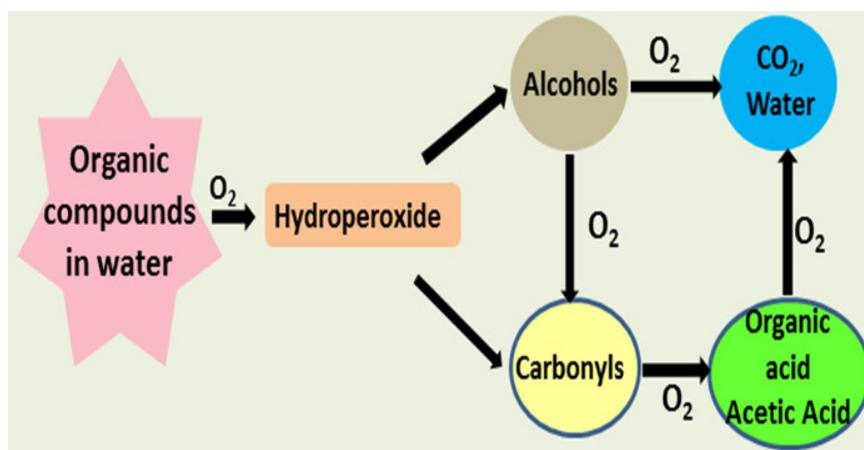


Fig. 7: Flow operational diagram of WAO process

Huge operational expenditure and investment is required to maintain a WAO system as it handles an extreme reaction environment.

Figure 8 illustrates Reactor design adopted for WAO system.

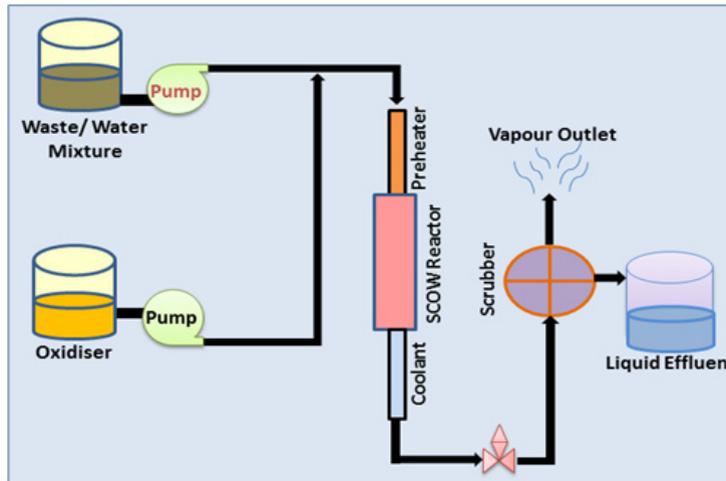


Fig. 8: Reactor design for SWOP system

SWO Employs supercritical condition refers to the extreme temperature and pressurized condition, where water changes its polarity and became a non-polar solvent to get miscible with the organic part. In supercritical condition, water can be mixed with the oxygen creating a homogeneous mixture which is perfect medium for organic degradation. When organic compounds and oxygen are dissolved in water above the critical point they are immediately brought into intimate molecular contact in a single

homogeneous phase. With no interface transport limitations at sufficiently high temperatures, the kinetics is fast and the oxidation reaction proceeds rapidly to completion. This supercritical water oxidation (SCOW) is also referred as hydrothermal oxidation (HTO). This process uses hydrogen peroxide in a homogeneous mixture to oxidize the toxic effluents above the critical point of water. If the organic material is in solid phase it requires the heterogeneous catalytic SCOW.

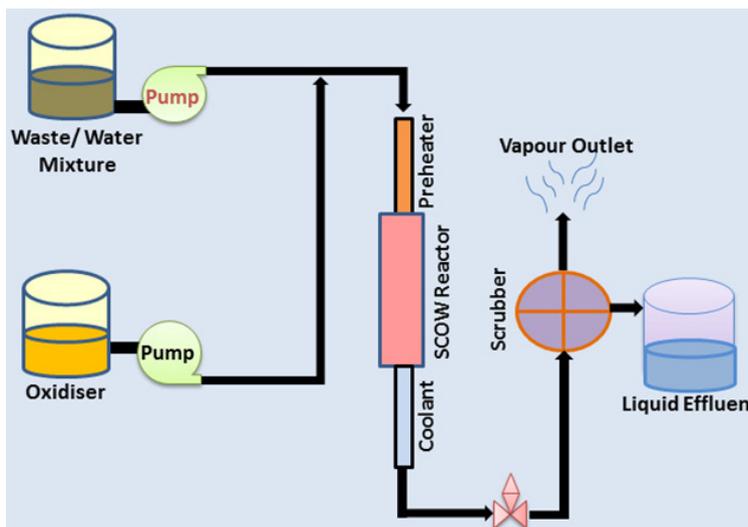


Fig. 9: Schematics of SCOW

It is most efficient method in case of environmental remediation as complete removal of oxidisable material can be achieved by this process. Till date inorganic substances like ammonia or cyanides can also be converted to CO_2 , H_2O , and N_2 . SCOW consists of four steps, starting from pressurizing the reagent, reaction, salt separation and depressurization. Wastewater and oxidant are mixed and fed in the SCOW reactor. The oxidants are normally heated before reaction and this reaction condition allows the exothermic reaction between the waste and oxidant. The heat energy obtained in the oxidation reaction helps to activate the reagent optimally to oxidizable condition. After the

treatment the salt precipitation is visible inside the reactor, because of reduced salt solubility. Though the process requires high energy, this demand can be recovered by utilization of this hot stream for preheating or energy production. A number of works that study in depth the organic reactions in SCW, focusing on the influence of the properties of water and in the kinetics modelling, has been developed over the last few years. The table 6 consists of the list of some organizations that have incorporated SCOW plant for water treatment. Figure 9 shows the schematics of a SWOP process for water/wastewater treatment while the table 6 lists the organization that incorporated the same.

Table 6: List of some organizations that have incorporated SCOW plant for water treatment

Compound	Treated Effluent	Removal efficiency	Ref.
ETH Zurich (Switzerland)	Methanol	TOC rem. 99.9%	[125]
ITC-CPV Karlsruhe (Germany)	Ethanol, Na_2SO_4 , Paper mill waste effluents	TOC rem. 99.9%	[126]
Sandia's EER (USA)	Isopropyl alcohol Military smokes and dye formulations	No Na_2SO_4 deposits in the transpiring wall	[127]
Pine Bluff Arsenal (USA)	Isopropyl alcohol Sugar and Na_2SO_4 Solutions Military smokes and dye formulations	TOC rem. 99.9%	[128]
U.S. Navy/Army's Dugway Proving Ground Facility (Utah, USA)	Naval wastes (Cl- and FI-containing) (71 h) Chemical weapons (231 h)	TOC rem. > 99.9% (Trials for Blue Grass chemical weapons destruction)	[129]
CEA (France)	Methanol	TOC rem. 99.9%	[130]

Conclusion

The review explicitly discussed on the robustness of various AOPs that has been extensively used for water management. Their treatment efficiency depended on various process parameters that were clearly reviewed. However, limitations such as high operational costs, high energy consumption and lower generation of the reactive species initiated the need for process intensifications. The strength

of the intensified system clarified their role on treating various pollutants. Though various AOPs for water treatment are discussed, the Heterogeneous Photocatalysis is most widely preferred over the rest of the processes for real-time applications. Over all the review presented the clear scenario of the AOPs for water and wastewater treatment with a benefit to the community.

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