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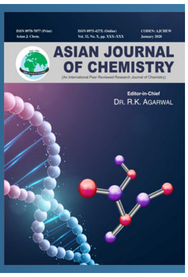

REVIEW

A Review on Advanced Oxidation Processes (AOPs) for Wastewater Remediation

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In 21st century, organic and domestic wastes and discharges from varied chemical and manufacturing industries to water bodies become a critical issue and challenge for the researchers, engineers and policy makers. Advanced oxidation processes (AOPs) are efficient, sustainable, economically viable and green techniques to elimination on-degradable organic pollutants by biological and traditional processes. A number of research articles have been published from the past two decades on the wastewater treatment using various advanced oxidation processes. The main objective of this review paper is to provide the quick view for researchers, academicians and scientists in the area of wastewater treatment using various types of AOPs, which incorporate green principles involves in the processes for removal of different pollutants and contaminants including dyes, phenols, pesticides, herbicides etc. from wastewaters, with emphasis on the degradation efficiency of various photocatalysts. The formation reactions of $^{\bullet}OH$ radical and the mechanisms of degradation of various organic pollutants in the wastewater is also discussed. This review covers various types of advanced oxidation processes, *viz*., ozone-based processes, photocatalysis and Fenton-based reactions.

Keywords: Advanced oxidation processes, Degradation, Hydroxyl radical, Photocatalyst, Wastewater, Dyes, Pesticides.

INTRODUCTION

Water covers 71% of the earth's surface but comprise only 2.5% fresh and potable earth's water. In the recent times, the presence of various potentially hazardous organic and inorganic compounds in industrial and municipal wastewaters is of major concern. These pollutants enter the water systems through different sources and depending on their stability and solubility, can be transported and distributed in the water system and could persist longer periods, either in dissolved form or in sediments. While, water consumption is periodically growing the problems related to provision of safe water and water treatment are increasing day to day in most of the developing countries. It becomes paramount to secure water from pollution and to develop cost effective remedial methods for its protection for sustainability of the today's environment [1-3].

Traditional wastewater treatment processes to treat polluted water from textile, paper and pesticides industry include chemical precipitation with alum or ferrous sulphate, which suffers from drawbacks such as production of a large volume of sludge leading to the disposal problem, the contamination of organic and inorganic substances in the treated wastewater, *etc*. Moreover these processes are inefficient to complete mineralization of hazardous pollutants. To overcome these problems advanced oxidation processes (AOPs) can acts as an alternatives or complementary method in established wastewater treatment and generate very reactive free radicals, especially hydroxyl radicals ($^{\bullet}OH$) generated *via* chemical (O_3/H_2O_2, O_3/OH^-), Fenton and photochemical (UV/O_3, O_3/H_2O_2, photo-Fenton, TiO_2, $ZnO/UV/O_3$, visible or solar light) reactions [4-7].

These technologies (*e.g*., photocatalytic oxidation, Fenton's chemistry and ozonation) can mineralize organic and inorganic pollutants completely and have been applied successfully for the degradation of hazardous pollutants into CO_2, H_2O and inorganic minerals [8,9]. Efficiency of these processes is depends on the production of different types of free radicals such as

TABLE-1
ESTABLISHED AND EMERGING TECHNOLOGIES

Established technologies	Emerging technologies
Hydrogen peroxide/Ozone	High Energy Electron Beamirradiation (E-beam)
Ozone/Ultraviolet irradiation	Cavitation (Sonication & Hydrodynamic)
Hydrogen peroxide/Ultraviolet irradiation	TiO_2, ZnO, $BaCrO_4$-catalyzed UV/visible and solar oxidation, Fenton's reaction

hydroxyl ($^{\bullet}OH$) (high standard potentials of 2.8 eV), superoxide ($O_2^{\bullet-}$), ozone, hydroperoxyl radicals ($HO_2^{\bullet}$), chlorine and fluorine radicals. These radicals are dominant oxidizing agent and expected to degrade adequately, mineralized water contaminants, alter them to less and even innocuous products, thereby providing pivotal solution for wastewater treatment [10-17].

As promising development in the research on advanced oxidation processes for water treatment, heterogeneous photocatalytic, ozonation and photo-Fenton processes are attracting the increasing interest due to their potentially higher effectiveness in the degradation, mineralization of hazardous organic pollutants and lower negative effect on water quality. So far, several metals oxide (*e.g.* MgO, Co_3O_4, ZnO, TiO_2, Al_2O_3), metal or metal oxides on different supports (*e.g.* Pr/Al_2O_3, Co/Al_2O_3, Au/Bi_2O_3, MnO_x/MWCNT, TiO_2/Silica-gel,TiO_2/Al_2O_3) have been reported as effective catalysts for photocatalytic oxidation, ozonation and photo-Fenton techniques. Different parameters also play an importat role in the performance of the degradation efficiency, such as catalyst doses, dye and pesticide concentrations, H_2O_2 concentration, solution pH, temperature *etc*. to find the best optimal operation conditions [18-22].

Advanced oxidation process (AOP) technologies: Advanced oxidation process can be broadly divided into two categories, *i.e.* established and emerging technologies [23]. Emerging technologies can be defined as technologies that have very limited, for example, full-scale applications in drinking water treatment (Table-1).

Most of the AOPs (Table-2) use a combination of strong oxidants (O_3 and H_2O_2), catalysts and irradiation (ultraviolet (UV), visible, ultrasound or electron beam). Different AOPs, which induced by light, are energy conservative and most favoured technologies for wastewater containing dyes and pesticides as cited by the huge literature data. Herein, some important categories of AOPs will be discussed, which are effectively used for the treatment of industrial wastewater containing hazardous organic compounds [24].

TABLE-2
LIST OF TYPICAL AOP SYSTEMS

Dark AOPs	Light driven AOPs
O_3 at elevated pH (> 8.5)	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/Ultrasound	O_3/H_2O_2/UV
O_3/AC (activated carbon)	H_2O_2/Fe^{2+}/UV, Visible or solar light (photo-Fenton)
O_3/Catalyst	
Electro-Fenton	UV, Visible/Photocatalyst
Ultrasound	H_2O_2/Photocatalyst/UV
H_2O_2/Ultrasound	O_3/ Photocatalyst/UV
Microwave	UV/Ultrasound
Wet air oxidation	Vacuum UV

Heterogeneous photocatalysis: Photocatalysis is an advanced oxidation processes applicable in the field of wastewater treatment. Several organic pollutants such as dyes and pesticides are degradable by photocatalysis. Thus, photocatalysis (homogeneous and heterogeneous) is considered one of the important, environmental friendly, cost effective and clean chemical technologies for wastewater treatment [25,26].

Heterogeneous photocatalysis is a light driven (UV, visible and solar light) photochemical reaction, accelerated by the action of various catalysts, *viz.* TiO_2, ZnO, BiOCl, $BaCrO_4$ and Bi_2MoO_6, *etc*. [27]. The mechanism of heterogeneous catalysis is based on the excitation of electrons from the valence band to the conduction band, which is caused by the light irradiation on the surface of catalyst. These migrating electrons and the holes created in the valence band can participate in redox reactions with hazardous pollutant absorbed on the surface of the photocatalyst [28,29]. The process does not require any chemical addition to produce $^{\bullet}OH$ radicals, which are generated by virtue of the semiconductor properties of TiO_2, ZnO, *etc*. Mechanism and the electron/hole generation processes of heterogeneous photocatalysis are discussed in various publications and reviews. Despite extensive studies, the mechanism of these heterogeneous photocatalytic reactions is still poorly understood due to its complexity. The ability of heterogeneous photocatalysis to degrade organic hazardous from wastewater were largely studied [30-34].

Degradation mechanism of heterogeneous photocatalysis is based on the concentration of hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{\bullet-}$) and $h\nu^+_{vb}$ which can be initiated by UV or visible irradiations in the presence of catalyst [35-38]. In this mechanism, catalyst particles are excited to produce positive holes in the valence band ($h\nu^+_{vb}$) with an oxidative capacity and negative electrons at the conduction band (e^-_{cb}) with a reductive capacity as follows :

With the reactions of OH^-, H_2O, and $O_2^{\bullet-}$ at the surface of photocatalyst, these holes and electrons can further form hydroxyl radicals.

$$\text{Catalyst} + h\nu_{\text{UV or Visible}} \rightarrow e^-_{cb} + h\nu^+_{vb} \quad (1)$$

$$h\nu^+_{vb} + OH^- \text{ (surface)} \rightarrow {}^{\bullet}OH \quad (2)$$

$$h\nu^+_{vb} + H_2O \text{ (absorbed)} \rightarrow {}^{\bullet}OH + H^+ \quad (3)$$

$$e^-_{cb} + O_2 \text{ (absorbed)} \rightarrow O_2^{\bullet-} \quad (4)$$

$$O_2 + e^-_{cb} + 2H^+ \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 + e^-_{cb} \rightarrow O_2^{\bullet-} + OH^- \quad (6)$$

$$O_2^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + OH^- \quad (7)$$

Oxidants such as H_2O_2 or O_3, additional $OH^{\bullet}$ may be produced under the UV and visible irradiation [39,40].

$$h\nu_{vb}^{+} + H_2O_2 \rightarrow 2OH^{\bullet} \quad (8)$$

$$\text{Organic pollutants} + {}^{\bullet}OH + O_2^{\bullet-} + h\nu_{vb}^{+} \rightarrow CO_2 + H_2O \text{ and mineral acids} \quad (9)$$

Xu *et al.* [41] investigated direct production pathway of $O_2^{\bullet-}$ and ${}^{\bullet}OH$ on the surface of $BiVO_4$ particles by the electron spin resonance technique. They proposed that $h\nu_{vb}^{+}$ are responsible for the direct production of ${}^{\bullet}OH$, which can degraded organic pollutants effectively in the aqueous system.

Effect of concentration of H_2O_2 on degradation of Congo red dye was studied by Yuksel [42], where at low concentration of H_2O_2, degradation of Congo red dye increased but at high concentration the value of rate of degradation of Congo red dye decreased. Hence, he concluded that at high concentration, H_2O_2 reacted with hydroxyl radicals to form hydroperoxide radicals which are less reactive than hydroxyl radicals and simulataneously also proposed mechanism of propagation and termination of hydroxyl radicals.

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (10)$$

$$2HO^{\bullet} \rightarrow H_2O_2 \quad (11)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O_2 + O_2 \quad (12)$$

$${}^{\bullet}OH + \text{Dye} \rightarrow \text{Degradation product} \quad (13)$$

$$HO_2^{\bullet} + \text{Dye} \rightarrow \text{Degradation product} \quad (14)$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \quad (15)$$

Photocatalytic degradation of reactive blue dye using V_2O_5 under solar light was studied and observed that the pH decreased at the end of reaction time, which is attributed to the degradation of reactive blue dye and producing organic acid. The oxidation reduction potential value at the end of reaction time is greater than its value at the beginning, hence V_2O_5 can be considered as a suitable catalyst for the oxidation process of the reactive blue dye [40]. Photocatalytic activities of titanium dioxide and titanium pillared purified clays, using 2,4-dichlorophenoxyacetic acid and 2,4-dichloro-phenoxypropionic acid as pesticides. Abdennouri *et al*. [43] concluded that these photocatalysts can effectively degrade selected pesticides and also suggested that the removal efficiency increases with the Ti content in pillared clay.

Considering the fact that the UV-Vis spectra of $BiGdO_3$ exhibited a strong optical absorption in visible region and the band gap of $BiGdO_3$ was estimated to be 2.25 eV, thus Luan *et al*. [44] achieved the photocatalytic efficiency of $BiGdO_3$ for mineralizing Direct orange 26 or direct red 23 in aqueous solution in the presence of visible light at 83.7% and 60.8% in 360 min, respectively. The photocatalytic oxidation mechanism of direct orange 26 due under visible light irradiation was proposed and concluded that $BiGdO_3$ possessed excellent suitable and efficient catalyst for textile industry wastewater treatment.

Efficiencies of ZnO and TiO_2 for photocatalytic decolouration of Safranine O dye were also investigated [45]. The highest percentage of degradation of 15 ppm of Safranine O dye was obtained in basic conditions with pH 11 at the optimum dosage of 0.8 g L^{-1} ZnO and 0.4 g L^{-1} TiO_2 under 60 min of UV light illumination for both the photocatalysts *viz*., ZnO and TiO_2. Similarly, malathion was degraded photocatalytically by TiO_2 in presence of UV radiations [46]. The rate of degradation of malathion was maximum at optimum concentration of catalyst (3.0 g/L) and pH 6.0.

Photocatalytic degradation of paraquat and malathion using ZnO/TiO_2 in presence of UV irradiations were also studied by Ali and Hassan [47]. They found that ZnO is suitable catalyst for degradation of malathion but TiO_2 is more efficient in degrading paraquat. Heterogeneous photocatalysis of acid yellow-17 (AY-17) dye on the surface of mesoporous TiO_2, SiO_2/TiO_2 and SiO_2 films in UV light was also reported by Smirnova *et al*. [48], where it was concluded that rate of degradation of acid yellow-17 is fast in the presence of anatase nanoparticles of TiO_2 and SiO_2/TiO_2 films but slow degradation was observed only in air and SiO_2 surface. The degradation mechanism of acid yellow-17 (AY-17) dye which is based on absorption spectra and LDI-MS data was also proposed. Pare *et al*. [49] successfully degraded malachite green dye photocatalytically in the presence of visible light using BiOCl. In this work, it is that addition of an optimal amount of hydrogen peroxide and potassium persulfate increases the degradation rate while NaCl and Na_2CO_3 decreases it.

Some researchers [50,51] noted that the mineralization of Azur B and methylene green dye in presence of visible light using $BaCrO_4$ was varied [5,51]. It is found that the mineralization efficiency of $BaCrO_4$ in visible light is more than that of UV light. Moreover, the value of COD increases while CO_2 value decreases during the mineralization of both dyes, this confirmed the complete mineralization of dyes. The mechanism suggested that the photocatalytic efficiency of the process can be exceeded effectively using green oxidizing agents such as H_2O_2 and $K_2S_2O_8$. Moreover, the photodegradation of dye employing artificial visible light with $BaCrO_4$ as photocatalyst has emerged as an effective and viable method. Sato *et al.* [52] used ZnO as an efficient photocatalyst for the degradation of methylene blue and reactive red 152 dyes. It is found that the mineralization of dyes were dependent on the various optimum parameters like dosage of catalyst, dye concentration and pH of the aqueous solution of dyes.

Photocatalytic degradation pathway of dyes and pesticides are very complex in nature. Dye molecules interact with O_2^-, ${}^{\bullet}OH_2$ or OH^- species to generate intermediates which ultimately lead to the formation of mineralized products. The excited coloured dye (dye*) (in the singlet or triplet state) will inject an electron to the conduction band of the photocatalyst. Hydroxyl radical (${}^{\bullet}OH$) being very powerful oxidizing agent (2.8 eV) degrades dye to non-toxic products [53-59].

Oxidation of pollutants by ozone-based AOPs

In traditional wastewater treatment techniques may be treated either by chemical or biological methods. These techniques often have some issues like time consumption and cost of treatment, the requirement for big facilities, formation of sludge and the existence of some potential pollutants which cannot be easily oxidized. Therefore, the implementation of advanced, innovative and green ozone based (AOPs) wastewater treatment methods that can solve these problems is vital [60,61].

Ozone (O_3) is a strong oxidant having oxidation potential of 2.07 V *vs*. SCE. Ozone shows high efficiency due to its short treatment application time and less concentration requirement. Ozone is also responsible for the generation of hydroxyl radicals in aqueous systems which are capable to degrade organic pollutants [62]. The literature survey shows that ozone and the ozone based advanced oxidation processes (AOPs) are effective to degrade hazardous organic pollutants.

Performance of ozone as a disinfectant for combined sewer overflow was studied by Leong *et al*. [63]. They found that the ozone decontamination represents a helpful substitute to chlorine and fluorine techniques because it does not produce poisonous secondary products and the extra degradation power (50% stronger oxidizer and acts over 3,000 times faster) bound to the dissolved ozone, helps the mineralization of many dyes and pesticides. This technique shows more peculiar advantages such as an increase in dissolved oxygen, decrease in chemical oxygen demand and improvement in aesthetic characteristics due to reduction in turbidity and colour. Jonnalagadda *et al*. [64] also reported that chlorination and UV radiations in the wastewater treatment do not provide these additional benefits.

Many ozone based AOPs are available for the production of hydroxyl radical [65]. These include photochemical and non-photochemical methods such as ozone at high pH (8-10), ozone + UV or visible irradiation, ozone + H_2O_2, ozone + H_2O_2 + UV, ozone + catalyst, ozone + catalyst + H_2O_2, ozone + ultrasound. Sindhi and Mehta [66] reported the effect of pH in the presence and absence of ozone and visible light on photocatalytic degradation of tetradifon pesticide by Mn/TiO_2 catalyst. The rate of degradation of tetradifon pesticide is very low at acidic pH due to the less reactivity of ozone but at high pH rate of degradation was increased due to increase in the concentration of hydroxyl radicals formation. Hence, it can be concluded that pH is most important factor, which can affect the rate of degradation of pollutants in aqueous system.

Various possible mechanisms have been proposed to explain the formation of $^{\bullet}OH$ radicals and the overall reaction involving $^{\bullet}OH$ generation is expressed as:

$$3O_3 + H_2O \rightarrow 2^{\bullet}OH + 4O_2 \quad (16)$$

The hydroxyl radical production is achieved by ozone irradiation (O_3) with ultraviolet radiation (UV) according to:

$$O_3 + h\nu_{UV} \rightarrow O_2 + \text{singlet oxygen} \quad (17)$$

$$\text{Singlet oxygen} + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \text{ (in moist air)} \quad (18)$$

$$\text{Singlet oxygen} + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2\text{(in water)} \quad (19)$$

$$\text{Organic pollutants} + {}^{\bullet}OH + O_2 \rightarrow CO_2 + H_2O \text{ and mineral acids} \quad (20)$$

Thus, hydroxyl radicals formed in the above equations can degrade hazardous organic pollutants [67].

Degradation of pollutants by ozone and hydrogen peroxide (peroxone): Peroxonation process is based on the coupling between ozone (O_3) and H_2O_2, which can generate hydroxyl radicals. Some researchers [68,69] reported that the peroxonation mechanism could be more effective than ozonation alone and in the presence of H_2O_2 the decomposition percentage of O_3 increases in water, which produces a larger number of very reactive $^{\bullet}OH$ radicals. Furthermore, organic pollutants which do not absorb ultraviolet or visible radiation efficiently, their percentage of degradation processes can be increased by adding hydrogen peroxide, when comes in contact with ozone undergoes an additional reaction and further promoting hydroxyl radical formation.

$$2O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH + 3O_2 \quad (21)$$

Degradation pathways of hazardous pollutants by ozone in the absence of catalyst: Legube and Leitner [70] investigated the mechanism of formation of hydroxyl radicals and the degradation pathway of organic pollutants in acidic and alkaline medium. In this mechanism, ozone can oxidize and transform an organic pollutant by direct or indirect pathway. In direct pathway ozone forms $^{\bullet}OH$ radicals in the presence of ultrasound, which react with the organic pollutants to form product, while in indirect mechanism, ozone reacts with hydroxide ions (OH^-) to form oxidants such as hydroxyl radical ($^{\bullet}OH$) which then reacts with the organic pollutants [70].

$$O_3\text{, aqueous solution + ultrasound} \rightarrow O_2\text{, aqueous solution} + O^{\bullet} \quad (22)$$

$$O^{\bullet} + H_2O \rightarrow 2OH^{\bullet} \quad (23)$$

$$OH^{\bullet} + \text{Organic Pollutants} \rightarrow \text{Organic Pollutants (Highly selective)} \rightarrow \text{Product} \quad (24)$$

$$O_3 + OH^- \rightarrow OH^{\bullet} + O_2^- + HO_2^{\bullet} \quad (25)$$

$$OH^{\bullet} + \text{Organic Pollutants} \rightarrow \text{Product} \quad (26)$$

$$HO_2^{\bullet} + O_2^- \rightarrow H_2O_2 \rightarrow \text{Oxidation or Reduction of Organic Pollutants} \rightarrow \text{Product} \quad (27)$$

Degradation mechanism of hazardous pollutants by ozone in the presence of catalyst: In the heterogeneous catalytic ozonation of organic pollutants, ozone and catalyst plays a significant role. Several studies were carried about heterogeneous catalytic system, and proposed a possible oxidation mechanism for organic pollutants [71]. There are two steps of mechanism: First step is based on the adsorption and desorption phenomenon. In this mechanism, catalysts act as adsorptive and provided large surface area to organic pollutants, also provided active sites simultaneously and combine with organic pollutant to form unstable complexes with low activation energy. Thereafter all the intermediates can be degraded on the surface of catalysts by ozone or $HO^{\bullet}$ radicals [71].

Second step is based on the redox-reaction, where catalyst plays a vital role in the formation of $HO^{\bullet}$ radicals. In this mechanism, reduced catalyst reacts with ozone to form $HO^{\bullet}$ radical. Organic pollutants get adsorbed on oxidized catalyst and itself get oxidized by an electron-transfer reaction also reduces catalyst.

The organic radical species $A^{\bullet}$ would be then easily removed from catalyst and subsequently oxidized by $HO^{\bullet}$ or ozone [72,73].

$$\text{Red. Catalyst} + O_3 \rightarrow HO^{\bullet} \quad (28)$$

$$\text{Oxd. Catalyst} + \text{Org. Pollutant A} \rightarrow \text{Red. Catalyst A}^{\bullet} \quad (29)$$

$$\text{Red. Catalyst A}^{\bullet} + \text{HO}^{\bullet} \rightarrow \text{Product} \quad (30)$$

Photo-Fenton process: The Fenton reaction was reported in 1894, in which the oxidative potential of H_2O_2 was enhanced, when iron is used as a catalyst under acidic conditions. Fenton is highly stable at room temperature, easy to handle and extremely useful source of oxidizing species ($HO^{\bullet}$ radicals) for organic pollutants degradation [74,75].

To increase the rate of degradation of organic compounds, processes is carried out in the presence of UV or visible light and the process is named as photo-Fenton process. Photo-Fenton method is effective in the treatment of wastewater containing dyes and pesticides and other hazardous mixture of organic wastes *viz*. 2,4-dichlorophenol, nonylphenol, polyethoxylate, chlorpyrifos insecticide *etc*. [76-80].

Degradation rate of sunset yellow FCF dye using copper loaded bentonite and H_2O_2 as photo-Fenton like reagent was also studied [65] and it is observed that the degradation rate depends on parameters involved. Oxidation of pharmaceutical sludge by Fenton process were investigated by Nithyanandam and Saravanane [81] and found that Fenton reaction has a short reaction time among all advanced oxidation processes and also concluded that iron and H_2O_2 are low-cost and non-toxic, due to its homogenous catalytic nature it has no mass transfer limitations and thus no energy involved as catalyst, it's commonly available, no need for special equipment and the process is easily to run and control. Hossain *et al.* [82] studied effect of various parameters on degradation of Eosin Y dye by Fenton's Process. However, the rate of degradation of Eosin Y decreases with increase in pH range from 2.5 to 4.5 and thus suggested that at low pH formation of hydroxyl radicals decreases due to H^+ ions in the aqueous solution but at high pH colloidal ferric species are formed which are responsible to decomposes of H_2O_2. Meanwhile, the effect of concentration of H_2O_2 on the rate of degradation of dye and observed that at high concen-tration of H_2O_2 the value of rate constant decreases because hydroxyl radicals reacts with H_2O_2 to form hydrogen dioxide radicals ($HO_2^{\bullet}$) which are less reactive than $^{\bullet}OH$. These radicals also react with hydroxyl radicals and produces H_2O_2.

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (31)$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O_2 \quad (32)$$

Some researchers [66] also discussed basic advantages of photo-Fenton method, they observed that this process is an efficient method for treatment of the different types of industrial and municipal wastewater, which not only remove the organic pollutants but also to reduce toxicity, BOD removal, odour and color removal, and the reduction in chemical oxygen demand (COD) should be a critical measure of the success of this method.

Degradation of diazinon by photo-Fenton like process was studied by Kazemizad et *al.* [65] under the optimal conditions (83.05% at 10 mg/L initial concentration, 30 min UV irradiation time, $[Fe^{o}]/[H_2O_2]$ molar ratio of 1:1 and pH 4) and 71.34% COD reduction was observed. They also suggested that photo-Fenton process can be used as a pretreatment step for the biological removal or post treatment of diazinon and other pesticides in presence of UV radiations in the aqueous environments. Formation of hydroxyl radicals and degradation mechanism involved in Fenton and photo-Fenton processes are given below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \quad (33)$$

$$Fe^{2+} + H_2O_2 \rightleftharpoons FeOOH^{+} + H^{+} \quad (34)$$

$$FeOOH^{+} + H^{+} \rightleftharpoons Fe(H_2O_2)^{2+} \quad (35)$$

TABLE-3
SUMMARY OF PHOTOCATALYTIC DEGRADATION OF DYES, PESTICIDES
AND OTHER ORGANIC COMPOUNDS BY ENVIRONMENTAL FRIENDLY AOPs

Dye/Pesticide/Sludge	Work	Ref.
Congo red	Effect of concentration of H_2O_2 on degradation of Congo red dye	[42]
Reactive blue	Photocatalytic degradation of reactive blue dye using V_2O_5 under solar light	[40]
2,4-D; 2,4-DP (Pesticides)	Photocatalytic degradation of pesticides by titanium dioxide and titanium pillared purified clays	[43]
Direct orange 26 or Direct red 23	Photocatalytic activity evaluation of $BiGdO_3$ nanoparticles under visible light	[44]
Safranine O	Photocatalytic decoloration of Safranine O by TiO_2 and ZnO	[45]
Malathion (insecticide)	Photocatalytic degradation of malathion by TiO_2 in presence of UV radiations	[46]
Paraquat (herbicide) and Malathion (insecticide)	Photocatalytic degradation of paraquat and malathion using ZnO/TiO_2 in presence of UV irradiations	[47]
Acridine yellow-17	Heterogeneous photocatalsis of AY dye on the surface of mesoporous TiO_2, SiO_2/TiO_2 and SiO_2 films in UV light	[48]
Malachite green	Photolytically degradation of Malachite green in the presence of visible light by BiOCl	[49]
Azur B & Methylene green	Mineralization of Azur B and methylene green dye in presence of visible light using $BaCrO_4$	[50,51]
Methylene blue and Reactive red 152	Methylene blue and Reactive red 152 degraded by ZnO	[52]
Tetradifon pesticide	Photocatalytic degradation of tetradifon pesticide by Mn/TiO_2 catalyst	[66]
Sunset yellow FCF	Degradation of sunset yellow FCF using copper loaded bentonite and H_2O_2 as photo-Fenton like reagent	[65]
Eosin Y	Degradation of eosin Y dye by Fenton's process	[82]
Diazinon (pesticide)	Degradation of diazinon by photo-Fenton-like process	[65]
Chlorobenzene	Rate of degradation of chlorobenzene in Fe^{2+}-catalyzed sodium percarbonate (SPC) system at different Fe^{2+} and SPC concentrations	[83]
Pharmaceutical sludge	Oxidation of pharmaceutical sludge by Fenton process	[81]

$$Fe^{2+} + H_2O_2 \rightleftharpoons Fe(H_2O_2)^{2+} \quad (36)$$

$$Fe(H_2O_2)^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (37)$$

$$Fe(H_2O_2)^{2+} \rightarrow FeO^{2+} + H_2O \quad (38)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \quad (39)$$

$$Fe^{3+} + H_2O_2 + h\nu \rightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+ \quad (40)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} or with H_2O_2:

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (41)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (42)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (43)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (44)$$

Hydroxyl radicals may react with hazardous organic pollutants and starting a chain reaction (eqn. 45):

$$\text{Organic pollutant} + {}^{\bullet}OH \rightarrow \text{Degraded products} \quad (45)$$

From the above mechanism, iron can be considered as a true catalyst [68,69]. Recently, rate of degradation of chlorobenzene in the Fe^{2+}-catalyzed sodium percarbonate (SPC) system at different Fe^{2+} and SPC concentrations and pH conditions were investigated by Zhang *et al*. [83]. In this work, an innovative Fenton system (SPC, $2Na_2CO_3{\cdot}3H_2O_2$), which is environmental friendly and economical process introduced instead of traditional Fe^{2+}/H_2O_2 system, which has overcome the problems of traditional Fenton techniques and also enhance the removal efficiency of organic pollutants. The mechanism regarding the formation of hydroxyl radicals on the surface of SPC, $2Na_2CO_3{\cdot}3H_2O_2$ is explained as follows:

$$2Na_2CO_3{\cdot}3H_2O_2 \rightarrow 2Na_2CO_3 + 3H_2O_2 \quad (46)$$

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (47)$$

Conclusion

An endorsement of the researchers, scientists and engineers for the implementation of advanced oxidation processes (AOPs) in wastewater treatment is indicated by the significant number of research publications in recent years. Photocatalysts like TiO_2, ZnO, SnO, NiO, Cu_2O, WO_3, Fe_3O_4, BiOCl and $BaCrO_4$ were extensively explored and utilized due to their non-toxic nature, high photosensitivity, wide band gap and high stability. Different systems such as catalyst/UV or visible and solar light process, catalyst/H_2O_2/UV light process, ozonation and Fenton′s reactions were employed for the removal of COD, TOC, degradation of dyes, phenolic compounds, pesticides and other potential organic pollutants from industrial and municipal wastewaters. The advantages that make heterogeneous photocatalytic techniques superior to conventional methods are their ability to remove contaminates in the range of part per billion (PPb), no generation of polycyclic compounds and sludge, high speed, low cost and environmental friendly. Photocatalysis processes offer a renewable, ecologically favourable and cost effective source of energy, like sunlight.

Ozone, which is a powerful oxidant, can be looked upon as an effective substitute for chlorine, fluorine and its derivatives in several applications. The combination O_3/H_2O_2, followed by an O_3/UV or visible system, is the most efficient and cost-effective technology for drinking water treatment sources. An advantage of the O_3/H_2O_2 process, which does not require maintenance such as cleaning and replacement of the UV lamps and the power requirements are usually low.

Fenton process is clean and economical and does not generate hazardous substances. Fenton reaction not only leads to degradation of dyes and pesticides from wastewater but also brings a significant COD reduction hence this adapts the treated wastewater prior to biological treatment. The major factors affecting these processes are the initial concentration of the dyes and pesticides, concentration of oxidizing agents, catalysts, light intensity, irradiation time and the nature of the wastewater′s solution (pH, presence of solids and other ions). The role of above parameters on AOPs performance is sufficiently described for different types of wastewaters. Review concludes that advanced oxidation processes are comparatively environmental friendly, economically viable and green processes for complete mineralization of dyes and pesticides in wastewater relative to other techniques.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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