ADVANCED OXIDATION PROCESSES AND THEIR APPLICATION IN THE TREATMENT OF DIFFERENT TYPES OF WASTEWATER SAMPLES

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Abstract. Over the years, urbanization has caused the quality of the water to decline gradually. The production of wastewater has been steadily rising alongside the growth of numerous businesses, including medicines, textiles, processed foods, and many more. Organic molecules from a variety of sources make up the majority of contaminants in wastewater. Some of these chemical molecules are not biodegradable, and it is challenging for anaerobic bacteria to break them down entirely. Because of the molecular structure of them, they can be quite persistent. Several advanced oxidation processes (AOPs) have been studied to remediate wastewater that contains trace organic chemicals (TrOCs). These include ozonation, Fenton oxidation, catalytic wet air oxidation, and photocatalytic oxidation. AOPs have excellent efficiencies, quick oxidation rates, and no secondary pollutants. Each AOP adheres to a particular mechanism in specific circumstances. In this article, we have comprehensively reviewed the underlying mechanism, and factors affecting oxidative pollutant degradation efficiency.

Keywords: advanced oxidation process, organic pollutant, photocatalysis, ozonation, Fenton oxidation

1 INTRODUCTION

Industrialization, urbanization, and commercialization have their fair contribution to the increased number of pollutants (e.g., pesticides, insecticides, personal care products, surfactants, pharmaceuticals, organic dyes, etc.) in water bodies resulting in a shortage of usable water ¹. These organic compounds are known to be biologically active ². Conventional methods are not much effective in removing and/or degrading these compounds due to the persistence related to their molecular properties and chemical structures ³. Although these chemicals are detected in trace amounts, prolonged exposure can cause adverse effects on human health as well as aquatic life. Therefore, treating these pollutants from wastewater is obligatory before discharging them⁴.

None of the conventional methods of wastewater treatment has been a universal solution. Several chemicals, biological, and physiochemical processes have been studied in order to find an efficient treatment for these trace organic compounds ⁵. Widely used physical techniques include adsorption ⁶, membrane separation ⁷ and sedimentation ⁸. Conventional physical methods cannot efficiently eliminate organic compounds from wastewater ⁹. This problem can be solved by using biological treatments to some extent. The most common biological methods include biofilm and activated sludge ¹⁰. However, biological processes also have their disadvantages including susceptibility to sludge swelling, high operating, and investment costs, and long pre-preparation cycles ¹¹.

A membrane bioreactor (MBR) can effectively remove pathogens and bulk organic pollutants. However, they do not remove persistent trace organic compounds (TrOCs) ¹². Therefore, many TrOCs pass through them. TrOCs with hydrophobic structures have electron donating groups (EDGs) that can be easily removed by MBR. The hydrophilic TrOCs, on the other hand, have functional groups called electron-withdrawing groups (EWGs) that are less biodegradable and are more difficult to remove. Properties of adsorbate TrOCs have a significant effect on the removal of TrOCs by activated carbon as well ¹³. Highly hydrophobic or non-polar TrOCs can be well removed by activated carbon but TrOC adsorption by activated carbon reduces significantly when there is the presence of interfering organic and inorganic species ¹⁴.

Chemical methods have emerged as a more efficient technique for wastewater treatment as they can quickly degrade the organic contaminants to a greater extent¹⁵. Advanced oxidation processes (AOPs) are considered as some of the best methods for organic wastewater treatment ¹⁶.
To decrease wastewater toxicity, AOPs have been used extensively, as their goal is to destroy certain pollutant structures and enhance their biodegradability. The reactions are characterized by the generation of reactive radicals (e.g., sulfate, hydroxyl) that oxidize contaminants into \( \text{H}_2\text{O} \), \( \text{CO}_2 \), and non-toxic inorganic compounds. AOPs have advantages including rapid oxidation rate, high mineralization efficiency, and no secondary pollution. Several AOPs, including sonochemical oxidation, Fenton oxidation, radical-based AOPs (SR-AOPs), photocatalytic oxidation, electrochemical oxidation, and microwave oxidation, can degrade these organic pollutants almost completely. Reactive oxygen species (ROS) are produced, including hydroxyl radicals, sulfates, and superoxide radicals. Radical generation mechanisms are different for different AOPs.

**Figure 1.** Treatment of various types of wastewaters using different types of AOPs. (A) Pharmaceutical wastewater, (B) Oily wastewater, (C) Dye wastewater & (D) Landfill leachate wastewater were treated by AOPs such as Fenton oxidation, ozonation, photocatalytic oxidation, CWAO, and SR-AOP.

Various activation methods are there to generate the radicals based on the AOPs such as photolytic oxidation, ozonation, electrochemical oxidation, Fenton and Fenton-like oxidation. A common and crucial step in each AOP is the generation of ROS which determines the oxidation capacity. In the real world, a single AOP might not be sufficient for the treatment of some organic waste streams. Additional organic matters (citric acid, humic acid, etc.) and inorganic ions (\( \text{NO}_3^- \), \( \text{Cl}^- \), \( \text{CO}_3^{2-} \)) may assist or prevent the role of a catalyst during the degradation process. As compared to a single technique, combining different AOPs has shown improved oxidation of pollutants, because of the synergistic effect of various ROS. The available literature is mainly focused on the degradation but not many have mentioned anything about the generation of by-products and their toxicity. To evaluate the AOP efficiency toxicity assay tool is suggested by Fernandez & Alba.

**ADVANCED OXIDATION PROCESSES**

1 Degradation by Photocatalysis

Photocatalysis includes the intra-excitation of a semiconductor photocatalyst that can degrade natural toxins. Beneath UV or sunlight illumination, an electron bounces from the valence band to the conduction band. This will create a positively charged hole (\( h^+ \)) and an electron within the valence and conduction bands. These electron-hole sets respond with the medium and generate ROS which degrades the organic pollutants as shown in figure 2.
Figure 2. Degradation pathway of organic pollutants by photocatalysis. The diagram depicts the generation of reactive oxygen species (superoxide and hydroxyl radicals) in the presence of a photocatalyst and the consequent degradation of organic molecules.

This is a green methodology for the progressed treatment of coloring wastewater, pharmaceutical wastewater, and industrial wastewater. Although TiO$_2$ has been the most utilized photocatalyst for TrOC degradation, recently new photocatalysts have been developed for better results. Alternatives of TiO$_2$ have shown enhanced degradation, e.g., ZnO, CuO, and CdS. UV lamps and solar light are commonly used as sources of UV irradiation.

Determinants of degradation efficiency in Photocatalysis

Compared to pure semiconductors, doping with noble metals has shown better electronic properties which can enhance photocatalytic degradation. While photogenerated electrons move to the noble metal, holes appear on the semiconductor surface resulting in suppressed recombination of electron-hole pair. Hence, despite the high cost, a very small amount of noble metals shows great photocatalytic efficiency.

The morphology of the photocatalyst also governs the quantum efficiency as it affects the porosity and surface area. If the morphology of TiO$_2$ is converted into hollow spheres, and nanotubes then the spacing between electron and hole pairs can be extended to a certain extent.

The nature and concentration of organic contaminants also affect their degradation by the photocatalytic oxidation method. At higher concentration, these organic molecules may create competition for the ROS and results in lower degradation. Functional groups present in TrOCs can determine the rate of degradation as they affect their attachment to the surface of the catalyst. Halo, nitro, or other EWG-containing compounds can easily bind to the catalyst surface at neutral pH.

A decrease in degradation has been observed if the catalyst concentration is increased beyond a certain limit, due to the lowered penetration of UV light. The effect of both initial concentrations of TiO$_2$ catalyst and diclofenac (DCF) has been investigated. DCF degradation primarily decreased by 99.5%, 61%, and 46% with the increase in initial DCF concentration as 5, 10, and 15 mg/L respectively.

pH change can enhance or reduce the chemisorption or physisorption of the TrOCs. Thus, controlling the extent of degradation.

The presence of a photocatalyst can also enhance the toxicity of treated effluent, making it necessary to separate the catalyst from the treated wastewater before discharging it. In real-world wastewater treatment, only a few uses for newly
designed catalysts have been recorded. Solar light photocatalysis is environmentally beneficial, however, it has yet to be established as a viable alternative to UV lamp irradiation.

1.2 Degradation by Ozonation

Ozone is a very unstable yet powerful oxidant with a redox potential of 2.07 V. It readily breaks into diatomic oxygen. Reaction progresses in two ways (figure 3a): direct and indirect ozonation. The method of direct attack on the organic matter is highly selective. In the direct method, two species are generated, one is electron-deficient oxygen, and the other is electron-rich reactive species. Generally, the direct reaction occurs with functional groups (e.g., -OH, -CH₃, unsaturation, -OCH₃) in an acidic medium. The electron-rich oxygen acts as a nucleophile and attacks organic compounds containing carbonyl or imine group, while electron-deficient oxygen behaves as an electrophile and reacts with groups having unsaturation, amines, etc. Indirect ozonation requires an alkaline medium. It refers to the decomposition of ozone into hydroxyl radical (●OH). These radicals attack organic pollutants unselectively and deform their structure by extracting hydrogen to form water. As a result, hydroxyl radical gets stabilized and TrOCs become radicals and execute further ozonation. The degradation of sulfaquinoxaline with an ozone dosage of 5.5 mg/L at pH 3 and 11 was investigated. Results show 99%, and 30% removal at pH 3 and 11, respectively.

Determinants of degradation efficiency in Ozonation

The degradation rate by ozonation depends upon the mass transfer efficiency of ozone. When the dosage is increased beyond a specific point, the solubility in aqueous media decreases, and the ozone usage rate decreases. Excess dosage may result in harmful by-products if competing ions such as halides, carbonates, and bicarbonates are present in the aqueous media.

Compounds containing phenolic groups are easily degraded by ozone due to the presence of high electron density. For instance, the non-phenolic compound (clofibric acid) was degraded by only 34% at 10mg/L ozone dosage and pH 7, whereas the phenolic compound (bisphenol A) was completely degraded only at 0.5 mg/L dosage at the same pH. Clofibric acid includes EWG which decreases its electron density as well. Hydroxyl radicals can degrade these types of substances at alkaline pH.

Although ozonation is a strong oxidation method and doesn’t create any secondary pollutant, still have some problems that include high process cost, high energy consumption, poor utilization rate, and unstable treatment effect. The efficiency of ozone oxidation can be improved, and energy consumption can be lowered by the combined set-up of the UV-O₃ oxidation process. This increases the rate of degradation and facilitates the degradation of a variety of organic pollutants. More free radicals are generated when ozone is irradiated with UV light. In addition, the ideal UV/O₃ process conditions were investigated to give theoretical support for the advancement of the UV/O₃ process and to fundamentally resolve issues that arise in real-world engineering applications. The ROS generation proceeds this way:

\[
\text{O}_3 + \text{H}_2\text{O} + \text{hv} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\]

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{●OH}
\]
Figure 3. (a) Degradation pathway by ozonation, (b) Fenton oxidation of organic molecules in the presence of Fe (+3)/Fe (+2) couple, hydrogen peroxide and electron donating species.

13 Degradation by Fenton Oxidation

During the Fenton oxidation process, highly oxidizing hydroxyl (●OH) radicals are generated by the chain reactions of Fe$^{2+}$ and H$_2$O$_2$. Hydroxyl radical can oxidize several organic and hazardous compounds by electron transfer (figure 3b). This technique is particularly used for the degradation of organic dyes and non-biodegradable compounds in landfill leachate.$^{57,58}$

Fe$^{2+}$ ions are oxidized to Fe$^{3+}$ ions during the process and get precipitated as Fe(OH)$_3$. These ferric ions act as scavengers.$^{59}$ At first, the reaction rate is fast as more ●OH radicals are present at low pH, but the rate decreases gradually due to the formation of peroxyl radicals$^{60}$. Fenton oxidation can take place in a homogeneous or heterogeneous manner. In an acidic aqueous media, homogenous oxidation occurs. Heterogenous oxidation happens at a high pH range and on the surface of the catalyst to generate ●OH radicals.$^{61}$

11 Fenton-like Oxidation

Fenton-like oxidation reaction provides a different pathway from conventional Fenton oxidation. It entails the production of a large number of free radicals in order to degrade contaminants. To create ●OH radicals, catalysts such as Cu$^{(+2)}$, Fe$^{(+2)}$, Fe$^{(+3)}$, metal foam-based and organic frameworks containing two metals(e.g., Co/Fe NC, Fe-Cu/MIL-101) can be utilized instead of solely Fe$^{(+2)}$.$^{62}$ H$_2$O$_2$ can be replaced by reagents like persulfate (PS), peroxysulfate (PDS) or peroxymonosulfate (PMS) to prevent the storage and transport loss of H$_2$O$_2$ in order to produce reactive oxygen species (ROS)$^{63}$. If UV photolysis and the Fenton process are combined, then a wide range of TrOCs can be degraded much more efficiently. This combined process is called the ‘photo-Fenton’ process. Its advantages include less reaction time, more ROS generation, and the requirement of less amount of Fenton reagents. Fe$^{(+3)}$ absorbs UV radiation and regenerates Fe$^{(+2)}$, thus producing more ●OH radicals from less iron salt.$^{64}$ Photo-Fenton process in acidic pH achieved 95% degradation while, in comparison, it was only 11 % by UV photolysis. However, maintaining the acidic pH is a disadvantage for the UV-Fenton process$^{64}$. The addition of mediators like citrate, oxalate, ethylenediamine-N, and EDTA has allowed the UV-Fenton process to take place at neutral pH.$^{65}$ These mediators, such as EDTA, form a water-soluble complex (i.e., Fe-EDTA) with the iron salt, causing the system to work in a basic pH without Fe$^{(+3)}$ precipitation$^{66}$. Determinants of degradation efficiency in Fenton Oxidation

At pH 3, complete degradation of amoxicillin took 90 minutes, while 80% degradation took 120 minutes at neutral pH. This demonstrates the importance of pH in determining the rate of degradation$^{67}$. The formation of ●OH radicals is limited at pH > 4 as H$_2$O$_2$ decomposes to yield O$_2$ and H$_2$O at this condition. As a result, the rate of TrOC degradation by the Fenton process slows down.

The ratio of [H$_2$O$_2$] to [Fe$^{3+}$] dose influences the degree of contamination degradation by Fenton oxidation. An excessive amount of H$_2$O$_2$ can also raise the process’ total cost, which is undesired. Degradation efficiency can be reduced by lowering the dosage. Only through experimentation can the best dose ratio be discovered. At pH 3, for example, full ibuprofen breakdown was seen at the optimum dose ratio of 1.5:1 of [H$_2$O$_2$]: [Fe$^{2+}$]$^{68}$. 14 Degradation by Catalytic Wet Air Oxidation (CWAO)

Wet air oxidation (WAO) cannot achieve complete mineralization of the organic pollutants as it’s very difficult to decompose small oxygen-containing compounds to give water and carbon dioxide in a single step. In this method, ●OH radicals are generated at high pressure and temperature that reacts with less toxic and more degradable small pollutants$^{69}$. Comparatively, catalytic wet air oxidation (CWAO) can function at ambient pressure and temperature to achieve more oxidation rate of contaminants dissolved in water. In the process, macromolecules are first decomposed into smaller ones by the catalysts at a certain pressure and temperature. Then these small molecules are further decomposed to give CO$_2$ and H$_2$O under the action of the same catalyst$^{70}$. Determinants of degradation efficiency in Catalytic Wet Air Oxidation (CWAO)

Recycling the catalyst that remains suspended in the operating unit is a disadvantage of CWAO. Also, the required conditions can sometimes be hard to deal with. It’s challenging to access the active sites of the powdered catalyst. A
standard porous alumina layer is commonly used to fix the catalyst particles and prevent them from escaping. Aluminum oxide has a high adsorption capacity, which inhibits the mass transfer of TrOCs. WAO is commonly used to purify concentrated wastewater containing high levels of TrOCs. Due to their strong reactivity, noble metals have been found to be more efficient than metal oxides. Pt-based CWAO was used to investigate the degradation of TrOCs such as amoxicillin, metoprolol, naproxen, and phenacetin. The parent chemical was found to be 80 percent degraded in 30 minutes. CWAO is a promising method for treating toxic, non-degradable, and hazardous pollutants in an environment-friendly manner.

15 Degradation by Sulfate-Radical-Based Advanced Oxidation Process (SR-AOP)

Unlike other oxidation processes mentioned above, the sulfate-radical-based advanced oxidation process (SR-AOP) utilizes sulfate radicals either with the combination of ●OH radicals or alone. To form sulfate radicals, it also requires activation. Generally, peroxydisulfate (PDS) or peroxymonosulfate (PMS) are used to generate the sulfate radicals. Both PDS and PMS are inactive without the application of external energy. PDS cannot readily release sulfate radicals compared to PMS, due to its symmetrical structure. Various methods of activation are used. Homogenous catalysts show better activation efficiency than non-homogenous catalysts when metals are used in the activation method. Noble metals (Pt, Ag, Au, etc.) and transition metals (Co, Fe, Mn, Cu, etc.) are commonly used for SR-AOPs. Ultrasound and UV activation methods utilize their high energy to create sulfate radicals from PDS and PMS.

Determinants of degradation efficiency in SR-AOPs

A key factor that affects the degradation efficiency of SR-AOPs is pH. Hydroxyl radicals get converted into water in acidic conditions. Sulfate radicals get converted into hydroxyl radicals when pH is raised to 8.5-9. Giannakis et al. have demonstrated the impact of pH on PDS and PMS.

Temperature also has a significant role in determining the efficiency of TrOC degradation by SR-AOP. Reaction temperature profoundly affects the generation of sulfate radicals from PDS and PMS. The degradation efficiency for Acid Orange 7 (AO7) azo dye was studied by using PS, PMS, and H₂O₂. PS showed 80% degradation efficiency within 40 min at 80 °C which is the best-known degradation efficiency for AO7.

Sulfate radicals are highly selective for organic compounds consisting of unsaturated and aromatic structures. Microwave radiations are commonly used for the activation of PS and PMS for generating sulfate radicals as shown in the equations below.
\[
S_2O_8^{2-} \rightarrow 2 \cdot SO_4^{2-} \text{(in presence of MW)}
\]

\[
HSO_5^- \rightarrow \cdot SO_4^- + \cdot OH
\]

Irradiation of MW on PS significantly reduces the activation energy and increases the rate of degradation. Increasing either PS concentration or power of MW can show better removal of organic matter from the wastewater. However, both should be increased to a certain level, beyond that there will be no improvement in TrOC degradation. It happens due to the scavenging effect and causes the termination of chain reactions of the sulfate radicals. Taguchi method can be utilized to determine the factors controlling the degradation by the MW-PS system. Experiments show that the power of MW is the key factor ruling the TrOC degradation.

2 APPLICATIONS

Studying all the advanced oxidation techniques can only be fruitful when they can be practically applied. There is a wide variety of applications of the AOPs for wastewater treatment. Here are the uses of the above-discussed AOPs in treating different types of wastewaters.

2 1 Treatment of Pharmaceutical Wastewater

Pharmaceutical wastewater consists of contaminants of diverse nature such as hazardous, and complex pharmaceutically active compounds (PhACs), residues with high BOD and COD, and volatile organic molecules. As most of them are generated by pharmaceutical outlets, they possess a serious threat to the ecosystem by getting accumulated in the environment. The existing technologies have shown poor rates of decomposition and it gives the idea that a combination of AOPs and other techniques can eliminate the pollutants completely.

2 1 1 Treatment of Pharmaceutical Wastewater by Fenton Oxidation

Various factors were changed to evaluate the degradation of real-world hospital wastewater. These include shorter reaction times, higher temperatures, and one-step reactions. As a result, the amount of \( \text{H}_2\text{O}_2 \) required was reduced, as was the iron content. With a low iron content (25 mg/L), Fe\(^{3+}\) and \( \text{H}_2\text{O}_2 \) dosage (1000 mg/L), full removal of phenol containing compounds, 70% removal OF COD, and 50% reduction in TOC were achieved at 90 °C in 1 h. By-products formed were formic and oxalic acids (short-chain organic acids) are known to be non-toxic.

2 1 2 Treatment of Pharmaceutical Wastewater by Ozonation

Liu et al. have shown that by combining the UV/O\(_3\) method with nanofiltration, 98% of antibiotics can be effectively eliminated. Firstly, nanofiltration separates the antibiotics from primary wastewater, then UV/O\(_3\) can further remove trace antibiotics from nano filtrate.

2 1 3 Treatment of Pharmaceutical Wastewater by Photocatalytic oxidation

Co-doped zinc oxide was accumulated onto \textit{Eichhornia crassipes} tissue which was synthesized to study the effect on water pollutants. This catalyst was tested for photocatalytic oxidation of methylene blue under UV irradiation. Within 45 min 99.6% dye was degraded on the 8\(^{th}\) day of cobalt accumulation.

2 1 4 Treatment of Pharmaceutical Wastewater by CWAO

Under ambient settings, the breakdown of bisphenol A (BPA), triclosan (TSC) and sulfamethoxazole (SMX) for electrocatalytic moist air oxidation was investigated. The extent of degradation by this system was 90.2%, 90.8%, and 92.9% for sulfamethoxazole, bisphenol A, and triclosan, respectively. The optimal operating conditions for an initial TrOC concentration of 40mg/L was 35.85°C, and 25mA applied current. The degradation of pharmaceutical sludge was investigated by CWAO using CuO-\( \text{CeO}_2\)/\( \gamma\)-\( \text{Al}_2\text{O}_3\) catalyst. This catalyst was synthesized by the wet impregnation method. Under optimal conditions maximum of 87.3% removal of volatile suspended solids and 72.6% removal of COD was observed at 260 °C within 60 min. Recently, electro-CWAO has been a topic of interest as it can operate at room temperature and pressure.

2 1 5 Treatment of Pharmaceutical Wastewater by SR-AOP

Modified rice straw biochar-copper oxide (RSBC-CuO) was fabricated by hydrothermal method and used to investigate phenacetin (PNT) degradation by activating PDS. 100% efficiency was observed just in 30 min. This combination possesses a wide range of pollutant degradation including aniline, p-chlorobenzoic acid, paracetamol, and sulfamethazine.
2.2 Treatment of Oily Wastewater

Generally, oily wastewater is released from food processing units and petrochemical industries, containing heavy metals, and volatile organic compounds (VOCs). These components are non-biodegradable and require a strong treatment method. Applications of AOPs for the degradation of oily wastewater are mentioned below:

2.2.1 Treatment of Oily Wastewater by Fenton Oxidation

Compared to the photo-Fenton system, the electro-Fenton system consumes less Fenton reagent. This system was used to investigate the decomposition of refinery oily wastewater. Variance in the current (0.5-2mA), electrolysis time (10-30min), and H₂O₂ concentration (10-50 ppm) was studied. And the COD removal was estimated to be 98% in 25 min. The downside of this process was the rise in energy consumption to 39.67kWh/m³.

2.2.2 Treatment of Oily Wastewater by Ozonation

Petrochemical wastewater was treated to study the degradation of organic contaminants, by using iron-nickel foam as a catalyst in catalytic ozonation. Under certain conditions, within 120 min 73%-96% of COD, and 40%-61% of dissolved organic carbon (DOC) were eliminated. Out of 66 detected organic pollutants, two third were completely removed. Some heavy metals along with Cl⁻ and NO₃⁻ were also treated to some extent.

2.2.3 Treatment of Oily Wastewater by Photocatalytic Oxidation

TiO₂ and vacuum UV oxidation system was used in the pretreatment of oily wastewater. Under 10 minutes of UV irradiation at pH 7, and 150 mg/L of TiO₂, this photocatalytic system achieved a 63% removal rate for COD. This shows that the degrading efficiency has significantly improved. The degradation and separation of synthetic oily water was investigated using a combination of membrane separation and photocatalytic oxidation approach with a hollow 2 wt% TiO₂-PVDF (polyvinylidene fluoride) fiber membrane. At a concentration of 250 ppm oil, the average flux of the membrane was approximately 73.04 L/m². When irradiated with UV, TrOC removal efficiency reached 80%.

2.2.4 Treatment of Oily Wastewater by CWAO

The degradation of oil refinery wastewater at low pressure (0.8 MPa) and low temperature (150°C) was investigated by using MW-assisted CWAO and granular activated carbon (5 wt.%) as a catalyst. Results show 90% efficiency of COD removal, and within 30 min ratio of BOD₅/COD biodegradability improved from 0.04 to 0.47.

2.2.5 Treatment of Oily Wastewater by SR-AOP

The degradation of palm oil mill wastewater was investigated to determine the efficiency of the electro-persulfate oxidation method. Under optimal conditions with 0.892g of S₂O₅²⁻, 45 min reaction time, 45 mA/cm² of current density, and pH 4, the capacity of COD and color removal reached 77.7% and 97.96%, respectively.

2.3 Treatment of Dyeing Wastewater

A large quantity of water is required in the various steps of the textile industry such as dyeing, printing, and finishing. Wastewater from various textile industries is disposed of in water bodies, which consists of different dyes, aerosols, particulate matter, sediments, oil, and grease particles. And all these are not easy to degrade. Hence, COD and BOD₅ values increase drastically resulting in the lowering of dissolved oxygen in the water, which affects the aquatic system adversely.

2.3.1 Treatment of Dyeing Wastewater by Fenton Oxidation

The Sono-Fenton oxidation method was used to examine the decolorization of Red 81. Within 75 min, 99% of decolorization was efficiently done. The factors affecting this rate of degradation are pH, ultrasonic frequency, [Fe²⁺], and [H₂O₂]. Ultrasonic frequency of 120 kHz, pH of 3, [Fe²⁺] = 0.2 g/L, [H₂O₂] = 5.1 × 10⁻³ mol/L were found to be the most optimal circumstances for this study. No significant effect of Cl⁻, NO₃⁻, CO₃²⁻, HCO₃⁻, and SO₄²⁻ on decolorization efficiency was observed.

2.3.2 Treatment of Dyeing Wastewater by Ozonation

Ozone oxidation for methyl orange was studied assisted with Ni-based double hydroxides in comparison to non-catalyzed ozonation. Catalytic ozonation has less reaction time, and an improved rate of COD removal, compared to normal ozonation. After 1 h, 72% COD was efficiently removed, while in non-catalytic ozonation only 30% efficiency was observed.

2.3.3 Treatment of Dyeing Wastewater by Photocatalytic Oxidation

Melamine foam coated with TiO₂ under sunlight was utilized as a catalyst to study the degradation of dye wastewater containing rhodamine B (RhB). This TiO₂-coated melamine foam has a porous structure and a high TiO₂ loading density. The carbonized scaffolding improved nanoparticle thermal stability and inhibited aggregation. When artificial light was
irradiated for 1 h, 98% RhB was decomposed. While 2 h time was required for 90% degradation of traditional dyeing wastewater under sunlight.  

2.3.4 Treatment of Dyeing Wastewater by CWAO  
A composite catalyst Mo-Cu-Fe-O was utilized to evaluate the degradation of crystal violet and cationic red GTL in ambient experimental settings. CuMoO₄ was formed when Mo⁶⁺ was diffused into the Cu-Fe-O crystal lattice. The catalyst Mo-Cu-Fe-O has active oxygen adsorption sites. After 1 h, 92.8% of crystal violet and 91.5% of cationic red GTL were efficiently degraded.  

2.3.5 Treatment of Dyeing Wastewater by SR-AOP  
The capacity of UV-irradiated LaZF@gRO was investigated to activate PDS for the degradation of RhB. Within 80 min, a 100% degradation was achieved. The catalytic activity of LaZF@gRO nanohybrid was two times higher than zinc spinel ferrite reduced graphene oxide. This can be considered as a green catalyst as it can be reused without losing its photocatalytic activity at least four times.  

2.4 Treatment of Landfill leachate  
Leachate from landfills is a bad-smelling, bio-toxic dark liquid with a complicated structure. It is composed of insoluble humic substances, aromatic compounds, metal ions (copper, lead, and chromium), and ammoniacal nitrogen. The activated sludge process can be utilized as a pretreatment step in landfill leachate degradation.  

2.4.1 Treatment of Landfill leachate by Fenton Oxidation  
Using a mix of electrochemical and Fenton oxidation, the degradation of semi-aerobic landfill leachate was examined. This combination had shown great efficiency in the treatment of semi-aerobic leachate, with the highest degradation rates of 93% and 92% for color and COD, respectively.  

2.4.2 Treatment of Landfill leachate by Ozonation  
The degradation of fulvic acid (FA) was studied by ozone decomposition in the presence of CeO₂/AC. FA is the main organic contaminant in landfill leachate and is bio-resistant and toxic. The catalyst used enhanced the contaminant degradation efficiency as compared to O₃/H₂O₂ system. With only 5% Ce loading and under hydrogen calcination at 450 °C, 83% FA had been removed in 30 min.  

2.4.3 Treatment of Landfill leachate by Photocatalytic Oxidation  
The rate of COD decomposition in leachate was determined by shining UV light on tungsten-carbon nanoparticles doped with TiO₂. Under the applied conditions of 550 mg/L initial COD concentration, 10.59 g/m² surface coating density, 40 W of light, 1 L/min flow rate, 84% of COD was removed.  

2.4.4 Treatment of Landfill leachate by CWAO  
From ‘mature’ to ‘old’ landfills the concentration of fulvic acid remains quite high. Degradation of the same was investigated by using activated carbon (AC) as the catalyst and K₂S₂O₈ as the promoter. The amount of AC and promoter, and temperature were the key factors affecting the degradation rate. Within 4 h and at 150 °C, almost 99% FA and 77.8% COD were removed.  

2.4.5 Treatment of Landfill leachate by SR-AOP  
PDS activation by ferrous ions was used to study COD removal from landfill leachate. The dosage of ferrous ions and PDS, the initial pH, and the current density all influenced the rate of COD breakdown. With increasing current density and PDS concentration, the efficiency dropped with increasing pH and increased with increasing current density and PDS concentration.  

Table 1: Treatment of various water pollutants (from different wastewater samples) using different advanced oxidation processes.  

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Method used</th>
<th>Wastewater type</th>
<th>Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veterinary antibiotics</td>
<td>Fenton-like oxidation</td>
<td>Pharmaceutical</td>
<td>74% antibiotics removed</td>
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</tr>
<tr>
<td>Landfill leachate</td>
<td>SR-AOP</td>
<td>Landfill leachate</td>
<td>67% TOC removed</td>
<td>[109]</td>
</tr>
<tr>
<td>Norfloxacin (NOR)</td>
<td>Photo-electrochemical oxidation</td>
<td>Pharmaceutical</td>
<td>100% NOR degradation, 83.9% TOC removed</td>
<td>[110]</td>
</tr>
<tr>
<td>Oily wastewater from restaurant</td>
<td>Photocatalytic oxidation</td>
<td>Oily water</td>
<td>63% COD &amp; 70% oil removed</td>
<td>[111]</td>
</tr>
<tr>
<td>Real dyeing wastewater</td>
<td>Electro-Fenton oxidation</td>
<td>Dyeing wastewater</td>
<td>75.2% COD removed</td>
<td>[112]</td>
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<td>------------------------</td>
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<tr>
<td>Fulvic acid (FA)</td>
<td>CWAO</td>
<td>Landfill leachate</td>
<td>100% conversion of FA, 77.8% COD removed</td>
<td>[113]</td>
</tr>
<tr>
<td>Hospital wastewater</td>
<td>Fenton oxidation</td>
<td>Pharmaceutical</td>
<td>100% phenolic, 70% COD, 50% TOC removed</td>
<td>[114]</td>
</tr>
<tr>
<td>Rh B</td>
<td>Photocatalytic oxidation</td>
<td>Dyeing wastewater</td>
<td>98% Rh B removed</td>
<td>[115]</td>
</tr>
<tr>
<td>Gasoline, engine oil &amp; diesel</td>
<td>Air diffusion-electrochemical oxidation-magnetic biochar</td>
<td>Oily wastewater</td>
<td>99.7% oil, 95% COD removed</td>
<td>[116]</td>
</tr>
<tr>
<td>Pharmaceutical sludge</td>
<td>CWAO</td>
<td>Pharmaceutical</td>
<td>72.6% COD, 87.3% volatile suspended solids removed</td>
<td>[117]</td>
</tr>
<tr>
<td>Raw landfill leachate</td>
<td>CWAO</td>
<td>Landfill leachate</td>
<td>83.7% decolorization, 56.8% COD&lt;sub&gt;Cr&lt;/sub&gt; removed</td>
<td>[118]</td>
</tr>
<tr>
<td>Rh B</td>
<td>SR-AOP</td>
<td>Dyeing wastewater</td>
<td>100% Rh B degraded</td>
<td>[119]</td>
</tr>
<tr>
<td>Triclosan (TCS), bisphenol A (BPA), sulfamethoxazole (SMX)</td>
<td>Electro-CWAO</td>
<td>Pharmaceutical</td>
<td>92.9% TCS, 90.8% BPA, 90.2% SMX mineralization</td>
<td>[120]</td>
</tr>
<tr>
<td>Cutting oil &amp; bulk feed</td>
<td>Photocatalytic oxidation combined with hollow fiber membrane</td>
<td>Oily wastewater</td>
<td>80% TOC degradation</td>
<td>[121]</td>
</tr>
<tr>
<td>Direct Red 81 (DR81)</td>
<td>Sono-Fenton oxidation</td>
<td>Dyeing wastewater</td>
<td>99% decolorization efficiency, 66.7% mineralization</td>
<td>[122]</td>
</tr>
<tr>
<td>Acetaminophen (ACT)</td>
<td>Photocatalytic oxidation</td>
<td>Pharmaceutical</td>
<td>100% ACT degradation, 61% mineralization</td>
<td>[123]</td>
</tr>
<tr>
<td>Fulvic acid (FA)</td>
<td>Catalytic ozonation</td>
<td>Landfill leachate</td>
<td>83% FA removed</td>
<td>[124]</td>
</tr>
<tr>
<td>Semi-aerobic sanitary landfill</td>
<td>Electrochemical oxidation</td>
<td>Landfill leachate</td>
<td>84% color, 70% BOD, and 68% COD were removed</td>
<td>[125]</td>
</tr>
</tbody>
</table>

### 3CONCLUSION

In this article, we have summarized the working principles and influencing factors of various advanced oxidation processes, followed by their application in real-world wastewater treatment. Although every method follows a different mechanism, the generation of ROS (e.g., $\bullet$OH, $\bullet$SO<sub>4</sub>–, and $\bullet$O<sub>2</sub>– etc.) is a common parameter for all AOPs. All ROS have a high oxidation capacity to degrade the organic pollutants present in wastewater. However, the rate of degradation depends on various factors such as pollutant concentration, pH, reagent concentration, reaction time, and a few more. The advantages of these growing wastewater treatment techniques are high degradation capacity and no formation of secondary pollutants. AOPs are classified based on methods used to generate ROS: photocatalysis, ozonation, photolysis, Fenton oxidation, sonolysis, CWAO, SR-AOP, and MW degradation. Different AOPs have their own limitations when it comes to practical implementation. Primarily, the high treatment cost and certain reaction conditions required, limit the efficiency of AOPs.
For instance, the Ozonation method requires an alkaline medium, whereas Fenton oxidation works well in acidic conditions. To achieve the best results in both cases pH should be strictly maintained, this pH regulation will lead to high treatment costs. The combination of AOP techniques has been observed to deliver more efficient results as compared to individual AOP treatment. This is an outcome of the synergistic effect of the two techniques, oxidation capacity gets increased to a higher extent. Pretreatment processes such as coagulation, sedimentation, and floatation can also be introduced to enhance the biochemical quality of wastewater. When electrochemical oxidation is combined with other AOPs, it prevents the inactivation of the electrode and widens the scope of application.

4 CHALLENGES

We live in an era of growing Industrialization. The need for finished goods has increased drastically over the decade. In the meantime, a lot of environmental problems have emerged. One of them is the lack of clean water, which is required on daily basis for different utilities. However, researchers are continuously working on reducing the wastewater generated, but the problem is not that easy to deal with. To enhance the water quality and degrade the various pollutants present, different AOP techniques are being investigated. Although these methods show positive signs for the betterment of wastewater treatment, there are various challenges too. This includes the generation of by-products in some of the oxidation processes which are more toxic than the original pollutant. To deal with this there should be a proper toxicology report prepared for each case. It will help in monitoring the toxicity level of treated wastewater, before discharging it into the water bodies. Another challenge is the use of appropriate catalysts. A catalyst is a major factor in any reaction, so its formation is also an important aspect. The preparation of the catalyst should be low cost and a green route for synthesis should be adopted, if possible. All in all, AOPs are the future of wastewater treatment, so innovative ideas should be explored for the reaction conditions, and beneficial combinations with traditional non-AOP methods should be examined.

5 REFERENCES


