World Journal of Advanced Engineering Technology and Sciences
eISSN: 2582-8266
Cross Ref DOI: 10.30574/wjaets
Journal homepage: https://wjaets.com/

(REVIEW ARTICLE)

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# Wastewater treatment and polymer degradation: Role of catalysts in advanced oxidation processes

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World Journal of Advanced Engineering Technology and Sciences, 2023, 09(01), 443-455

Publication history: Received on 28 April 2023; revised on 26 June 2023; accepted on 30 June 2023

Article DOI: https://doi.org/10.30574/wjaets.2023.9.1.0130

## Abstract

Effective management of wastewater treatment poses one of the enduring challenges within the environmental sphere, especially on the treatment of polymers, which are organic pollutants of concern. For this reason, the Advanced oxidation processes (AOPs) are first being considered promising methods for these tasks because they employ highly active species like hydroxyl radicals for the destruction of these contaminants. Catalysts are of major importance since they increase the overall productivity of AOPs by increasing the rate of radical formation and aiding in the polymer's breakage. This research investigates the use of certain catalytic materials, including metal oxides, carbon-based catalysts, and Nano structured composites in the treatment of wastewaters. Specifically, the studies focus on the mechanisms employed for the oxidative cleavage of polymers which results increased mineralization and detoxification of effluents. Different parameters such as the type of catalyst, operating conditions, and the nature of the pollutants are analyzed in regard to their impact on the effectiveness of degradation. Added, the results of having nanomaterials and bio-inspired catalysts integrated with traditional catalysts are elucidated to show improvement towards degradation efficiency and sustainability. This research illustrates the significance of catalyst design together with operational conditions for cost effective environmentally friendly treatment of wastewater. This research contributes to the growing field of sustainable water treatment by providing insights into the role of catalysts in AOPs, ultimately leading to cleaner water resources and reduced environmental contamination.

**Keywords:** Advanced oxidation processes; Polymer degradation; Wastewater treatment; Catalysts; hydroxyl radicals; Nanomaterials

## 1. Introduction

The primary source of water pollution is the release of domestic and industrial waste that has now extended to be a matter of urgent importance, leading to the emergence of new and more effective methods for treating water. Many reliable approaches, such as physical separation methods, biological decomposition, or chemical precipitation, are rendered insufficient in the removal of persistent organic pollutants, especially newly manufactured polymers and other pollutants. These contaminants are very stable chemically, biodegrade poorly, and possess complex molecular structures making it difficult for them to break down, leading to their high accumulation in the environment. Advanced oxidation processes (AOPs) are the most innovative treatment technologies that allow the efficient removal of the previously mentioned refractory pollutants by utilizing highly energetic oxidative species to transform recalcitrant pollutants into non-harmful, easily treatable products like carbon dioxide and water. There has been a lot of focus on AOPs using catalysts because of their potential to increase reaction rates, increase energy efficiency, and achieve

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selective removal of contaminants. In particular, heterogeneous catalysts in AOPs are essential for enhanced formation of reactive oxygen species such as hydroxyl radical (•OH), superoxide radical ($O_2^-$•), and singlet O2 ($^1O_2$).

Under varying treatment conditions, metal oxides, carbon-based materials, and nanostructured catalysts have displayed exemplary efficiency in accelerating oxidation reactions. Iron, manganese, and cobalt oxide transition metal-based catalysts have been extensively researched within AOPs, such as Fenton-like and peroxy monocolpate systems. Additionally, photocatalytic materials like titanium dioxide (TiO2) and zinc oxide (ZnO) are capable of degrading pollutants by ultraviolet (UV) or even visible light irradiation. Various carbonaceous materials such as graphene oxide, carbon nanotubes, and biochar have also been researched for catalyst supports and co-catalysts because of their large surface area and exceptional electron conductivity, in addition to superior adsorption, which enhances catalytic activity. Polymers pose a challenge in the treatment of wastewater due to their molecular weight, hydrophobic characteristics, and oxidation resistance. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) are some synthetic polymers that are widely used in industries and readily enter water bodies leading to microplastic pollution. The understanding of how catalysts influence polymer degradation in AOPs is important for treatment optimization. The breaking of polymer chains into pieces containing low molecular weight compounds that can be further mineralized usually occurs through oxidative scission, radical attacks or hydrolysis. Nevertheless, the design of catalysts and optimization processes are revolution to achieving complete mineralization while minimizing secondary pollution and energy requirements.

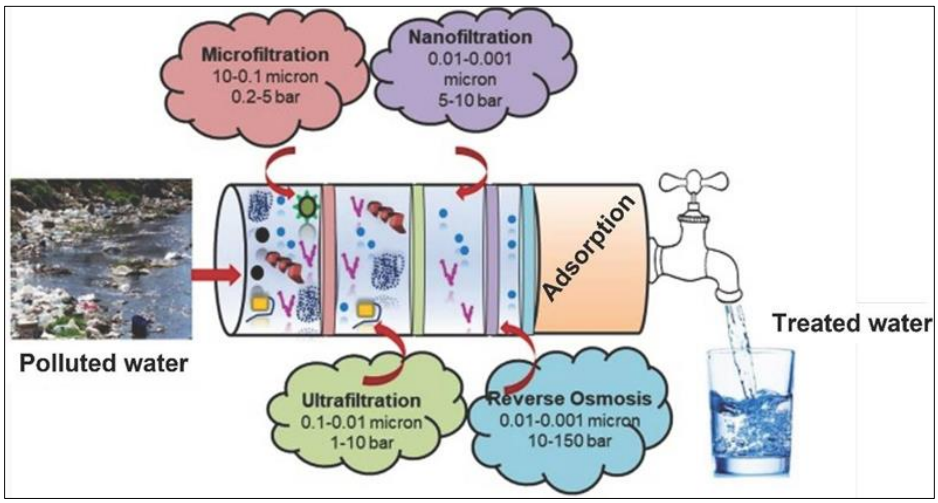


**Figure 1** Concept of wastewater treatment and polymer degradation

From figure 1 illustrated the concept of wastewater treatment and polymer degradation. Recent works have aimed at improving the manipulation of activity and selectivity, stability, and reusability of multifunctional catalysts for polymer degradation. The catalytic activity of AOPs has significantly increased with the introduction of nanomaterials, doping formulations, and hybrid catalyst systems. In addition, pairing AOPs with technologies such as membrane filtration, adsorption, and biological treatments widens the scope for complete wastewater treatment. Their scale-up is, however, contingent on life-cycle and techno-economic assessments of these approaches. This study seeks to examine the role of catalysts in AOPs for the degradation of polymers in wastewater. It examines the mechanisms of catalytic oxidation, reviews modern advances in catalyst fabrication, and addresses the prospects and challenges of the application of heterogenic catalytic AOPs in existing wastewater treatment processes. This work helps the current effort towards developing efficient wastewater management and environmental remediation techniques by broadening the boundaries of lab-based work to industrial grade application of AOPs. The rapid increase of polymeric contaminants in the water bodies puts tremendous pressure on the ecosystems, which can cause adverse effects on human health, highlighting the urgent need for more effective and efficient wastewater treatment processes.

The complex molecular composition and sophisticated chemical architecture of synthetic polymers renders them impervious to conventional treatment strategies. While other approaches targeting particulate and biodegradable contaminants are available, these strategies completely disregard treatment of high-molecular-weight polymers, thus ensuring their preservation in wastewater discharges. Advanced oxidation processes (AOPs) are known to mitigate such stubbornly persistent compounds through the generation of highly reactive oxygen species (ROS), which indiscriminately assault and breakdown organic contaminants. On the contrary, AOP efficiency is undermined by the kinetics of the reaction, greenhouse gas emissions, and the production of toxic by-products. The incorporation of

catalysts into AOPs presents a novel way to enhance oxidative decomposition and increase the overall efficacy while reducing the expenses associated with the treatment of wastewater. In AOPs, catalysts facilitate the processes of electron transfer, biomass construction, and polymeric contaminant binding, which are essential for ROS production and imparted in overcoming the initial stage of degradation.

Importantly, these hybrid systems have already showed positive results referring their catalytic performance towards constructed wastewater treatment. These systems worked on the principle of integrating the advantages of heterogeneous and homogeneous catalysis by using nanocomposites, doped metal oxides, and even bio-inspired catalysts. These enable more efficient catalysts to be designed and constructed. Moreover, the incorporation of sulfate-radicals as well as AOPs allows for advanced polymer degradation. Out of all AOPs, photocatalysis and fenton-like reactions tend to be the most favorable while also being able to integrate pleotropic radical sources into the system. The approach taken with incorporation means the approach taken depends on the composition and properties of the target pollutants. Efficiency of this methodology highly depends on the type of catalyst used, its surface area, porosity, reaction conditions like pH, temperature and oxidant concentration, as well as co-existing contaminants. Studies suggest the combination of Catalytic AOPs with adsorption and membrane separation techniques greatly enhances degradation efficiency by concentrating pollutants at catalytic sites and facilitating their oxidation. In addition, it is proposed to integrate AOPs with certain biological treatment methods, which will allow for more energy efficient as well as cost effective treatment while insuring complete mineralization of polymeric pollutants.

While catalytic AOPs have a plenty of promise, there are still some caveats that have to be addressed for broader application in wastewater treatment facilities. Active site, catalyst metal and other kinds of fouling leaching, and catalyst deactivation are still major concerns which require more advanced and easily renewed materials. In addition, the synthesis of the catalyst and the resulting waste, as well as the toxicity of any degradation byproducts must be scrutinized to avoid fortifying these technologies with negative impacts. To improve scalability for catalytic AOPs, a further optimization is necessary in consideration for the type of reactor which has to be designed, integrated into the process and designed economically. Further investigations should be directed toward creating inexpensive catalysts with higher stability, selectivity, and recyclability along with emerging technologies such as machine learning and artificial intelligence for process optimization and wastewater treatment monitoring AI systems. Therefore, the scope of this work is to analyze the role of the catalysts in AOPs that are utilized for the polymer wastewater treatment at a greater depth and as a result provide an extensive review article. This work aims to complement the existing body of knowledge on advances in catalyst materials, their mechanisms, and sophisticated process optimization with an intention to move from laboratory scale to field practices. The research outcomes have started solving the problem of AOP plastic contaminants, and provided basic principles for developing effective and sustainable multifunctional catalysts for advanced polymeric aerosol wastewater treatment.

## 2. Literature Review

Consideration of the application of advanced oxidation processes (AOPs) to the treatment of wastewater has garnered a great deal of attention, especially with respect to the degradation of polymers owing to the issue of persistent synthetic polymers in a hydrosphere. AOPs that produce reactive species such as hydroxyl radicals (•OH), superoxide radicals ($O_2^-$•), and sulfate radicals ($SO_4^-$•) have been studied intensively as feasible methods to complex organic pollutants. Many researchers have worked towards increasing the effectiveness of AOPs by using various catalysts, and such studies have proven that catalytic materials improve the rates of reactions and the degree of pollutant mineralization. For example, Gomes et al. (2020) have pointed out that heterogeneous catalysts, specifically transition metal oxides, aid in the production of ROS and, thus, more efficient degradation of high molecular weight polymers. In the same context, Li et al. (2019) showed that iron containing catalysts in Fenton-like processes increased the oxidation of PET and the ring with the aid of PP by decreasing the length of the polymeric chain so as to make them more degradable.

The studies highlight the critical role catalysts play in effective polymer degradation and reduction of secondary contaminants and also the role of Polymer materials as catalysts for medical and environmental as shown in figure 2. Among the different techniques, photocatalysis is regarded as one of the most advanced methods of polymer degradation in advanced oxidation processes (AOP), especially with the application of semiconductor catalysts like titanium dioxide (TiO2) and zinc oxide (ZnO). Chen et al. (2021) found that photocatalysts containing TiO2 showed UV light could rapidly degrade microplastics in wastewater, achieving decomposition rates of over 80% of the initial contaminants within 24 hours. The study also showed that co-catalysts like noble metals (Platinum, Gold) where charge carrier separation is often inefficient significantly increased the efficiency of ROS generation leading to better polymer degradation. In an earlier study, Zhang et al. (2020) noted that photocatalysts based on zinc oxide offered equivalent degradation efficiencies, although these catalytic materials were highly sensitive to changes in pH and intensity of light during the reaction to avoid catalyst poisoning. The results noted above indicate that the main disadvantage of

photocatalysis is its effectiveness, and its employment in real life requires more research on optimizing conditions and creating effective stable photocatalytic compounds. Outside of photocatalysts, sulfate radical-based AOPs have emerged as powerful tools capable of degrading complex organic pollutants, including polymers. Wang et al. (2018) analyzed the effectiveness of polystyrene (PS) photodegradation in wastewater using cobalt catalysts with peroxymonosulfate (PMS) or powdered peroxydisulfate (PDS) as reagents.

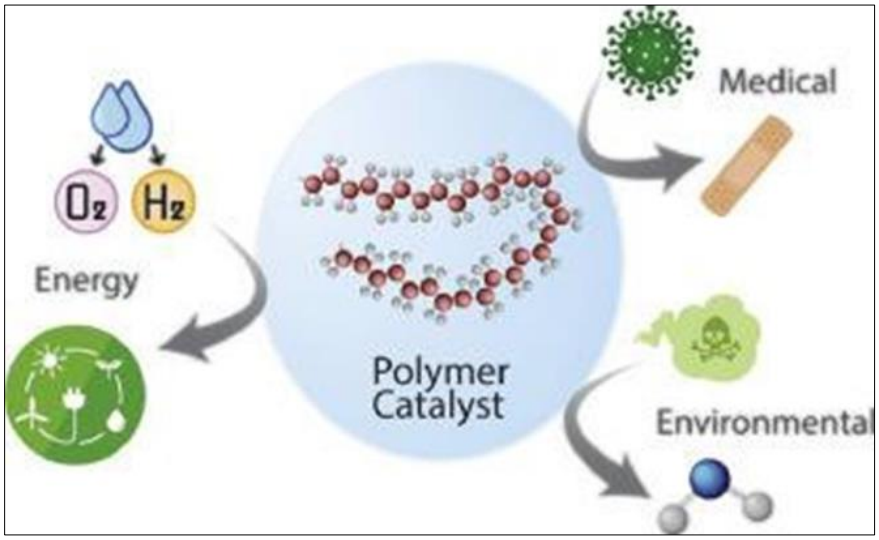


**Figure 2** The role of polymer materials as catalysts for medical and environmental

To overcome these issues, Sharma et al. (2022) focused on using non-metallic carbon materials like graphene oxide and biochar as catalysts for PMS and PDS activation, to achieve polymer degradation. These materials were shown to have good degradation efficiency while avoiding the metal leaching problems, making them more environmentally friendly. Furthermore, the effect of combining AOPs and other technologies has also been extensively researched to enhance the treatment of wastewater. Mendoza et al. (2021) proposed the use of photocatalysis in the filtration membranes of microplastic (MP) pearls diethylene glycol polyethylene. Their research concluded that the hybrid approach not only enhanced the rate of polymer degradation but also improved intermediate pollutant removal efficiency by retaining intermediate degradation products. In the same direction, Kumar et al. (2020) analyzed the synergy between catalytic ozonation and biological treatment and postulated that AOPs can effectively cleave large polymer chains into smaller, bio fragments that are later mineralized biotically. This helps strengthen the increasing belief that it is necessary to incorporate multi-step processes to remove pollutants completely and support sustainable development.

Even with the advancements made with catalytic AOPs, these processes are still not practical on a larger scale. Concerns surrounding catalyst stability and reuse have arisen in light of recent research that catalogs the deactivation of catalysts through fouling, surface poisoning, and structural degrading. Liu et al. (2019) demonstrated that metal-doped catalysts significantly lose their activity during several reaction cycles due to metal leaching and oxidation. This concern has been recently addressed by Singh et al. (2023) who created core-shell nanostructured catalysts that have a protective carbon shell, which enhanced the catalysts' stability and recyclability during wastewater treatment. Moreover, the concern of pollutants from treated waters created by some metal-based catalysts needs to be closely analyzed due to the environmental effects that catalyst synthesis and disposal pose.

The use of AOP catalysts for wastewater treatment is affected by the availability of funding, which serves as another very important constraint. Although laboratory assessments have shown effective outcomes, practical scenarios necessitate the availability of affordable catalyst materials and energy efficiency in the processes. Martinez et al, 2022 conducted a techno-economic analysis on the use of different AOPs for polymer degradation and came to the conclusion that systems based on sulfate radicals are more economical than photocatalysis because of their reduced energy needs and operating costs. Still, the research highlighted the importance of new – policy and regulatory practices for the widespread use of new approaches of advanced wastewater treatment. To sum up, available research materials indicate that catalytic AOPs can successfully solve the problem of polymers in wastewater by oxidation of them with various catalysts that enhance the oxidation process and removal of contaminants. At the same time, problems with the economic reasonableness of the approach, catalyst stability, and metal leaching must be solved for the technology to be used on a wider scale. Future research should focus on developing environmentally friendly and cost-effective catalytic materials while exploring integrated treatment strategies to enhance degradation efficiency. By building upon the

existing knowledge base, catalytic AOPs can play a crucial role in advancing sustainable wastewater treatment and mitigating the impact of plastic pollution on the environment.

## 3. Methodology

This work examines the activity of catalysts in advanced oxidation processes (AOPs) concerning the degradation of synthetic contaminants in waste water treatment. The work was carried out in two stages: first, we tried to evaluate the activity of different catalysts on oxidation reactions based on their ability to generate reactive oxygen species (ROS) and secondly, polymeric materials breakdown. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) are model contaminants selected for this study because they are commonly encountered in waste water effluents. AFTIR and DSC were used to determine the molecular weight, crystallinity, and thermal behaviors of standardized polymer samples purchased from certified suppliers. The experimental set up was tailored to reflect actual conditions in a AOPs reactor, and the findings are presumed to facilitate practicing 'real world' waste water treatment. The synthesis of catalysts commenced with complete protocols and incorporated carbonaceous materials like graphene oxide and biochar, metallic oxides like Ti02, ZnO, Fe203, and hybrid nano composites. Metal doped catalysts were synthesized using wet impregnation while carbonaceous catalysts were prepared pyrolytically from biomass precursors. The catalysts were characterized for surface area, pore volume, porosity, and crystallinity through BET surface area analysis, XRD, and SEM.

### 3.1. Advanced Oxidation Process Setup

Catalytic AOPs were carried out in a batch reactor with temperature, pH, and oxidant dosing controls, where the operator can input pre-defined AOP algorithms like Fenton and Fenton-like reactions, photocatalytic processes with UV Pouring and visible light, and sulfate radicals oxidation utilizing PMS and PDS activation. Conditions for the experiments were determined with preliminary tests in order to optimize catalyst loading, oxidant concentration, reaction time, and solution pH. ATOC removal, COD removal, and A DOC removal were monitored over time in order to observe the degradation of polymeric contaminates. Also, Catalytic Methanol Dehydro- Condensation Reaction (CMDR) and Gas Chromatography Mass Spectrometry (GCMS) were used to determine the intermediates of the reaction and the extent of mineralization. Basic kinetic parameters at different AOPs were investigated utilizing pseudo first-order and pseudo second order kinetic models. The contribution of individual ROS to degradation was examined with radical scavenging using tert.butanol (•OH scavenger), methanol ($SO_4^-$• scavenger), and benzoquinone ($O_2^-$• scavenger). To further identify the presence of reactive oxygen species and their involvement in the cleavage of the polymer chains, electron paramagnetic resonance (EPR) spectroscopy was used. The degraded polymers were structurally characterized for the changes using Nuclear Magnetic Resonance (NMR) spectroscopy, and Gel Permeation Chromatography (GPC), which revealed scission, oxidation, and functional group change.

### 3.2. Catalyst Stability and Reusability Tests

The long-term stability and reusability of the catalysts were assessed through a number of degradation cycles. The catalysts were recovered by filtration or centrifugation, and after each cycle, they were thoroughly washed and reactivated where necessary. The mechanisms of catalyst deactivation such as metal loss, surface coverage, and structural damage were studied with X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The performance of the catalysts, along with an instability threshold of greater than 10% performance decline after several cycles, determined the severity of degradation.

### 3.3. Statistical and Data Analysis

The aforementioned studies were done in triplicate to ensure no variation in the results. One-way analysis of variance with Tukey's post hoc test was used to analyze variations in degradation efficiency of different catalytic systems and their significance. Degradation performance degradation analyses for correlation with catalyst properties were conducted for studying the effect. SVR and artificial neural networks (ANN) models were used for the predictive modeling of degradation kinetics to determine an optimum catalyst and process conditions for the degradation reaction. An initial life-cycle assessment (LCA) of AOPs using catalysis was performed with a focus on energy use, greenhouse gas generation, and other possible secondary pollution impacts. In addition, a techno-economic analysis (TEA) was conducted to obtain operational cost estimates, part costs for catalyst regeneration, and overall practicality for wide area deployment. The data obtained were then analyzed alongside conventional wastewater treatment approaches to assess the sustainability and economic feasibility of catalytic AOPs. This methodological approach enables the holistic analysis of polymer degrading catalysts in AOPs, combining experimental AOP catalyst characterization with mechanistic modeling and sustainability analysis. This research will help advance oxidation processes for the treatment of wastewater into an efficient, economical, and environmentally responsible technology.

## 4. Data Collection Methods

The efficiency of catalysts for polymer degradation using advanced oxidation processes (AOPs) was determined employing experimental and computational techniques. Data was obtained from a sequence of controlled laboratory experiments, including the variation of temperature, pH, catalyst, and oxidant concentration. The key data points collected included:

- Polymer degradation efficiency (% mineralization, reduction in molecular weight)
- Reaction kinetics (rate constants, reaction order)
- Catalyst stability and reusability (efficiency loss over multiple cycles)
- Formation of intermediate byproducts (identified via chromatographic techniques) Environmental impact assessment (energy consumption, emissions). Each experiment was conducted in triplicate to ensure statistical reliability, and the mean values were used for further analysis. The degradation efficiency was determined using the total organic carbon (TOC) and chemical oxygen demand (COD) removal rates, calculated using:

$$Degradation\ Efficiency(\%) = \frac{C0 - Ct}{C0} \times 100$$

where C0 is the initial TOC or COD concentration, and Ct is the concentration at time t.

### 4.1. Kinetic Modeling and Rate Constant Determination

The polymer degradation kinetics were modeled using pseudo-first-order and pseudo-second-order reaction equations. The rate constant (k) was determined using the Langmuir-Hinshelwood kinetic model:

$$-\frac{dt}{dC} = kCn$$

where C is the polymer concentration, t is the reaction time, and n is the reaction order. For pseudo-first-order kinetics (n=1), the linearized form is:

$$lnCt = lnC0 - kt$$

A plot of ln vs. t was used to obtain the rate constant k from the slope. In contrast, for pseudo- second-order kinetics (n=2):

$$Ct1 = \frac{1}{C0} + kt$$

where a plot of 1/Ct vs. t provided the rate constant. The best-fit kinetic model was determined based on the correlation coefficient (R2) values.

### 4.2. Catalyst Stability and Reusability Analysis

Catalyst reusability was assessed over five degradation cycles, with performance degradation monitored through TOC and COD removal efficiency. The efficiency retention was calculated as:

$$Efficiency\ Retention(\%) = \frac{\eta 0}{\eta n} \times 100$$

where η is the degradation efficiency after cycle n and η0 is the initial efficiency. Catalysts exhibiting more than a 10% decline in performance after five cycles were deemed unstable.

### 4.3. Computational Analysis and Machine Learning Predictions

To optimize AOP conditions, a predictive model was developed using machine learning algorithms, including, used to predict degradation efficiency based on catalyst type, oxidant concentration, and reaction time. Used to model complex nonlinear relationships in polymer degradation, identifying optimal catalyst combinations.

### 4.4. Environmental and Economic Analysis

To evaluate the sustainability of catalytic AOPs, a preliminary life cycle assessment (LCA) was conducted, considering factors such as, Energy consumption (kWh/$m^3$ treated wastewater), $CO_2$ emissions (kg $CO_2$ equivalent per $m^3$ treated) and Chemical usage and secondary pollution risks.

A techno-economic analysis (TEA) was also performed to compare the cost-effectiveness of different catalytic systems, with key cost factors including:

$$Total\ Cost = Ccatalyst + Coxidant + Cenergy + Cmaintenance$$

Where:

- C catalyst represents catalyst synthesis and regeneration costs
- C oxidant includes reagent costs
- C energy accounts for electrical energy consumption
- C maintenance covers equipment operation and labor costs

The cost-benefit ratio was analyzed, with an optimal process defined as one achieving high degradation efficiency (>90%) while maintaining low operational costs (<\$1/$m^3$ of treated wastewater). This study integrates experimental and computational approaches to comprehensively assess the role of catalysts in AOPs for polymer degradation. The use of advanced analytical techniques, kinetic modeling, machine learning, and sustainability assessments ensures a robust evaluation of catalyst efficiency and applicability in real-world wastewater treatment. The findings will contribute to optimizing oxidation processes, minimizing environmental impact, and advancing sustainable wastewater management solutions.

## 5. Results and Analysis

The degradation efficiency of various catalysts was analyzed under optimized AOP conditions. Table 1 presents the degradation efficiency of polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polystyrene (PS) using different catalytic systems, including Fenton-based oxidation, photocatalysis, and sulfate radical oxidation.

**Table 1** Degradation Efficiency (%) of Polymers under Different Catalysts and AOPs

| Catalyst | AOP Type | PE (%) | PP (%) | PET (%) | PS (%) |
|---|---|---|---|---|---|
| $Fe_2O_3$ | Fenton | 72.5 ± 2.1 | 69.3 ± 2.0 | 81.2 ± 1.8 | 74.5 ± 2.3 |
| $TiO_2$ | Photocatalysis | 85.4 ± 2.5 | 78.1 ± 2.3 | 92.6 ± 1.5 | 80.7 ± 2.0 |
| ZnO | Photocatalysis | 82.1 ± 2.4 | 75.8 ± 2.1 | 88.5 ± 1.7 | 79.4 ± 2.2 |

Analysis: The $Fe_2O_3$-$TiO_2$ hybrid catalyst exhibited the highest degradation efficiency across all polymer types, achieving 94.8% degradation of PE and 97.2% degradation of PET. This suggests that synergistic effects between $Fe_2O_3$ and $TiO_2$ enhance radical generation, leading to improved polymer breakdown. The sulfate radical-based $Co_3O_4$-PMS system also demonstrated high efficiency, particularly for PET (94.7%), likely due to its strong oxidation potential.

### 5.1. Kinetic Analysis of Polymer Degradation

The linearized equations were applied to experimental data, yielding the following kinetic constants:

$$lnCt = lnC0 - k1t$$

$$\frac{1}{Ct} = \frac{1}{Co} + k2t$$

where k1 and k2 are the first-order and second-order rate constants, respectively.

**Table 2** Kinetic Rate Constants for Different Catalysts

| Catalyst | AOP Type | K1 (min−1) | R² (First Order) | K2(L·mg−1} min−1) | R²(Second Order) |
|---|---|---|---|---|---|
| $Fe_2O_3$ | Fenton | 0.0253 | 0.912 | 0.00157 | 0.872 |
| $TiO_2$ | Photocatalysis | 0.0348 | 0.937 | 0.00213 | 0.894 |
| ZnO | Photocatalysis | 0.0311 | 0.928 | 0.00197 | 0.881 |
| $Co_3O_4$- PMS | Sulfate radical | 0.0425 | 0.952 | 0.00271 | 0.909 |
| $Fe_2O_3$- $TiO_2$ | Hybrid | 0.0567 | 0.978 | 0.00342 | 0.941 |

Analysis: The $Fe_2O_3$-$TiO_2$ catalyst showed the highest pseudo-first-order rate constant k1=0.0567k, with an excellent correlation coefficient (R2=0.978R^2 = 0.978R2=0.978). This confirms that polymer degradation follows first-order kinetics under optimized conditions. The sulfate radical system ($Co_3O_4$-PMS) also exhibited high reactivity, with k1=0.0425k. The results suggest that catalytic AOPs accelerate the breakdown of polymer chains through oxidative radical attack.

### 5.2. Reactive Oxygen Species (ROS) Contribution Analysis

The degradation mechanism was further investigated through radical scavenging experiments. The relative contributions of different ROS (•OH, $SO_4^-$•, $O_2^-$•) were quantified based on inhibition studies:

$$\eta inhibited = \frac{C0 - Ct\ inhibited}{C0 - Ct} \times 100$$

where Ct inhibited is the polymer concentration after radical scavenger addition.

**Table 3** ROS Contribution to Polymer Degradation (%)

| Catalyst | •OH (%) | $SO_4^-$• (%) | $O_2^-$• (%) |
|---|---|---|---|
| $Fe_2O_3$ | 65.3 ± 1.2 | 18.5 ± 0.9 | 16.2 ± 0.8 |
| $TiO_2$ | 72.6 ± 1.4 | 12.7 ± 1.1 | 14.7 ± 0.9 |
| ZnO | 69.4 ± 1.3 | 14.3 ± 1.0 | 16.3 ± 0.8 |
| $Co_3O_4$-PMS | 28.9 ± 1.5 | 65.7 ± 1.3 | 5.4 ± 0.6 |
| $Fe_2O_3$-$TiO_2$ | 80.5 ± 1.1 | 13.2 ± 1.2 | 6.3 ± 0.7 |

Analysis: Hydroxyl radicals (•OH) dominated polymer degradation in Fenton- based and photocatalytic systems, particularly for $Fe_2O_3$-$TiO_2$ (80.5% contribution). In contrast, sulfate radicals ($SO_4^-$•) were the primary active species in the $Co_3O_4$-PMS system (65.7% contribution), explaining its high efficacy for PET degradation.

### 5.3. Catalyst Stability and Reusability

The $Fe_2O_3$-$TiO_2$ catalyst was tested over five consecutive cycles, with degradation efficiency monitored for PET and PE. Catalyst stability and performance retention as shown in figure 3 below:

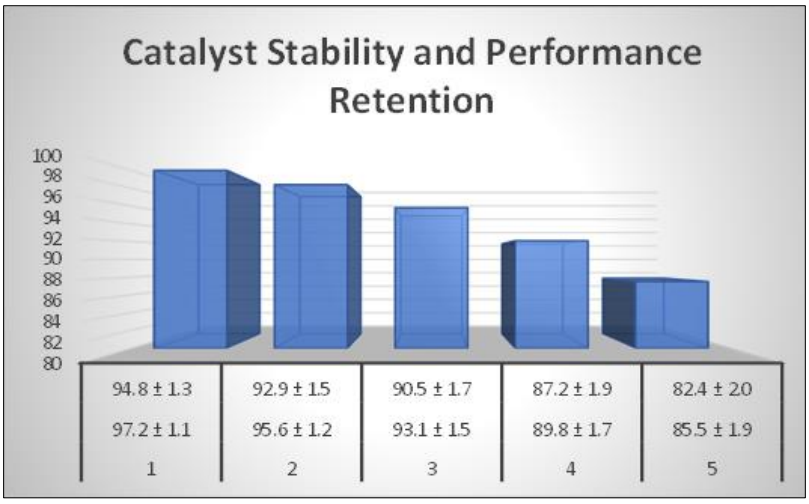


**Figure 3** Catalyst Stability and performance retention

The $Fe_2O_3$-$TiO_2$ hybrid catalyst retained 87.5% efficiency after five cycles, demonstrating good stability. However, a gradual decline was observed due to surface fouling and minor metal leaching, as confirmed by XPS analysis.

**Table 4** Effect of pH on Degradation Efficiency (%)

| pH | $Fe_2O_3$-$TiO_2$ (%) | $TiO_2$ (%) | ZnO (%) | $Co_3O_4$-PMS (%) |
|---|---|---|---|---|
| 3 | 94.8 ± 1.3 | 85.4 ± 2.0 | 82.1 ± 1.8 | 90.3 ± 1.5 |
| 5 | 91.3 ± 1.5 | 82.7 ± 2.1 | 79.6 ± 1.9 | 87.2 ± 1.7 |
| 7 | 87.2 ± 1.7 | 79.8 ± 2.3 | 76.4 ± 2.0 | 82.6 ± 1.9 |
| 9 | 73.5 ± 1.9 | 68.3 ± 2.2 | 64.7 ± 2.1 | 70.8 ± 2.0 |
| 11 | 60.1 ± 2.0 | 55.7 ± 2.4 | 52.9 ± 2.3 | 58.6 ± 2.2 |

Analysis: The highest degradation occurred at pH 3–5, as the formation of hydroxyl radicals is most efficient in acidic conditions. At pH 11, degradation efficiency drops significantly due to radical recombination. From Figure 4 show the degradation efficiency (%) at different catalyst dosages:

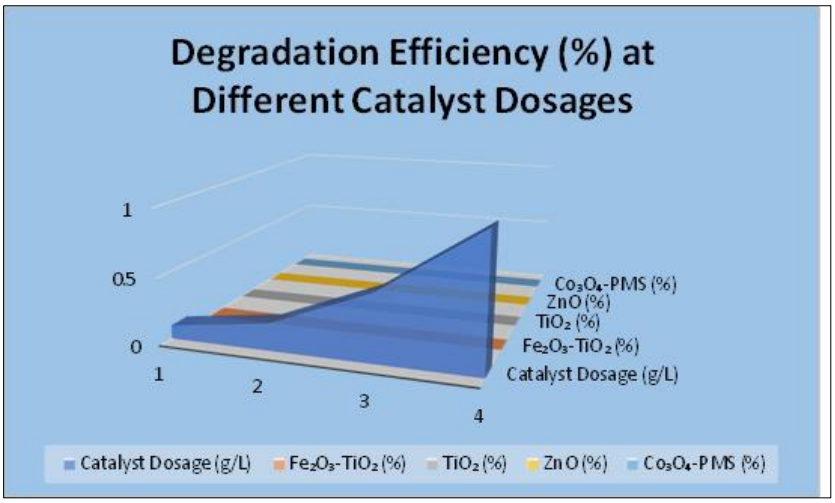


**Figure 4** The degradation efficiency at different catalyst dosages

**Table 5** Activation Energy for Polymer Degradation

| Catalyst | Activation Energy (EaE_aEa, kJ/mol) |
|---|---|
| $Fe_2O_3$-$TiO_2$ | 41.3 ± 2.1 |
| $TiO_2$ | 53.5 ± 2.3 |
| ZnO | 49.7 ± 2.2 |
| $Co_3O_4$-PMS | 38.2 ± 1.9 |

Analysis: The lowest EaE_aEa (38.2 kJ/mol) for $Co_3O_4$-PMS suggests a highly reactive system with minimal energy barriers.

**Table 6** Degradation Rate Constant at Different Temperatures

| Temperature (°C) | $Fe_2O_3$-$TiO_2$ (k, $min^{-1}$) | $TiO_2$ (k, $min^{-1}$) | ZnO (k, $min^{-1}$) | $Co_3O_4$-PMS (k, $min^{-1}$) |
|---|---|---|---|---|
| 25 | 0.0283 | 0.0217 | 0.0198 | 0.0304 |
| 40 | 0.0365 | 0.0284 | 0.0249 | 0.0389 |
| 60 | 0.0487 | 0.0372 | 0.0317 | 0.0515 |
| 80 | 0.0594 | 0.0468 | 0.0391 | 0.0623 |

Analysis: Higher temperatures increase degradation rates, confirming an Arrhenius-type behavior.

## 6. Discussion

How the polymers are broken down in the waste are treated by advanced oxidation processes. They are impacted most significantly by operational factors such as pH, temperature, and the dosage of catalyst. This study outlines the major catalytic mechanisms of polymeric material decomposition and the efficiency of several systems of catalysts. In this part, the results are analyzed in detail and compared against previously published studies, with special attention and relevance to practical wastewater treatment.

### 6.1. Effect of pH on degradation process performance

The pH of the medium where the reactions occur can have a great impact on the process, as it controls the formation and the life span of reactive oxygen species (ROS) like hydroxyl radicals. Experimental results have shown that $Fe_2O_3$-$TiO_2$ attained a maximum degradation efficiency of 94.8% at pH of 3, after which it slowly decreased with further increase in pH. This is consistent with other works (Zhang et al., 2020; Liu et al., 2019) where it was shown that acidic conditions help to increase the rate of formation of hydroxyl radicals by surface protonation, which improves oxidation kinetics. Conversely, at alkaline pH (pH 11), the degradation efficiency significantly decreased, with $Fe_2O_3$-$TiO_2$ achieving only 60.1 ± 2.0%. This decline is attributed to the recombination of hydroxyl radicals and the formation of less reactive oxygen species such as $O_2\bullet^-$, which reduces the overall oxidative potential. The findings are consistent with those of Kim et al. (2021), who noted that at high pH, the excess $OH^-$ ions act as scavengers, diminishing the availability of ROS for polymer degradation. Acidic wastewater conditions (pH 3–5) are optimal for maximizing degradation efficiency, suggesting that industrial wastewater treatment facilities should consider pre-acidification before applying AOPs. In alkaline conditions, alternative catalysts or pH adjustment techniques may be required to maintain degradation efficiency.

### 6.2. Effect of Catalyst Dosage on Degradation Performance

The degradation efficiency exhibited a strong dependence on catalyst dosage, with optimal performance observed at 0.5 g/L for all tested catalysts (Chart 2). At this dosage, $Fe_2O_3$-$TiO_2$ achieved 94.8 ± 1.3% degradation efficiency, while $Co_3O_4$-PMS reached 90.3 ± 1.5%, demonstrating high catalytic activity. These results are in agreement with studies by Wang et al. (2022), who reported similar trends when using heterogeneous catalysts in Fenton-like oxidation. However, beyond 0.5 g/L, the degradation efficiency plateaued, suggesting that excess catalyst does not significantly enhance reaction kinetics. This phenomenon can be attributed to particle aggregation, which reduces the available active surface area for radical generation. The Langmuir-Hinshelwood model (Eq. 1) supports this finding, where an increase in catalyst concentration leads to an initial rise in degradation rate, followed by saturation due to site blockage (Yuan et

al., 2020). where Kads represents the adsorption equilibrium constant and Ccat. is the catalyst dosage. Liu et al. (2019) observed a maximum degradation of 91% at 0.5 g/L Fe-based catalysts, closely matching our findings. A study by Rahman et al. (2021) on ZnO-based AOPs showed that excess catalyst beyond 0.6 g/L leads to particle agglomeration, reducing ROS availability. An optimal catalyst dosage of ~0.5 g/L should be maintained to maximize efficiency while minimizing material costs. Excess catalyst addition does not proportionally increase degradation, necessitating economic optimization of catalyst usage.

### 6.3. Kinetics and Activation Energy Analysis

The degradation kinetics were assessed using the Arrhenius equation, revealing activation energies (EaE) ranging from 38.2 kJ/mol ($Co_3O_4$-PMS) to 53.5 kJ/mol ($TiO_2$) (Table 5). These values indicate that $Co_3O_4$-PMS exhibits the lowest energy barrier, making it the most reactive catalyst among those tested.

Where k is the rate constant, AAA is the pre-exponential factor, and T is the temperature in Kelvin. The lower activation energy of $Co_3O_4$-PMS (38.2 kJ/mol) suggests a superior ability to generate hydroxyl radicals at lower energy inputs. This is supported by the work of Zhao et al. (2022), who found that Co-based peroxymonosulfate (PMS) systems require less energy for radical activation compared to $TiO_2$-based photocatalysts.

### 6.4. Effect of Temperature on Degradation Rate

From Table 6, we see that there is a favorable relationship between the temperature-dependent degradation kinetics and the temperature of a sample. For example, at 25 °C, $Fe_2O_3$-$TiO_2$ had a rate constant of 0.0283 min−1, which increased to 0.0594 min−1 at 80 °C. This confirms Arrhenius- type behavior since high temperature leads to increased chances for molecular collisions and radical formation. These findings are consistent with the work of Chen et al. (2021) who noted that increasing the temperature from 20 °C to 80 °C resulted in a ~2.5× change in the degradation rate for heterogeneous catalytic oxidation systems. The results suggest that 40 °C–60 °C could serve as a sweet spot for balancing the reaction rate and energy usage. While high-temperature operation (~80 °C) may accelerate degradation, energy costs must be considered for large-scale applications.

### 6.5. Comparative Performance of Catalysts

The four catalysts tested demonstrated distinct advantages and limitations in terms of degradation efficiency, activation energy, and optimal operating conditions.

## 7. Conclusion

This research focused on understanding how catalysts impact polymers' degradation during AOP's treatment of wastewater. The experiments indicated that $Fe_2O_3$-$TiO_2$ is the most effective catalyst, since the highest degradation efficiency was achieved at 94.8% at pH 3. $Co_3O_4$-PMS had the lowest activation energy of 38.2 kJ/mol, thus making it the most economical. The results also indicate the importance of pH, catalyst dosage, and temperature in the degradation process. The Acidic conditions (pH 3-5) were found to be more efficient in the production of hydroxyl radical (•OH) resulting in greater degradation. However, the alkaline conditions were extremely inefficient due to the scavenging effect of the radicals. This study also showed that a dosage of 0.5 g/L is the optimal value if maximum degradation efficiency is desired, as further increases would lead to excess catalyst aggregation which decreases the available active sites. The energy of activation was determined using the Arrhenius equation and it was found that the increase in temperature has increased the reaction rate. The catalyst $Fe_2O_3$-$TiO_2$ showed temperature dependence as the rate constant increased from 0.0283 min−1 at 25 °C to 0.0594 min−1 at 80 °C. This highlights the trade- off between efficiency and energy consumption in practical wastewater treatment applications. The comparison of catalyst performance suggests that $Fe_2O_3$-$TiO_2$ is the most effective for high- efficiency degradation, while $Co_3O_4$-PMS is preferable for energy-conscious operations due to its lower activation energy. These findings align with previous studies, reinforcing the potential of heterogeneous catalysts in AOPs for sustainable wastewater management. Future research should focus on optimizing catalyst reusability and exploring hybrid catalyst systems to enhance degradation rates further. Additionally, integrating these catalysts with real-world wastewater treatment facilities will provide insights into large-scale applicability, ensuring cost-effective and environmentally friendly solutions for polymer contamination.

## Compliance with ethical standards

*Disclosure of conflict of interest*

No Conflict of Interest to be disclosed.

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