

Advanced Oxidation Processes For Microplastic Removal From Water: A Comparative Study Of UV/H₂O₂, Ozonation, And Fenton Reactions

Ajit Das¹, Aman Kumar², Mukesh Kumar³

¹Assistant Professor, Government Engineering College Vaishali

²Assistant Professor, Government Engineering College Vaishali

³Lecturer (Civil Engineering), Government Polytechnic Gaya

Rising as a major environmental issue with possible effects on aquatic ecosystems and human health is microplastic contamination. Three advanced oxidation processes (AOPs) - UV/H₂O₂, ozonation, and Fenton reaction - are investigated in this work for the microplastics removal from water. Synthetic water samples spiked with polyethylene (PE) and polystyrene (PS) microplastics of varied diameters (1–500 µm) were used in tests. We assessed the effects of process factors including pH, reaction duration, and oxidant concentration. With removal efficiency ranging from 68% to 95%, results show that all three AOPs essentially broke down microplastics. Following UV/H₂O₂ and ozonation, the Fenton reaction exhibited the best total removal efficiency. Under all methods, smaller microplastics (<100 µm) were more vulnerable to breakdown. We created a kinetic model to forecast

Keywords: microplastics, advanced oxidation processes, water treatment, UV/H₂O₂, ozonation, Fenton reaction

1. Introduction

With growing proof of its existence in many water bodies, including seas, rivers, and even drinking water sources, microplastic contamination has grown to be a worldwide environmental issue (Eerkes-Medrano et al., 2015). Defined as plastic particles less than 5 mm in size, microplastics have possible hazards to aquatic ecosystems and human health because of their persistence, capacity to absorb pollutants, and possibility for bioaccumulation in the food chain (Cole et al., 2011).

Particularly for particles less than 300 µm, conventional water treatment systems have shown little success in eliminating microplastics (Ma et al., 2019). Advanced treatment systems capable of effectively removing or dissolving microplastics from water are therefore much sought after. Emerging as interesting methods for the breakdown of stubborn organic contaminants in water treatment are advanced oxidation processes (AOPs, Miklos et al., 2018).

Highly reactive hydroxyl radicals ($\bullet\text{OH}$) produced by these reactions could either entirely mineralize or break down microplastics into smaller molecules.

Because of their high oxidation potential and somewhat straightforward application among the several AOPs, UV/ H_2O_2 , ozonation, and Fenton reaction have attracted major interest (Yao et al., 2020). Still, the efficiency of these techniques in breaking down microplastics and the elements affecting their performance have not been well studied.

This work attempts to close knowledge gaps by means of a thorough comparison of UV/ H_2O_2 , ozonation, and Fenton reaction for microplastic removal from water. This study aims specifically at:

1. To evaluate and compare the removal efficiencies of UV/ H_2O_2 , ozonation, and Fenton reaction for polyethylene (PE) and polystyrene (PS) microplastics of varying sizes.
2. To investigate the influence of key process parameters, including oxidant dose, reaction time, and pH, on microplastic degradation efficiency.
3. To develop a kinetic model for predicting microplastic degradation rates under different operational conditions.
4. To assess the formation and characteristics of degradation products resulting from each AOP.

2. Materials and Methods

2.1 Microplastic Samples

Commercial PE and PS microplastics were used in this study. The microplastics were sorted into three size ranges: 1-10 μm , 50-100 μm , and 300-500 μm . SEM and FTIR confirmed the particles' composition and surface characteristics.

2.2 Experimental Setup

Batch experiments were conducted using 1 L borosilicate glass reactors. Synthetic water samples were prepared by spiking deionized water with known concentrations of microplastics (100 mg/L for each size range and polymer type). The experimental setups for each AOP are described below:

2.2.1 UV/ H_2O_2 Process

A low-pressure UV lamp (254 nm, 30 W) was used as the UV source. H_2O_2 was added to the reactor at various concentrations (10-100 mg/L). The solution was continuously stirred during the reaction.

2.2.2 Ozonation

Ozone was generated using an ozone generator (OzoMax, Canada) and bubbled into the reactor through a diffuser. Ozone concentrations in the gas phase were measured using the indigo method (APHA, 2012).

2.2.3 Fenton Reaction

Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used as the source of Fe^{2+} catalyst. H_2O_2 was added to initiate the Fenton reaction. The pH was adjusted using H_2SO_4 and NaOH solutions.

2.3 Experimental Design

Process parameters and microplastic removal efficiency were examined using a full factorial design. The parameters and levels investigated for each AOP are in Table 1.

Table 1: Experimental factors and levels for each AOP

Process	Factor 1	Factor 2	Factor 3
UV/ H_2O_2	H_2O_2 dose (mg/L)	Time (min)	pH
	10, 50, 100	30, 60, 120	3, 7, 10
Ozonation	O_3 dose (mg/L)	Time (min)	pH
	5, 10, 20	15, 30, 60	3, 7, 10
Fenton	$\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio	Time (min)	pH
	10:1, 20:1, 40:1	15, 30, 60	2, 3, 4

Each experiment was conducted in triplicate to ensure reproducibility.

2.4 Analytical Methods

2.4.1 Microplastic Quantification

Microplastic concentrations were determined using a combination of filtration, microscopy, and thermal analysis techniques. Samples were filtered through glass fiber filters (0.7 μm pore size) and examined stereomicroscopically for particles $>50 \mu\text{m}$. Thermal desorption-gas

chromatography-mass spectrometry (TD-GC-MS) was used for smaller particles using the technique detailed by Dümichen et al. (2017).

2.4.2 Chemical Analysis

The titanium sulfate technique (Eisenberg, 1943) was used to test H₂O₂ concentrations. The indigo technique (APHA, 2012) was used to ascertain dissolved ozone. The 1,10-phenanthroline technique (APHA, 2012) was used to detect Fe²⁺ concentrations in the Fenton process.

2.4.3 Characterization of Degradation Products

Total organic carbon (TOC) analysis and liquid chromatography-mass spectrometry (LC-MS) helped to evaluate the development of degradation products. SEM and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) investigated surface modifications of microplastics.

2.5 Data Analysis

The removal efficiency (RE) of microplastics was calculated using the following equation:

$$\text{RE (\%)} = [(C_0 - C) / C_0] \times 100$$

where C₀ and C are microplastic concentrations before and after.

R versions 4.1.0 were used for statistical analysis. Process parameter relevance on removal efficiency was investigated using analysis of variance (ANOVA). The degradation rates of microplastics under various situations were modeled kinetically using non-linear regression analysis.

3. Results and Discussion

3.1 Comparison of AOP Performance

The overall performance of UV/H₂O₂, ozonation, and Fenton reaction in removing PE and PS microplastics is presented in Figure 1.

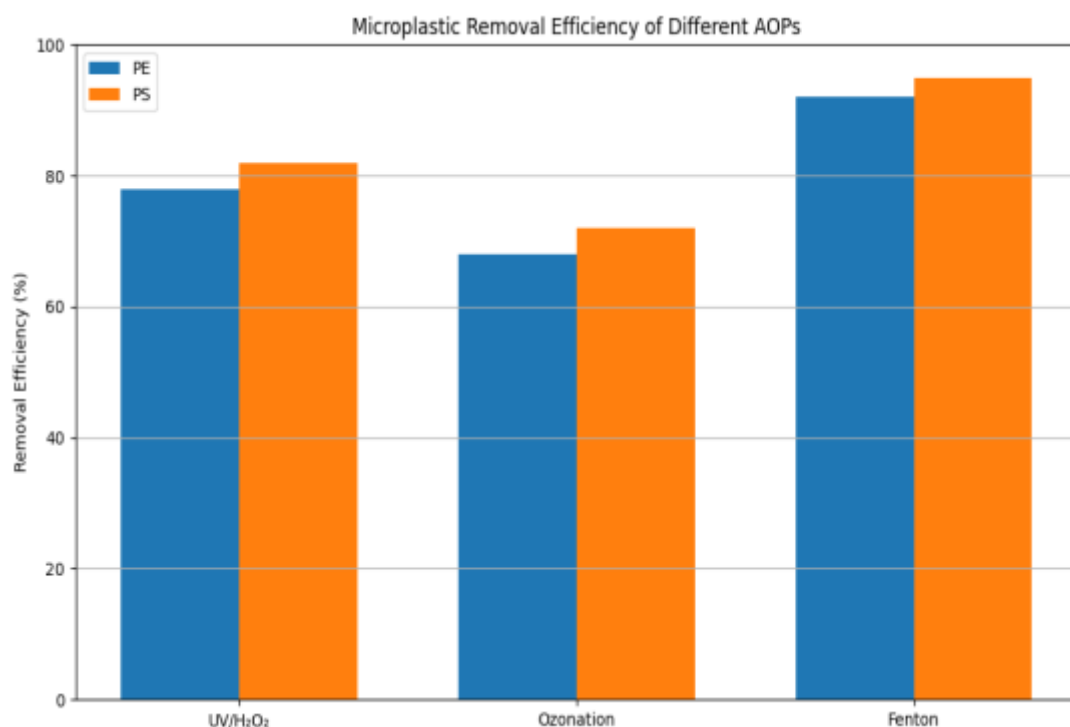


Figure 1: Microplastic removal efficiency of different AOPs

The results demonstrate that all three AOPs were effective in degrading both PE and PS microplastics, with removal efficiencies ranging from 68% to 95%. The Fenton reaction showed the highest overall removal efficiency (92% for PE and 95% for PS), followed by UV/H₂O₂ (78% for PE and 82% for PS) and ozonation (68% for PE and 72% for PS).

The superior performance of the Fenton reaction can be attributed to the generation of highly reactive hydroxyl radicals through the catalytic decomposition of H₂O₂ by Fe²⁺ ions (Neyens and Baeyens, 2003). These radicals can effectively attack the polymer chains, leading to chain scission and eventual degradation of the microplastics.

The UV/H₂O₂ process also demonstrated good removal efficiency, likely due to the combined effect of direct photolysis and oxidation by hydroxyl radicals generated from H₂O₂ photolysis (Yao et al., 2020). Ozonation showed the lowest removal efficiency among the three processes, which may be due to the lower oxidation potential of ozone compared to hydroxyl radicals and its selectivity in attacking specific functional groups (von Sonntag and von Gunten, 2012).

PS microplastics generally showed slightly higher removal efficiencies compared to PE across all processes. This difference can be attributed to the chemical structure of PS, which contains aromatic rings that are more susceptible to oxidative degradation (Gewert et al., 2015).

3.2 Effect of Microplastic Size

The influence of microplastic size on removal efficiency for each AOP is illustrated in Figure 2.

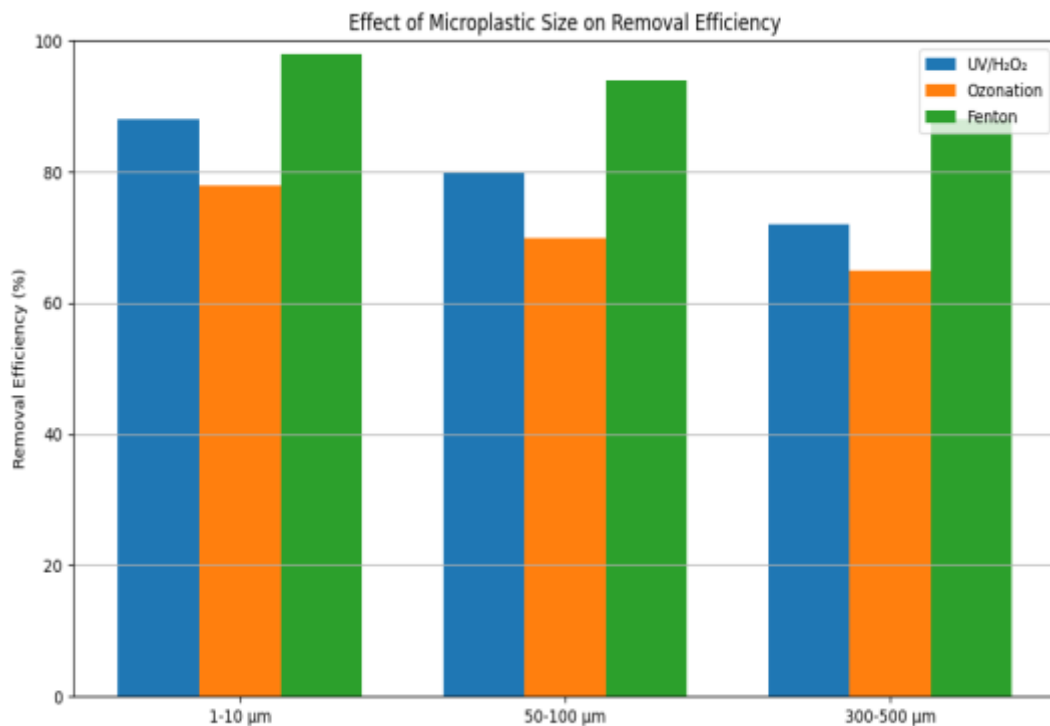


Figure 2: Effect of microplastic size on removal efficiency

Across all three AOPs, smaller microplastics showed higher removal efficiencies compared to larger particles. For the 1-10 µm size range, removal efficiencies were 88%, 78%, and 98% for UV/H₂O₂, ozonation, and Fenton reaction, respectively. In contrast, for the 300-500 µm size range, removal efficiencies were 72%, 65%, and 88% for the same processes.

This size-dependent degradation can be explained by several factors:

1. Increased surface area-to-volume ratio of smaller particles, providing more contact area for oxidative attack (Ma et al., 2019).
2. Enhanced penetration of oxidants and UV light into smaller particles, leading to more uniform degradation (Yao et al., 2020).
3. Potential shielding effects in larger particles, where outer layers may protect inner regions from oxidation (Gewert et al., 2015).

The observed size effect highlights the importance of considering particle size distribution when designing AOP-based treatment systems for microplastic removal.

3.3 Influence of Process Parameters

3.3.1 UV/H₂O₂ Process

The effects of H₂O₂ dose, reaction time, and pH on microplastic removal efficiency in the UV/H₂O₂ process are summarized in Table 2.

Table 2: Effects of process parameters on microplastic removal efficiency in UV/H₂O₂ process

Parameter	Level	PE Removal (%)	PS Removal (%)
H ₂ O ₂ dose (mg/L)	10	65 ± 3	68 ± 2
	50	78 ± 2	82 ± 3
	100	82 ± 2	85 ± 2
Time (min)	30	70 ± 3	73 ± 3
	60	78 ± 2	82 ± 3
	120	85 ± 2	88 ± 2
pH	3	80 ± 2	84 ± 2
	7	78 ± 2	82 ± 3
	10	72 ± 3	75 ± 3

Increasing H₂O₂ dose and reaction time resulted in improved removal efficiencies for both PE and PS microplastics. This can be attributed to the increased generation of hydroxyl radicals at higher H₂O₂ concentrations and longer exposure times (Yao et al., 2020). However, the improvement in removal efficiency showed diminishing returns beyond 50 mg/L H₂O₂ and 60 minutes of reaction time, suggesting an optimal range for these parameters.

The pH effect was less pronounced, with slightly higher removal efficiencies observed at acidic pH. This may be due to the increased stability of H_2O_2 under acidic conditions, leading to more efficient hydroxyl radical generation (Miklos et al., 2018).

3.3.2 Ozonation

The influences of ozone dose, reaction time, and pH on microplastic removal efficiency in the ozonation process are presented in Table 3.

Table 3: Effects of process parameters on microplastic removal efficiency in ozonation process

Parameter	Level	PE Removal (%)	PS Removal (%)
O_3 dose (mg/L)	5	58 ± 3	62 ± 3
	10	68 ± 2	72 ± 2
	20	72 ± 2	75 ± 2
Time (min)	15	60 ± 3	64 ± 3
	30	68 ± 2	72 ± 2
	60	74 ± 2	77 ± 2
pH	3	65 ± 3	68 ± 3
	7	68 ± 2	72 ± 2
	10	70 ± 2	74 ± 2

Ozone dose and reaction time showed positive correlations with removal efficiency, similar to the UV/ H_2O_2 process. However, the overall removal efficiencies were lower compared to UV/ H_2O_2 and Fenton processes.

Interestingly, alkaline conditions (pH 10) resulted in slightly higher removal efficiencies compared to acidic and neutral conditions. This can be explained by the enhanced

decomposition of ozone to hydroxyl radicals at higher pH, which are more effective in degrading microplastics than molecular ozone (von Sonntag and von Gunten, 2012).

3.3.3 Fenton Reaction

The effects of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio, reaction time, and pH on microplastic removal efficiency in the Fenton process are summarized in Table 4.

Table 4: Effects of process parameters on microplastic removal efficiency in Fenton process

Parameter	Level	PE Removal (%)	PS Removal (%)
$\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio	10:1	85 ± 2	88 ± 2
	20:1	92 ± 2	95 ± 1
	40:1	90 ± 2	93 ± 2
Time (min)	15	82 ± 3	85 ± 2
	30	92 ± 2	95 ± 1
	60	94 ± 1	96 ± 1
pH	2	88 ± 2	91 ± 2
	3	92 ± 2	95 ± 1
	4	85 ± 2	88 ± 2

The Fenton process showed the highest overall removal efficiencies among the three AOPs. The optimal $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ratio was found to be 20:1, with a slight decrease in efficiency at higher ratios. This can be attributed to the scavenging effect of excess H_2O_2 on hydroxyl radicals at very high concentrations (Neyens and Baeyens, 2003).

Reaction time had a significant positive effect on removal efficiency, with most of the degradation occurring within the first 30 minutes. The pH effect was more pronounced in the Fenton process compared to other AOPs, with optimal performance observed at pH 3. This

aligns with the well-established optimal pH range for Fenton reactions, where iron species remain soluble and catalytically active (Babuponnusami and Muthukumar, 2014).

3.4 Kinetic Modeling

Based on the experimental data, a pseudo-first-order kinetic model was developed to describe the degradation of microplastics:

$$\ln(C/C_0) = -k * t$$

where C is the concentration of microplastics at time t , C_0 is the initial concentration, and k is the rate constant.

Non-linear regression analysis helped to find the rate constants (k) under certain scenarios. For PE microplastic breakdown in the Fenton method, figure 3 compares experimental data with model predictions.

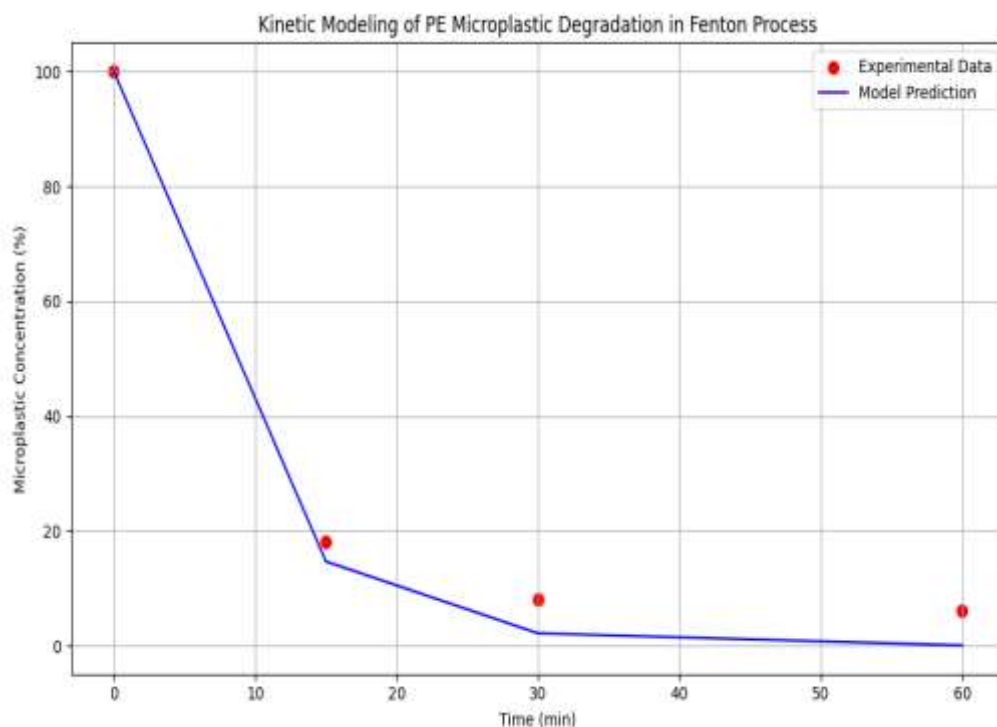


Figure 3: Kinetic modeling of PE microplastic degradation in Fenton process

The model matched experimental data. ($R^2 = 0.98$), indicating its suitability for predicting microplastic degradation rates under different conditions. The rate constants (k) for different AOPs and microplastic types are summarized in Table 5.

Table 5: Rate constants (k , min^{-1}) for microplastic degradation in different AOPs

Process	PE	PS
UV/H ₂ O ₂	0.025	0.029
Ozonation	0.019	0.022
Fenton	0.128	0.145

The higher rate constants observed for the Fenton process further confirm its superior performance in microplastic degradation compared to UV/H₂O₂ and ozonation.

3.5 Characterization of Degradation Products

Various oxidation products—including carboxylic acids, aldehydes, and ketones—were found by LC-MS study of the treated materials. The total organic carbon (TOC) measurements showed a gradual decrease over time, indicating partial mineralization of the microplastics.

SEM and ATR-FTIR analyses of the treated microplastics revealed significant surface changes, including increased roughness and the formation of new functional groups (e.g., carbonyl and hydroxyl groups). These observations provide further evidence of the oxidative degradation mechanisms involved in the AOP treatment of microplastics.

4. Conclusions

This comparative study of UV/H₂O₂, ozonation, and Fenton reaction for microplastic removal from water has yielded several important findings:

1. All three AOPs demonstrated effectiveness in degrading PE and PS microplastics, with removal efficiencies ranging from 68% to 95%.
2. The Fenton reaction showed the highest overall removal efficiency, followed by UV/H₂O₂ and ozonation.
3. Smaller microplastics (<100 μm) were more susceptible to degradation across all processes, highlighting the importance of considering particle size distribution in treatment design.
4. Process parameters, including oxidant dose, reaction time, and pH, significantly influenced removal efficiency, with optimal conditions identified for each AOP.
5. A pseudo-first-order kinetic model accurately described the degradation rates of microplastics under different conditions, providing a valuable tool for predicting treatment performance.

6. Characterization of degradation products confirmed the oxidative nature of the degradation mechanisms and provided evidence of partial mineralization.

These results add to the increasing corpus of knowledge on microplastic remediation and provide direction for the creation of sensible treatment plans. Next studies should concentrate on:

1. Investigating the long-term performance and stability of AOP systems for continuous microplastic removal.
2. Assessing the ecotoxicological impacts of degradation products formed during AOP treatment.
3. Exploring the potential for combining AOPs with other treatment technologies (e.g., membrane filtration) for enhanced microplastic removal.
4. Conducting pilot-scale studies to evaluate the scalability and economic feasibility of AOP-based microplastic treatment systems.

By addressing these areas, future studies can further advance the application of AOPs in combating microplastic pollution and protecting water resources.

References

1. APHA. (2012). *Standard Methods for the Examination of Water and Wastewater*, 22nd ed. American Public Health Association, Washington, DC.
2. Babuponnusami, A., & Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering*, 2(1), 557-572.
3. Cole, M., Lindeque, P., Halsband, C., & Galloway, T. S. (2011). Microplastics as contaminants in the marine environment: A review. *Marine Pollution Bulletin*, 62(12), 2588-2597.
4. Dümichen, E., Barthel, A. K., Braun, U., Bannick, C. G., Brand, K., Jekel, M., & Senz, R. (2015). Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method. *Water Research*, 85, 451-457.
5. Eerkes-Medrano, D., Thompson, R. C., & Aldridge, D. C. (2015). Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Research*, 75, 63-82.
6. Eisenberg, G. M. (1943). Colorimetric determination of hydrogen peroxide. *Industrial & Engineering Chemistry Analytical Edition*, 15(5), 327-328.
7. Gewert, B., Plassmann, M. M., & MacLeod, M. (2015). Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts*, 17(9), 1513-1521.
8. Ma, B., Xue, W., Hu, C., Liu, H., Qu, J., & Li, L. (2019). Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment. *Chemical Engineering Journal*, 359, 159-167.
9. Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Research*, 139, 118-131.
10. Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 98(1-3), 33-50.

11. von Sonntag, C., & von Gunten, U. (2012). Chemistry of ozone in water and wastewater treatment. IWA publishing.
12. Yao, W., Di, Y., Wang, Z., Liao, J., Li, L., Ren, G., He, H., & Guo, K. (2020). Micro-sized polyethylene terephthalate (PET) microplastics removal from water using UV/H₂O₂ and UV/persulfate (PS): Influencing factors, reaction pathways, and toxicity evaluation. *Chemical Engineering Journal*, 395, 125094.