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# The treatment of high concentration wastewater in the natural gas processing industry

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The operation of the Cansolv tail gas treatment device in natural gas plants generates acidic and alkaline wastewater from the venturi unit and amine purification unit (APU), respectively. The APU wastewater is complex in composition and contains hard-to-degrade organic matter, which can adversely impact the normal functioning of the water treatment system. This study assesses the efficacy of three ozone-based advanced oxidation processes (ozone (O<sub>3</sub>), ozone/hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), and ozone/Fenton (O<sub>3</sub>/Fenton)) for treating Cansolv wastewater, with chemical oxygen demand (COD) and total organic carbon (TOC) serving as indicators of organic degradation. The findings demonstrate that all three processes effectively eliminate coloration and reducible sulfur, with O<sub>3</sub>/Fenton exhibiting superior performance in removing organic substances. The treated wastewater has a clarified light-yellow appearance with residual COD levels at 43 mg L<sup>-1</sup>. Under the optimum Fenton oxidation conditions (initial pH 5, H<sub>2</sub>O<sub>2</sub> dosage 97.8 mmol L<sup>-1</sup>, FeSO<sub>4</sub>·7H<sub>2</sub>O dosage 550 mg L<sup>-1</sup>), average TOC and COD removal rates reached 50% and 97%, respectively. After a treatment duration of 60 minutes, the wastewater demonstrated an enhanced membrane-specific flux, confirming the effectiveness of the O<sub>3</sub>/Fenton oxidation process in mitigating membrane fouling while ensuring the stable operation of the wastewater treatment system.

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## 1. Introduction

The Cansolv exhaust gas treatment device has been utilized in various industries, including natural gas processing, petrochemicals, smelting, and coal-fired power plants to selectively remove sulfur dioxide from exhaust gases using organic amine solutions. This technology offers significant technical advantages and environmental benefits.<sup>1</sup> However, the pre-wash unit (venturi) and amine purification unit (APU) in the Cansolv device generate large volumes of acidic and alkaline wastewater, respectively. These wastewaters undergo treatment through a flocculation softening – ultrafiltration – ion – exchange – two-stage reverse osmosis process to produce freshwater for reuse and concentrated water for evaporation crystallization. This zero – wastewater discharge system reduces water consumption. Nevertheless, the intake quality of APU wastewater exhibits considerable fluctuations in practical applications due to its complex composition containing numerous recalcitrant organic compounds.<sup>2</sup> The treatment of highly alkaline APU wastewater at certain gas purification plants has been explored using conventional electrocatalytic oxidation and biochemical oxidation methods in practical applications. However, the methods

were intricate, requiring an additional 2 hours reaction time and pH adjustment within a range of 3–5.

The application of advanced oxidation processes (AOPs) in water treatment and reclaimed water reuse has garnered significant attention and implementation in various countries and regions.<sup>3–7</sup> Previous studies have investigated the treatment efficacy of the UV-Fenton process within different pH ranges for actual drilling wastewater. Both the acidic UV-Fenton process and the neutral modified UV-Fenton process effectively treated the wastewater, resulting in effluent BOD<sub>5</sub>/COD ratios of 0.53 and 0.6, respectively.<sup>5</sup> In the field of AOPs, especially ozone-based AOPs, integrated with other oxidation techniques, have been extensively employed for the removal of recalcitrant contaminants in diverse water matrices.<sup>8–11</sup> Ozone (O<sub>3</sub>) and its derivative hydroxyl radicals (·OH) possess remarkable electron affinity and oxidative potential, ranking second only to Fluorine.<sup>12–14</sup> The O<sub>3</sub> molecule can directly or selectively react with water impurities and undergo decomposition *via* a chain reaction mechanism, generating ·OH.<sup>15,16</sup> The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation process, derived from the development of O<sub>3</sub> oxidation process, has promising potential in advanced wastewater treatment owing to its non-selectivity and absence of secondary pollution.<sup>17</sup> The ·OH concentration is effectively increased through the addition of H<sub>2</sub>O<sub>2</sub>, thereby facilitating the degradation of organic matter in wastewater.<sup>18</sup> In previous studies, after O<sub>3</sub>/H<sub>2</sub>O oxidation, long-chain unsaturated organic compounds (C > 40, double bond equivalents > 20) were degraded into short-chain aldehydes and low molecular weight

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fatty acids, and the subsequent Fenton oxidation effectively removed refractory organic matter.<sup>3</sup> The O<sub>3</sub>/Fenton oxidation process is particularly well-suited for the treatment of recalcitrant organic wastewater, as it combines the potent oxidation capabilities of O<sub>3</sub> with the highly reactive ·OH species generated through the Fenton reaction, which exhibits strong electrophilic characteristics.<sup>19,20</sup> This synergistic approach enables comprehensive degradation of a wide range of organic compounds present in wastewater. In our previous study, we investigated the effects of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>/Fenton oxidation on the wastewater of APU unit at the organic molecular level, ultimately determining that the O<sub>3</sub>/Fenton process exhibits superior oxidation efficacy.<sup>3</sup>

Therefore, this study primarily investigates the impacts of three advanced oxidation processes (AOPs), namely O<sub>3</sub> oxidation, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation, and O<sub>3</sub>/Fenton oxidation, on the APU wastewater produced by Cansolv device. The focus is mainly on evaluating changes in COD and TOC levels. Specifically, the three oxidation methods were examined to identify the factors influencing the treatment of APU wastewater and determine the optimal process conditions. Key parameters such as initial O<sub>3</sub> dosage, H<sub>2</sub>O<sub>2</sub> dosage, FeSO<sub>4</sub>·7H<sub>2</sub>O dosage, and pH value were thoroughly examined to achieve this objective.

## 2. Materials and methods

### 2.1 Materials

The experimental wastewater came from APU unit of the Cansolv device at a natural gas purification plant in China. The sample was pale yellow and transparent, with a faint pungent smell and a little suspension matter, which might have been due to iron ions and organic matter. The metal content, sulfide, pH, COD, and TOC in wastewater were obtained by different testing methods. 30% H<sub>2</sub>O<sub>2</sub> was guaranteed reagent, and the other reagents such as FeSO<sub>4</sub>·7H<sub>2</sub>O, NaOH, concentrated sulfuric acid were the analytical reagents. All agents were purchased from Cologne Chemical Reagent Plant in China. The central laboratory apparatus included an O<sub>3</sub> generator (QJ-8006K, Guangzhou Quanju Ozone Technology Co, Ltd), a total organic carbon meter (SHIMADZU TOC-LCP, Japan) *et al.*

### 2.2 O<sub>3</sub> oxidation process

The O<sub>3</sub> generator produced ozone by utilizing a pure oxygen stream and introduced it into the liquid bulk through a gas diffuser. The O<sub>3</sub> generator maintained a constant concentration of 9 g h<sup>-1</sup>, and all experiments were conducted under ambient temperature conditions. After a reaction time of 15 minutes, a noticeable improvement in chromaticity was observed, indicating enhanced clarity. O<sub>3</sub> treatment durations of 5, 15, 30, 60, and 90 minutes were selected for subsequent analysis of COD and TOC levels.

### 2.3 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation process

The treatment of a 200 mL wastewater sample with O<sub>3</sub> was conducted in a 1 L reactor, where O<sub>3</sub> was generated using an O<sub>3</sub> generator and continuously introduced into the water at a rate

of 9 g h<sup>-1</sup>. Furthermore, various dosages of H<sub>2</sub>O<sub>2</sub> (1 mL, 2 mL, 3 mL, and 4 mL) were added to the reactor. After 1 h treatment time, any remaining oxidants in the samples were neutralized using sodium thiosulfate. The treated water samples were stored at a temperature of 4 °C for subsequent analysis to evaluate COD and TOC levels as indicators of the reaction oxidation process.

### 2.4 O<sub>3</sub>/Fenton oxidation process

The O<sub>3</sub>/Fenton oxidation process was conducted in a 1 L reactor at ambient temperature. Different dosages of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O, as well as various pH levels, were employed to determine the optimal conditions for achieving maximum COD and TOC removals. O<sub>3</sub> was continuously added into 200 mL wastewater through a gas diffuser, maintaining a constant concentration of 9 g h<sup>-1</sup>. H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O were added into the wastewater to investigate the degradation effect on organic matter and determine the most effective dosages. The resulting residue was allowed to settle for 30 minutes, while the treated water was stored at 4 °C for subsequent analysis of water quality parameters, specifically COD and TOC measurements.

Gas chromatography-mass spectrometry (GC-MS) was used to study the oxidation of organic matter in wastewater. The surface morphology and chemical composition of the membranes treated with different oxidation wastewater were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

## 3. Results and discussion

### 3.1 Analysis of water quality

The results of water quality tests conducted on the APU wastewater are presented in Table 1. The analysis revealed that the wastewater exhibited an alkaline nature with a high concentration of sodium ions, while other metal ion levels met the standard requirements. Both ammonia nitrogen and chloride

Table 1 Water quality tests results for APU wastewater

Parameter	Unit	Values
Na <sup>+</sup>	mg L <sup>-1</sup>	344.0
K <sup>+</sup>	mg L <sup>-1</sup>	0.0
Ca <sup>2+</sup>	mg L <sup>-1</sup>	0.0
Mg <sup>2+</sup>	mg L <sup>-1</sup>	0.0
Fe <sup>3+</sup>	mg L <sup>-1</sup>	0.0
Ba <sup>2+</sup>	mg L <sup>-1</sup>	0.0
pH	—	11.5
Total alkalinity (CaCO <sub>3</sub> )	mg L <sup>-1</sup>	2222.2
CO <sub>3</sub> <sup>2-</sup>	mg L <sup>-1</sup>	10.5
HCO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	25.5
Turbidity	NTU	21.3
Ammonia nitrogen	mg L <sup>-1</sup>	6.3
Chloride	mg L <sup>-1</sup>	550.2
Sulfide	mg L <sup>-1</sup>	473.8
SO <sub>3</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	mg L <sup>-1</sup>	1369.4
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	10 580.1
COD	mg L <sup>-1</sup>	1838.8
TOC	mg L <sup>-1</sup>	293.6

levels were found to be within the limits set by the Chinese wastewater discharge standard, which stipulates values below  $15 \text{ mg L}^{-1}$  and  $1000 \text{ mg L}^{-1}$ , respectively. However, sulfide levels and organic content exceeded the prevailing regulations for wastewater effluent in China.

The membrane contamination was primarily attributed to the high organic matter content, which exceeded the design threshold of the Cansolv wastewater treatment unit. Additionally, the elevated sulfur content in the wastewater surpassed standard levels, resulting in a need to remove reduced sulfur along with organic matter and its subsequent conversion into sulfate.

### 3.2 $\text{O}_3$ oxidation process

During  $\text{O}_3$  oxidation process, complex organic matter in APU wastewater is transformed into simpler intermediates, primarily micromolecular esters and phenols. As a result, the pH of the wastewater decreases from 11.52 to 6.78 after undergoing  $\text{O}_3$  oxidation treatment. The alkaline nature of the wastewater facilitated  $\text{O}_3$  induction by hydroxide ions ( $\text{OH}^-$ ), leading to the generation of hydroxyl radicals ( $\cdot\text{OH}$ ). These highly reactive radicals react with the organic matter, resulting in the decomposition of macromolecular substances.<sup>21,22</sup> Overall, it can be concluded that the application of  $\text{O}_3$  oxidation process proves to be an advanced and suitable technology for treating APU wastewater.

The solubility of  $\text{O}_3$  in water and the change in sulfide content after a 60 minutes reaction at different  $\text{O}_3$

concentrations are illustrated in Fig. 1. When the treatment time was 60 minutes and the  $\text{O}_3$  concentration was  $5 \text{ g L}^{-1}$ , minimal oxidation effect was observed with sulfide content remaining at  $473.1 \text{ mg L}^{-1}$ . This can be attributed to the relatively low solubility of  $\text{O}_3$  in water, approximately  $22.9 \text{ mg L}^{-1}$ , which is insufficient for effective sulfide deoxidization. However, increasing the  $\text{O}_3$  concentration from  $5 \text{ g L}^{-1}$  to  $10 \text{ g L}^{-1}$  resulted in a rapid decrease in sulfide content to less than  $1 \text{ mg L}^{-1}$ , achieving over 99.9% removal efficiency. At higher  $\text{O}_3$  concentrations of  $15 \text{ g L}^{-1}$  and  $20 \text{ g L}^{-1}$ , the sulfide content further decreased to only  $0.5 \text{ mg L}^{-1}$  and  $0.3 \text{ mg L}^{-1}$ , respectively. Notably, when exceeding a concentration of  $10 \text{ g L}^{-1}$ , the amount of dissolved  $\text{O}_3$  in water increased significantly with saturated solubility reaching about  $132.3 \text{ mg L}^{-1}$ .

When introduced into the wastewater,  $\text{O}_3$  partially dissolved and reacted with the organic matter, thereby facilitating the conversion of undissolved  $\text{O}_3$  into dissolved  $\text{O}_3$  (Fig. 1). As the reaction progressed,  $\text{O}_3$  was gradually consumed, leading to its dissolution in water approaching saturation. Notably, it was observed that the equilibrium dissolution of  $\text{O}_3$  in wastewater exceeded that in deionized water.

The variations in sulfide, sulfate ( $\text{SO}_4^{2-}$ ), sulfite ( $\text{SO}_3^{2-}$ ), and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) concentrations in the wastewater under experimental conditions of  $10 \text{ g per L O}_3$  concentration and a treatment time of 60 minutes are presented in Table 2. The initial content of reducible sulfur in the wastewater was found to be similar to the sulfate concentration after treatment. During the  $\text{O}_3$  oxidation process, all reduced sulfur present in APU wastewater can be completely oxidized to  $\text{SO}_4^{2-}$ , without generating any secondary pollutants.

The initial concentration of COD in the wastewater was  $909.5 \text{ mg L}^{-1}$ , and it gradually decreased with increasing  $\text{O}_3$  oxidation time. Within the first 5 minutes, there was a significant reduction in COD from  $909.4 \text{ mg L}^{-1}$  to  $697.8 \text{ mg L}^{-1}$ , corresponding to a decrease of 23.3%. Among different treatment durations, the most efficient removal of organic matter occurred during the 60 minutes period. After 60 minutes of treatment,  $\text{O}_3$  effectively degraded most of the macromolecular organic matter in the wastewater, converting it into micromolecular organic matter. Consequently, the COD level remained stable and decreased to approximately  $556.6 \text{ mg L}^{-1}$  (Fig. 2).

The removals of COD and TOC were investigated at various treatment durations and  $\text{O}_3$  concentrations. The highest COD elimination was achieved at an  $\text{O}_3$  concentration of  $22.5 \text{ g L}^{-1}$  (Fig. 3a). Within the initial 45 minutes, there was a significant increase in COD removal, reaching a peak removal of 45.7% at

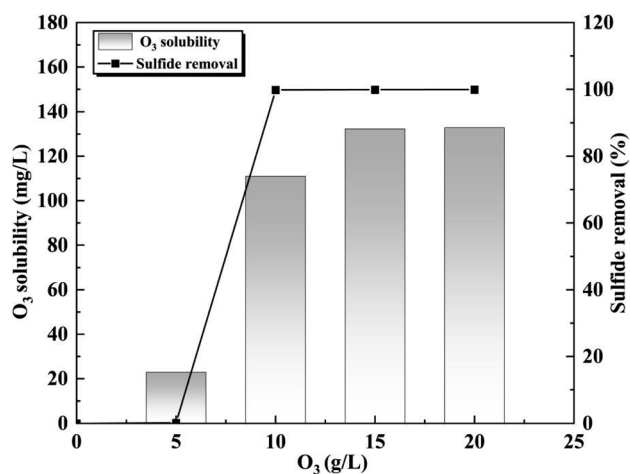


Fig. 1 The solubility of  $\text{O}_3$  in water and sulfide removal under different  $\text{O}_3$  concentration.

Table 2 The concentration of reducible sulfur and sulfate in water samples before and after  $\text{O}_3$  oxidation process

Index	Unit ( $\text{mg L}^{-1}$ )					
	Before $\text{O}_3$ oxidation process			After $\text{O}_3$ oxidation process		
	Sulfide	$\text{SO}_3^{2-}$ and $\text{S}_2\text{O}_3^{2-}$	$\text{SO}_4^{2-}$	Sulfide	$\text{SO}_3^{2-}$ and $\text{S}_2\text{O}_3^{2-}$	$\text{SO}_4^{2-}$
	473.8	1067.4	9773.6	0.3	1.2	11303.6

60 minutes. This COD removal process was attributed to the generation of abundant  $\cdot\text{OH}$  by  $\text{O}_3$  oxidation. However, excessive  $\cdot\text{OH}$  concentration can lead to self-quenching, resulting in a reduced utilization rate of  $\text{O}_3$ . Consequently, when the  $\text{O}_3$  concentration was increased to  $30 \text{ g L}^{-1}$ , the COD removal decreased accordingly due to this phenomenon.

The solubility of  $\text{O}_3$  in wastewater was limited, thus, even with an  $\text{O}_3$  concentration of  $15 \text{ g L}^{-1}$ , only approximately 20% COD removal could be achieved. It was found that an appropriate dosage of  $\text{O}_3$  facilitated the degradation of organic pollutants effectively. During the ozonation process using  $\text{O}_3$  as an oxidant, macromolecular organic matter present in wastewater underwent transformation into micromolecular organic matter which led to fluctuations in measured TOC levels (Fig. 3b). Although ozonation has the ability to disrupt the structure of the original organic matter and generate intermediates with simpler structures, achieving complete mineralization solely through ozonation remains challenging for most organic matter compounds.<sup>3</sup> Therefore, additional oxidation processes need to be integrated alongside  $\text{O}_3$  oxidation for effective treatment.

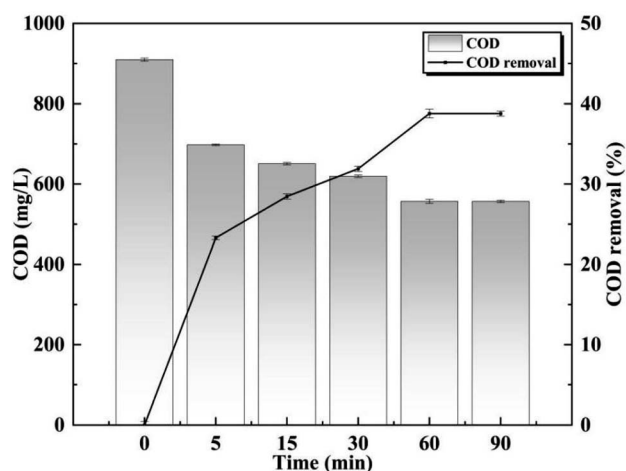


Fig. 2 The COD concentrations and removal with  $\text{O}_3$  treatment time.

### 3.3 $\text{O}_3/\text{H}_2\text{O}_2$ oxidation process

To further enhance the removal of COD and TOC, the impact of different dosages of  $\text{H}_2\text{O}_2$  on organic degradation was investigated in the  $\text{O}_3/\text{H}_2\text{O}_2$  oxidation process. Initially, the concentrations of COD and TOC decreased and then increased as the dosage of  $\text{H}_2\text{O}_2$  increased (Fig. 4). However, when the dosage exceeded 2 mL, excessive  $\text{H}_2\text{O}_2$  and the intermediate product  $\text{HO}_2^-$  reacted with  $\cdot\text{OH}$ . The COD decreased to  $510.7 \text{ mg L}^{-1}$ , achieving a maximum removal efficiency of 60.6% at a dosage of 2 mL  $\text{H}_2\text{O}_2$ . Furthermore, with a further increase in  $\text{H}_2\text{O}_2$  dosage, TOC initially increased but gradually decreased thereafter until reaching its lowest value at a dosage of  $255.7 \text{ mg L}^{-1}$ .

The degradation of organic matter by  $\text{O}_3$  occurs through both direct and indirect oxidation, while  $\text{H}_2\text{O}_2$  primarily acts as a potent oxidant dependent on the  $\cdot\text{OH}$  produced during its decomposition.<sup>23</sup>  $\text{H}_2\text{O}_2$  exhibits instability under alkaline conditions,<sup>23,24</sup> and an optimal  $\text{H}_2\text{O}_2$  amount in wastewater enhances the transfer of  $\text{O}_3$  to water.<sup>24,25</sup> This generates a significant quantity of  $\cdot\text{OH}$  that synergistically degrades organic matter with  $\text{O}_3$ , effectively reducing COD and TOC.

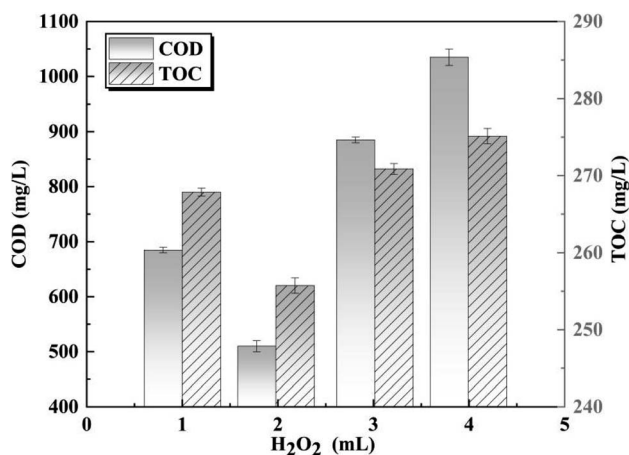


Fig. 4 COD and TOC concentration at different  $\text{H}_2\text{O}_2$  dosages under  $\text{O}_3/\text{H}_2\text{O}_2$  oxidation process.

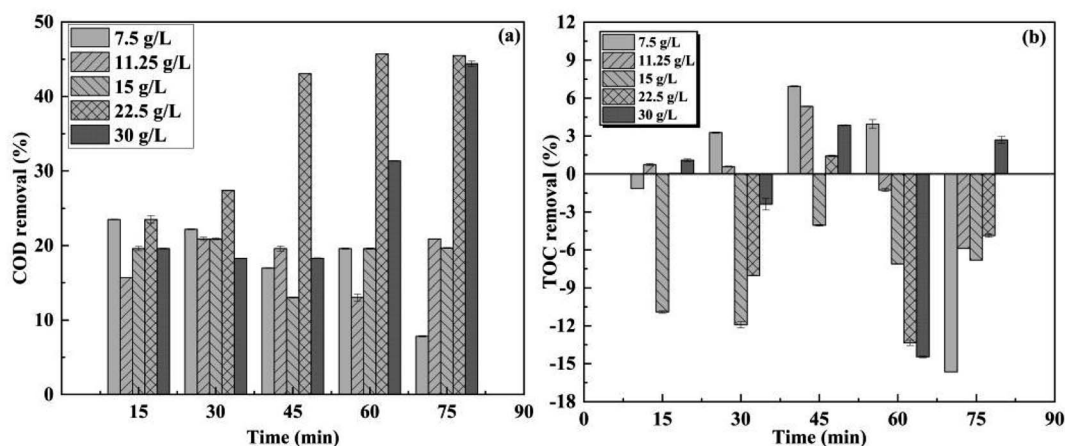
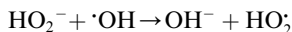
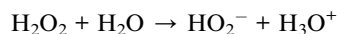
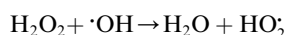


Fig. 3 (a) The COD removal and (b) the TOC removal under different  $\text{O}_3$  treatment time.

Nevertheless, excessive  $\text{H}_2\text{O}_2$  and its intermediate  $\text{HO}_2^-$  react with  $\cdot\text{OH}$  produced by the  $\text{O}_3$  decomposition, and the main reaction mechanism is as follows.<sup>26,27</sup>



Elevated concentrations of  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  typically result in an enhanced production of  $\cdot\text{OH}$ , but excessive utilization can give rise to detrimental consequences. Hence, it is crucial to assess the optimal  $\text{H}_2\text{O}_2/\text{O}_3$  ratio for attaining maximum degradation of pollutants.

### 3.4 $\text{O}_3$ /Fenton oxidation process

The  $\text{O}_3$  oxidation process comprises two modes of oxidation, namely direct oxidation under acidic conditions and indirect oxidation under alkaline conditions. These modes generate a significant quantity of  $\cdot\text{OH}$  radicals.<sup>27</sup> Considering the highly alkaline nature of the APU wastewater, the primary oxidation mechanism gradually shifted from indirect  $\text{O}_3$  oxidation to direct  $\cdot\text{OH}$  oxidation. After undergoing the process of  $\text{O}_3$  oxidation, the water became weakly acidic, thus creating favorable conditions for the occurrence of the Fenton reaction. The Fenton reaction involved the generation of additional  $\cdot\text{OH}$ , and the reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  produced highly reactive  $\cdot\text{OH}$ , which effectively degraded complex organic matter, including aromatic and heterocyclic unsaturated organic matter.<sup>28–30</sup> In the  $\text{O}_3$ /Fenton oxidation process, precise determination of the appropriate dosage is crucial for achieving optimal oxidation and subsequent decolorization. Therefore, it was imperative to investigate the optimum oxidative effect of different dosages of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  to determine the ideal agent dosage.

The oxidation efficiency of wastewater treated by  $\text{O}_3$ /Fenton oxidation process in the Cansolv device was investigated. As

shown in Fig. 5a, an increase in  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage significantly enhanced COD removal when  $\text{H}_2\text{O}_2$  dosage was 2 mL. A COD removal of 95% was achieved with a dosage of 2.88 mmol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage, highlighting its crucial role in the organic degradation process within the  $\text{O}_3$ /Fenton system. However, when  $\text{H}_2\text{O}_2$  dosage was increased to 4 mL, COD initially increased and then decreased with increasing  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  content. The highest point of COD removal (98%) was reached at a  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  content of 2.16 mmol. The decline in COD removal with an addition of 2.88 mmol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  can be attributed to excessive  $\cdot\text{OH}$  consumption by  $\text{Fe}^{2+}$  ions within the system, leading to impaired oxidation.<sup>27</sup>

After adding 2 mL and 4 mL of  $\text{H}_2\text{O}_2$ , the removal of TOC increased with an increase in  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  content. The optimal TOC removal rates were found to be 49% and 55%, respectively. This suggests that a higher dosage of  $\text{H}_2\text{O}_2$  dosage generates more  $\cdot\text{OH}$ , thereby enhancing the organic degradation of organic compounds and improving TOC removal to some extent.<sup>31</sup> When the  $\text{H}_2\text{O}_2$  dosage was fixed at 4 mL, further increasing the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage resulted in a continuous increase in TOC removal without reaching equilibrium. However, excessive  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage in the  $\text{O}_3$ /Fenton oxidation process led to increased alkali consumption during subsequent decolorization, resulting in significant formation of ferric hydroxide sludge.<sup>32,33</sup> Considering COD and TOC removal efficiencies as well as economic factors, it was determined that the optimal dosages for the  $\text{O}_3$ /Fenton oxidation process were 2 mL  $\text{H}_2\text{O}_2$  and 2.88 mmol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

The impact of the  $\text{O}_3$ /Fenton oxidation process on COD removal within the pH range of 3 to 6 was investigated. Fenton exhibited superior oxidation efficacy at a pH of 3, while under alkaline conditions, the  $\text{O}_3$  oxidation process demonstrated greater effectiveness. Therefore, the optimal performance was achieved when employing the  $\text{O}_3$ /Fenton oxidation process with a value of 5 for pH.

In the  $\text{O}_3$ /Fenton oxidation process, a pH that is too low would hinder the oxidation of  $\text{O}_3$  in the solution, while a pH that is too high would diminish the effectiveness of Fenton's reagent. Under alkaline conditions,  $\text{Fe}^{2+}$  undergoes rapid

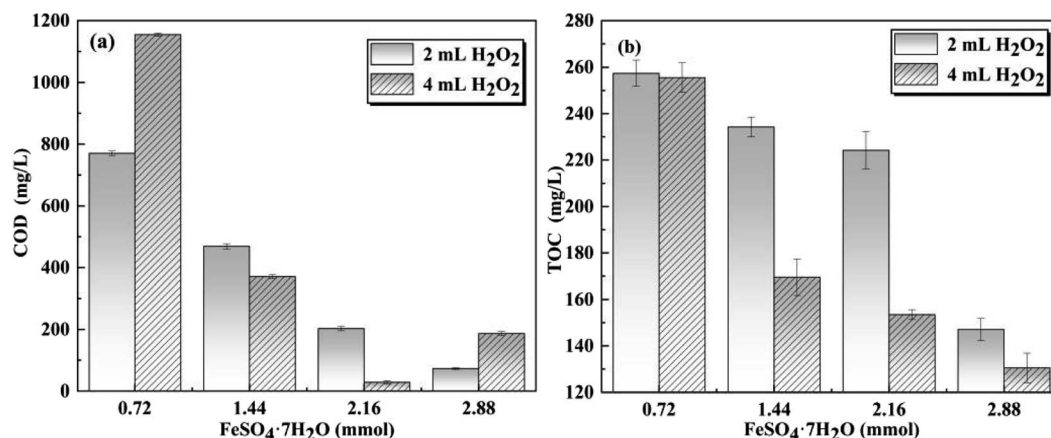


Fig. 5 COD (a) and (b) TOC under different  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ .

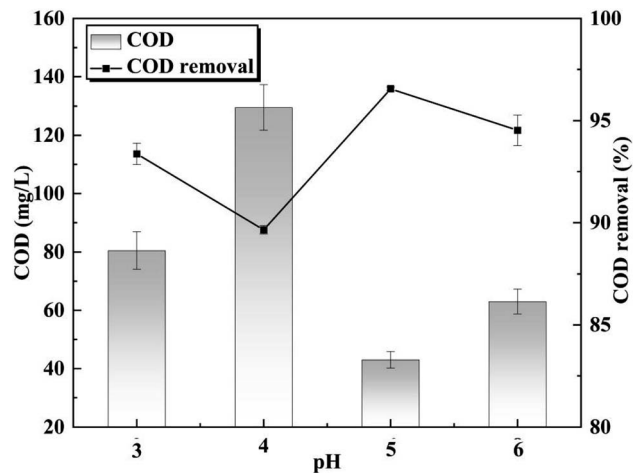


Fig. 6 COD removal during the  $O_3$ /Fenton oxidation process under varying pH conditions.

oxidized to  $Fe^{3+}$ , resulting in precipitation of ferric hydroxide.<sup>29,33</sup> Additionally,  $H_2O_2$  acts as a weak acid and easily ionizes under neutral and alkaline conditions. When the wastewater pH exceeds 5, there is a significant reduction in  $H_2O_2$  concentration, leading to a decrease in  $\cdot OH$  concentration within the system (Fig. 6). A pH of 5 creates an optimal environment for the  $O_3$ /Fenton oxidation process, leading to a 97% decrease in COD removal.

The composition of APU wastewater before and after the  $O_3$ /Fenton process was compared using GC-MS analysis, as depicted in Fig. 7. The red line represents the organic analysis of the treated APU wastewater. Initially, the wastewater predominantly contained polycyclic aromatic hydrocarbons (PAHs) and long-chain ester organic matter, with dibutyl phthalate (DBP) comprising 60% of the total proportion. After undergoing  $O_3$  reaction (electrophilic substitution and cycloaddition), the esters and phenolic organic compounds in the system can be effectively decomposed into more stable intermediates.

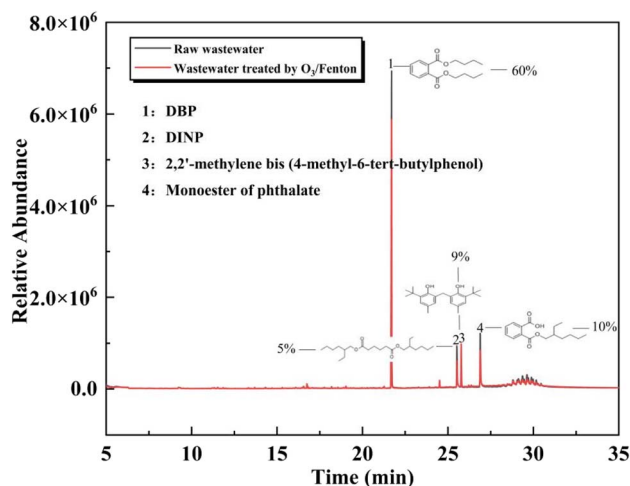


Fig. 7 GC-MS before and after  $O_3$ /Fenton oxidation process.

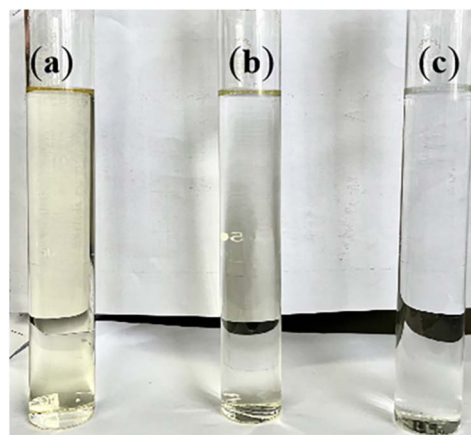


Fig. 8 Different chromatic characteristics of raw APU wastewater (a), wastewater treated by  $O_3/H_2O_2$  process (b), wastewater treated by  $O_3$ /Fenton process (c).

Subsequently, following Fenton reaction, the intermediates in the wastewater are efficiently mineralized.<sup>3,34</sup> Thus, a significant reduction in organic composition within the wastewater was observed after a 1 hour  $O_3$ /Fenton oxidation process.

In Fig. 8, the wastewater treated by the  $O_3/H_2O_2$  process and  $O_3$ /Fenton process respectively exhibit high clarity level. The  $O_3/H_2O_2$  process achieved a 61% reduction in COD and a 13% reduction in TOC. The  $O_3$ /Fenton process exhibited the highest removal efficiency for complex organic matter in APU wastewater, resulting in a significant decrease of 97% in COD and 55% in TOC (Table 3). This process effectively degraded macromolecular organic matter into smaller and simpler structures, and even led to complete mineralization of the organic matter.<sup>3</sup>

As shown in Fig. 9, membrane flux was assessed using a high-pressure flat membrane apparatus, which compared the effects of different oxidation processes on mitigating membrane fouling. Initially, the membrane flux of various wastewater samples exhibited a gradual decrease within the first 200 minutes, with a relatively consistent decline rate. However, as the filtration time increased, the decline rate in membrane flux became increasingly inconsistent among the different wastewaters. For raw APU wastewater, the membrane

Table 3 The efficacy of three distinct oxidation processes in treatment

Parameter ( $mg L^{-1}$ )	Different processes		
	$O_3$	$O_3/H_2O_2$	$O_3$ /Fenton
Original sulfide	473.8	473.8	473.8
Sulfide	0.32	0.25	0.2
Sulfide removal (%)	99.9	99.9	99.9
Original COD	1383	1383	1383
Original TOC	293.6	293.6	293.6
COD	846.4	539.4	41.5
TOC	273	255	132
COD removal (%)	38.8	61	97
TOC removal (%)	7	13	55

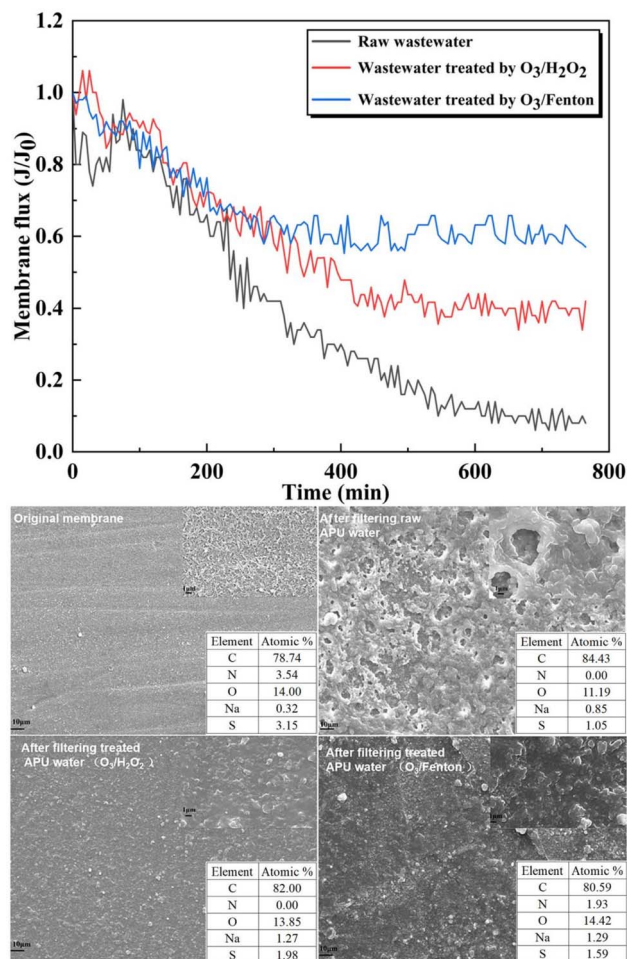


Fig. 9 The membrane flux and SEM-EDS analysis of different membrane surfaces.

flux exhibited a rapid and nearly complete reduction after 600 minutes treatment, indicating the occurrence of severe membrane fouling. The raw APU wastewater caused dense irregularities and micron-sized pores on the surface of the utilized membrane along with a thick layer of contaminants. The  $O_3/H_2O_2$  process resulted in a slight increase in membrane flux by approximately 40%, indicating an improved efficiency of this approach for organic matter treatment. The  $O_3$ /Fenton oxidation process maintained a consistent state at approximately 60% of the initial membrane flux due to its surface uneven pore structure, which facilitates water flow through reverse osmosis membranes. Furthermore, apparent enhancement in membrane flux was observed during wastewater treatment using  $O_3$ /Fenton process, suggesting gradual decomposition of organics with enhanced treatment.

From SEM-EDS analysis of membrane surface, the original reverse osmosis membrane is dense and smooth with numerous nanoporous structures, and the C, O, N, S contents of the membrane surface are 78.74%, 14.00%, 3.54% and 3.15%, respectively. After filtering raw APU water, the membrane surface exhibited a multitude of microporous irregular

structures within the organic contaminant layer, and the C, O, N, S contents of the membrane surface are 84.43%, 11.19%, 0.00% and 1.05%, respectively. These pollutants persistently accumulated on the membrane during the flushing process, resulting in membrane blockage and reduced lifespan. After  $O_3/H_2O_2$  oxidation process, there was a decrease in C content from 84.43% to 82.00% while an increase in O content from 11.19% to 13.85%, indicating organic degradation on the membrane surface. In the  $O_3$ /Fenton oxidation process, incorporation of Fenton reagent enhanced the oxidation effect, leading to a reduction in C content from 84.43% to 80.59%, approaching that of the initial membrane at 78.74%. Furthermore, the O and N contents are 14.42% and 1.93%, resulted in an approach towards the initial membrane surface. The decline in C content signifies continuous reduction of organic matter on the membrane surface during Cansolv wastewater treatment. The addition of  $FeSO_4 \cdot 7H_2O$  in the  $O_3$ /Fenton oxidation process promotes organic degradation and effectively prevents the formation of an organic pollution layer on reverse osmosis membrane surface.

According to the field test conducted at a natural gas plant, the electrocatalytic oxidation process achieved a remarkable 95% conversion rate of reduced sulfur, while the COD removal rate reached 40%. However, when the wastewater was subjected to biochemical oxidation treatment, it exhibited an unexpected increase in COD levels instead of reduction, indicating poor biodegradability of the APU unit wastewater. In contrast,  $O_3$ /Fenton oxidation process significantly enhanced the COD removal rate to 97%. These findings unequivocally demonstrate that the  $O_3$ /Fenton oxidation process represents the most optimal combined approach for treating wastewater originating from APU unit of Cansolv device.

## 4. Conclusion

This study conducted a comprehensive comparison of the degradation performance of three  $O_3$ -based oxidation processes ( $O_3$  only,  $O_3/H_2O_2$ , and  $O_3$ /Fenton) for APU wastewater treatment. The degradation efficiency towards organic matter exhibited variations among the different  $O_3$ -based oxidation processes. In the case of the  $O_3$ /Fenton oxidation process, the addition of Fenton reagent effectively reduced organic matter in wastewater and eliminated the organic layer adhered to the membrane surface. This approach successfully addressed membrane fouling issues during Cansolv wastewater treatment, resulting in a significant reduction in COD (97%) and TOC (55%). The proposed wastewater treatment scheme aligns with circular economy principles and holds potential for pollution reduction, enhancement of industrial environmental performance, improved efficiency, and compliance with ecolabel criteria.

## Conflicts of interest

There are no known competing financial interests or personal relationships that could affect the work reported in this article.

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## References

- 1 M. Davoudi, S. Samieirad, H. R. Mottaghi, *et al.*, The main sources of wastewater and sea contamination in the south pars natural gas processing plants: Prevention and recovery, *J. Nat. Gas Sci. Eng.*, 2014, 137–146.
- 2 M. F. V. Dooren, P. Astrup and T. K. Mikkelsen, Influence of Cansolv tail gas treatment unit on natural gas purification plant and discussion on optimization measures, *Chem. Eng. Oil Gas*, 2022, 138–146.
- 3 W. J. Hu, Y. Qu, J. Xiong, *et al.*, Wastewater from natural gas Cansolv desulfurization process: Comprehensive characterization and effective removal of organic compounds, *Sci. Total Environ.*, 2024, **911**, 168681.
- 4 Y. Wang, H. Q. Li and L. M. Ren, Organic matter removal from mother liquor of gas field wastewater by electro-Fenton process with the addition of H<sub>2</sub>O<sub>2</sub>: effect of initial pH, *R. Soc. Open Sci.*, 2019, **6**, 191304.
- 5 W. Chen, C. Zou, X. Li, *et al.*, The treatment of phenolic contaminants from shale gas drilling wastewater: A comparison with UV-Fenton and modified UV-Fenton processes at neutral pH, *RSC Adv.*, 2016, 90682–90689.
- 6 Z. G. Liu, W. Zhou, X. L. Liu, *et al.*, Study on Treatment Performance of Desulfurization Wastewater by Zero-Valent Iron Fenton-like Process, *Separations*, 2023, 451.
- 7 Z. Liu, K. Demeestere and S. Van Hulle, Comparison and performance assessment of ozone-based AOPs in view of trace organic contaminants abatement in water and wastewater: A review, *J. Environ. Chem. Eng.*, 2021, 105599.
- 8 C. C. Chang, C. Y. Chiu, C. Y. Chang, *et al.*, Combined photolysis and catalytic ozonation of dimethyl phthalate in a high-gravity rotating packed bed, *J. Hazard. Mater.*, 2009, 287–293.
- 9 A. C. Mecha and M. N. Chollom, Photocatalytic ozonation of wastewater: a review, *Environ. Chem. Lett.*, 2020, 1491–1507.
- 10 M. Mehrjouei, S. Mueller and D. Moeller, A review on photocatalytic ozonation used for the treatment of water and wastewater, *Chem. Eng. J.*, 2015, 209–219.
- 11 G. H. Zheng, B. T. Xia and X. U. Jing, Comparison of O<sub>3</sub>, UV/O<sub>3</sub>, and UV/O<sub>3</sub>/PS Processes for Marine Oily Wastewater Treatment: Degradation Performance, Toxicity Evaluation, and Flocc Analysis, *Water Res.*, 2022, 119–234.
- 12 P. Asaithambi, R. Govindarajan, M. B. Yesuf, *et al.*, Enhanced treatment of landfill leachate wastewater using sono-ozone-electrocoagulation process: role of process parameters on color, COD and electrical energy consumption, *Process Saf. Environ. Prot.*, 2020, 212–218.
- 13 W. S. Liu, K. Xiao, J. Li, *et al.*, Efficient removal of organic contaminants in real shale gas flowback water using Fenton oxidation assisted by UV irradiation: Feasibility study and process optimization, *Process Saf. Environ. Prot.*, 2022, 687–697.
- 14 B. Kasprzykhordern, M. Ziolek and J. Nawrock, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, *Appl. Catal., B*, 2003, 639–669.
- 15 M. M. Bello, A. A. A. Raman, *et al.*, A review on approaches for addressing the limitations of Fenton oxidation for recalcitrant wastewater treatment, *Process Saf. Environ. Prot.*, 2019, 119–140.
- 16 S. N. Malik, P. C. Ghosh, A. N. Vaidya and A. Asghar, Hybrid ozonation process for industrial wastewater treatment: Principles and applications: A review, *J. Water Proc. Eng.*, 2020, 101–193.
- 17 Z. P. Gu, W. M. Chen, F. Wang, *et al.*, Transformation and degradation of recalcitrant organic matter in membrane bioreactor leachate effluent by the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process, *Environ. Sci.: Water Res. Technol.*, 2019, 1748–1757.
- 18 C. L. Jung, Y. Deng, R. Z. Zhao, *et al.*, Chemical oxidation for mitigation of UV-quinching substances (UVQS) from municipal landfill leachate: Fenton process versus ozonation, *Water Res.*, 2017, 260–270.
- 19 E. C. Catalkaya and F. Kargi, Color, TOC and AOX removals from pulp mill effluent by advanced oxidation processes: a comparative study, *J. Hazard. Mater.*, 2007, 244–253.
- 20 W. Sun, Z. L. Lu, Z. Y. Zhang, *et al.*, Ozone and Fenton oxidation affected the bacterial community and opportunistic pathogens in biofilms and effluents from GAC, *Water Res.*, 2022, 118–495.
- 21 E. Rezae, B. Jafari, M. Abbasi, *et al.*, Hybridized microfiltration-Fenton system for the treatment of greywater, *J. Environ. Chem. Eng.*, 2023, 109–725.
- 22 T. Lu, Y. Chen, M. Liu, *et al.*, Efficient degradation of evaporative condensing liquid of shale gas wastewater using O<sub>3</sub>/UV process, *Process Saf. Environ. Prot.*, 2019, 175–183.
- 23 V. Fontanier, V. Farines, J. Albet, *et al.*, Study of catalyzed ozonation for advanced treatment of pulp and paper mill effluents, *Water Res.*, 2006, 303–310.
- 24 A. Vinayak and G. B. Singh, Biodecolorization of reactive black 5 using magnetite nanoparticles coated Bacillus sp. RA5, *Mater. Today: Proc.*, 2022, 1523–1526.
- 25 E. M. Aieta, K. M. Reagan, J. S. Lang, *et al.*, Advanced Oxidation Processes for Treating Groundwater Contaminated With TCE and PCE: Pilot-Scale Evaluations, *J.-Am. Water Works Assoc.*, 1988, 64–72.
- 26 I. A. Balcioglu and M. Oetker, Treatment of pharmaceutical wastewater containing antibiotics by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes, *Chemosphere*, 2002, 85–95.
- 27 J. J. Pignatello, E. Oliveros and A. Mac Kay, Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.*, 2006, 1–84.
- 28 B. Enric, M. Eva, S. Roser, *et al.*, Aniline mineralization by AOPs: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, *Appl. Catal., B*, 1998, 31–42.
- 29 P. V. Nidheesh, Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review, *RSC Adv.*, 2015, 40552–40577.



- 30 J. Yang, H. Zhang, Z. Zhang, *et al.*, Degradation of 2, 4-dinitrophenol in aqueous solution by microscale Fe<sub>0</sub>/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> process, *Environ. Eng. Sci.*, 2019, 207–218.
- 31 N. Hassanshahi and A. Karimi-Jashni, Comparison of photo-Fenton, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and photocatalytic processes for the treatment of gray water, *Ecotoxicol. Environ. Saf.*, 2018, 683–690.
- 32 F. Al Momani, D. W. Smith and M. G. El-Din, Degradation of cyanobacteria toxin by advanced oxidation processes, *J. Hazard. Mater.*, 2008, 238–249.
- 33 J. H. Ma, W. J. Song, C. C. Chen, *et al.*, Fenton Degradation of Organic Compounds Promoted by Dyes under Visible Irradiation, *Environ. Sci. Technol.*, 2005, 5810–5815.
- 34 F. Wang, Y. Huang, P. Wen, *et al.*, Transformation mechanisms of refractory organic matter in mature landfill leachate treated using an Fe-participated O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process, *Chemosphere*, 2021, 128198.