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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_3), ozone/hydrogen peroxide (O_3/H_2O_2), and ozone/Fenton (O_3/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_3/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^{-1}. Under the optimum Fenton oxidation conditions (initial pH 5, H_2O_2 dosage 97.8 mmol L^{-1}, $FeSO_4 \cdot 7H_2O$ dosage 550 mg L^{-1}), 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_3/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.[1] 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.[2] 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.[3–7] 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_5/COD ratios of 0.53 and 0.6, respectively.[5] 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.[8–11] Ozone (O_3) and its derivative hydroxyl radicals ($^{\bullet}OH$) possess remarkable electron affinity and oxidative potential, ranking second only to Fluorine.[12–14] The O_3 molecule can directly or selectively react with water impurities and undergo decomposition *via* a chain reaction mechanism, generating $^{\bullet}OH$.[15,16] The O_3/H_2O_2 oxidation process, derived from the development of O_3 oxidation process, has promising potential in advanced wastewater treatment owing to its non-selectivity and absence of secondary pollution.[17] The $^{\bullet}OH$ concentration is effectively increased through the addition of H_2O_2, thereby facilitating the degradation of organic matter in wastewater.[18] In previous studies, after O_3/H_2O 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.[3] The O_3/Fenton oxidation process is particularly well-suited for the treatment of recalcitrant organic wastewater, as it combines the potent oxidation capabilities of O_3 with the highly reactive $^{\bullet}OH$ species generated through the Fenton reaction, which exhibits strong electrophilic characteristics.[19,20] 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_3/H_2O_2 and O_3/Fenton oxidation on the wastewater of APU unit at the organic molecular level, ultimately determining that the O_3/Fenton process exhibits superior oxidation efficacy.[3]

Therefore, this study primarily investigates the impacts of three advanced oxidation processes (AOPs), namely O_3 oxidation, O_3/H_2O_2 oxidation, and O_3/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_3 dosage, H_2O_2 dosage, $FeSO_4\cdot 7H_2O$ 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_2O_2 was guaranteed reagent, and the other reagents such as $FeSO_4\cdot 7H_2O$, 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_3 generator (QJ-8006K, Guangzhou Quanju Ozone Technology Co, Ltd), a total organic carbon meter (SHIMADZU TOC-LCP, Japan) *et al.*

2.2 O_3 oxidation process

The O_3 generator produced ozone by utilizing a pure oxygen stream and introduced it into the liquid bulk through a gas diffuser. The O_3 generator maintained a constant concentration of 9 g h^{-1}, 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_3 treatment durations of 5, 15, 30, 60, and 90 minutes were selected for subsequent analysis of COD and TOC levels.

2.3 O_3/H_2O_2 oxidation process

The treatment of a 200 mL wastewater sample with O_3 was conducted in a 1 L reactor, where O_3 was generated using an O_3 generator and continuously introduced into the water at a rate of 9 g h^{-1}. Furthermore, various dosages of H_2O_2 (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_3/Fenton oxidation process

The O_3/Fenton oxidation process was conducted in a 1 L reactor at ambient temperature. Different dosages of H_2O_2 and $FeSO_4\cdot 7H_2O$, as well as various pH levels, were employed to determine the optimal conditions for achieving maximum COD and TOC removals. O_3 was continuously added into 200 mL wastewater through a gas diffuser, maintaining a constant concentration of 9 g h^{-1}. H_2O_2 and $FeSO_4\cdot 7H_2O$ 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^+	mg L^{-1}	344.0
K^+	mg L^{-1}	0.0
Ca^{2+}	mg L^{-1}	0.0
Mg^{2+}	mg L^{-1}	0.0
Fe^{3+}	mg L^{-1}	0.0
Ba^{2+}	mg L^{-1}	0.0
pH	—	11.5
Total alkalinity ($CaCO_3$)	mg L^{-1}	2222.2
$CO_3{}^{2-}$	mg L^{-1}	10.5
$HCO_3{}^{-}$	mg L^{-1}	25.5
Turbidity	NTU	21.3
Ammonia nitrogen	mg L^{-1}	6.3
Chloride	mg L^{-1}	550.2
Sulfide	mg L^{-1}	473.8
$SO_3{}^{2-}$, $S_2O_3{}^{2-}$	mg L^{-1}	1369.4
$SO_4{}^{2-}$	mg L^{-1}	10 580.1
COD	mg L^{-1}	1838.8
TOC	mg L^{-1}	293.6

levels were found to be within the limits set by the Chinese wastewater discharge standard, which stipulates values below 15 mg L^{-1} and 1000 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 O_3 oxidation process

During 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 O_3 oxidation treatment. The alkaline nature of the wastewater facilitated O_3 induction by hydroxide ions (OH^-), leading to the generation of hydroxyl radicals ($^{\bullet}OH$). These highly reactive radicals react with the organic matter, resulting in the decomposition of macromolecular substances.[21,22] Overall, it can be concluded that the application of O_3 oxidation process proves to be an advanced and suitable technology for treating APU wastewater.

The solubility of O_3 in water and the change in sulfide content after a 60 minutes reaction at different O_3 concentrations are illustrated in Fig. 1. When the treatment time was 60 minutes and the O_3 concentration was 5 g L^{-1}, minimal oxidation effect was observed with sulfide content remaining at 473.1 mg L^{-1}. This can be attributed to the relatively low solubility of O_3 in water, approximately 22.9 mg L^{-1}, which is insufficient for effective sulfide deoxidization. However, increasing the O_3 concentration from 5 g L^{-1} to 10 g L^{-1} resulted in a rapid decrease in sulfide content to less than 1 mg L^{-1}, achieving over 99.9% removal efficiency. At higher O_3 concentrations of 15 g L^{-1} and 20 g L^{-1}, the sulfide content further decreased to only 0.5 mg L^{-1} and 0.3 mg L^{-1}, respectively. Notably, when exceeding a concentration of 10 g L^{-1}, the amount of dissolved O_3 in water increased significantly with saturated solubility reaching about 132.3 mg L^{-1}.

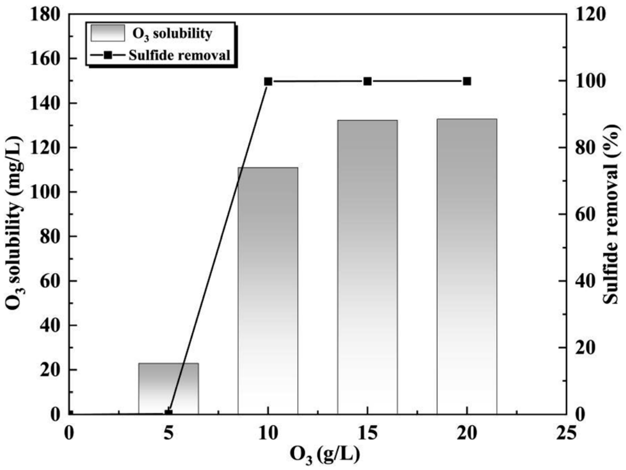


Fig. 1 The solubility of O_3 in water and sulfide removal under different O_3 concentration.

When introduced into the wastewater, O_3 partially dissolved and reacted with the organic matter, thereby facilitating the conversion of undissolved O_3 into dissolved O_3 (Fig. 1). As the reaction progressed, O_3 was gradually consumed, leading to its dissolution in water approaching saturation. Notably, it was observed that the equilibrium dissolution of O_3 in wastewater exceeded that in deionized water.

The variations in sulfide, sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), and thiosulfate ($S_2O_3^{2-}$) concentrations in the wastewater under experimental conditions of 10 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 O_3 oxidation process, all reduced sulfur present in APU wastewater can be completely oxidized to SO_4^{2-}, without generating any secondary pollutants.

The initial concentration of COD in the wastewater was 909.5 mg L^{-1}, and it gradually decreased with increasing O_3 oxidation time. Within the first 5 minutes, there was a significant reduction in COD from 909.4 mg L^{-1} to 697.8 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, 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 mg L^{-1} (Fig. 2).

The removals of COD and TOC were investigated at various treatment durations and O_3 concentrations. The highest COD elimination was achieved at an O_3 concentration of 22.5 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

Table 2 The concentration of reducible sulfur and sulfate in water samples before and after O_3 oxidation process

	Unit (mg L^{-1})					
	Before O_3 oxidation process			After O_3 oxidation process		
Index	Sulfide	SO_3^{2-} and $S_2O_3^{2-}$	SO_4^{2-}	Sulfide	SO_3^{2-} and $S_2O_3^{2-}$	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 ˙OH by O_3 oxidation. However, excessive ˙OH concentration can lead to self-quenching, resulting in a reduced utilization rate of O_3. Consequently, when the O_3 concentration was increased to 30 g L^{-1}, the COD removal decreased accordingly due to this phenomenon.

The solubility of O_3 in wastewater was limited, thus, even with an O_3 concentration of 15 g L^{-1}, only approximately 20% COD removal could be achieved. It was found that an appropriate dosage of O_3 facilitated the degradation of organic pollutants effectively. During the ozonation process using 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.[3] Therefore, additional oxidation processes need to be integrated alongside O_3 oxidation for effective treatment.

3.3 O_3/H_2O_2 oxidation process

To further enhance the removal of COD and TOC, the impact of different dosages of H_2O_2 on organic degradation was investigated in the O_3/H_2O_2 oxidation process. Initially, the concentrations of COD and TOC decreased and then increased as the dosage of H_2O_2 increased (Fig. 4). However, when the dosage exceeded 2 mL, excessive H_2O_2 and the intermediate product HO_2^- reacted with ˙OH. The COD decreased to 510.7 mg L^{-1}, achieving a maximum removal efficiency of 60.6% at a dosage of 2 mL H_2O_2. Furthermore, with a further increase in H_2O_2 dosage, TOC initially increased but gradually decreased thereafter until reaching its lowest value at a dosage of 255.7 mg L^{-1}.

The degradation of organic matter by O_3 occurs through both direct and indirect oxidation, while H_2O_2 primarily acts as a potent oxidant dependent on the ˙OH produced during its decomposition.[23] H_2O_2 exhibits instability under alkaline conditions,[23,24] and an optimal H_2O_2 amount in wastewater enhances the transfer of O_3 to water.[24,25] This generates a significant quantity of ˙OH that synergistically degrades organic matter with O_3, effectively reducing COD and TOC.

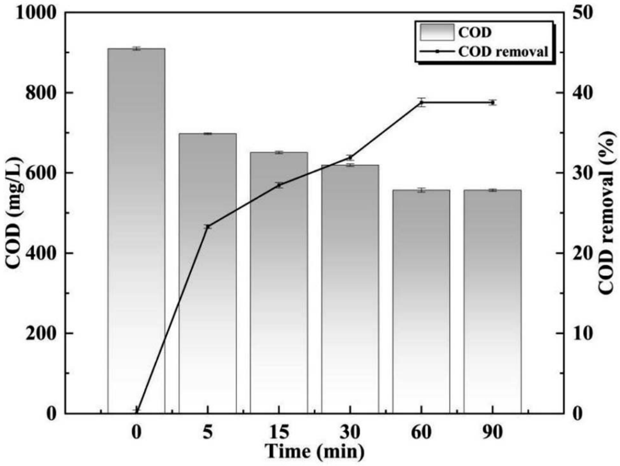


Fig. 2 The COD concentrations and removal with O_3 treatment time.

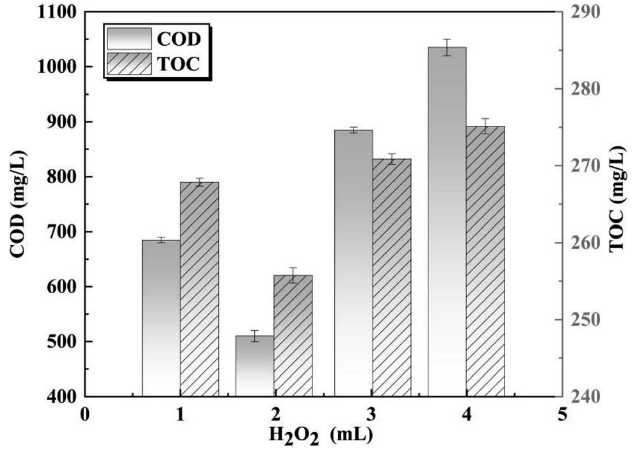


Fig. 4 COD and TOC concentration at different H_2O_2 dosages under O_3/H_2O_2 oxidation process.

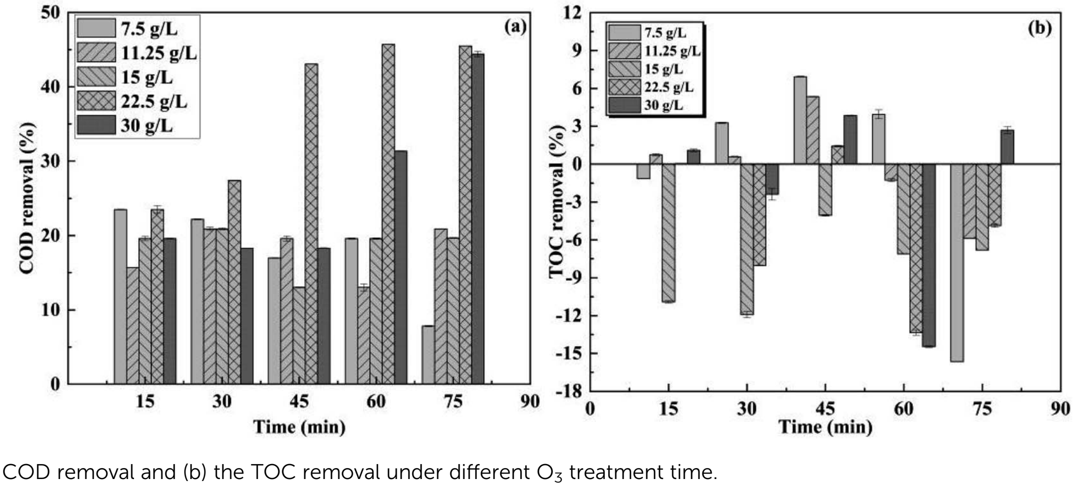


Fig. 3 (a) The COD removal and (b) the TOC removal under different O_3 treatment time.

Nevertheless, excessive H_2O_2 and its intermediate HO_2^- react with $^{\bullet}OH$ produced by the O_3 decomposition, and the main reaction mechanism is as follows.[26,27]

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet}$$

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$$

$$HO_2^- + {}^{\bullet}OH \rightarrow OH^- + HO_2^{\bullet}$$

Elevated concentrations of H_2O_2 and O_3 typically result in an enhanced production of $^{\bullet}OH$, but excessive utilization can give rise to detrimental consequences. Hence, it is crucial to assess the optimal H_2O_2/O_3 ratio for attaining maximum degradation of pollutants.

3.4 O_3/Fenton oxidation process

The 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 $^{\bullet}OH$ radicals.[27] Considering the highly alkaline nature of the APU wastewater, the primary oxidation mechanism gradually shifted from indirect O_3 oxidation to direct $^{\bullet}OH$ oxidation. After undergoing the process of 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 $^{\bullet}OH$, and the reaction between Fe^{2+} and H_2O_2 produced highly reactive $^{\bullet}OH$, which effectively degraded complex organic matter, including aromatic and heterocyclic unsaturated organic matter.[28–30] In the 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 $FeSO_4 \cdot 7H_2O$ and H_2O_2 to determine the ideal agent dosage.

The oxidation efficiency of wastewater treated by O_3/Fenton oxidation process in the Cansolv device was investigated. As shown in Fig. 5a, an increase in $FeSO_4 \cdot 7H_2O$ dosage significantly enhanced COD removal when H_2O_2 dosage was 2 mL. A COD removal of 95% was achieved with a dosage of 2.88 mmol $FeSO_4 \cdot 7H_2O$ dosage, highlighting its crucial role in the organic degradation process within the O_3/Fenton system. However, when H_2O_2 dosage was increased to 4 mL, COD initially increased and then decreased with increasing $FeSO_4 \cdot 7H_2O$ content. The highest point of COD removal (98%) was reached at a $FeSO_4 \cdot 7H_2O$ content of 2.16 mmol. The decline in COD removal with an addition of 2.88 mmol $FeSO_4 \cdot 7H_2O$ can be attributed to excessive $^{\bullet}OH$ consumption by Fe^{2+} ions within the system, leading to impaired oxidation.[27]

After adding 2 mL and 4 mL of H_2O_2, the removal of TOC increased with an increase in $FeSO_4 \cdot 7H_2O$ content. The optimal TOC removal rates were found to be 49% and 55%, respectively. This suggests that a higher dosage of H_2O_2 dosage generates more $^{\bullet}OH$, thereby enhancing the organic degradation of organic compounds and improving TOC removal to some extent.[31] When the H_2O_2 dosage was fixed at 4 mL, further increasing the $FeSO_4 \cdot 7H_2O$ dosage resulted in a continuous increase in TOC removal without reaching equilibrium. However, excessive $FeSO_4 \cdot 7H_2O$ dosage in the O_3/Fenton oxidation process led to increased alkali consumption during subsequent decolorization, resulting in significant formation of ferric hydroxide sludge.[32,33] Considering COD and TOC removal efficiencies as well as economic factors, it was determined that the optimal dosages for the O_3/Fenton oxidation process were 2 mL H_2O_2 and 2.88 mmol $FeSO_4 \cdot 7H_2O$.

The impact of the 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 O_3 oxidation process demonstrated greater effectiveness. Therefore, the optimal performance was achieved when employing the O_3/Fenton oxidation process with a value of 5 for pH.

In the O_3/Fenton oxidation process, a pH that is too low would hinder the oxidation of O_3 in the solution, while a pH that is too high would diminish the effectiveness of Fenton's reagent. Under alkaline conditions, Fe^{2+} undergoes rapid

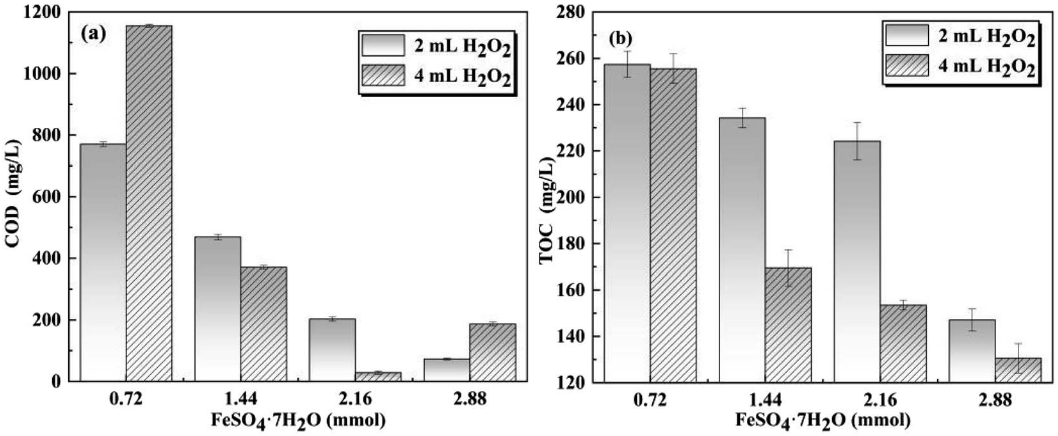


Fig. 5 COD (a) and (b) TOC under different $FeSO_4 \cdot 7H_2O$ and H_2O_2.

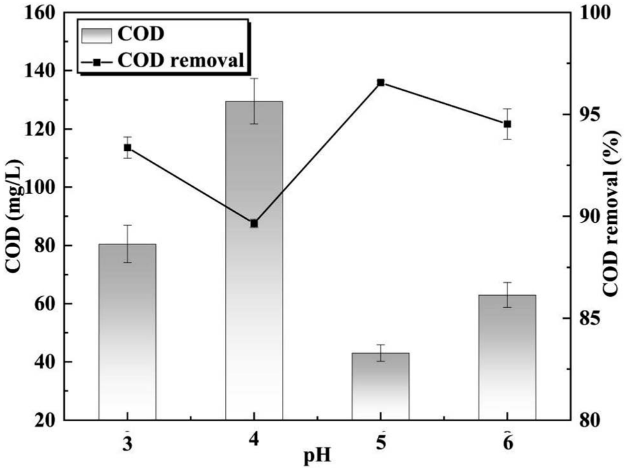


Fig. 6 COD removal during the O_3/Fenton oxidation process under varying pH conditions.

oxidized to Fe^{3+}, resulting in precipitation of ferric hydroxide.[29,33] 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 $^{\bullet}OH$ 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. Subsequently, following Fenton reaction, the intermediates in the wastewater are efficiently mineralized.[3,34] Thus, a significant reduction in organic composition within the wastewater was observed after a 1 hour O_3/Fenton oxidation process.

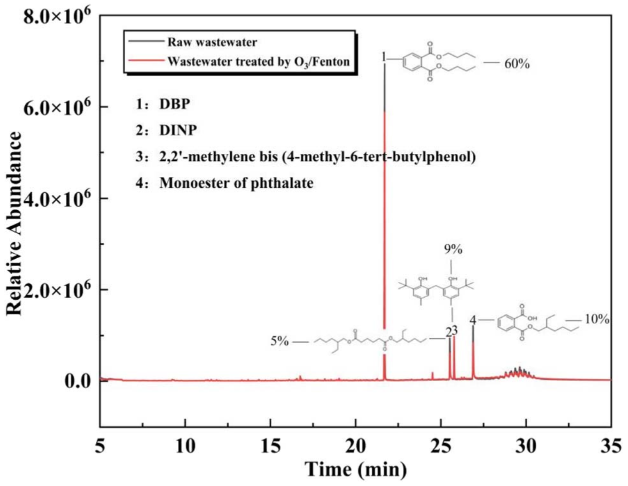


Fig. 7 GC-MS before and after O_3/Fenton oxidation process.

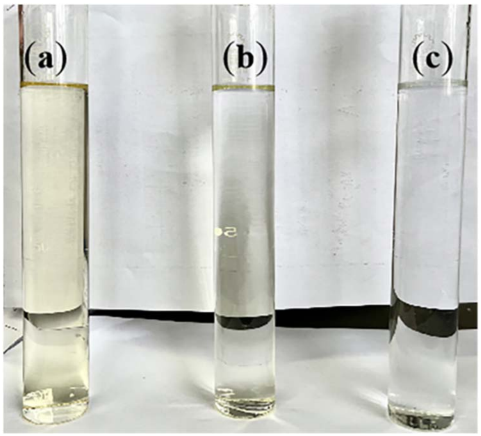


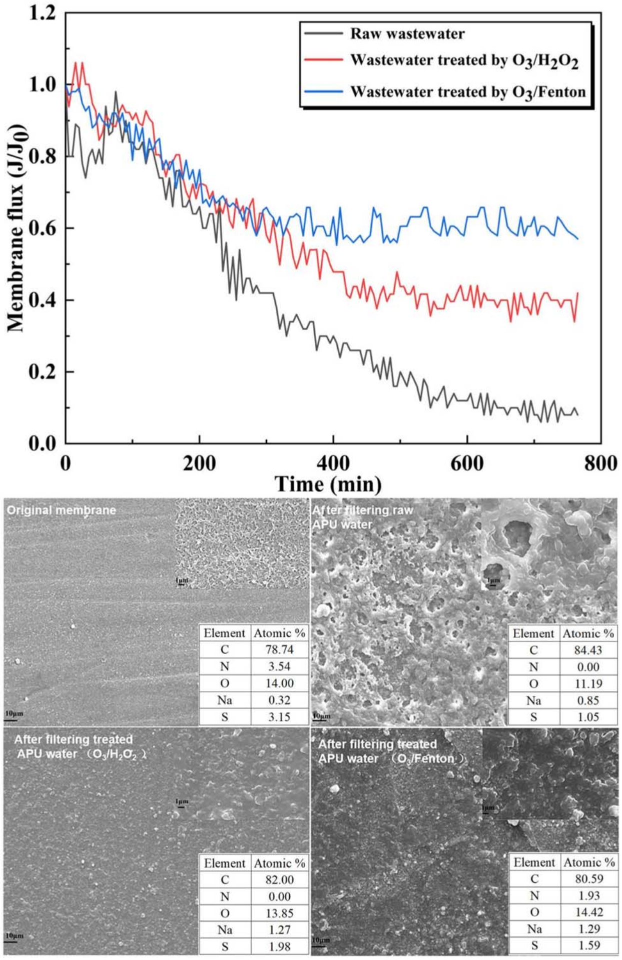
Fig. 8 Different chromatic characteristics of raw APU wastewater (a), wastewater treated by O_3/H_2O_2 process (b), wastewater treated by O_3/Fenton process (c).

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.[3]

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

	Different processes		
Parameter (mg L^{-1})	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



Element	Atomic %
C	78.74
N	3.54
O	14.00
Na	0.32
S	3.15

Element	Atomic %
C	84.43
N	0.00
O	11.19
Na	0.85
S	1.05

Element	Atomic %
C	82.00
N	0.00
O	13.85
Na	1.27
S	1.98

Element	Atomic %
C	80.59
N	1.93
O	14.42
Na	1.29
S	1.59

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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