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Application of airlift ceramic ultrafiltration membrane ozonation reactor in the degradation of humic acids

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ABSTRACT

A novel airlift reactor for the removal and degradation of humic acids (HAs) was presented and employed, combining a ceramic membrane reactor with a pressurized ozonation process. The degradation of organic matter was enhanced since HA could be effectively rejected in the reactor by adopting TiO_2 ultrafiltration membrane with an average pore size of 5.5 nm. Ozone was pressurized into the reactor to improve both the reaction and the separation processes. In addition, the application of compressed gaseous ozone can alleviate membrane fouling by reaction with HAs to reduce the thickness of filter cake. Thanks to the effective retention and catalytic ozonation of the TiO_2 membrane, the removal rate of COD_{Cr} and TOC increased to 91.0, 70.0% from 61.0, 36.5%, respectively, compared with a conventional airlift reactor. Further, the ratio of BOD_5/COD increased to 0.52 from 0.01, which means the biodegradability of the feed solution was significantly improved with the reactor, thus it could play an important role in improving the efficiency of water treatment and reducing the cost of downstream biological steps.

Keywords: Ceramic membrane; Ozonation; Airlift membrane reactor; Humic acids

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1. Introduction

Humic substances represent a major fraction of dissolved natural organic matter (NOM) in surface water, usually accounting for 50–90% of the total dissolved NOM [1,2]. Mounting investigation has shown that humic substances are the major precursors in the formation of trichloromethane compounds and other disinfection by-products after water chlorination [3–6]. Humic substances also have a high ability to form complex with various heavy metal ions and toxic organic pollutants in water, which leads to the formation of indissoluble and toxic matter [7]. Hence, the removal of humic substances has been an essential topic in water treatment for improving the quality of direct drinking water.

The application of membrane filtration for the treatment of water and wastewater has expanded rapidly over the last two decades due to its effective performance of removing particles, micro-organisms and organic matter from surface waters [8,9]. Nevertheless,

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one of the major obstacles in using membrane filtration is an increase in operational cost because of the decrease in the permeate flux due to membrane fouling and concentration polarization. Numerous studies have been explored in order to decrease membrane fouling and control concentration polarization, such as changing membrane structure parameters (size and shape of pores, surface roughness, and porosity) and optimizing technology (coupling with other techniques, enhanced flux based on gas–liquid two-phase flow) [10–13].

Ozone is currently used for water treatment because of its high oxidation and disinfection potential [14,15]. In an ozonation process, the total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) of wastewater will decrease due to the destruction of the aromaticity and depolymerization, causing the high apparent molecular weight (MW) fractions to decrease and the carboxylic functions to increase [3,6,16]. Ozonation and pre-ozonation have been proven to be an effective way to reduce the membrane fouling and enhance the permeate flux by the degradation of high MW NOM [17,18]. However, the polymeric membranes, commonly used in water treatment industry, have low chemical resistance and tend to degrade by ozone [19]. To avoid this, some researchers had adopted to dislodge ozone, before the solution flows into the membrane modules, by nitrogen to make sure that the ozone is not getting in touch with the membrane, which increases the operational cost greatly [10].

Ceramic membranes have more advantages than polymeric membranes to combine with ozonation of thermally, chemically mechanical stable, longer lifetimes [20,21], and most importantly, the ozone resistant [22]. The use of hybrid ozonation–ceramic membrane can efficiently reduce membrane fouling. The thickness of the foulant layer will be decreased by the ozonation of organic foulant into small molecules, reduce the adsorption on the membrane surface by change the hydrophobic aromatic groups to more hydrophilic groups and the catalytic properties of metal oxides in the separation layer of membrane [23]. In recent years, the reactive catalytic ceramic membrane has been developed, which manifested itself as an improved recovery of the permeate flux because of good performance of catalytic activity when combined with ozonation [24,25]. Furthermore, the hybrid ozonation–ceramic membrane systems have also proven to be an effective way to control the formation of carcinogenic bromate by reducing the ozone exposure and improving the ozone utilization [26–28].

The airlift membrane reactor can remove pollution and serve as an effective device in the treatment of water by combining a membrane separation technology and reaction process [29]. The operating principle of this reactor is to utilize the density difference between the fluid in a vertical membrane tube with a sparged gas and that of a feed tank, in which the liquid level is at the same or lower height than the sparged tube [30]. In this process, the gas simultaneously provides the driving force for fluid circulation and the transmembrane pressure (TMP) for membrane filtration, while the sparged gas will react with the fluid. Compared with the traditional membrane reactor, the airlift membrane reactor is considered to be an effective, simple and low-cost technique [31,32]. It can increase the shear force at the membrane surface by facilitating the formation of slug flow and enhance the membrane permeation flux via alleviating concentration polarization phenomenon [29,33,34].

Hence, in this paper, we introduced a method to remove and degrade humic acids (HAs) by using an airlift ceramic membrane ozonation reactor (ACMOR). Ozone has three functions in this membrane reactor, such as providing TMP, circulating liquid, and reaction with pollutant. The compressed ozone gas entered into the membrane reactor by a gas sparger forms a gas—liquid two-phase flow to drive the circulation of the feed solution and react with HA. A TiO_2 ultrafiltration (UF) membrane with an average pore size of 5.5 nm was implicated. The effects of pressurized ozone in the reactor on the membrane permeate performance and the efficiency of improving water quality (UV_{254}, TOC, COD_{Cr}, and BOD_5) were investigated.

2. Materials and methods

2.1. HAs sample

Aldrich-humic acid (53680, technical grade Sigma-Aldrich) was used as a model substance although, it is a terrestrial peat-derived humic material and its weight-averaged MW is larger than typical aquatic HA [35]. It has been widely used as a model foulant by many membrane researchers since it is easily available and well characterized [36].

An HA stock solution was prepared and diluted to the required feed solution concentrations with deionized water. The pH was adjusted by adding either HCl or NaOH. All aqueous solutions were prepared with deionized water.

2.2. UF membrane

The ceramic UF membrane was fabricated via an improved polymeric sol–gel method. The sol containing P123 was obtained according to that reported in our previous works [37]. The tubular support with an average pore size of 50 nm (8 mm in inner diameter, 100 mm in length, and 2 mm in wall thickness) was provided by Membrane Science & Technology Research Center (Nanjing, China). The sol was dip coated on the support and then aged at 60℃ 35% RH for 12 h. The obtained gel was calcined at 400℃ for 4 h in air with the heating rate of 0.5℃/min to burn off the polymer template. All the procedures were repeated four times to obtain crack-free TiO_2 UF membrane. Characteristics of the membrane are shown in Table 1. The scanning electron microscopy (SEM) image in Fig. 1 shows that the surface of the membrane is homogeneous throughout the whole area and no defects can be found. Fig. 2 shows the cross-sectional SEM image of the composite membrane. The thin TiO_2 layer with an approximate thickness of 1.5 μm can be seen clearly on the right side of the composite membrane.

2.3. Experimental apparatus

The airlift ceramic UF membrane ozonation reactor used in these experiments is shown in Fig. 3. It consists of an ozone-pressurized system (E-1, E-2, E-3, E-4, E-5) and a ceramic membrane reactor. Ozone was produced from dry air using an ozone generator (E-1 NPA-15, NIPPON Co., Ltd China), and then pressurized with a pneumatic booster pump (E-3). The compressed ozone was introduced into the reactor through a gas diffuser at the bottom of the reactor. Storage tanks (E-2, E-5) were used as pressure buffer tanks. The gaseous ozone concentration was controlled by changing the voltage, applied to the ozone generator. The airlift reactor included a volume of 800 mL feed tank and the membrane module, in which tubular ceramic membrane was sealed with O-ring, was flange mounted with the reactor. The volumetric gas flow rate was adjusted by a calibrated flow meter and the TMP was regulated through a back pressure valve V2 at the gas outlet of the reactor. At last, a 5% potassium iodide (KI) solution was employed as the absorption solution for residual ozone tail gas. The operating condition for this system is shown in Table 2.

Table 1
Characteristics of the membrane employed in this study

Parameters	UF membrane
Material	TiO_2
Type	Tubular
Average pore size (nm)	5.5
Membrane surface area (cm^2)	23.6
Type of filtration	Cross-flow
Pure water flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)	155

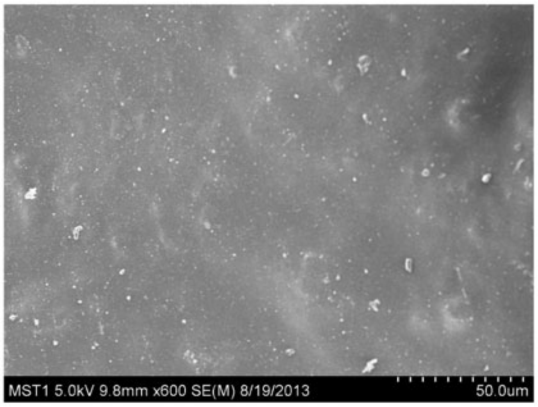


Fig. 1. SEM image of the surface of the TiO_2 UF membrane.

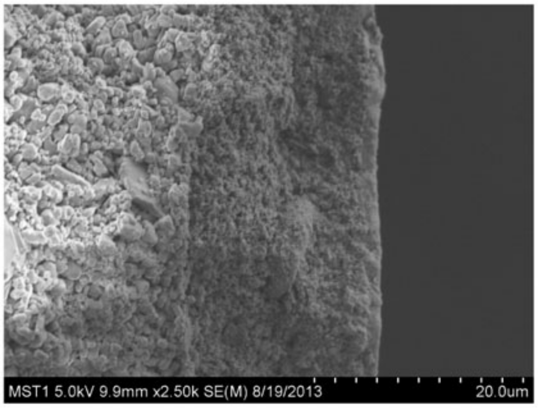
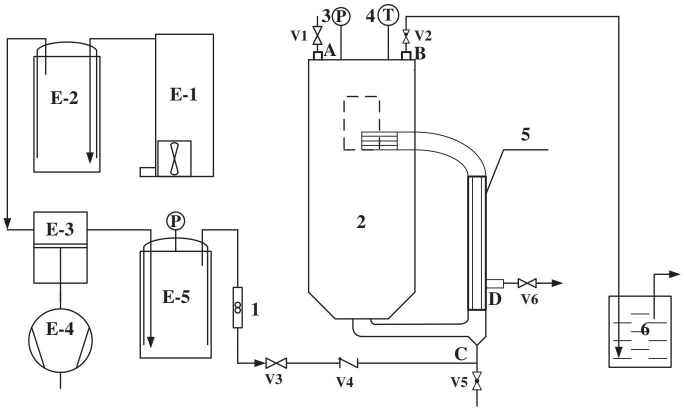


Fig. 2. SEM image of the cross-section of the TiO_2 UF membrane.

2.4. Analytical methods

The morphology of the surface and cross-section of the membrane were examined by a high-resolution scanning electron microscope (SEM, S4800, Hitachi, Japan). The gaseous ozone concentration was determined by iodometry using KI solutions to calculate the amount of ozone in the gaseous phase. The TOC concentration was determined by a TOC-VCPH (Shimadzu, Japan) and a detection limit of 0.004 mg L^{-1}. COD_{Cr} was obtained by a DRB200 (HACH, USA), while biological oxygen demand within 5 d (BOD_5) was measured with a BOD TraK analyzer (HACH, USA). A UV/VIS spectrophotometry (UV-3600 spectrophotometer, Shimadzu, Japan) was carried out to



E-1: ozone generator
E-2: buffer tank
E-3: pneumatic booster pump
E-4: air compressor
E-5: storage tank

1: flowmeter
2: feed tank
3: pressure gauge
4: thermometer
5: membrane module
6: KI solution

A: feed port
B: gas outlet
C: gas inlet
D: permeation outlet
V1-V6: valves

Fig. 3. Schematic of the airlift ceramic UF membrane ozonation reactor.

Table 2
Operating condition for the system

Parameters	
TMP (MPa)	0.15–0.35
Temperature (℃)	25 ± 0.5
Ozone gas flow rate (L min^{-1})	5
Gaseous ozone concentration (mg/L)	8, 15, 25, 50
Diameter of gas diffuser (mm)	1.5

determine the evaluation of the HA degradation. Two different wavelengths were measured; UV$_{254}$ was used for aromatic compounds, while the removal of color was performed at 400 nm [38]. Removal rates of HA were determined using the following formulae [16]:

$$\frac{C_f}{C_i} = \frac{\mathrm{UV}_{254(t)}}{\mathrm{UV}_{254(0)}} \tag{1}$$

$$R = \frac{C_i - C_f}{C_i} \times 100\% \tag{2}$$

where R is the removal rate of HA (%), C_i is the concentration of feed solution, and C_f is the concentration after the reaction, while UV$_{254(0)}$ and UV$_{254(t)}$ are the absorbance of the HA solution at 254 nm at the initial time and the reaction time "t", respectively.

The HA concentration in permeate samples of the membrane (C_p) was analyzed using the same method mentioned above, and the retention of the membrane (r) was calculated using the following formula:

$$r = \frac{C_i - C_p}{C_i} \times 100\% \tag{3}$$

3. Results and discussion

3.1. Effect of ozone on membrane flux

Gas sparging has proven to be an effective way to enhance membrane permeates flux due to the forming gas–liquid two-phase flow. In Fig. 4, normalized flux (J/J_0) vs. operation time was presented under different operation conditions including: (a) static UF (no gas–-liquid two-phase flow circulating in the system), (b) UF with compressed nitrogen (forming gas–liquid two-phase fluid by compressed nitrogen), and (c) UF in the ACMOR (forming gas–liquid two-phase fluid by compressed ozone). The critical stable normalized flux was improved from 0.37 to 0.46 compared with a static UF. The possible reason was that, it enhanced the shear force on the membrane surface via formation of a gas–liquid two-phase flow when introducing the sparging nitrogen into this system [33] that disrupted the concentration polarization layer and hindered the formation of fouling layer to enhance the UF process. And, the normalized flux was further improved with compressed ozone instead of nitrogen since the

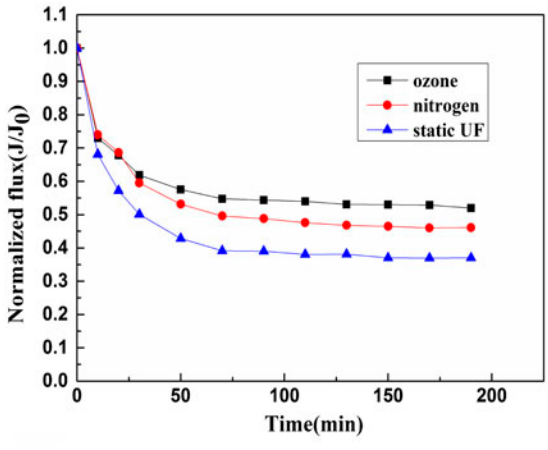


Fig. 4. Effect of ozone and nitrogen on flux: C_i of 10 mg L^{-1}, pressure of 0.35 MPa, gaseous ozone concentration 8 mg/L, gas flow rate of 5 L min^{-1}, pH of 10.

reaction of ozone and hydroxy radicals with NOM could effectively reduce the thickness and resistance of the filer cake formed during filtration. Fig. 5 shows the relationships between the ozone concentration and the normalized flux, the greater the ozone gas concentration, the greater the normalized flux. With the ozone gas concentration increase from 8 to 25 mg/L, there was a significant increase in normalized flux from 0.52 to 0.75, respectively. As the ozone gas concentration further increased from 25 to 50 mg/L, the normalized flux had a little change. The synergetic mechanism of catalytic ozonation and gas–liquid TiO_2 membrane UF are shown in Fig. 6. Gas slugs, which contain ozone, were formed in a vertical channel of ceramic tubular membrane. As reported by Nawrocki [39], hydroxyl groups are present on TiO_2 membrane surface in water. These hydroxyl groups react with dissolved ozone to generate radicals intermediates ($O_2^{\cdot-}$ and $HO_2^{\cdot}$), which can act as the initiator of chain reactions to produce hydroxyl radicals.

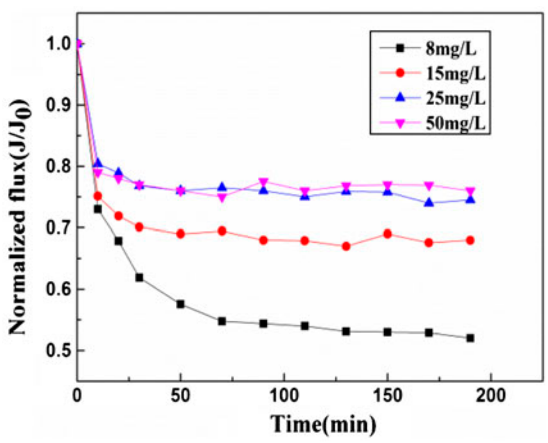


Fig. 5. Effect of gaseous ozone concentration on flux: C_i of 10 mg/L, pressure of 0.35 MPa, gas flow rate of 5 L min^{-1}, pH of 10.

3.2. *Effect of pressure on membrane performance*

The evolution of the permeate flux at different pressures is shown in Fig. 7. The flux decreased in the initial 50 min to a steady-state level. Simultaneously, we observed that the rate of decline for the permeate flux increased with increasing pressure and this phenomenon could be attributed to the increase in thickness and the compactness of the fouling layer [29,40]. When increasing the pressure, the accumulation of organic matter in the fouling layer was enhanced and reduced the difference of the critical steady flux at different pressures. The values for the steady state permeate fluxes were 138, 129, and 120 L/m^{2}h for pressures of 0.35, 0.25, and 0.15 MPa, respectively. Thus, the flux could not be effectively increased by the increase in pressure. Meanwhile, the variation of rejection rates with filtration time at different pressures is given in Fig. 8. It was observed that the retention rate was enhanced with filtration time due to the formation of fouling layer on the membrane surface and/or partially blocking the membrane pores. The retention rate of HA slightly decreased with the increase in pressure, that reached 96.7, 95.6, and 94.8% at 90 min when the pressure was varied to 0.15, 0.25, and 0.35 MPa, respectively.

3.3. *Effect of ACMOR on TOC and COD removal*

The removal rate of TOC and COD_{Cr} were investigated when employing ACMOR and ozonation alone (Figs. 9–12). It was found that 70% TOC and 91% COD_{Cr} were removed via ACMOR after 60 min, which were obviously higher than the results from the airlift reactor with ozonation alone. Under the ozonation alone condition, the removal rate of TOC and COD were improved with increasing ozonation time. But after 60 min, only 36.5% TOC and 61% COD were removed. These results reveal that single ozonation is insufficient to mineralize marine HA to carbon dioxide and water, which is in agreement with the work of Imai et al. [16].

In Fig. 9, at the first 10 min, the TOC had a sharp decrease to 3.9 mg/L from the initial concentration (20.5 mg/L), and then it increased slightly to 6.3 mg/L

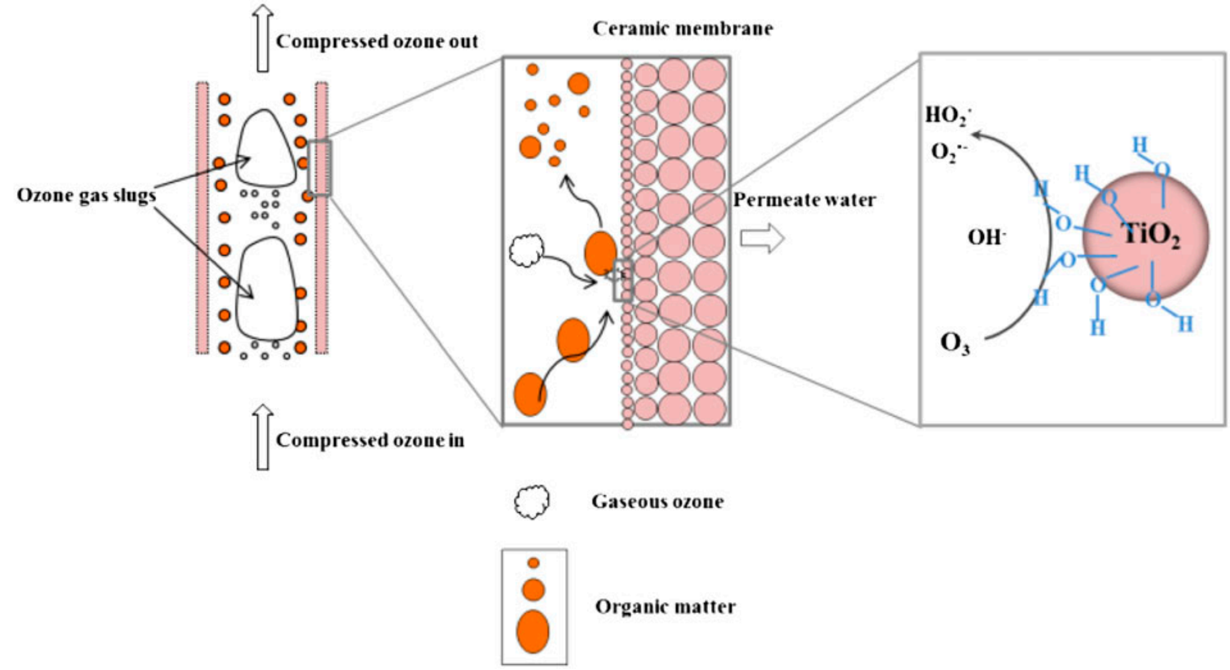


Fig. 6. Mechanism of compressed ozone enhanced permeate flux in ceramic tubular membrane.

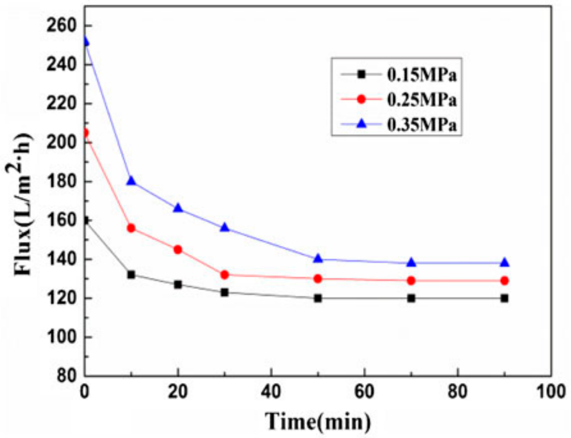


Fig. 7. Permeate flux evolution at different pressures: C_i of $10\,\mathrm{mg\,L^{-1}}$, gaseous ozone concentration of $8\,\mathrm{mg\,L^{-1}}$, pH of 10, and gas flow rate of $5\,\mathrm{L\,min^{-1}}$.

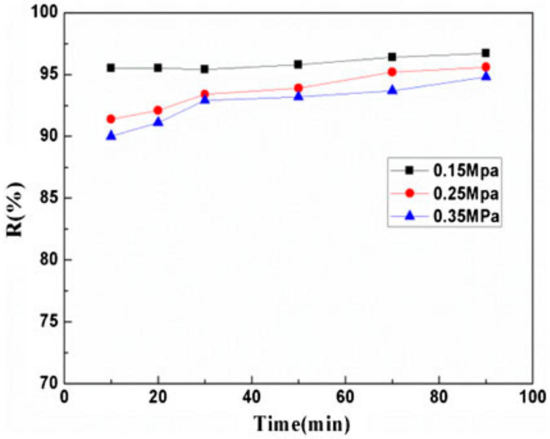


Fig. 8. HA retention at different pressures: C_i of $10\,\mathrm{mg\,L^{-1}}$, gaseous ozone concentration of $8\,\mathrm{mg\,L^{-1}}$, pH of 10, and gas flow rate of $5\,\mathrm{L\,min^{-1}}$.

with time, and the removal rate decreases from 80 to 70% in 60 min. The reason was that the HA had been rejected at the beginning, and then decomposed into small MW organic matter. The small organic compounds could diffuse through the pores of membrane and resulted in rejection of only relatively large MW organic compounds during filtration. This also demonstrates that high MW organic matter was degraded into low MW organic matter by ozonation; however, complete removal was impossible [16,41]. Moreover, ozonation combined with membrane filtration as an advanced process resulted in the removal of COD_{Cr}. In Fig. 10, the COD_{Cr} decreased from 64.5 to 5.8 mg/L and the removal rate of COD_{Cr} was stabilized at 91% with reaction and filtration time. It means that ceramic UF membrane with a small pore size has a preferable removal rate for TOC and COD_{Cr} from this experiment.

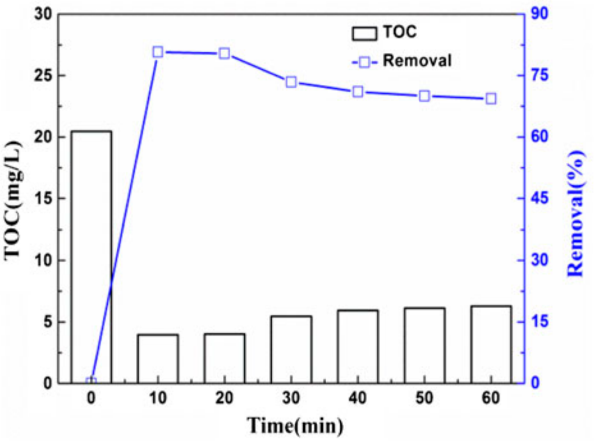


Fig. 9. Effect of ozonation and membrane filtration on TOC: C_i of $10\,\mathrm{mg\,L^{-1}}$, ozone concentration of $50\,\mathrm{mg\,L^{-1}}$, pH of 10, gas flow rate of $5\,\mathrm{L\,min^{-1}}$, and pressure of 0.15 MPa.

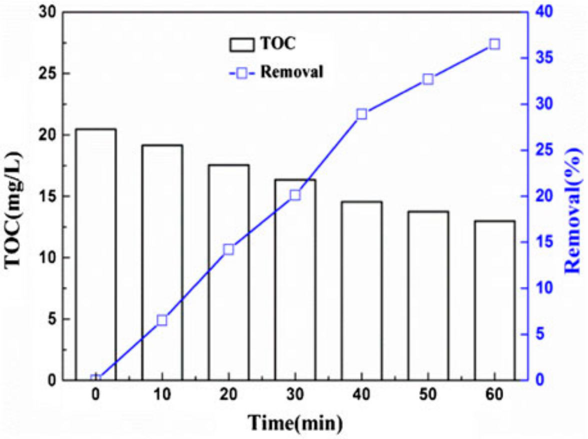


Fig. 11. Effect of ozonation on TOC: C_i of $10\,\mathrm{mg\,L^{-1}}$, ozone concentration of $50\,\mathrm{mg\,L^{-1}}$, pH of 10, gas flow rate of $5\,\mathrm{L\,min^{-1}}$, and pressure of 0.15 MPa.

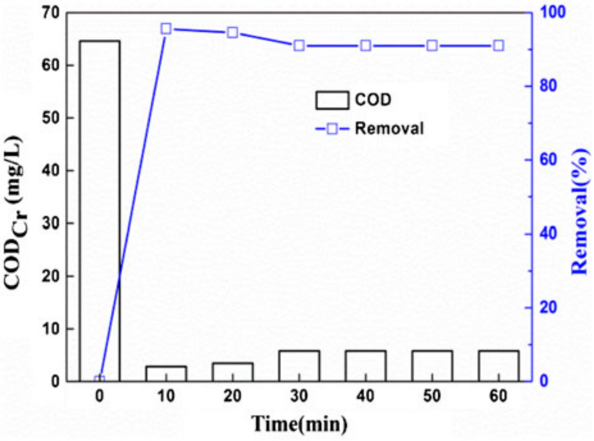


Fig. 10. Effect of ozonation and membrane filtration on $\mathrm{COD_{Cr}}$: C_i of $10\,\mathrm{mg\,L^{-1}}$, ozone concentration of $50\,\mathrm{mg\,L^{-1}}$, pH of 10, gas flow rate of $5\,\mathrm{L\,min^{-1}}$, and pressure of 0.15 MPa.

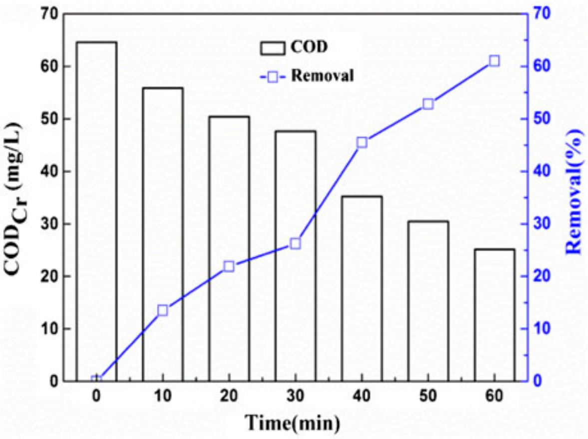


Fig. 12. Effect of ozonation on $\mathrm{COD_{Cr}}$: C_i of $10\,\mathrm{mg\,L^{-1}}$, ozone concentration of $50\,\mathrm{mg\,L^{-1}}$, pH of 10, gas flow rate of $5\,\mathrm{L\,min^{-1}}$, and pressure of 0.15 MPa.

The appearance changes of HA solution over time by two different operation ways are shown in Fig. 13. The color of the HA solution became weaker with increasing reaction time. The color removal reached 95% by ACMOR (Fig. 13(b)) at 60 min, which is higher than by ozonation alone (Fig. 13(a)) about 75%. This also demonstrated that the removal of HA by the ACMOR was very efficient.

3.4. Effect of ozonation on biodegradability

We further evaluated the biodegradability of the solution treated by the ACMOR via examining the evolution of the ratio of $\mathrm{BOD_5/COD}$. In Fig. 14, the value of the feed solution is about 0.01 and then increased to 0.52 after treated with ozone for 60 min. The reason was that pressurized ozone broke down (or rearranged) the molecular structures of organic matter, converting the non-biodegradable organics to more biodegradable substances, which simultaneously alleviated membrane fouling and enhanced the flux. The improvement in HA biodegradability makes this method remarkably important in the application of the ACMOR to wastewater treatment for improving the efficiency and reducing the burden of the further biological steps.

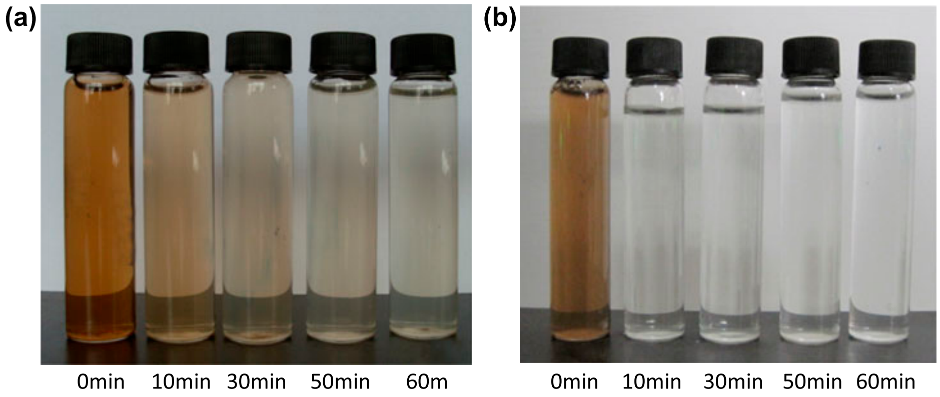


Fig. 13. The appearance of solutions at different times (from 0 to 60 min): (a) refers to ozonation alone and (b) refers to ACMOR.

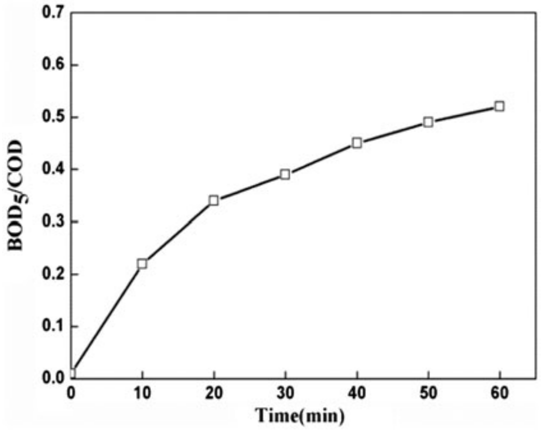


Fig. 14. The change in biodegradability during ozonation: C_i of 50 mg L^{-1}, ozone concentration of 50 mg L^{-1}, pH of 10, gas flow rate of 5 L min^{-1}, and temperature of 50℃.

3.5. Membrane cleaning

Membrane fouling causes severe flux decline and affects the quantity of the water produced. The pure water flux even decreases by 50% compared with fresh membrane, if not adopt any membrane cleaning measures, because the organic matters could deposit onto membrane surface or into membrane pores. In this experiment, the TiO_2 UF ceramic membrane could be regenerated via an easy chemical cleaning procedure: the ceramic membrane was cleaned with 2% NaOH solution at 75℃ for 60 min after each experiment, followed by thorough rinsing with deionized water. The results of the cleaning tests, after each experiment, are presented in Fig. 15, and the flux recovery ratio is higher than 90% of the flux of the new membrane.

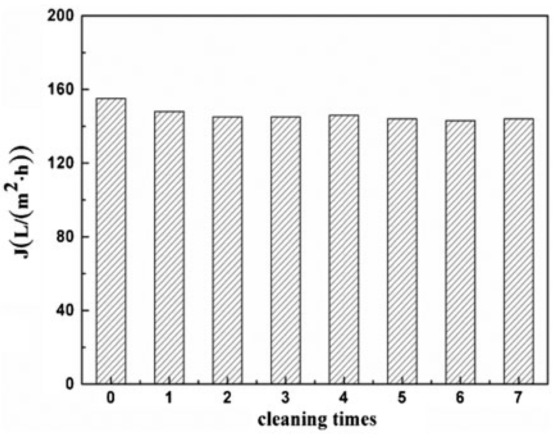


Fig. 15. The recovery of membrane cleaning flux.

4. Conclusion

The new ACMOR was demonstrated to be a very efficient technology in the degradation of HAs, when compared with currently solely applied ozonation or membrane filtration process. The compressed ozone has a great effect on TiO_2 membrane permeate flux by relieving concentration polarization and decreasing membrane fouling. The permeate flux increased with the increase in gas ozone concentration. The degradation of organic matter was improved via the effectively rejection HA of TiO_2 UF membrane. In addition, compressed gas zone significantly enhanced biodegradability by degrading the high MW organic matter (HAs) to low MW organic matter. Thus, this technology has potential application in the purification of wastewater and the degradation of other organic pollutants in wastewater.

Acknowledgments

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