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Can Heat-Activated Peroxymonosulfate Be Used as a Pretreatment to Mitigate Fouling for Membrane Distillation: Performance of Individual Organics?

Mingxiang Liu ^{1,*}, Lei Zhang ^{1,*}, Le Han ² , Caihua Mei ¹, Changwen Xu ¹, Rui Yuan ¹ and Chunxia Geng ³

¹ School of Civil Engineering and Architecture, Chuzhou University, Chuzhou 239000, China

² Key Laboratory of Eco-Environments in Three Gorges Reservoir Region, Ministry of Education, College of Environment and Ecology, Chongqing University, Chongqing 400044, China

³ Beijing Water Planning Institute, Beijing 100089, China

* Correspondence: liumingxiang2022@126.com (M.L.); zhanglei@chzu.edu.cn (L.Z.)

Abstract: Heat-activated persulfate preoxidation was recently proposed as a potential approach to mitigate membrane fouling in membrane distillation (MD) for treating actual water. However, the possible mitigation mechanism involved has not yet been elucidated. In this study, we explored the relationship between membrane fouling and the pretreatment of natural organic matter (NOM) solutions with peroxymonosulfate (PMS). Individual humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA) contaminants were chosen as model NOM samples. The degradation efficiency of heat-activated PMS preoxidation was investigated. The removal rates of organic contaminants improved as the PMS dose and activation temperature of the feed increased. Specific flux (J/J_0) measurements coupled with multiple characterizations were performed to assess the fouling behavior. The fouling data showed that when pretreatment was conducted without PMS, pure HA caused the most severe fouling, followed by pure BSA, whereas pure SA caused almost no membrane fouling. After PMS preoxidation, the oxidation products of the NOM unexpectedly caused more fouling, despite the reduction in the amount of the NOM. Further work is needed to evaluate fouling mitigation when working with complex streams.

Keywords: membrane distillation; membrane fouling; natural organic matter; heat-activated peroxymonosulfate oxidation



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1. Introduction

Membrane distillation (MD) is a thermal separation process in which the driving force for mass transfer is the vapor pressure gradient created by the temperature difference between the sides of a hydrophobic microporous membrane [1,2]. Superior to pressure-driven membrane processes, MD can theoretically reach a nonvolatile rejection rate of 100% while having minimal mechanical requirements for membrane materials and modules [3,4]. Moreover, compared to conventional distillation and multistage vacuum evaporation processes, MD can be performed at lower temperatures and consumes lesser energy [5].

Although MD is a promising technique for desalination and water purification [6,7], the industrial application of MD has not yet fully matured [8]. Membrane fouling is one of the primary problems hindering its scale-up and is manifested in the forms of surface fouling and pore blocking [9]. The fouling of membrane surfaces aggravates the temperature and concentration polarization effects and increases the mass transfer resistance [10]. Blockages in membrane pores result in reductions of the pore size and porosity of the membrane [11,12], thus affecting the transfer rate of water vapor in the pores. Therefore, membrane fouling could reduce the membrane permeability and increase the heat transfer resistance, ultimately leading to a rapid flux decline [13]. In addition, severe membrane fouling could induce membrane wetting, which is responsible for the deterioration of the

effluent quality [14,15]. Based on the nature of the feed solution, fouling can be classified into biological, inorganic, and organic fouling [9,16]. The adsorption and deposition of natural organic matter (NOM) constitutes the most common type of organic fouling, where the NOM is primarily made up of humic substances, proteins, polysaccharides, carboxylic acids, extracellular polymers, and other substances [17]. Liu et al. [18] found that humic acid (HA) is more prone to adsorption on the surfaces of hydrophobic membranes due to hydrophobic interaction forces and electrostatic interactions, leading to irreversible membrane fouling. Tan et al. [19] explored the effect of HA fouling on MD and found that HA contamination caused a considerable decrease in the flux, mainly due to the concave interfaces inside the small pores of the foulants, leading to a decrease in the vapor pressure. Naidu et al. [20] found that bovine serum albumin (BSA) also has considerable fouling potential, whereas alginate acid causes minimal fouling because of its hydrophilic nature. Interestingly, in a recent study by Wang et al. [21], HA formed a dense protective layer that hindered inorganic scaling, making HA play a mitigative role in membrane scaling/wetting when MD was performed for sea water desalination. Organic fouling is typically accompanied by biological and/or inorganic fouling during the treatment of actual water, and the resulting complex fouling mechanism is difficult to elucidate. Nanomaterial modification of MD membranes has shown potential in enhancing their performance, including their flux, selectivity, and antifouling properties. However, the high cost and difficulty in scaling up the fabrication process remain significant challenges [22].

Advanced oxidation processes (AOPs) are promising technologies for pollutant degradation as they produce hydroxyl radicals ($\bullet\text{OH}$) and sulfate radicals ($\text{SO}_4^{\bullet-}$). Among the oxidants, persulfates, including peroxymonosulfate (PMS) and peroxydisulfate (PDS), are often preferred due to their high stability and low cost [23–25]. PMS and PDS can be activated to produce $\text{SO}_4^{\bullet-}$ and/or $\bullet\text{OH}$ by providing an energy input (heat, light, and ultrasound) and incorporating transition metal ions and carbonaceous materials, among other means [26]. Asif et al. [27] first proposed heat-activated persulfate oxidation as a pretreatment strategy for MD applications. Subsequent studies have verified the effectiveness of this strategy in degrading contaminants in raw water, thus reducing membrane fouling [28–30]. Since MD is a thermal separation process, no additional heat source is required for persulfate activation. In addition, secondary contamination is eliminated because no chemical activators are needed. The use of persulfates can result in lower operational costs for membrane distillation by reducing the frequency of cleaning and maintenance as well as increasing the overall lifespan of the membranes. Therefore, preoxidation with persulfates activated by the hot feed in the MD process is an effective strategy for membrane fouling mitigation and effluent quality improvement. In the MD-AOP hybrid process developed by Han et al. [29], a hot feed is utilized to activate PDS and successfully control the membrane fouling/wetting caused by sodium dodecyl sulfate (SDS). Asif et al. [28] found that although protein-like substances are mainly responsible for algogenic organic matter (AOM) fouling in MD, it can be degraded by $\bullet\text{OH}$ and the singlet oxygen ($^1\text{O}_2$) generated from heat-activated PMS, thus alleviating 27–100% of AOM fouling. Ding et al. [30] revealed the fouling control mechanism through molecular fate mapping in a heated PDS activation–MD hybrid process. They found that organics with a high unsaturation degree that prefer to develop into membrane foulants could be effectively destroyed during the pretreatment process. High-molecular-weight (MW) organic compounds were broken down into lower-MW ones. These lower-MW compounds were more easily absorbed into the membranes of MD. At the same time, the complexation between cations and organics was reduced, which hindered inorganic scaling. Studies on the propensity of, and mechanisms underlying, organic fouling mitigation in persulfate oxidation coupled with ultrafiltration (UF) have been conducted [31–34]. According to Cheng et al. [34] Fe(II)/PMS oxidation can alleviate the UF fouling caused by salt-free HA–SA–BSA. However, unlike UF, MD is performed at higher water temperatures, lower operating pressures, and with different membrane materials. Therefore, the laws and mechanisms of UF may not apply to MD.

To evaluate the fouling degree caused by various NOM compounds and to comprehend the effect of persulfate preoxidation from the perspective of organic fouling excluding biological/inorganic fouling, we utilized a direct-contact membrane distillation (DCMD) system in conjunction with heat-activated PMS (heat/PMS) preoxidation to treat single NOM solutions. HA, BSA, and sodium alginate (SA) were utilized as target NOM contaminants to represent humic substances, proteins, and polysaccharides, respectively. The degradation efficiency of heat/PMS preoxidation was investigated using dissolved organic carbon (DOC) measurements, ultraviolet absorbance spectrometry at 254 nm (UV_{254}), and fluorescence excitation-emission matrices (EEMs). Real-time fluxes were monitored to reflect the rate and extent of membrane fouling. The fouling behaviors of the fouled membranes were characterized and assessed by scanning electron microscopy (SEM), attenuated total reflectance–Fourier transform infrared (ATR-FTIR) spectroscopy, and water contact angle (WCA) analyses. The research is anticipated to facilitate the development of precise pretreatment strategies for MD.

2. Materials and Methods

2.1. Membranes and Reagents

A hydrophobic, electronegative polytetrafluoroethylene (PTFE) flat-sheet membrane with a mean pore diameter of 0.22 μm , porosity of 70–80%, and thickness of 100 μm was obtained from Chuangwei Filter Equipment Company (Haining, China). HA (BR, $\geq 90\%$ purity), BSA (BR, $\geq 98\%$ purity), and SA (AR, $\geq 98\%$ purity) were purchased from Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Analytical grade potassium peroxydisulfate (PMS, $\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$, $\geq 98\%$ purity), sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\geq 99\%$ purity), hydrochloric acid (HCl, 36–38% purity), and sodium hydroxide (NaOH, $\geq 96\%$ purity) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). In this research, the concentration of each NOM (HA, BSA, and SA) solution was fixed at 20 mg L^{-1} , slightly higher than the DOC of surface water. Two gram per liter organic stock solutions of NOM were prepared as follows: 2 g HA was dissolved in 800 mL of 0.01 mol L^{-1} NaOH and stirred for 24 h. Subsequently, the pH was adjusted to 7.0 ± 0.1 using 1 mmol L^{-1} HCl, and the solution was diluted to 1000 mL using ultrapure water. Two grams each of BSA and SA were separately dissolved in 1000 mL ultrapure water under 12 h of stirring. Prior to the preoxidation tests, PMS and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ powders were separately dissolved in ultrapure water to prepare their respective stock solutions (0.10 mol L^{-1}). All stock solutions were stored in the dark at 4 $^\circ\text{C}$ and were used within three months.

2.2. Experimental Procedures

2.2.1. Heat-Activated PMS Preoxidation

Heat/PMS pretreatment experiments were performed in a glass beaker placed in a magnetically stirred water bath (ZNCL-GS, Jieyang Instrument, Shanghai, China). PMS was added to initiate the reaction when the desired temperature was reached. The time required for each preoxidation experiment was 60 min, and then equal stoichiometric amounts of $\text{Na}_2\text{S}_2\text{O}_3$ were added to quench the oxidation reaction. The activation temperature was controlled at 80 $^\circ\text{C}$ to study the degradation efficiency under different PMS doses (0, 0.4, and 0.8 g L^{-1}). A constant PMS dose of 0.4 g L^{-1} was used to study the degradation efficiency at different activation temperatures (60 $^\circ\text{C}$, 70 $^\circ\text{C}$, 80 $^\circ\text{C}$, and 90 $^\circ\text{C}$). Samples were gathered every 10 min and then immediately placed in a cold bath (0 $^\circ\text{C}$) in order to quench the reaction without affecting the analysis, as explained in Section 2.2.1.

2.2.2. DCMD Process

The laboratory-scale DCMD setup (Figure 1) was composed of two water circulation systems (hot side and cold side) and a membrane module with an effective area of $8.5 \times 6.5 \text{ cm}^2$ with cavities 2 mm in height on the hot and cold sides of the PTFE membrane. Two peristaltic pumps (DIPump550, Kamoer, Shanghai, China) were used for water

circulation at the same speed of 300 rpm, which enabled a constant crossflow velocity of 6.16 cm s^{-1} on both sides of the membrane. The feed temperature was set to the preoxidation temperature using an electric thermostatic water bath (BHS-2, Joanlab, Huzhou, China). The cold-side inlet temperature was constantly controlled at 20°C using a thermostatic condensation bath (XODC-0506, Xianou, Nanjing, China). The volume of the hot-side feed was 2 L, and 300 mL of ultrapure water was added to the permeate tank to start the cold-side circulation. Each MD process was run for 12 h. The permeate volume was calculated as the weight increase of the permeate tank, which was connected to an online digital balance (Jinkehua, Jinhua, China). The permeation flux and specific flux (SF) were calculated using Equations (1) and (2), respectively, as follows:

$$J = V / (A \times t) \quad (1)$$

where J refers to the permeate flux ($\text{L m}^{-2} \text{ h}^{-1}$), V refers to the permeate volume (L), A refers to the effective area of the membrane (m^2), and t refers to the operating time (h).

$$\text{SF} = J / J_0 \quad (2)$$

where SF represents the specific flux, J represents the permeate flux ($\text{L m}^{-2} \text{ h}^{-1}$), and J_0 represents the initial permeate flux ($\text{L m}^{-2} \text{ h}^{-1}$) in the first 10 min of operation.

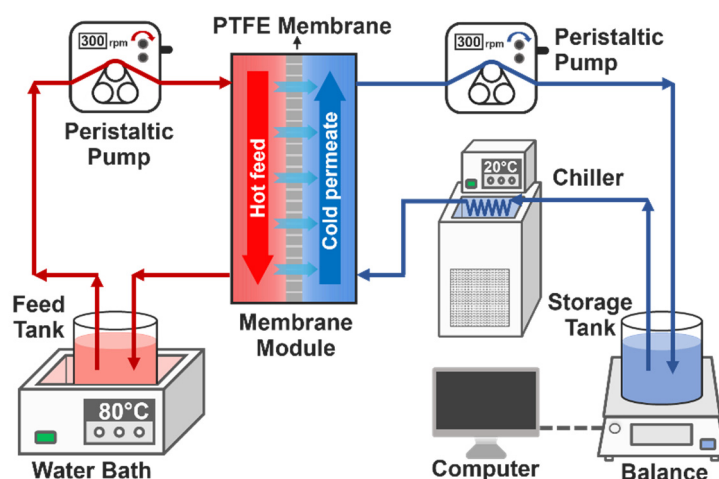


Figure 1. Schematic of the laboratory-scale DCMD setup.

After each experiment had been conducted in triplicate, membrane samples were collected. Each PMS-MD hybrid experiment was labeled in the form HA/SA/BSA-n-m, with n and m representing the PMS concentration (g L^{-1}) and reaction temperature ($^\circ\text{C}$), respectively.

2.3. Analytical Methods

UV_{254} , DOC, and EEM analyses were performed to characterize the oxidation products. A UV-visible spectrometer (UV-3000, Mapada, Shanghai, China) was used at 254 nm for UV_{254} analysis, and a total organic carbon analyzer (N/C-3100, Analytikjena, Jena, Germany) was used for the DOC analysis. A molecular fluorescence absorption spectrometer (F-7000, Hitachi Limited, Tokyo, Japan) equipped with a gas light source was used for the EEM measurements.

The degree of membrane fouling and the shape of the membrane foulants were observed using SEM (S-4800, Hitachi, Japan). ATR-FTIR (Tensor 27, Bruker, Billerica, MA, USA) spectroscopy was performed to identify the functional groups on the virgin and fouled membrane surfaces. WCA analysis was performed to detect the changes in the hydrophobicity of the membrane surface before and after the MD operation. Static WCA

measurements were performed using a contact angle measurement system (DSA30, KRÜSS Scientific, Hamburg, Germany).

3. Results and Discussion

3.1. Effect of Heat/PMS on Organic Degradation

DOC measurements were performed to characterize the amount of dissolved organic matter, and UV₂₅₄ measurements were conducted to characterize the organics containing unsaturated bonds or aromatic chromophores [35]. Figures 2 and 3 clearly demonstrate that heat/PMS oxidation can considerably degrade the model NOM samples. Equation (3) illustrates that the O–O bond of PMS is cleaved to form SO₄^{•−} and •OH when adequate heat is supplied, leading to the degradation of NOM [36].

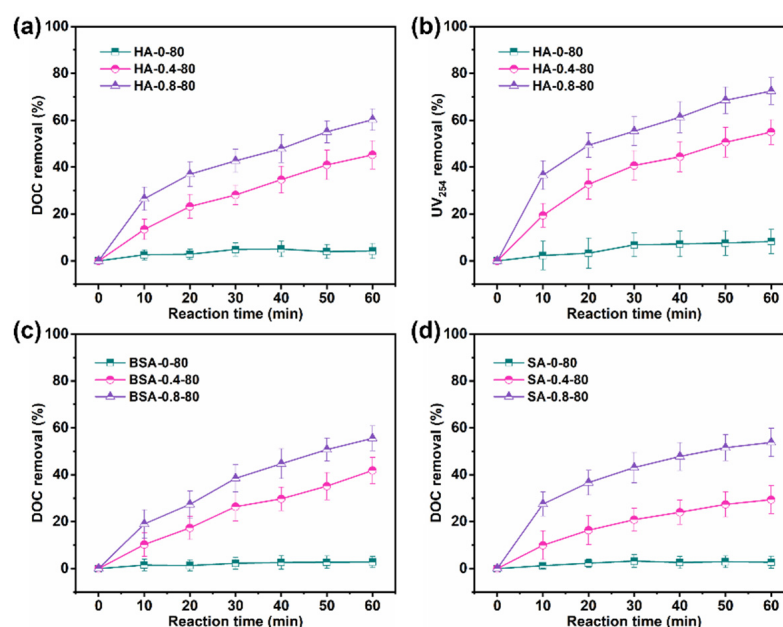


Figure 2. Influence of the PMS dose on the DOC removal rates for (a) individual HA, (c) BSA, (d) SA, and (b) the UV₂₅₄ removal rate for individual HA. Pretreatment conditions: [PMS] = 0, 0.4, and 0.8 g L^{−1}, temperature = 80 °C.

The effect of the PMS dose was explored by regulating the reaction temperature at 80 °C. According to Figure 2, the removal of each organic compound was negligible in the absence of PMS, indicating that the pyrolysis reaction (at a reaction temperature of 80 °C or below) was not effective for reducing the amount of NOM in the feed solution within 60 min of the reaction. When PMS was added for preoxidation, the removal rates of both DOC and UV₂₅₄ increased with the PMS dose. An increase in the PMS dose from 0.4 to 0.8 g L^{−1} within 60 min of the reaction resulted in a rise in the DOC removal rates from 45.2%, 41.8%, and 29.4% to 60.2%, 55.5%, and 53.8%, for individual HA, BSA, and SA, respectively. An increasing PMS dose can enhance the reaction rate by providing more reactive radicals (SO₄^{•−} and •OH) to react with the organic pollutants [26]. Notably, DOC (Figure 2a) had a lower HA removal rate than UV₂₅₄ (Figure 2b), primarily due to the fact that the NOM structure tends to break down into small molecules rather than being completely mineralized into CO₂ and H₂O because of the higher energy requirements of the latter [31,33].

The influence of temperature on the DOC removal rates for NOM was further investigated (Figure 3). In all cases, the degradation efficiency of NOM was limited at a reaction temperature of 60 °C, likely because PMS is difficult to thermally activate at tem-

peratures below 60 °C due to its high peroxide bond dissociation energy [37]. However, the DOC removal rate increased significantly when the temperature reached 70 °C. When the temperature increased from 70 °C to 90 °C, the DOC removal rates for HA, BSA, and SA increased from 35.7%, 31.1%, and 22.9% to 55.3%, 51.5%, and 45.0%, respectively, at 60 min. A higher temperature can promote the generation of reactive radicals and enhance the reaction rate between the radicals and NOM [26,36]. Therefore, the degradation of NOM was more complete at higher temperatures, as demonstrated by the significantly increased DOC removal rates at temperatures above 70 °C. Similarly, DOC showed a lower removal efficiency than UV₂₅₄, further demonstrating that some of the NOM in raw water was only oxidized to organic intermediates. Interestingly, at the beginning of the reaction at 60 °C, DOC removal occurred to a lower extent with an increase in temperature, but UV₂₅₄ removal occurred to a higher extent under the same conditions, indicating that NOM is more inclined to be destroyed rather than mineralized at the initial stage at a reaction temperature of 60 °C.

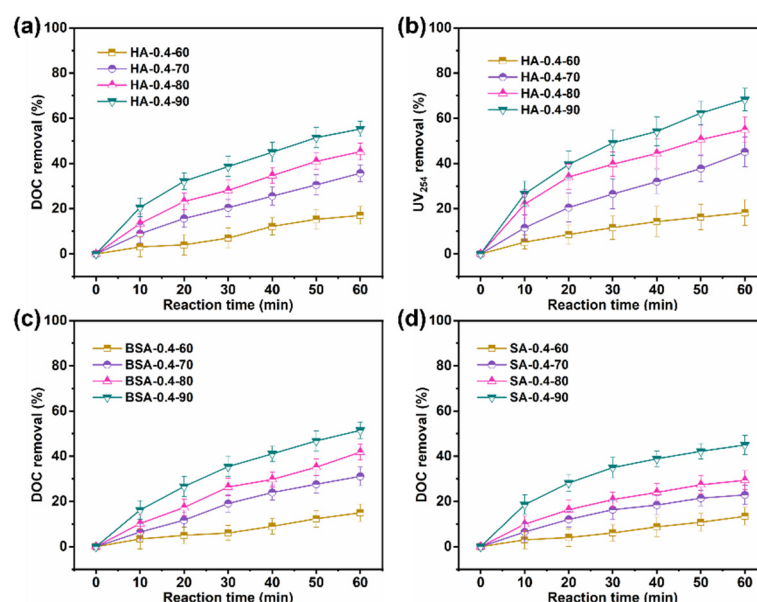


Figure 3. Influence of the activation temperature on the DOC removal rates for (a) individual HA, (c) BSA, (d) SA, and (b) the UV₂₅₄ removal rate for individual HA. Pretreatment conditions: temperature = 60, 70, 80, and 90 °C, [PMS] = 0.4 g L⁻¹.

The fluorescence EEMs were used to explore the influence of heat/PMS preoxidation on the removal of the fluorescent components (Figure 4). SA was not investigated here because polysaccharides cannot show fluorescence [38]. Figure 4a shows a significant peak (C1, Ex/Em: 275 nm/435 nm) in the HA spectrum, representing humic-like substances [31,39]. After 60 min of heat/PMS oxidation, peak C1 vanished completely (Figure 4b). Figure 4c reveals that the BSA spectrum has two significant peaks, peak C2 (Ex/Em = 280 nm/335 nm) and peak C3 (Ex/Em = 230 nm/330 nm), representing aromatic protein and tryptophan-like substances, respectively [40]. The fluorescence intensities of peaks C2 and C3 were zero after 60 min of heat/PMS preoxidation (Figure 4d). The EEM results suggest that the fluorescent components of HA and BSA were substantially degraded in the preoxidation processes.

3.2. Impact of Heat/PMS Pretreatment on MD Performance

The effect of the increase in the salt ion concentration caused by adding PMS was assessed. The mixed (HA–BSA–SA) solution with and without PMS (beforehand, a stoichiometric amount of Na₂S₂O₃ was added to the PMS solution, causing the PMS to lose its oxidation capacity) was treated by MD. As illustrated in Figure 5, the permeate flux of

the feed solution with PMS decreased faster due to the following reasons: (i) the driving force for mass transfer was reduced due to the increase in the concentration polarization effect [41]; (ii) the required driving force increase due to the decrease in the saturated vapor pressure of the feed solutions [42]; and (iii) as the electronegativity of the NOM and membrane decreased, the electrostatic repulsion between organic and membrane surfaces decreased, enabling easier adsorption of NOM on the membrane surface [43].

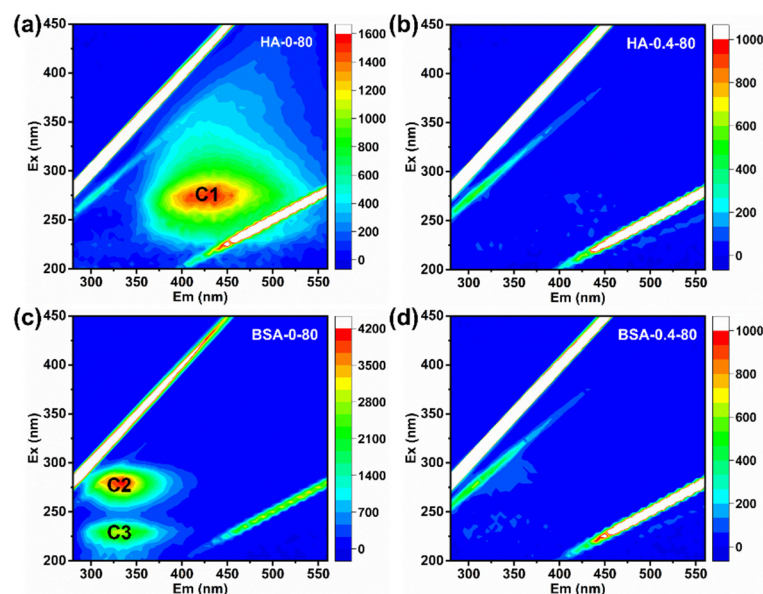


Figure 4. Fluorescence EEM spectra of (a) HA treated with 0 g L^{-1} PMS, (b) HA treated with 0.4 g L^{-1} PMS, (c) BSA treated with 0 g L^{-1} PMS, and (d) BSA treated with 0.4 g L^{-1} PMS. Pretreatment conditions: temperature = 80°C , $[\text{PMS}] = 0.4 \text{ g L}^{-1}$, reaction time = 60 min. Peak C1: Ex/Em: 275 nm/435 nm, peak C2: Ex/Em = 280 nm/335 nm and peak C3: Ex/Em = 230 nm/330 nm.

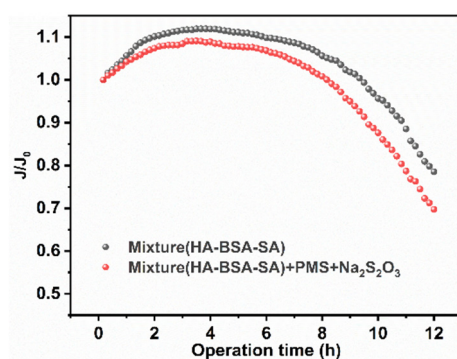


Figure 5. Effect of the increase in the salt ion concentration caused by adding PMS: $[\text{PMS}] = 0.4 \text{ g L}^{-1}$, temperature = 80°C .

Figures 6 and 7 show the flux behavior observed during the treatment of NOM solutions under various pretreatment conditions. For both HA and BSA, regardless of the addition of PMS, the SF curves exhibited three stages. In Stage I, a slow flux increase was seen in the initial periods, likely due to the increased hydrophilicity of the PTFE membrane as some NOM was adsorbed on the membrane. In Stage II, the slow flux decline continued in the middle period as the deposition and adsorption of NOM proceeded, blocking the transport paths of water vapor. In Stage III, the flux decline accelerated during the final period. This rapid flux decline was likely due to further membrane fouling, which aggravated the differential concentration and temperature polarizations. Due to the separation properties of DCMD, contaminants accumulate in the boundary layer of the

MD membrane, leading to concentration polarization, which prevents the passage of water vapor through the membrane [9]. However, pure and oxidized SA have consistently shown steady flux trends, probably because SA is less likely to cause membrane fouling [20].

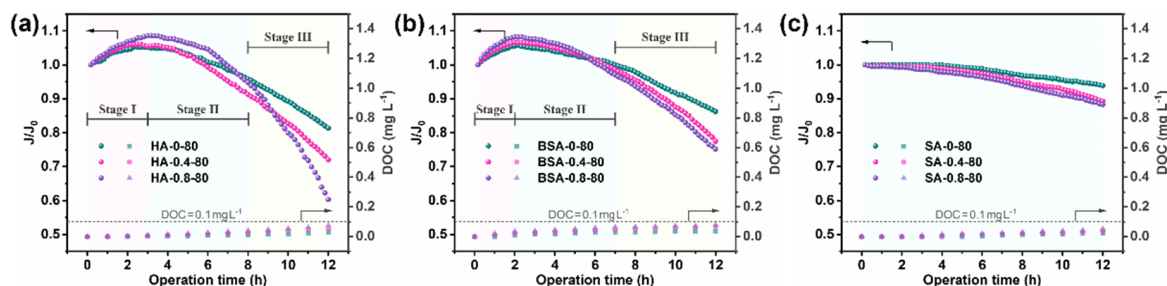


Figure 6. Effect of the PMS dose on the permeate flux and effluent quality (DOC) during MD operation of individual (a) HA, (b) BSA, and (c) SA. Pretreatment conditions: [PMS] = 0, 0.4, and 0.8 g L^{−1}, temperature = 80 °C.

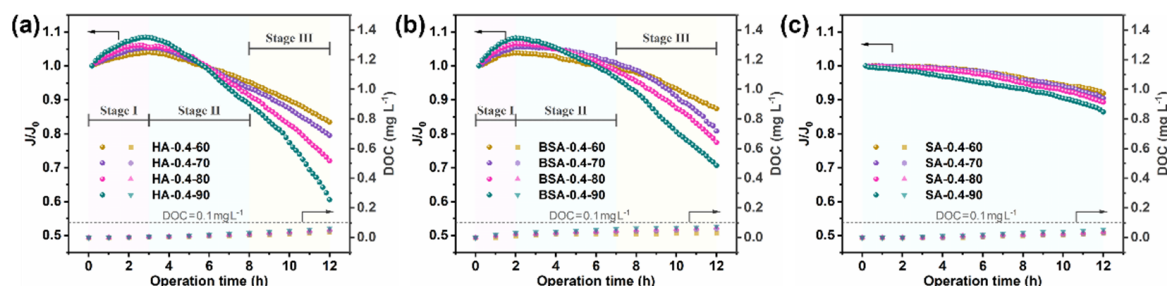


Figure 7. Influence of the activation temperature on the permeate flux and effluent quality during the MD operation of individual (a) HA, (b) BSA, and (c) SA. Pretreatment conditions: temperature = 60 °C, 70 °C, 80 °C, and 90 °C, [PMS] = 0.4 g L^{−1}.

Figure 6 shows the changes in SF over time at different PMS doses. When pure NOM solutions are treated, the SF values of pure HA, BSA, and SA reached 0.81, 0.86, and 0.94, respectively, during an operation time of 12 h, with HA showing the sharpest decline. However, after 12 h of 80 °C/0.8 g L^{−1} heat/PMS pretreatment, the SF values of oxidized HA, BSA, and SA decreased to 0.60, 0.75, and 0.88, respectively, where the oxidized NOM solutions all showed more significant flux declines, especially oxidized HA and BSA. The influence of temperature on the permeate flux was evaluated at a constant PMS dose of 0.4 g L^{−1}. Figure 7 shows that the diminishing rate trend of the SF gradually reversed as the temperature increased from 60 °C to 90 °C, whereas the final J/J_0 values decreased from 0.83, 0.87, and 0.92 to 0.61, 0.71 and 0.86 for HA, BSA, and SA respectively. Additionally, samples of MD effluents were collected hourly to monitor the effluent quality, which could indicate the loss of the membrane filtration functionality triggered by membrane wetting. The DOC of each MD effluent was below 0.1 mg L^{−1}, and the DOC removal was consistently greater than 99%, demonstrating the outstanding removal performance of the MD process.

3.3. Characterization of Fouled MD Membranes

3.3.1. SEM Analysis

SEM was used to observe the surface morphology of the membrane, assess the membrane fouling degree and shape of the foulants, and compare them with those of the virgin PTFE membrane. Figure 8a,b displays a fiber-nodule microporous structure in the virgin PTFE membrane [44]. The contaminated membranes were covered with a dense layer of contaminants after 12 h of MD to treat pure HA (Figure 8c) and oxidized HA (Figure 8d). Moreover, the organic deposits on the fouled membrane of oxidized HA were distinctly

smaller than those for pure HA. As shown in Figure 8e, most parts of the membrane fouled by pure BSA were deposit-free; however, the membrane fouled by oxidized BSA was completely covered with organic contaminants (Figure 8f). This indicates that subjecting BSA to heating and oxidation enhances its adsorption on the hydrophobic membrane. However, the fouled membrane appeared to be relatively fresh after 12 h of treatment with pure and oxidized SA solutions (Figure 8g,h, respectively), indicating that little SA was deposited or adsorbed on the membrane. This conclusion is consistent with the findings of Naidu et al. [20], who suggested that a hydrophilic, organic SA compound had a minimal fouling impact on the MD operation. The SEM images confirmed that the oxidized NOM produced by heat/PMS oxidation preferentially adhered to the PTFE membrane during MD.

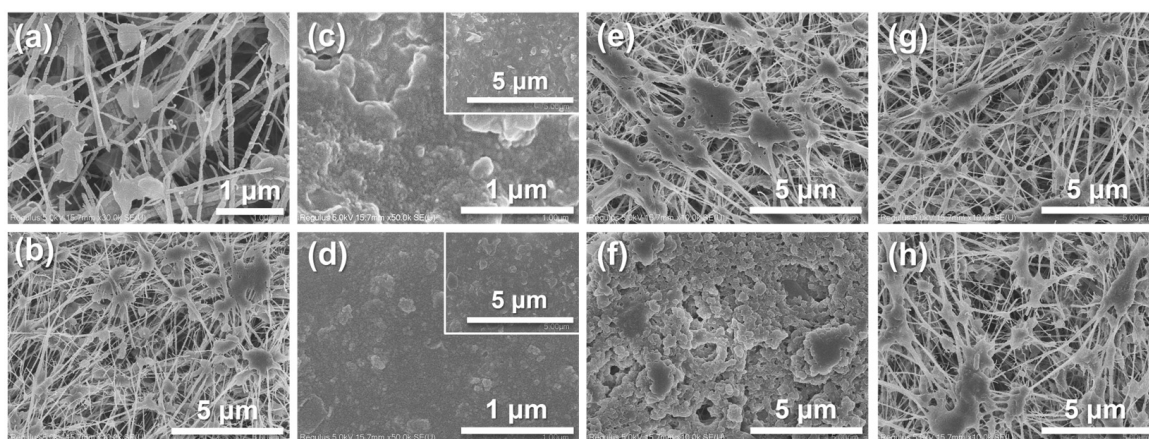


Figure 8. SEM images of the virgin (a,b) and fouled membrane surfaces after treating native HA (c), BSA (e), SA (g) and oxidized HA (d), BSA (f), and SA (h). Pretreatment conditions: [PMS] = 0.4 g L^{−1}, temperature = 80 °C.

3.3.2. ATR-FTIR Analysis

ATR-FTIR spectroscopy was utilized for identifying the functional groups of the membrane foulants (Figure 9). In the spectra of the virgin PTFE membrane, two strong peaks appeared at 1201 cm^{−1} and 1140 cm^{−1}, corresponding to the stretching vibrations of the asymmetric and symmetric C–F bonds [45]. Another band appeared at 635 cm^{−1}, corresponding to the bending modes of the C–C skeleton [46,47]. The membranes fouled by pure and oxidized HA showed new peaks at 3691 cm^{−1}, 2923–2854 cm^{−1}, 1708–1578 cm^{−1}, 1030 cm^{−1}, and 917 cm^{−1}, denoting the stretching vibrations of the alcoholic O–H, C–H, C=O, C–O, and carboxylic O–H groups, respectively. The differences between the peaks of pure HA and oxidized HA indicate the transformation of organic molecules after oxidation. Additionally, the peaks associated with PTFE were weakened, implying that membranes fouled with both native and oxidized HA are covered with a layer of humic substances. The membranes fouled by oxidized BSA showed different peaks at 3478 cm^{−1}, 1739 cm^{−1}, and 1045 cm^{−1}, denoting the N–H groups, C=O, and C–H groups of the peptide bonds in BSA, respectively. However, the membranes fouled by pure BSA were almost indistinguishable from the virgin PTFE membrane. Similar results were also observed for pure and oxidized SA, indicating that SA is unlikely to cause membrane fouling, regardless of its preoxidation status.

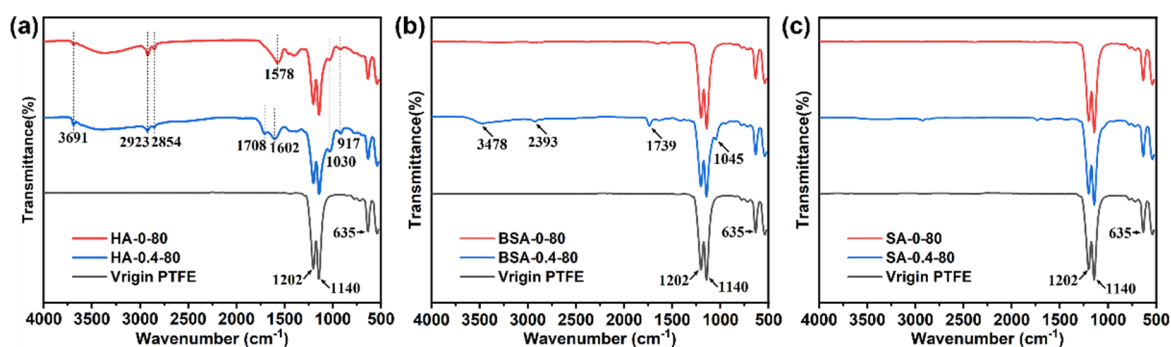


Figure 9. ATR-FTIR spectra of the virgin PTFE membrane and membranes fouled by pure and oxidized NOMs: (a) HA, (b) BSA, and (c) SA. Pretreatment conditions: $[PMS] = 0.4 \text{ g L}^{-1}$, temperature = 80°C .

3.3.3. Hydrophobicity Analysis

The influence of fouling on the hydrophobicity was assessed by measuring the WCA of the virgin and fouled MD membranes. The WCA results were consistent with the SEM and ATR-FTIR results (Figure 10). In NOM solutions that did not undergo PMS preoxidation, pure HA (WCA of 98.2°) caused the biggest reduction in hydrophobicity, followed by pure BSA (WCA of 113.3°), in comparison with the virgin PTFE membrane (WCA of 139.0°), implying the deposition of hydrophilic contaminants. However, pure SA (WCA of 136.9°) only induced a slight decrease in the hydrophobicity, demonstrating that individual SA caused little membrane fouling. After pretreatment with heat/PMS, only oxidized HA showed a negligible change in hydrophobicity, whereas both oxidized SA (WCA of 128.1°) and BSA (WCA of 69.5°) caused severe decreases in hydrophobicity, with the heat/PMS oxidation of BSA causing the greatest decrease in hydrophobicity. This is possibly because heat/PMS oxidation changed the molecular properties of NOM, making it more susceptible to membrane adhesion.

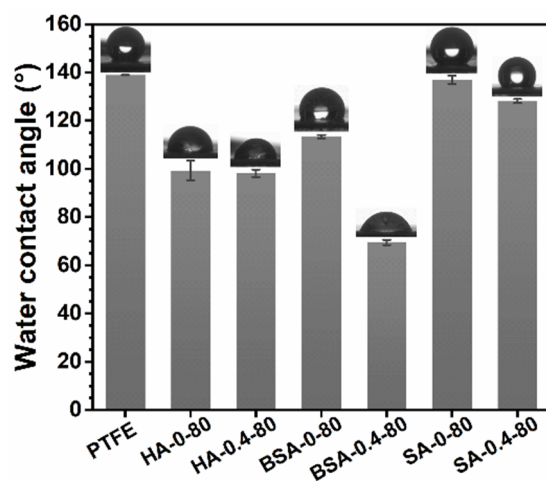


Figure 10. Water contact angles of the virgin membrane and membranes fouled by pure and oxidized NOM: HA, BSA, and SA. Pretreatment conditions: Temperature = 80°C , $[PMS] = 0.4 \text{ g L}^{-1}$.

The results for the flux performances and characterizations conducted to assess the membrane fouling degree with or without preoxidation contradict those of previous studies in which the feed solutions all contained ions (Table 1). Therefore, it can be inferred that pretreatment can only successfully mitigate MD fouling in saline solutions of organic matter. Large organic molecules can be broken down into smaller ones during the pretreatment process, and these would easily assemble on the membrane surface, resulting in fouling. It can be speculated that the reduction in inorganic fouling is the reason for the effect of PMS pretreatment, because the degradation of the organic matter would consequently

reduce the binding of salt ions to organic matter. Therefore, follow-up studies are needed to investigate the effect of salt ions on organic fouling in the AOP-MD hybrid process.

Table 1. Feed solutions used in previous studies.

Feed Solutions	Organics	Cations	References
Secondary effluent + a mixture of micropollutants	NOM and micropollutants (amitriptyline, trimethoprim, etc.)	Zn^{2+} , Cu^{2+} , Ca^{2+} , Fe^{3+} , K^{+} , etc.	Asif et al., 2019 [27]
Surface water	AOM	Ca^{2+} , Mg^{2+} , Al^{3+} , etc.	Asif et al., 2021 [28]
SDS + NaCl	SDS	Na^{+}	Han et al., 2022 [29]
Secondary effluent/surface water	NOM	Ca^{2+} , Mg^{2+} , Fe^{3+} , K^{+} , etc.	Ding et al., 2022 [30]

4. Conclusions

The study investigated single-organic membrane fouling by examining different model organics individually. Individual salt-free NOM solutions were selected as the target contaminants for the PMS-MD hybrid process. The findings demonstrate that, in contrast to pure NOM solutions, the degree of membrane fouling increased surprisingly for preoxidized NOM solutions, as summarized below:

1. NOM was notably degraded after 60 min of heat/PMS pretreatment using a PMS dose of 0.4 g L^{-1} and a reaction temperature of 80°C . The DOC removal results indicate that the amount of NOM was considerably reduced because some of the NOM was partially mineralized. The greater removal of UV_{254} compared with DOC indicates that some NOM decomposed to small molecules, whereas the fluorescent compounds HA and BSA were completely degraded.
2. For pure NOM solutions that did not undergo heat/PMS pretreatment, pure HA caused the most severe membrane fouling, followed by pure BSA; however, there was little adherence of pure SA to the membrane.
3. When PMS was added for pretreatment, the oxidized NOM solutions caused a more severe flux decline and a higher fouling degree, despite the reduction in the NOM concentration, especially for oxidized HA and BSA. On one hand, the oxidized NOM had a lower MW, which made it easier to adsorb on the membrane. On the other hand, the introduction of the PMS oxidant and quencher increased the ionic strength of the feed solution, which reduced the permeability in the MD process.

Overall, this study demonstrates that the organic fouling degree cannot be reduced even after the considerable degradation of NOM by heat/PMS pretreatment. Therefore, the ideal mitigation effect reported in previous studies in actual water treatments was most likely mainly due to a reduction in inorganic fouling. The degradation of NOM could hinder the complexation of inorganic cations and organic matter. Hence, further investigations are required to determine the impact of this pretreatment approach on the fouling of inorganic-organic mixed membranes. Specifically, understanding how organic molecule properties and their interactions with salt ions during oxidation affect the degree of membrane fouling in membrane distillation (MD) is necessary to optimize MD performance.

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