Humic acid fouling mitigation by ultrasonic irradiation in membrane distillation process

Deyin Hou^{a,b,*}, Lijuan Zhang^c, Zhangxin Wang^d, Hua Fan^e, Jun Wang^{a,b,*}, Hongjing Huang^e

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^b Beijing Key Laboratory of Industrial Wastewater Treatment and Reuse, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^c School of Environmental and Chemical Engineering, Nanchang Hangkong University, Jiangxi 330063, PR China

^d Department of Civil and Environmental Engineering, Vanderbilt University, PMB 51831, 2301 Vanderbilt Place, Nashville, TN 37235-1831, United States

^e School of Environmental and Chemical Engineering, Nanchang University, Jiangxi 330031, PR China

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ABSTRACT

A novel ultrasonic assisted direct contact membrane distillation hybrid process was designed and the effect of ultrasonic irradiation on humic acid (HA) fouling mitigation during membrane distillation process was investigated. Although permeate flux declines were negligible (less than 5%) for the ranges of HA concentration studied, ultrasonic irradiation could enhance the permeate flux more than 30% without destroying HA rejection. The higher the concentration factor was, the larger the ultrasonic enhancement of permeate flux could be obtained. Severe permeate flux decline can be found when CaCl_2 was added into the HA solution. The presence of Ca^{2+} would aggravate HA organic fouling phenomenon and resulted in a thick and dense HA fouling layer on membrane surface. The HA fouling increased heat transfer resistance and reduced the pores available for vapor transfer, both the permeate flux and thermal efficiency of the PTFE membrane declined. Under ultrasonic irradiation, ultrasonic wave refreshed the liquid-membrane interface continuously and alleviated the deposition of HA aggregates. Therefore, although there were still some HA fouling scattered on membrane surface, most of the membrane pores could be kept open and clean, the relative permeate flux can maintain above 94% and was hardly affected by concentration factor increasing.

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1. Introduction

Membrane distillation (MD) is a promising thermally driven desalination technology and usually used a hydrophobic membrane as separation media [1]. Compared with other desalination processes such as nanofiltration (NF), reverse osmosis (RO) and conventional evaporation, MD has several unique advantages such as: (1) lower operating temperature and vapor space required than conventional distillation, (2) lower operating pressure than RO, (3) theoretically 100% salt rejection, (4) unlimited by high osmotic pressure, and (5) lower energy consumption than multistage vacuum evaporation [2–5].

Although there have been extensive studies on the application of MD for water desalination, removal of organic matters in drinking water production, treatment of water and wastewater, recovery of valuable components, and treatment of radioactive wastes

[6–11], the industrial implementation of MD is not yet feasible and significant advancements are still needed to reach the theoretical cost competitiveness and develop market share growth [12]. Like all other membrane processes, fouling in MD is of particular importance, as fouling can alter membrane surface properties, change membrane pore structure, potentially lead to wetting of membrane pores and ultimately cause a decline in membrane permeability [13,14]. In recent years, a number of studies have investigated the effect of fouling on the overall MD process utilizing different types of membranes such as flat-sheet and hollow fibers, as well as using different modules [15]. However, the majority of works focus on the negative effects and mitigation strategies of inorganic membrane scaling such as CaSO_4 , CaCO_3 and SiO_2 [16–18]. As far as we know, there are limited studies dedicated to organic fouling in the MD process.

It has been acknowledged that natural organic matter (NOM) is one of the primary causes for the membrane permeability decline due to organic fouling [19]. It was reported that humic substances and low molecular weight organics are the main constituents of NOM present in natural water sources such as surface water,

* Corresponding authors at: Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China.

E-mail addresses: dyhou@rcees.ac.cn (D. Hou), junwang@rcees.ac.cn (J. Wang).

ground water and seawater [20]. Furthermore, humic acid (HA) has been identified as the principal NOM foulant in membrane processes [21]. With regards to the MD process, it is deemed necessary to pay more attention on HA fouling because it has been demonstrated that HA is adsorbed more favorably onto hydrophobic membrane surface [22]. Khayet and Mengual [23] investigated the treatment of HA solutions through direct contact membrane distillation (DCMD), it was found that the extent of HA fouling was affected by HA concentration, feed pH and transmembrane temperature difference. Srisurichan et al. [24] studied the effects of ionic strength, divalent ion and feed pH on HA fouling, flux declines were less than 6% for the ranges of HA concentration, ionic strength, and pH studied. The presence of calcium ions had a marked effect on HA fouling, Ca^{2+} formed complexes with HA and resulted in coagulation on the polyvinylidene fluoride (PVDF) membrane surface. Naidu et al. [25] reported that the HA fouling in MD was influenced by temperature, salinity (NaCl) and inorganic scalant (CaSO_4), and HA can penetrate through the hydrophobic membrane and present in permeate. Meng et al. [26] also found that HA penetrated through both virgin and superhydrophobic PVDF membranes even without the occurrence of partial pore wetting, and they proposed adsorption–desorption foulant migration mechanism through the membrane to explain this experimental phenomena.

Fouling in MD is generally less serious than that in pressure-driven membrane processes, however, reduction of fouling by NOM in MD process, such as HA, is still one of the major challenges. Srisurichan et al. [24] found that pure water rinsing was not sufficient to recover the initial permeate flux, while HA fouling was easily removed with a 0.1 M NaOH solution and 100% flux recovery was attained. It is also reported that thermal heating in MD may influence the characteristics of HA, and alternating temperature changes can clean HA fouling in some extent [27]. Nevertheless, it is worth highlighting that the HA fouling control methods used in pressure-driven membrane processes may be full of important reference value. For example, Hong and Elimelech [28] added chelating agent (EDTA) into feed water in NF membrane process, reduced HA fouling significantly and also improved the cleaning efficiency dramatically. Because the presence of divalent cation has a marked effect on HA fouling, selective removal of divalent cation via pretreatment was suggested to reduce the adverse effect of divalent ions [29]. In addition, antiscalants were widely used to control inorganic scales such as CaCO_3 and CaSO_4 formed on NF or RO membrane surfaces, Yang et al. [30] tried to use a benign antiscalant polyaspartic acid to mitigate HA fouling on RO membrane. HA fouling decreased with Ca^{2+} concentration increasing in the presence of polyaspartic acid, and it was a feasible approach for HA fouling control by dosing antiscalant.

Ultrasonic wave is referred to the acoustic wave with the frequency between 20 kHz and 10 MHz. Several concomitant effects, such as mechanics, thermotics and cavitation effect, during the propagation of ultrasonic wave in various media, have been recognized to be beneficial to many physical and chemical processes [31]. For membrane separation processes, the ultrasonic technique is used mainly in membrane fouling monitoring, membrane cleaning and membrane flux enhancement [32–36]. Li et al. [37–39] applied ultrasonic technique as a non-destructive, real-time, in situ measuring technique for direct monitoring of membrane fouling and cleaning during ultrafiltration (UF) and RO, and found that the ultrasonic technique was a useful technique for the non-destructive investigation of fouling and cleaning in membrane applications. Kobayashi et al. [40–44] introduced ultrasonic technique to create novel anti-fouling membrane processes for membrane water treatments, it was reported that ultrasonic irradiation during membrane filtration was very effective in removing foulants from membranes. Massive evidences exist that

the ultrasonic effect is useful for water cleaning of fouled membrane, the ultrasonic cleaning presents advantages and is an effective method compared with other typical cleaning methods using physical and chemical methods [45–47].

Although the ultrasonic irradiation has been successfully applied to enhance the performance of pressure-driven membrane separation process such as microfiltration (MF), UF, NF and RO, relatively few studies have been carried out with the use of ultrasonic to mitigate HA fouling in MD process. The objective of this paper is to introduce ultrasonic irradiation into DCMD process to develop a novel ultrasonic assisted direct contact membrane distillation (USDCMD) hybrid process and to investigate the influence of ultrasonic irradiation on HA fouling mitigation. Compared with traditional physical and chemical methods for membrane fouling control, ultrasonic irradiation is expected to be a real-time, in situ membrane fouling mitigation technique and can also ensure MD system continuous operation without chemicals addition and membrane drying.

2. Experimental

2.1. Materials and membrane module

The polytetrafluoroethylene (PTFE) hydrophobic hollow fiber membrane with a mean pore diameter of 0.26 μm , supplied by DD Water Group Co., Ltd. (China), was chosen to fabricate membrane modules. The hollow fibers in the number of 40 pieces were assembled into a polyester tube (diameter $d_{\text{in}}/d_{\text{out}} = 15/20 \text{ mm/mm}$) with two UPVC T-tubes and two ends of the bundle of fibers were sealed with solidified epoxy resin to compose a membrane module. The effective membrane length was 100 mm for each membrane module. The characteristics of the membrane and membrane modules are presented in Table 1.

2.2. USDCMD setup

The USDCMD experimental setup is schematically shown in Fig. 1. The hot feed stirred continually by a magnetic stirrer flowed through the shell side of the fibers, and the cold distillate flowed through the lumen side. The initial volumes of the feed and the distillate were 4.0 L and 0.25 L, respectively. Both solutions were circulated in the membrane module with the help of two magnetic pumps (MP-15RN, Shanghai Seisun Pumps, China). The feed and the distillate flowed co-currently through the module, and the circulation feed rate (V_f) was 0.25 m/s, while the cold side (V_p) being 1.0 m/s. The feed temperature ($T_{f-\text{inlet}}$) was fixed at 53 °C by a Pt-100 sensor and a heater connected to an external thermostat (XMTD-2202, Yongshang Instruments, China). The distillate temperature ($T_{p-\text{inlet}}$) kept at 20 °C by a spiral glass heat exchanger immersed in the constant temperature trough of the cooler (SDC-6, Nanjing Xinchun Biotechnology, China). The temperature of both fluids was monitored at the inlet and outlet of the membrane module using four Pt-100 thermoresistances connected to a digital

Table 1
The characteristics of the membrane material and the membrane module.

Membrane and module	Properties
Membrane material	PTFE
Mean pore diameter (μm)	0.26
Porosity (%)	45.07
Inner diameter of hollow fiber (mm)	0.80
Membrane thickness (mm)	0.39
Number of hollow fibers	40
Effective membrane length (mm)	100
Effective membrane area (cm^2)	198.4

Fig. 1. Schematic diagram of USDCMD system.

Fig. 2. Effect of HA concentration on the process of DCMD concentration of HA solution.

meter (Digit RTD, model XMT-808, Yuyao Changjiang Temperature Meter Instruments, China) with an accuracy of ± 0.1 °C. An electric conductivity monitor (CM-230A, Shijiazhuang Create Instrumentation Technologies, China) was used to monitor the distillate water quality.

In order to investigate the influence of ultrasonic irradiation on HA fouling mitigation, the membrane module was immersed vertically in a water bath ($15 \times 15 \times 42$ cm³), transducers were adhered to the four outside surfaces of the water bath stainless steel shell. The ultrasonic bath was capable of generating ultrasonic with a frequency of 20 kHz and an acoustic power of 260 W. The ultrasonic irradiation device was supplied by Quanyi Electronic Equipment Co., Ltd. (Baoding, China).

Fig. 4. Effect of ultrasound irradiation on the permeate flux during HA solution concentration process.

2.3. Experimental

Humic acid was supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Feed solutions were prepared by dissolving a pre-weighed quantity of HA powder in deionized water obtained from the Milli-Q system (Millipore, USA), followed by filtration through a $0.45 \mu\text{m}$ filter to exclude initial deposition of bulk suspended solids on the membrane. The solution pH was adjusted to 7.0 by addition of small quantities of 0.1 M NaOH as needed before MD experiment starting. The HA concentration of the permeate were evaluated by measuring the absorbance using a Hach DR-5000 UV–Vis spectrophotometer (Hach, USA) at 207 nm. This wave-

Fig. 3. Morphological image of the PTFE membrane after HA solution concentration experiment: (a) with the initial HA concentration of 10 mg/L and (b) with the initial HA concentration of 50 mg/L.

Fig. 5. Effect of ultrasound irradiation on the process of DCMD concentration of HA solution.

Fig. 6. Effect of ultrasound irradiation on permeate HA concentration.

length gave a maximum absorbance over the HA concentration range in the obtained permeate.

During MD process, all the feed solutions were no make-up water added into the feed tank, which meant that the feed was gradually concentrated. The concentration factor K can be calculated by the following equation:

$$K = \frac{Q_o}{Q_o - Q_p} \quad (1)$$

where Q_o is the initial quantity of feed (kg), Q_p is the cumulative permeate production (kg). The permeate flux J was calculated by the following equation:

$$J = \frac{\Delta W}{A \Delta t}, \quad (2)$$

where J is the permeate flux ($\text{kg/m}^2\text{h}$), ΔW is the quantity of distillate (kg), A is the effective area of flat-sheet membrane (m^2) and Δt is the sampling time (h). The relative permeate flux J_R was used to describe the change of membrane permeability with the concentration factor increase:

$$J_R = \frac{J}{J_o} \quad (3)$$

where J_o is the initial permeate flux ($\text{kg/m}^2\text{h}$). When the concentration factor reached 4.0, the MD process was stopped, and a new membrane module was used for each experiment in this study. At the completion of each experiment, the membrane was removed from the membrane module for further analysis and excess liquid on the membrane surface was allowed to drain off by gently tilting the hollow fiber.

2.4. Membrane surface analysis

The HA fouling on the membrane surface was observed by using a HITACHI S-3000N scanning electron microscope (SEM) (Hitachi Ltd., Japan). The fouled membranes were dried in a desiccator, and sputtered with platinum using a HITACHI E-1010 Ion Sputtering device for SEM observation. Elemental analysis of the fouled membrane surface was accomplished using energy dispersive X-ray spectroscopy (EDS) detector. The fouled membrane samples were handled gently and without any excessive forces to ensure that the fouling remained intact.

3. Results and discussions

3.1. The effect of humic acid concentration

The solutions containing 10 mg/L and 50 mg/L HA were tested for concentration by DCMD, respectively. The permeate flux as a function of concentration factor is illustrated in Fig. 2.

It was found that the HA concentration had little effect on the permeate flux and the organic foulant HA did not cause notable flux decline with the concentration factor increase. For different HA concentration, the initial permeate fluxes of the PTFE hollow fiber membranes were almost the same and about $1.76 \text{ kg/m}^2\text{h}$. With the concentration factor increasing, the relative permeate

Fig. 7. Morphological image of the PTFE membrane after HA solution concentration experiment: (a) in the absence of ultrasonic irradiation and (b) in the presence of ultrasonic irradiation.

fluxes can still keep constant during the DCMD concentration operation. When the concentration factor reached 4.0, the permeate flux declined less than 5% compared with the initial permeate flux for the feed with different HA content.

The SEM micrographs of the PTFE membranes used in different feed concentration process are presented in Fig. 3. It can be found that the membrane surface still kept clean when the experiments ending, and these results indicated negligible HA fouling, even the HA concentration was as high as 50 mg/L, which was consistent with the findings of Srisurichan [24] and Khayet [48]. On the contrary, in the pressure-driven membrane separation process such as MF, UF and NF of the solutions with lower HA concentration [21],

the permeate flux would decline significantly in a very short time. Being different from pressure-driven membrane process, MD is a thermally driven process and there is a thermally driven vapor transport through non-wetted porous hydrophobic membrane where the driving force is the partial vapor pressure difference across the two sides of membrane pores. In MD process, the feed solution to be treated cannot permeate into the membrane pores. Therefore, the HA would not deposit in membrane pores. Furthermore, due to the lower operating pressure of the process, even there were HA aggregates formed on the membrane surface, the deposition would be less compact and be easily flushed off the membrane surface, slightly affect the transport resistance.

3.2. Ultrasonic irradiation effect on DCMD of humic acid solution

The effect of ultrasonic irradiation on absolute permeate flux and relative permeate flux are shown in Figs. 4 and 5, respectively. It can be seen that ultrasonic irradiation really increased the permeate flux. Although the permeate flux seemed to be hardly affected by the concentration factor increasing both in the presence and absence of ultrasonic irradiation, the slight rise of the ratio of membrane permeate flux with and without ultrasonic irradiation as shown in Fig. 4 indicated that the higher the concentration factor was, the more obvious the ultrasonic enhancement of permeate flux could be obtained. When the concentration factor varied from 1.0 to 4.0, the ratio of permeate flux with and without ultrasonic irradiation enhanced from 1.30 to 1.37. With the concentration factor increasing, both the feed viscosity and the boundary layer thickness increased, which would aggravate concentration polarization on the membrane surface and cause the permeate flux decline in some extent. Ultrasonic irradiation can bring mechanical and thermal effects and generate powerful shock wave and microstreaming with high speed, which were ben-

Fig. 8. Effect of calcium ion on the process of DCMD concentration of HA solution.

Fig. 9. Morphological image of the PTFE membrane after HA solution concentration experiment: (a) in the absence of calcium ion, (b) in the presence of 2 mM CaCl_2 , (c) in the presence of 10 mM CaCl_2 , and (d) in the presence of 20 mM CaCl_2 .

eficial to reduce the boundary layer, intensified eddy diffusion and relieve the negative effect of concentration factor increase on the mass transfer of DCMD process.

The ultrasonic irradiation can enhance permeate flux, however, it should be certified whether the PTFE hollow fibers can maintain excellent HA rejection under ultrasonic irradiation. In Fig. 5, it can be seen that the permeate conductivity declined with the elapse of operation time in the presence or absence of ultrasonic irradiation, which meant that the permeate quality was even better than the deionized water. The PTFE membranes kept good HA rejection and all permeate HA concentration were below 0.40 mg/L with and without ultrasonic irradiation as shown in Fig. 6. Furthermore, as can be found from Fig. 7, there was no obvious difference

between the surface SEM images of the PTFE membranes before and after ultrasound irradiation. For the PTFE hollow fiber membrane, both the performance stability and membrane morphology were hardly influenced by ultrasonic irradiation, which indicated that the PTFE membrane was suitable to be utilized in ultrasonic assisted direct contact membrane distillation hybrid process to mitigate HA fouling.

3.3. The effect of calcium ion

Calcium ion is a major cation in natural and waste waters, thus, the effect of calcium ion was studied in the present paper. The initial feed solution contained 50 mg/L HA and the concentration of

Fig. 10. SEM-EDS analysis of the fouling scattered on membrane surface: (a) in the presence of 2 Mm CaCl_2 , (b) in the presence of 10 Mm CaCl_2 , and (c) in the presence of 20 Mm CaCl_2 .

the salt CaCl_2 in feed solution was in the range of 0–20 mM. The curves for relative permeate flux with concentration factor under various conditions are shown in Fig. 8. It is clearly different from the DCMD of pure HA, the results reveal the flux decline when the salt CaCl_2 was added into the HA solution. As can be seen from Fig. 8, the relative permeate flux J/J_0 decline at the end of experiment increased from 4.8% to 23.7% as Ca^{2+} concentration increased from 0 to 20 mM, and the decline of relative permeate flux increased with increasing calcium ion concentration.

According to HSAB theory, the divalent cation Ca^{2+} is a hard acid, which easily interacts with hard bases such as $-\text{COO}^-$. Since HA contains negatively charged carboxyl groups, Ca^{2+} can act like a binding agent of two carboxyl functional groups and form complexes, which cause the humic acids aggregate. On the other side, the addition of cation Ca^{2+} also reduced electrostatic repulsion between HA molecules and that between HA and PTFE hydrophobic membrane surface. The presence of divalent cation Ca^{2+} would aggravate HA organic fouling phenomenon via charge neutralization, complexation and formation of calcium bridges. The SEM micrographs shown in Fig. 9 obviously confirmed that the presence of divalent cation Ca^{2+} in feed solution aggravated HA organic fouling. With the increase of calcium ion concentration, the membrane fouling became worse and worse. It can be found that there were some foulants scattered on membrane surface when 2 mM CaCl_2 was added into the HA solution, then the membrane foulants formed loose aggregates with 10 mM CaCl_2 addition, the PTFE membrane was finally covered by a dense fouling layer in the presence of 20 mM CaCl_2 . Certainly, the SEM-EDS analysis presented in Fig. 10 revealed that the deposit on the membrane surface was the complex formed by HA and divalent cation Ca^{2+} , and the calcium content in membrane foulants increased with the salt CaCl_2 concentration increasing.

It is well known that membrane distillation is a simultaneous heat and mass transfer process. The deterioration of permeate flux due to HA fouling may be attributed to two factors, the reduction of surface area available for vaporization as the fouling blocked the pore entrances, and the fouling layer may decrease the heat transfer driving force. Even though there has been no report on the heat transfer resistance of the fouling layer, it is expected that such a layer will reduce the temperature polarization coefficient, and the temperature polarization coefficient reflects the heat transfer efficiency of the process in some extent.

During MD process, heat transport can be divided into the latent heat due to water vaporization and the heat conduction across the membrane. The heat transfer from the hot feed to the cold stream induced temperature decrease from the inlet of the shell side to the outlet and vice versa for the lumen side. Thermal efficiency (evaporation efficiency, EE) was defined as the ratio

between the heat which contributed to evaporation and the total heat exchanged between two streams. Because distillate water flows through the fiber lumen side, there is no other heat transfer except for heat from the fiber shell side. The total heat exchange can be calculated from the enthalpy difference between the inlet and outlet of the distillate. EE can be calculated by the following equation [49]:

$$EE = \frac{Q_{\text{diff}}}{Q_T} = \frac{Q_{\text{diff}}}{Q_{\text{diff}} + Q_{\text{cond}}} = \frac{J \cdot A \cdot H_v}{V_p \cdot \bar{C}_p (T_{p-\text{outlet}} - T_{p-\text{inlet}})} \quad (4)$$

Fig. 12. Effect of ultrasound irradiation on the process of DCMD concentration of HA solution containing calcium ion: (a) 2 Mm CaCl_2 , (b) 10 Mm CaCl_2 , and (c) 20 Mm CaCl_2 .

Fig. 11. Effect of calcium ion on thermal efficiency of the DCMD process.

Fig. 13. Morphological image of the PTFE membrane after HA solution concentration experiment under ultrasonic irradiation: (a) in the presence of 2 mM CaCl_2 , (b) in the presence of 10 mM CaCl_2 , and (c) in the presence of 20 mM CaCl_2 .

where A is the effective permeate area of the membrane module, $T_{p\text{-outlet}}$ is the cold distillate temperature at the outlet of membrane module. $\bar{C}_p$ is the average specific heat of water, which can be simplified as a constant value 4200 J/(kg K). H_v is the latent heat of vaporization, in the range of temperature 273–373 K, H_v can be expressed as [50]:

$$H_v = 2024.3 + 1.7535 \cdot T \quad (5)$$

where T is the average temperature, and $T = \frac{T_{p\text{-inlet}} + T_{p\text{-outlet}}}{2}$, in K.

As shown in Fig. 11, the calculated thermal efficiency was around 12% for the DCMD process of pure HA solution, the EE value declined with the salt CaCl_2 addition and the EE value was less than 10% in the presence of 20 mM CaCl_2 . With the concentration factor increasing, the EE value also decreased, and the EE fell down to 7.5% at end of the concentration experiment in the presence of 20 mM CaCl_2 . According to Eq. (4), it can be clearly found that the high permeate flux meant higher EE value and the latent heat of water evaporation became the main contribution to total heat transfer. As for the DCMD process with low permeate flux, the heat

loss due to heat conduction across the membrane was the major contribution to total heat transfer and the EE value became lower. The presence of divalent cation Ca^{2+} induced the EE decrease may be attributed to two factors: the permeate flux decline and the thermal conductivity increase with the fouling layer formation.

3.4. Ultrasonic irradiation effect on humic acid fouling mitigation

To investigate the influence of ultrasonic irradiation on HA fouling in the presence of divalent cation Ca^{2+} , DCMD concentration experiments were carried out with ultrasonic irradiation. The initial feed solution contained 50 mg/L HA and the concentration of the salt CaCl_2 in feed solution was varied in the range of 2–20 mM. Except for the additional ultrasonic irradiation, other operating parameters were in accordance with the previous experiments. The result of the mixed solution concentration through USDCMD is shown in Fig. 12.

The permeate flux increased markedly in the presence of ultrasonic irradiation as indicated in Fig. 12. The higher the concentra-

Fig. 14. SEM-EDS analysis of the fouling scattered on membrane surface in presence of ultrasonic irradiation. Feed solution: 50 mg/L HA+20 mM CaCl_2 .

Fig. 15. Schematic illustration of ultrasonic irradiation effect on HA fouling mitigation.

tion of calcium ion in feed, the more obvious the ultrasonic enhancement of relative permeate flux could be obtained. It also can be found that the enhancement of relative permeate flux increased with concentration factor increasing. As can be seen from Fig. 12(c), in the presence of 20 mM CaCl_2 , the relative permeate flux maintained 94% when the concentration factor reached 4.0 with ultrasonic irradiation. In contrast, the relative permeate flux declined considerably in the absence of ultrasonic irradiation and the relative permeate flux went down to 76.3% when the concentration factor reached 4.0. The ultrasonic irradiation can effectively mitigate the HA fouling, which can be observed from the images of the membrane surface morphology. The difference between the surface morphologies of the membranes fouled with HA in the absence and presence of ultrasonic irradiation can be found by comparing Figs. 9 and 13. In the presence of ultrasonic irradiation, although there were some foulant aggregates scattered on the membrane surface, the membrane surface became much cleaner

than that without ultrasonic irradiation. The most noticeable fouling mitigation effect was demonstrated in concentration process of the feed containing 20 mM CaCl_2 , there was no overall fouling layer covered on the membrane surface and the foulants were scattered and not as a whole when the experiment ended, it looked like that the hydrophobic membrane was still porous and most of the membrane pores kept open. The SEM-EDS analysis presented in Fig. 14 also demonstrated that it was possible a large part of the membrane surface maintained clean in the presence of ultrasonic irradiation.

The schematic illustration of the ultrasonic irradiation effect on mitigation of HA fouling during MD process was given in Fig. 15. Although the HA molecules in the feed solution became coiled and compact configuration from the stretched and linear configuration in presence of divalent cation Ca^{2+} [28] and the HA fouling was aggravated, ultrasonic irradiation could effectively mitigate membrane fouling caused by HA and prevented the permeate flux decline due to ultrasonic cleaning of the PTFE membrane surface. Ultrasonic wave can bring significant mechanical and thermal effects, and generated powerful shock wave and microstreaming with high speed. The mechanical effect promoted turbulence, reduced the boundary layer and intensified eddy diffusion. The microstreaming, shock wave and acoustic vortex streaming can continuously stimulate the liquid-membrane interface, therefore refreshed the interface and alleviated the deposition of HA aggregates. On the other side, due to ultrasonic irradiation, it became impossible to form an integral HA fouling layer covered the membrane surface, which was also beneficial to maintain permeate flux.

4. Conclusions

In the present work, an ultrasonic assisted direct contact membrane distillation hybrid process was designed and the influence of ultrasonic irradiation on HA membrane fouling mitigation during DCMD process was investigated.

Although the initial HA concentration did not affect permeate flux characteristics under experimental ranges, ultrasonic irradiation could enhance the permeate flux more than 30% without destroying HA rejection and all permeate HA concentration were below 0.40 mg/L. It was also found that the higher the concentration factor was, the larger the ultrasonic enhancement of permeate flux could be obtained.

Severe permeate flux decline can be found when the salt CaCl_2 was added into the HA solution. The presence of Ca^{2+} would aggravate HA organic fouling phenomenon via charge neutralization, complexation and formation of calcium bridges. Without liquid

penetration into the membrane pores, the HA aggregates scattered on the membrane surface, and resulted in a thick and dense HA fouling layer. The fouling layer increased heat transfer resistance and reduced the pores available for water vaporization. As a result, both the permeate flux and thermal efficiency declined.

Ultrasonic wave can bring significant mechanical and thermal effects, and generated powerful shock wave and microstreaming with high speed. The mechanical effect promoted turbulence, reduced the boundary layer and intensified eddy diffusion. The microstreaming, shock wave and acoustic vortex streaming can continuously stimulate the liquid-membrane interface, therefore refreshed the interface and alleviated the deposition of HA aggregates. Under ultrasonic irradiation, although there were some HA fouling scattered on membrane surface, most of the membrane pores kept open and clean and the relative permeate flux can maintain about 94% when the concentration factor reached 4.0.

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