Control of protein (BSA) fouling by ultrasonic irradiation during membrane distillation process

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ABSTRACT

Ultrasonic irradiation was introduced into membrane distillation process and the influence of ultrasonic irradiation on protein (bovine serum albumin, BSA) fouling control was investigated. Although the initial BSA concentration did not affect permeate flux in experimental ranges, the feed concentration increasing caused permeate BSA raise due to partial wetting of the hydrophobic membrane. The ultrasonic irradiation could enhance permeate flux about 20% without modification of the hydrophobicity/hydrophilicity of BSA in feed. The higher the concentration factor was, the larger the ultrasonic enhancement of permeate flux could be. Severe permeate flux decline can be found when the salt CaCl_2 was added into the BSA solution. The presence of Ca^{2+} would aggravate membrane fouling because the BSA molecules interacted with each other via salt bridging and formed BSA-Ca complex. The BSA aggregates scattered on membrane surface and resulted in a dense fouling layer. With ultrasonic irradiation, ultrasonic wave refreshed liquid-membrane interface continuously and alleviated the deposition of BSA aggregates. Therefore, although there were still some small foulant aggregates scattered on membrane surface, most of the membrane pores kept open and clean, the relative permeate flux can maintain about 98% and was hardly affected by concentration factor increasing.

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1. Introduction

Membrane distillation (MD) is an emerging thermally separation process using a microporous hydrophobic membrane as separation media [1]. Compared with other desalination processes such as nanofiltration (NF), reverse osmosis (RO) and conventional thermal evaporation, the potential advantages of MD are as follows: (1) lower operating temperature required than conventional distillation, (2) lower operating pressure than RO, (3) 100% (theoretical) rejection of non-volatile solute, (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 from water, treatment of wastewater and recovery of valuable components [6–9], the industrial implementation of MD is not yet feasible

because of the following four major factors [10,11]: (1) low permeate flux of the hydrophobic membrane, (2) membrane fouling and membrane pore wetting, (3) long term performance instability, and (4) optimization and development of effective MD process system. Among these considerations, membrane fouling 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 [12].

In recent years, a number of studies have investigated the effect of fouling on MD process, however, the majority of works focus on the negative effects and mitigation strategies of inorganic scaling such as CaSO_4 , CaCO_3 and SiO_2 [13–15]. As far as we know, there are limited studies dedicated to organic fouling in MD process. Protein-like substances have been identified as one of the major membrane foulants in wastewater treatment, seawater desalination and reclamation applications [16]. With regards to MD process, it is deemed necessary to pay more attention on protein fouling because the hydrophobic membrane surfaces show an especially high tendency to get fouled by proteins due to the strong foulant-membrane affinity [17].

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Severe protein fouling was observed during MD process for aqueous solutions containing organic compounds at representative concentrations, for example, Naidu et al. [18] investigated the membrane fouling development in direct contact membrane distillation (DCMD) using synthetic model solutions of bovine serum albumin (BSA), they found significant fouling and the BSA feed solution showed more significant deposits on membrane surface with less significant pore penetration. Gryta [19] performed concentration of NaCl solution containing natural organic matters (NOMs) by MD, it was found that the presence of NOMs in feed caused the fouling formation and led to rapid flux decline and the major component of the fouling layer was composed mainly of protein and sodium chloride. Hausmann et al. [20] found some minerals and proteinaceous material would penetrate into the membrane for DCMD of whey while skim milk caseins seemed to form a protective layer on membrane surface, they judged calcium playing a stronger role on adhesion in the presence of whey proteins. Thygesen et al. [21] used polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes to remove ammonia from model manure via MD, it was also revealed that the protein was one of the main components in the fouling layer deposited on both PP and PTFE membranes.

It has been demonstrated that boiling and filtration of saline wastewater can reduce the occurrence of protein fouling [22], the wastewater was boiled for 30 min and then was filtered out using a filter paper after cooling to room temperature, this method effectively prevented a rapid flux decline in DCMD. Feed pretreatment with microfiltration (MF) and ultrafiltration (UF) can remove partial protein containing in model manure solution, which was beneficial to permeate flux maintenance, Zarebska et al. [23] also found that the Novadan cleaning agents were the most successful in removing proteins compared with deionized water and NaOH/citric acid. So far, the investigations of protein fouling mitigation and membrane cleaning specially for MD process are still scarce. Nevertheless, it is worth highlighting that the protein fouling control and membrane cleaning methods used in pressure-driven membrane processes may be full of important reference value. Cui and Wright [24] created a gas–liquid two-phase flow across the UF membrane surface by injecting air into the feed stream, suppressed the BSA polarization layer and enhanced the permeate flux dramatically. In addition, the addition of a polyelectrolyte [25] and antiscalant polyaspartic acid [26] to the BSA solution can significantly reduce protein fouling for the PVDF MF membrane and BW30 RO membrane, respectively. Membrane cleaning is a key step to restore the initial flux and to continue the regular separation, both surfactant solutions [27] and saline solutions [28] are common and effective agents using for cleaning of UF membrane fouled by protein. It was also reported that the oxidative cleaning with NaClO would increase the membrane hydrophilicity and improve the initial permeate flux [29].

In recent years, application of ultrasonic technique has been tentatively introduced into membrane filtration processes. Ultrasonic wave is referred to the acoustic wave with the frequency between 20 kHz and 10 MHz [30] and the ultrasonic is used mainly in membrane fouling monitoring, membrane cleaning and membrane flux enhancement [31–35]. Li and Mairal et al. [36,37] applied ultrasonic technique as a non-destructive, real-time, in situ measuring technique for direct monitoring of membrane fouling and cleaning during UF and RO, and found that the ultrasonic technique was a useful technique for the investigation of fouling and cleaning in membrane applications. Xu et al. [38] 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 studies showed that the ultrasonic effect was useful for the fouled mem-

brane cleaning, as an alternative tool, ultrasonic cleaning was more efficient compared with other typical cleaning methods using physical and chemical methods [39,40].

Although ultrasonic irradiation has been successfully applied to enhance the performance of different pressure-driven membrane separation process, relatively few studies have been carried out with the use of ultrasonic to mitigate protein fouling in MD process. The objective of this paper is to introduce ultrasonic irradiation into DCMD process and to investigate the influence of ultrasonic irradiation on protein 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 PTFE hydrophobic hollow fibers with a mean pore diameter of 0.26 μm , supplied by DD Water Group Co., Ltd. (China), were chosen to fabricate membrane modules. The SEM images of the PTFE membrane are shown in Fig. 1. Forty pieces of hollow fibers were assembled into a polyester tube (diameter $d_{\text{in}}/d_{\text{out}} = 15/20$ 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 characteristics of the membrane and membrane modules are presented in Table 1.

2.2. Membrane distillation setup

The MD experimental setup is schematically shown in Fig. 2. 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 was 0.25 m/s, while the cold side being 1.0 m/s. The feed temperature 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 kept at 20 °C by a spiral glass heat exchanger immersed in the constant temperature trough of the cooler (SDC-6, Nanjing Xincheng 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 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 protein 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. 1. SEM images of the pristine PTFE membrane: (a) cross section, (b) inner surface, (c) outer surface.

Table 1

The characteristics of membrane material and 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

2.3. Experimental

The protein foulant was bovine serum albumin (BSA, purity > 98%, Sinopharm Chemical Reagent, China). According to the manufacturer, the molecular weight of the BSA was about 66 kDa. The pre-weighed BSA was dissolved in deionized water obtained from the Milli-Q system (Millipore, USA), then mixing of the solution was performed for over 24 h to ensure complete BSA dissolution. The filtered solution was stored in sterilized glass bottles at 4 °C and the solution pH was adjusted to 7.0 by addition of small quantities of 0.1 M NaOH or 0.1 M HCl as needed before MD experiment starting. The BSA concentration of the permeate

Fig. 2. Schematic diagram of the experimental DCMD set-up.

were evaluated by measuring the absorbance using a Hach DR-5000 UV–Vis spectrophotometer (Hach, USA) at 221 nm. This wavelength gave a maximum absorbance over the BSA 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 weight 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 (kg/m² h), ΔW is the increment of the weight of distillate (kg), A is the effective area of flat-sheet membrane (m²) 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 (kg/m² h). When the concentration factor reached 4.0, the MD process was stopped. 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 BSA 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.

2.5. Fluorescence spectra for BSA

Fluorescence spectra for BSA were measured with a fluorescence spectrophotometer (Hitachi, Model F-7000). The blank sample was MilliQ water. The F-7000 system program was employed for data processing with an excitation range of 200–500 nm and an emission range of 200–600 nm. Fluorescence data from each single measurement then was combined to construct three-dimensional fluorescence spectra and fluorescence excitation-emission matrices (EEMs) that containing fluorescence intensity as a function of both excitation and emission wavelengths. SigmaPlot 11.0 was used to obtain the 3D-EEM fluorescence spectroscopy in which Ex/Em maxima can be identified.

3. Results and discussions

3.1. Concentration of BSA solution

The solutions containing 100 mg/L and 500 mg/L BSA were tested for concentration by DCMD, respectively. The permeate flux as a function of concentration factor is illustrated in Fig. 3. It was

found that the BSA concentration had little effect on the permeate flux and the organic foulant BSA did not cause notable flux decline with the concentration factor increase. For the different BSA concentration, the initial permeate fluxes of the PTFE hollow fiber membranes were almost the same and about 1.80 kg/m² h. With the concentration factor increasing, the relative permeate fluxes can still keep constant. 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 BSA content.

Although all the BSA rejection efficiency could be over 99%, the feed concentration increasing still caused the permeate BSA concentration raise as shown in Fig. 3, which may be attributed to partial wetting phenomenon. According to Meng et al. [41], the BSA can migrate through hydrophobic membrane through an adsorption-desorption mechanism. It was also reported that proteins were easy to be adsorbed on hydrophobic surfaces due to their hydrophobic or amphoteric character [42]. During the DCMD process, BSA would be adsorbed onto the membrane surface and the BSA adsorbed at the edge of the pores migrated due to hydrogen bonding between unattached carboxylic or amino groups on the molecule and water vapor. The water vapor penetrated through membrane from feed to permeate with the help of the difference of vapor pressure, meanwhile, the BSA was also transmitted to permeate and dissolved through continuous adsorption-desorption cycles. With the feed concentration increasing, both the feed viscosity and the boundary layer thickness increased, which would aggravate the membrane wetting and cause more BSA to be adsorbed onto the membrane surface. As a result, the permeate BSA concentration increased with feed BSA concentration increasing.

The SEM micrographs of the PTFE membranes used in different feed concentration process are presented in Fig. 4. Although it looks that the membrane surface can keep clean when the experiment ending with the initial feed BSA concentration of 100 mg/L, the images of the PTFE membrane used for 500 mg/L BSA concentration confirmed several scattered fouling plots on the membrane surface. Certainly, the SEM-EDS analysis presented in Fig. 5 revealed that the deposit on the membrane surface was mainly composed of BSA, with smaller amounts of sodium chloride. Being different from pressure-driven membrane process, MD is a thermally driven process and there is a vapor transport through porous hydrophobic membrane where the driving force is the partial vapor pressure difference across the two sides of membrane pores. Because of the lower operating pressure of the MD process, even there were several BSA aggregates formed on the membrane surface, the deposition would be less compact and only cause a slight permeate flux decline.

3.2. Ultrasonic irradiation effect on DCMD of BSA solution

The effect of ultrasonic irradiation on DCMD concentration process of the feed solution containing 500 mg/L BSA was investigated in the present study and the relative permeate flux during DCMD process is shown in Fig. 6. It can be seen that ultrasonic irradiation increased the permeate flux. The higher the concentration factor was, the more obvious the ultrasonic enhancement of permeate flux could be. 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 beneficial to reduce the boundary layer, intensified eddy diffusion and relieve the negative effect of concentration factor increase on the mass transfer of DCMD process.

Fig. 3. Effect of BSA concentration on DCMD concentration process. The co-current flow velocities of the streams in the membrane module were 0.25 m/s and 1.0 m/s in the feed stream and distillate stream, respectively. The feed and distillate temperatures were 53 and 20 °C, respectively.

Fig. 4. Morphological images of the PTFE membrane after BSA solution concentration experiment: (a) with the initial BSA concentration of 100 mg/L and (b) with the initial BSA concentration of 500 mg/L.

Fig. 5. SEM-EDS analysis of the fouling scattered on membrane surface with the initial BSA concentration of 500 mg/L.

Fig. 6. Effect of BSA concentration on DCMD concentration process in the presence of ultrasonic irradiation. The co-current flow velocities of the streams in the membrane module were 0.25 m/s and 1.0 m/s in the feed stream and distillate stream, respectively. The feed and distillate temperatures were 53 and 20 °C, respectively. The frequency and power of ultrasonic irradiation were 20 kHz and 260 W, respectively.

The ultrasonic irradiation can enhance permeate flux, however, it should be confirmed whether the PTFE hollow fibers can maintain excellent BSA rejection under ultrasonic irradiation. In Fig. 6, it is presented that the permeate BSA concentration with ultrasonic irradiation was higher than that without ultrasonic irradiation. The higher the feed concentration factor, the more the BSA permeated the hydrophobic membrane. This result meant that the ultrasonic irradiation accelerated the BSA penetrate through the membrane. However, the hydrophobic membrane still kept more than 99% BSA rejection. The SEM micrographs of the PTFE membrane under ultrasonic irradiation are shown in Fig. 7, there was no foulant deposited on the membrane surface and the PTFE membrane kept clean in the presence of ultrasonic irradiation compared with that without ultrasonic irradiation.

Fig. 8 presents the 3D-EEM spectra of the BSA solutions with and without ultrasonic irradiation. Region I, II, III and IV represents tyrosine-like organics, tryptophan-like organics, fulvic-like organics, aromatic protein and humic acid-like organics, respectively [43,44]. Whether with the ultrasonic irradiation or not, the significant fluorescence peaks are appeared in the same regions. According to the locations of the fluorescence peaks, the classes were the aromatic protein (peaks located at Ex/Em = 250–330 nm/220–330 nm) and tyrosine-like organics (peaks located at Ex/Em = 200–250 nm/220–330 nm). The fluorescence spectrum analysis results indicated that ultrasonic irradiation did not cause the degradation or modification of the BSA and the hydrophobicity/hydrophilicity of the BSA solution was maintained under ultrasonic irradiation, which may be attributed to the low ultrasonic irradiation power.

Fig. 7. Morphological image of the PTFE membrane after BSA solution concentration experiment in the presence of ultrasonic irradiation: (a) 1000 $\times$ and (b) 2000 $\times$.

Fig. 8. 3D-EEM spectra of BSA solution: (a) without ultrasonic irradiation and (b) with ultrasonic irradiation.

3.3. The effect of calcium ion

Calcium ion is a major cation in natural and waste waters and the effect of the divalent cation Ca^{2+} on membrane fouling is

shown in Fig. 9. Be greatly different from the DCMD of pure BSA solution, the results clearly reveal the considerable flux decline, with the relative permeate flux J/J_0 of 0.73 at the end of the concentration experiment when the salt CaCl_2 was added into the BSA solution.

The aggravated fouling phenomenon occurred in the presence of Ca^{2+} because Ca^{2+} could form ionic bridge between two adjacent carboxyl groups from different peptide chains in BSA [45], resulting in a denser fouling layer on membrane surface as shown in Fig. 10. The reported iso-electric point of BSA is 4.7–4.9 [46], so BSA is negatively charged at pH 7. In the presence of calcium chloride, the BSA interacted with Ca^{2+} and formed BSA-Ca complex through ionic bridge between two adjacent carboxyl groups, therefore the salt CaCl_2 effectively reduced the negative charge of BSA at pH 7. The protein dissolved in water is present in the form of micelle, in general, the more negative charge will cause micelles to repel each other due to same charges, and remain micelle system stable and dispersed. On the contrary, as the negative charge of BSA decreases, the proteins tend to aggregate and deposit on membrane surface. The deposited proteins would form a dense fouling layer because these proteins could interact with each other via salt bridging. The fouling layer covered most part of membrane surface, which subsequently led to permeate flux decline.

In Fig. 10, it can be clearly found that the PTFE membrane was covered by a fouling layer due to the presence of divalent cation Ca^{2+} . Certainly, the SEM-EDS analysis revealed that the deposit on the membrane surface was the complex formed by BSA and calcium chloride.

3.4. Ultrasonic irradiation effect on BSA fouling mitigation

To investigate the influence of ultrasonic irradiation on BSA fouling, DCMD concentration of the feed containing 500 mg/L BSA and 20 mM CaCl_2 was carried out in the presence of ultrasonic irradiation. Except for the additional ultrasonic irradiation, other operating parameters were in accordance with the previous experiments. The result of the mixed solution concentration is shown in Fig. 11.

The permeate flux increased markedly in the presence of ultrasonic irradiation. The higher the concentration factor was, the more obvious the ultrasonic enhancement of permeate flux could be. As can be seen from Fig. 11, the relative permeate flux maintained 98% when the concentration factor reached 4.0 in the presence of ultrasonic irradiation. In contrast, the relative permeate

Fig. 9. Effect of calcium ion on the process of DCMD concentration of BSA solution. The co-current flow velocities of the streams in the membrane module were 0.25 m/s and 1.0 m/s in the feed stream and distillate stream, respectively. The feed and distillate temperatures were 53 and 20 °C, respectively.

Fig. 10. SEM-EDS analysis of the fouling scattered on membrane surface in presence of calcium ion.

flux decreased considerably in the absence of ultrasonic irradiation and the relative permeate flux declined to 73% when the concentration factor reached 4.0. The ultrasonic irradiation can effectively mitigate the BSA fouling, which can be observed from the images of the membrane surface morphology. The difference between the surface morphologies of the membranes fouled with BSA in the absence and presence of ultrasonic irradiation can be clearly found by comparing Figs. 10 and 12. In the presence of ultrasonic irradiation, although there were some small foulant aggregates scattered on the membrane surface, there was no overall fouling layer covered the membrane surface and the foulants were scattered and not as a whole, so the hydrophobic membrane was still porous and most of the membrane pores kept open. The SEM-EDS analysis presented in Fig. 13 revealed that the deposit on the membrane surface was the complex formed by CaCl_2 and a small amount of BSA, which also demonstrated that it was possible that the ultrasonic irradiation can effectively mitigate BSA fouling.

The schematic illustration of the ultrasonic irradiation effect on mitigation of BSA fouling during MD process was given in Fig. 14. Although the BSA molecules would interact with each other via salt bridging and form BSA-Ca complex in presence of divalent cation Ca^{2+} , and the BSA fouling was aggravated, ultrasonic irradiation could effectively mitigate membrane fouling caused by BSA 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 BSA aggregates. On the other side, due to ultrasonic irradiation, it became impossible to form an integral BSA fouling layer covered the membrane surface, which was also beneficial to maintain permeate flux.

Fig. 11. Effect of ultrasound irradiation on the process of DCMD concentration of BSA solution containing calcium ion. The co-current flow velocities of the streams in the membrane module were 0.25 m/s and 1.0 m/s in the feed stream and distillate stream, respectively. The feed and distillate temperatures were 53 and 20 °C, respectively. The frequency and power of ultrasonic irradiation were 20 kHz and 260 W, respectively.

Fig. 12. Morphological image of the PTFE membrane after BSA solution concentration experiment in the presence of ultrasonic irradiation: (a) 1000 $\times$ and (b) 20,000 $\times$.

Fig. 13. SEM-EDS analysis of the fouling scattered on membrane surface in presence of ultrasonic irradiation.

Fig. 14. Schematic illustration of ultrasonic irradiation effect on BSA fouling mitigation.

4. Conclusions

In the present work, ultrasonic irradiation was introduced into membrane distillation process and the influence of ultrasonic irradiation on protein fouling mitigation was investigated.

Although the initial BSA concentration did not affect permeate flux in experimental ranges, the feed concentration increasing caused the permeate BSA concentration raise due to partial wetting of the hydrophobic membrane. Ultrasonic irradiation could enhance the permeate flux about 20%, the higher the concentration factor was, the larger the ultrasonic enhancement of permeate flux could be. In addition, ultrasonic irradiation did not cause the modification of the hydrophobicity/hydrophilicity of the BSA because of the low ultrasonic irradiation power.

Severe permeate flux decline can be found when the salt CaCl_2 was added into the BSA solution. The presence of Ca^{2+} would aggravate BSA organic fouling because the BSA molecules would interact with each other via salt bridging and form BSA- Ca complex. The BSA aggregates scattered on the membrane surface, and resulted in a dense BSA fouling layer. The fouling layer increased mass transfer resistance and reduced the pores available for water vapor transmission, and the permeate flux declined.

Ultrasonic wave can bring significant mechanical and thermal effects, and generated powerful shock wave and microstreaming with high speed. The liquid-membrane interface was continuously stimulated and refreshed. Therefore, although there were still some small foulant aggregates scattered on membrane surface, most of the membrane pores kept open and clean and the relative permeate flux can maintain about 98% when the concentration factor reached 4.0 in the presence of ultrasonic irradiation.

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References

- [1] K.Y. Wang, T.S. Chung, M. Gryta, Hydrophobic PVDF hollow fiber membranes with narrow pore size distribution and ultra-thin skin for the fresh water production through membrane distillation, *Chem. Eng. Sci.* 63 (2008) 2587–2589.
- [2] K.W. Lawson, D.R. Lloyd, Membrane distillation, *J. Membr. Sci.* 124 (1997) 1–25.
- [3] A. Chafidz, S. Al-Zahrani, M.N. Al-Otaibi, C.F. Hoong, T.F. Lai, M. Prabu, Portable and integrated solar-driven desalination system using membrane distillation for arid remote areas in Saudi Arabia, *Desalination* 345 (2014) 36–49.
- [4] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, *J. Membr. Sci.* 331 (2009) 31–39.
- [5] E. El-Zanati, K.M. El-Khatib, Integrated membrane-based desalination system, *Desalination* 205 (2007) 15–25.
- [6] A. Alkhudhiri, N. Darwish, N. Hilal, Produced water treatment: application of air gap membrane distillation, *Desalination* 309 (2013) 46–51.
- [7] F. Banat, S. Al-Asheh, M. Qtaishat, Treatment of waters colored with methylene blue dye by vacuum membrane distillation, *Desalination* 174 (2005) 87–96.
- [8] A. Criscuolo, J. Zhong, A. Figoli, M.C. Carnevale, R. Huang, E. Drioli, Treatment of dye solutions by vacuum membrane distillation, *Water Res.* 42 (2008) 5031–5037.
- [9] H.Y. Liu, J.L. Wang, Treatment of radioactive wastewater using direct contact membrane distillation, *J. Hazard. Mater.* 261 (2013) 307–315.
- [10] D.Y. Hou, G.H. Dai, H. Fan, H.J. Huang, J. Wang, An ultrasonic assisted direct contact membrane distillation hybrid process for desalination, *J. Membr. Sci.* 476 (2015) 59–67.
- [11] M.M. Teoh, T.S. Chung, Membrane distillation with hydrophobic macrovoid-free PVDF-PTFE hollow fiber membranes, *Sep. Purif. Technol.* 66 (2009) 229–236.

- [12] L.D. Tijting, Y.C. Woo, J.S. Choi, S. Lee, S.H. Kim, H.K. Shon, Fouling and its control in membrane distillation—a review, *J. Membr. Sci.* 475 (2015) 215–244.
- [13] S. Shirazi, C.J. Lin, D. Chen, Inorganic fouling of pressure-driven membrane processes—a critical review, *Desalination* 250 (2010) 236–248.
- [14] F. He, K.K. Sirkar, J. Gilron, Studies on scaling of membranes in desalination by direct contact membrane distillation: CaCO_3 and mixed $\text{CaCO}_3/\text{CaSO}_4$ systems, *Chem. Eng. Sci.* 64 (2009) 1844–1859.
- [15] L.D. Nghiem, T. Cath, A scaling mitigation approach during direct contact membrane distillation, *Sep. Purif. Technol.* 80 (2011) 315–322.
- [16] E. Celik, L. Liu, H. Choi, Protein fouling behavior of carbon nanotube/polyethersulfone composite membranes during water filtration, *Water Res.* 45 (2011) 5287–5294.
- [17] R. Miao, L. Wang, N. Mi, Z. Gao, T.T. Liu, Y.T. Lv, X.D. Wang, X.R. Meng, Y.Z. Yang, Enhancement and mitigation mechanisms of protein fouling of ultrafiltration membranes under different ionic strengths, *Environ. Sci. Technol.* 49 (2015) 6574–6580.
- [18] G. Naidu, S. Jeong, S.J. Kim, I.S. Kim, S. Vigneswaran, Organic fouling behavior in direct contact membrane distillation, *Desalination* 347 (2014) 230–239.
- [19] M. Gryta, Fouling in direct contact membrane distillation, *J. Membr. Sci.* 325 (2008) 383–394.
- [20] A. Hausmann, P. Sancio, T. Vasiljevic, M. Weeks, K. Schroën, S. Gray, M. Duke, Fouling mechanisms of dairy streams during membrane distillation, *J. Membr. Sci.* 441 (2013) 102–111.
- [21] O. Thygesen, M.A.B. Hedegaard, A. Zarebska, C. Beileites, C. Krafft, Membrane fouling from ammonia recovery analyzed by ATR-FTIR imaging, *Vib. Spectrosc.* 72 (2014) 119–123.
- [22] M. Gryta, M. Tomaszewska, K. Karakulski, Wastewater treatment by membrane distillation, *Desalination* 198 (2006) 67–73.
- [23] A. Zarebska, Á.C. Amor, K. Ciurkot, H. Karring, O. Thygesen, T.P. Andersen, M.B. Hägg, K.V. Christensen, B. Norddahl, Fouling mitigation in membrane distillation processes during ammonia stripping from pig manure, *J. Membr. Sci.* 484 (2015) 119–132.
- [24] Z.F. Cui, K.I.T. Wright, Gas-liquid two-phase cross-flow ultrafiltration of BSA and dextran solutions, *J. Membr. Sci.* 90 (1994) 183–189.
- [25] M. Pinelo, C. Ferrer, A.S. Meyer, G. Jonsson, Controlling the rejection of protein during membrane filtration by adding selected polyelectrolytes, *Sep. Purif. Technol.* 85 (2012) 54–60.
- [26] Q.F. Yang, Y.Q. Liu, Y.J. Li, Control of protein (BSA) fouling in RO system by antiscalants, *J. Membr. Sci.* 364 (2010) 372–379.
- [27] R. Naim, I. Levitsky, V. Gitis, Surfactant cleaning of UF membranes fouled by proteins, *Sep. Purif. Technol.* 94 (2012) 39–43.
- [28] M.J. Corbatón-Báguena, S. Álvarez-Blanco, M.C. Vincent-Vela, Cleaning of ultrafiltration membranes fouled with BSA by means of saline solutions, *Sep. Purif. Technol.* 125 (2014) 1–10.
- [29] I. Levitsky, A. Duek, E. Arkhangelsky, D. Pinchev, T. Kadoshian, H. Shetrit, R. Naim, V. Gitis, Understanding the oxidative cleaning of UF membranes, *J. Membr. Sci.* 377 (2011) 206–213.
- [30] L.Y. Liu, Z.W. Ding, L.J. Chang, R.Y. Ma, Z.R. Yang, Ultrasonic enhancement of membrane-based deoxygenation and simultaneous influence on polymeric hollow fiber membrane, *Sep. Purif. Technol.* 56 (2007) 133–142.
- [31] R. Sanderson, J.X. Li, L.J. Koen, L. Lorenzen, Ultrasonic time-domain reflectometry as a non-destructive instrumental visualization technique to monitor inorganic fouling and cleaning on reverse osmosis membranes, *J. Membr. Sci.* 207 (2002) 105–117.
- [32] J.X. Li, R.D. Sanderson, E.P. Jacobs, Ultrasonic cleaning of nylon microfiltration membranes fouled by Kraft paper mill effluent, *J. Membr. Sci.* 205 (2002) 247–257.
- [33] A. Mirzaie, T. Mohammadi, Effect of ultrasonic waves on flux enhancement in microfiltration of milk, *J. Food Eng.* 108 (2012) 77–86.
- [34] C. Zhua, G.L. Liu, C.S. Cheung, C.W. Leung, Z.C. Zhu, Ultrasonic stimulation on enhancement of air gap membrane distillation, *J. Membr. Sci.* 161 (1999) 85–93.
- [35] M. Cai, S.N. Zhao, H.H. Liang, Mechanisms for the enhancement of ultrafiltration and membrane cleaning by different ultrasonic frequencies, *Desalination* 263 (2010) 133–138.
- [36] X.H. Li, J.X. Li, J. Wang, H. Wang, B.Q. He, H.W. Zhang, W.S. Guo, H.H. Ngo, Experimental investigation of local flux distribution and fouling behavior in double-end and dead-end submerged hollow fiber membrane modules, *J. Membr. Sci.* 453 (2014) 18–26.
- [37] A.P. Mairal, A.R. Greenberg, W.B. Krantz, Investigation of membrane fouling and cleaning using ultrasonic time-domain reflectometry, *Desalination* 130 (2000) 45–60.
- [38] M.L. Xu, X.H. Wen, X. Huang, Z.Y. Yu, M. Zhu, Mechanisms of membrane fouling controlled by online ultrasound in an anaerobic membrane bioreactor for digestion of waste activated sludge, *J. Membr. Sci.* 445 (2013) 119–126.
- [39] S.R. Gonzalez-Avila, F. Prabowo, A. Kumar, C.D. Ohi, Improved ultrasonic cleaning of membranes with tandem frequency excitation, *J. Membr. Sci.* 415–416 (2012) 776–783.
- [40] C. Loderer, D. Pawelka, W. Vatie, P. Hasal, W. Fuchs, Dynamic filtration—Ultrasonic cleaning in a continuous operated filtration process under submerged conditions, *Sep. Purif. Technol.* 119 (2013) 72–81.
- [41] S. Meng, Y. Ye, J. Mansouri, V. Chen, Fouling and crystallisation behaviour of superhydrophobic nano-composite PVDF membranes in direct contact membrane distillation, *J. Membr. Sci.* 463 (2014) 102–112.
- [42] A. Bottino, G. Capannelli, O. Monticelli, P. Piaggio, Poly(vinylidene fluoride) with improved functionalization for membrane production, *J. Membr. Sci.* 166 (2000) 23–29.
- [43] W. Chen, P. Westerhoff, J.A. Leenheer, K. Booksh, Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter, *Environ. Sci. Technol.* 37 (2003) 5701–5710.
- [44] A. Baker, M. Curry, Fluorescence of leachates from three contrasting landfills, *Water Res.* 38 (2004) 2605–2613.
- [45] H.J. Mo, K.G. Tay, H.Y. Ng, Fouling of reverse osmosis membrane by protein (BSA): effects of pH, calcium, magnesium, ionic strength and temperature, *J. Membr. Sci.* 315 (2008) 28–35.
- [46] K. Nakamura, K. Matsumoto, Properties of protein adsorption onto pore surface during microfiltration: effects of solution environment and membrane hydrophobicity, *J. Membr. Sci.* 280 (2006) 363–374.