Study on concentrating primary reverse osmosis retentate by direct contact membrane distillation

Dan Qu, Jun Wang, Bin Fan, Zhaokun Luan*, Deyin Hou

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences, Beijing 100085, China
Tel/Fax: +86-10-62849150; email: luanzk@rcees.ac.cn

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Abstract

The direct contact membrane distillation (DCMD) applied for the concentration of the primary reverse osmosis (PRO) retentate was presented in the paper. All the experiments were carried out using the self-made hydrophobic polyvinylidene fluoride (PVDF) membranes. The DCMD process (permeate flux and conductivity) and membrane fouling phenomenon were investigated. Three kinds of PRO retentate (direct PRO retentate, silica bearing PRO retentate, and iron and manganese bearing PRO retentate) were used in the experiments. During the whole period of investigation, the membranes were found to be thermally stable and good separation characteristics. The RO was fed with the tap water with the recovery of 50%. After DCMD process, the whole water recovery can be significantly enhanced to 98.8%. Membrane fouling was observed during the process. Membrane clogging caused by the formed deposit (CaCO_3 , CaSO_4 , and silicate) was the main reason of the membrane efficiency reduction. It was found that CaCO_3 formed at first during the process, and can be alleviated even eliminated by acidification. When the PRO retentate was concentrated a high level, CaSO_4 formed and caused a sharp decline of module efficiency. During the DCMD process of silica bearing PRO retentate, silica may co-precipitate with soluble metals to form silicate at alkaline solutions while colloid silica may form at acidic solutions. The influence of iron and manganese is not significant.

Keywords: Direct contact membrane distillation; Reverse osmosis; Recovery; Membrane fouling

1. Introduction

Reverse osmosis (RO) has been widely used in the preparation of industrial pure water and other fields such as chemical engineering and environmental engineering. At present, the

recovery of primary reverse osmosis (PRO) is usually kept at 50–75%. In the above range of water recovery, the retentate volume is significant and thus represents a loss of valuable water resource and a major disposal challenge. Currently the available methods to improve RO recovery are using water soluble polymeric anti-scalants. Even though, the recovery is still kept at

*Corresponding author.

a low level about 75–85% [1]. Other pretreatment methods such as accelerated precipitation softening (APS) for secondary or higher levels of RO process were also investigated. It was reported that a laboratory bench-scale system for evaluating enhanced water recovery via RO desalting (50–75%), followed by APS treatment and subsequently secondary RO desalting to achieve total recovery of 95–98% [2]. Here, a hydrophobic membrane process – membrane distillation (MD) was considered.

MD is a thermally driven process that involves transport of water vapor through a porous hydrophobic membrane [3]. During MD of solutions with non-volatile solutes, only water vapor can be transferred through the membrane, so theoretically the MD process enables the production of pure water from natural water. In addition, it is less dependent on the initial salinity of the feed as well as a higher salt rejection ratio. And it is less demanding in membrane's mechanical strength. Thus, MD is often proposed for desalination [4–6] and other applications such as the concentration of juice and the separation of volatile metabolites [7, 8].

The principal obstacle in MD process is associated with membrane fouling and wettability [9]. The latter phenomenon is responsible not only for a decline of the plant efficiency, but also a damage of the module over a short time. The feed type has a considerable influence on membrane fouling. The PRO retentate with low content of organic compounds decreased the possibility of membrane wettability. Thus, it is possible to enhance water recovery by MD process. Meanwhile, the industrial pure water is obtained. It is significant in economizing water resource.

However, the PRO retentate contains high content of inorganic ions such as Ca^{2+} , HCO_3^- , SO_4^{2-} , SiO_3^{2-} and so on. At higher temperature and levels of recovery, the concentration of ions on the membrane feed-side may exceed the solubility limit such as CaCO_3 and CaSO_4 , which may

lead to permeate flux decline and even wetting phenomenon. During pressure-driven membrane process (NF and RO), the CaCO_3 and CaSO_4 scaling potential assessment has been described in many papers. Sheikholeslami [10] used the scaling potential index (SPI) to assess the scaling potential for sparing soluble salts in RO and NF units. Samir et al. [11] used molar ratio as a tool for prediction of scaling potential in RO systems. Sangho Lee et al. [12] also discussed the scale formation mechanism in various NF modules. However, CaCO_3 and CaSO_4 scaling was just mentioned to be found during MD process [13–15]. Few discussions about the scaling potential and different scaling properties were presented. Chernyshov et al. [16] had ever used Lias and Govind method to model temperature and salt concentration distribution in membrane distillation feed channel and concluded that if the solubility of salt decreases with temperature, maximum supersaturation can occur in the bulk of the flow rather than at the membrane surface. It can be used to explain the CaCO_3 and CaSO_4 scaling phenomenon during MD process. Recently, Fei He et al. [17] analyzed the CaSO_4 scaling potential in hollow fiber membrane in terms of the saturation index profiles during the crossflow DCMD.

Silica was considered to be a problematic foulant during membrane process. In naturally occurring waters, silica is weakly ionized and existed as monosilicic acid while at higher concentrations, monosilicic acid polymerizes to form larger polysilicic acids, the larger of which are of a colloidal size. In neutral or slightly alkaline solutions, silica can also co-precipitate with soluble metals forming silicate [18]. Sheikholeslami et al. had done a lot of works on silica fouling during RO process [19–23]. Iron and manganese are also the two common ions in natural water, and it was reported that membrane fouling with $\text{Fe}(\text{OH})_3$ occurs both in the strongly acidic or alkaline medium during RO process [24]. So, all the inorganic ions mentioned above may limit the

module efficiency and their fouling mechanism during the MD process should be investigated.

Direct contact membrane distillation (DCMD) is one of the four basic configurations of MD, in which the feed and the permeate are directly separated by the membrane. And DCMD is considered to be the most simple, economic and efficient configurations. Thus, in the present paper, DCMD was applied for concentrating the PRO retentate to enhance the water recovery. Three different kinds of PRO retentate (direct PRO retentate, silica bearing PRO retentate, and iron and manganese bearing PRO retentate) were used in the experiments. DCMD performance in terms of flux and conductivity stability was observed throughout the whole experiment periods. And also membrane fouling was observed during the process.

2. Experimental

2.1. Membrane modules and the DCMD unit

The membrane module was made by a polyester tube and two UPVC T-tubes. The outside/inside diameters of the module were 20 mm/15 mm and the effective length of the module was 100 mm. The module was equipped with 50 hydrophobic hollow fiber PVDF membranes. The outside/inside diameters of the membrane were 1 mm/0.6 mm, respectively. The porosity, average pore radius and the membrane thickness were 80%, 0.15 μm and 0.2 mm, respectively. The total efficient area of the module was calculated for the internal diameter of hollow fiber membrane and amounted to 94.20 cm^2 .

The experimental setup is shown in Fig. 1. The DCMD installation was consisted of two thermostatic cycles, the feed one and the permeate one, which were connected to the membrane module. Both the feed and the permeate were pumped from the bottom to the upper part of the module assembled in a vertical position. The feed flowed inside the capillaries, whereas the permeate

Fig. 1. Membrane distillation setup: (1) feed reservoir; (2) membrane module; (3) permeate reservoir; (4) water bath; (5) cooling coil; (6) pump; (7) thermometer; and (8) conductivity monitor.

flowed through the intertubular space. Two magnetic pumps were used to provide the flow of the feed preheated in the thermostatic bath and the permeate cooled through the cooling coil. There were 4 thermometers equipped on both the inlet and the outlet of the feed and the permeate sides. The permeate flux was measured by the overflow volume of the permeate reservoir.

2.2. The primary reverse osmosis retentate

The PRO retentate was used as the basic feed in the presented paper. The RO system was one unit of the direct drinking water preparation system, which consisted of ozone oxidation, catalyze oxidation and active carbon filtration before the RO system to get rid of organic compounds. No antiscalants were used. So the total organic carbon (TOC) analysis revealed that the PRO retentate contained less than 1 mg L^{-1} of the TOC. The RO was supplied with the tap water with the recovery of 50%. The conductivity of PRO retentate varied from 980 to 1200 $\mu\text{S cm}^{-1}$. The pH was about 7.90 in average. The average concentrations of the major ions were as follows: Ca^{2+} 376.00 mg L^{-1} , Mg^{2+} 203.00 mg L^{-1} , Cl^{-} 56.75 mg L^{-1} , SiO_3^{-} 11.22 mg L^{-1} , HCO_3^{-} 9.25 mmol L^{-1} and CO_3^{2-} 0.35 mmol L^{-1} . Additional $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were added in the PRO retentate

for special experimental needs. All the reagents were analytical grade.

2.3. DCMD experiments

New modules were used for each experimental series. During each series, the DCMD installation worked non-stop until the permeate flux declined significantly and then rinsed the module with 2% HCl. After rinsing the module, other correlative experiments were performed on the same module. The initial flow rate of the feed was 0.60 m s^{-1} , whereas the permeate flow rate was 0.18 m s^{-1} during all the experiments. And the inlet temperature of the feed and the permeate were $50 \pm 1^\circ\text{C}$ and $20 \pm 1^\circ\text{C}$, respectively.

2.4. Analysis methods

The permeate conductivity was measured by an online conductivity monitor. The concentration of Ca^{2+} was determined with EDTA titration, and the concentration of SO_4^{2-} was measured by the spectrophotometer (DR/4000U, HACH, USA). The analysis for soluble silica was carried out

using molybdosilicate method and the spectrophotometer. The morphology and the composition of the fouling matter was studied using scanning electron microscopy (S-3000N, HITACHI, Japan) coupled with energy dispersion spectrometry (Genesis, EDAX, USA). The membrane samples were made by liquid nitrogen and then dried in the oven at 50°C . Then the samples were sputter coated with gold and examined. The accelerating voltage was 5 kV.

3. Results and discussion

3.1. DCMD process of the PRO retentate

The experimental results shown in Fig. 2 (stage I) demonstrated the direct application of the PRO retentate as a feed. At the initial stage of the experiments, an increase of permeate flux from $10.50 \text{ kg m}^{-2} \text{ h}^{-1}$ to $11.40 \text{ kg m}^{-2} \text{ h}^{-1}$ was observed, just as reported in other works [9, 25]. There were two explanations based on the PP membrane experiments for the initial flux increase. One reason may be associated with a change of the membrane morphology [25]. It

Fig. 2. Variation of the efficiency during the DCMD process.

was reported that a significant increase of membrane pores were observed after the water contact experiments, which lead to the reduction of resistance of the vapor transfer across the membrane. Another reason was the asymmetrical structure of the membrane reported by Gryta [9]. It was pointed that the pores on the membrane surface were larger, what may lead pores to be filled with water. It caused a decrease of thickness of the gas diffusion paths and consequently the DCMD efficiency was increased.

The SEM images of membranes are shown in Fig. 3. The morphology of the PVDF membrane was uniform with the finger-like pores outside and the sponge structure in the center. However, the pores on the inner membrane surface were not obvious at a low magnify factor ($500\times$) (Fig. 3a₁), while the sponge structure was clear

in sight (Fig. 3b₁). At a larger magnify factor ($2000\times$) (Fig. 3a₂), the pores in the membrane surface come into sight with a small diameter. Obviously, the pores on the membrane surface were much smaller than the sponge pores, so the reason of flux increase was not related to the larger pores on the membrane surface. The observations performed with new membrane (Fig. 3a₂ and b₂) and the membrane collected from the module after 5 h of the MD performance (Fig. 3a₃ and b₃) did not reveal any significant differences in the morphology (both the surface and the cross-section). However, a slight increase of pore size, difficult to assess visually, can lead the reduction of the resistances of vapor diffusion across the membrane and the permeate flux may increase. The permeate conductivity kept decreasing during the process and it indicated

Fig. 3. SEM images of the PVDF membranes: (a₁) inner surface of fresh membrane ($500\times$); (a₂) inner surface of fresh membrane ($2000\times$); (a₃) inner surface of the membrane after DCMD experiment; (b₁) cross section of the fresh membrane ($500\times$); (b₂) cross section of the fresh membrane ($2000\times$); and (b₃) cross section of the membrane after DCMD experiment.

that no wettability phenomenon occurred. The observed initial permeate flux increase may also result from the dissolved gas transferring across the membrane when heated. Several preliminary experiments by our group have showed that soluble micro bubble may lead to an enhancement of permeate flux.

After the initial increase, a continual decline of the permeate flux was found. A large amount of deposit was found in the inlet of the membrane module (Fig. 4). A concentration decrease of HCO_3^- from 9.25 to 1.43 mmol L^{-1} was found in the feed, what indicated the flux decline was associated with the formation of CaCO_3 , just as reported in other work [15]. The feed flow rate decreased from initial 0.60 to 0.45 m s^{-1} when the permeate flux decreased to 7.53 $\text{kg m}^{-2} \text{h}^{-1}$ after 50 h running. So it can be assumed that the feed flow decrease caused by the deposit clogging was the main reason for the decrease of the module efficiency. It is because that the feed was pumped with magnetic pump; therefore, an increase of the feed flow resistance caused a decline of the flow rate. A decrease of the flow rate caused an unfavorable increase of the temperature polarization and comprises a possible reason of the observed

reduction of the module efficiency [9]. The feed flow rate can be entirely restored by rinsing the module with 2% HCl. The permeate conductivity kept decline and stabilized at about 3.5 $\mu\text{S cm}^{-1}$ at last, which indicated that the PVDF membrane exhibited a stable hydrophobicity.

The results presented in Fig. 2 (stage II) were obtained after the acidification of the PRO retentate. The solution pH was adjusted to 6.0. There was a sharp increase of the permeate conductivity at the beginning of the process. It was resulted from the CO_2 , which was not degassed completely after acidification, crossing the membrane to the permeate side. After the initial increase, the permeate conductivity was stabilized at about 3 $\mu\text{S cm}^{-1}$. The problem of CaCO_3 was alleviated by acidification, so the permeate flux declined only 20% after 200 h running after acidification (stage II). Then a sharp flux decline was observed. Up to the permeate flux decline, the PRO retentate was concentrated about 40 times as the initial concentration and the whole water recovery increased up to 98.8%.

At high levels of water recovery, CaSO_4 crystallization may take place when Ca^{2+} and SO_4^{2-} on the feed side exceed the solubility limit of CaSO_4 . Figure 5 illustrates the changes of Ca^{2+} and SO_4^{2-} during the process, which demonstrates the formation of CaSO_4 . Chernyshov et al. [16] used Lias and Govind method to model temperature and salt concentration distribution in membrane distillation feed channel and concluded that if the solubility of salt decreases with temperature, maximum supersaturation can occur in the bulk of the flow rather than at the membrane surface. Our previous research [26] proved that CaCO_3 and CaSO_4 were prone to precipitate in bulk solutions rather than at membrane surface, and CaSO_4 precipitate can lead to a faster flux decline than CaCO_3 precipitate. This phenomenon can be explained by the different morphology between them. CaCO_3 has a hexagonal structure, and was more tenacious and compact; while CaSO_4

Fig. 4. SEM micrograph of CaCO_3 deposit collected from the inlet of the module.

Fig. 5. Changes of Ca^{2+} and SO_4^{2-} concentration during DCMD process.

had a needle shape and was loosely attached [27]. So in the experiment, CaCO_3 was found to attach to the feed container and the tubes, the probability of clogging the membrane module was decreased. While CaSO_4 was found moving freely in the solution, once it formed, it would lead to a rapid clogging of the module, which would cause a sharp flux decline.

The feed PRO retentate pH was adjusted to 4.0 in stage III. Until the end of the process, the problem of scaling was eliminated just as reported in other works [19]. All the experiments mentioned above were at a laboratory scale, further research should be considered.

3.2. DCMD process of silica bearing PRO retentate

Additional $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was added in PRO retentate, and the initial silica concentration of PRO retentate was 50 mg L^{-1} . Permeate flux and conductivity is shown as a function of elapsed time in Fig. 6. The feed solution pH was adjusted to 6.0 at stage I. Along with the

decomposition of HCO_3^- when heated, the solution pH increased and stabilized at about 8.0. A lot of deposit was found in the inlet of the module. The EDS analysis of the deposit demonstrated that the deposit contained a large amount of Si, C and Ca with a trace amount of Mg. The deposit could be assumed as a mixture of CaCO_3 and silicate. At alkaline pH, silica may co-precipitate with soluble metals to form magnesium silicate (Mg_2SiO_4) or calcium silicate (Ca_2SiO_4). Furthermore, silica may be adsorbed onto the surface of insoluble metal hydroxide compounds, such as $\text{Mg}(\text{OH})_2$ or MgCO_3 [18].

The feed solution pH was adjusted to 4.0 at stage II. The observed initial flux decline was due to the impurity clogging the module. After the washing of the module, the module efficiency recovered to the initial level. The performance kept stable until the PRO retentate was concentrated about 40 times. Then the sharp flux decline occurred. A large amount of deposit was found at the module inlet, while only a little deposit was found on the membrane surface. The EDS analysis (Fig. 7) showed the deposit was mainly

Fig. 6. Variation of the efficiency during the DCMD process of silica bearing PRO.

consisted of Si, S, C, Ca, Cl, O and a trace amount of Cu and Mg. The deposit was assumed as a mixture of calcium scaling and colloid silica.

There are two relevant categories of silica fouling, namely precipitation fouling and particulate fouling. Precipitation is a glasslike scale formed on the surface due to concentration polarization. On the other hand, particulate fouling is the accumulation of colloids, formed

initially in bulk solution or the boundary layer and then deposit on the membrane surface [19, 20, 23]. The silica fouling potential is dependent on the concentration of dissolved silica exceeding the amorphous silica equilibrium solubility of the solution. In RO processes, concentration polarization phenomenon is significant, so the silica concentration adjacent to the membrane surface is highly supersaturated; precipitation

Fig. 7. SEM-EDS of the deposit collected from the module inlet.

and particulate fouling were both common and then the initial silica feed concentration may affect the silica fouling [20].

However, during the DCMD process, temperature polarization phenomenon plays a more important role than concentration polarization in the heat and mass transfer process. So silica fouling phenomenon may be different from the pressure-driven membrane processes. Precipitation of monomeric silica on the membrane surface was not found during the process. The SEM analysis showed a mixture of colloid silica and calcium scaling formed during the process. It seems that particulate fouling occurred when the bulk silica concentration is high enough to reach the silica polymerize concentration. The further discussion about silica fouling during DCMD process should be investigated.

3.3. DCMD process of iron and manganese bearing PRO retentate

Additional $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were added to PRO retentate and the initial

iron and manganese concentration of PRO retentate were kept at 1 mg L^{-1} and 0.5 mg L^{-1} , respectively. The solution pH was adjusted to 6.0. As seen in Fig. 8, the permeate flux began to decline when the installation run 75 h. It was found that the major reason of the observed permeate flux decline was the formation of the deposit at the inlet of the module. The SEM-EDS analysis demonstrated that the deposit collected from the module inlet was mainly Ca, C and O, with a smaller amount of Cl. It can be concluded that CaCO_3 was still the main cause of the reduction of membrane efficiency and the influence of iron and manganese is not significant. An initial permeate conductivity increase due to the CO_2 generated from acidification was observed, and then the permeate conductivity kept at a stable level. At the end of this process, the permeate conductivity increased, which was also found during the former experiments. One of the reasons causing an increase of permeate conductivity may be associated with the partial wetting phenomenon. Few larger pores which lead a low LEPw were still in

Fig. 8. Variation of the efficiency during DCMD process of high iron and manganese PRO retentate.

existence, where ions can transfer directly across to the permeate side. During the DCMD process of low concentration solutions, with a constant permeate flux and low salinity, the permeate conductivity kept at about $3.0\text{--}3.5\ \mu\text{S cm}^{-1}$. But accompany with the flux decline and the feed salinity increase, partial wetting phenomenon became serious and lead to a slight permeate conductivity increase. Another reason was the hydraulic pressure on the feed side was slightly higher than that of the permeate side when the flow channel was clogged by the deposit, which additionally enhanced the possibility of leakage and consequently the permeate contamination.

All the experiments mentioned above were investigated at a laboratory level. Now, the pilot scale performance was being carried on the power plant for investigation. The stability and efficiency should be further considered.

4. Conclusions

The results of the present work have suggested that the PRO retentate (with the recovery 50%) can be concentrated about 40 times by direct contact membrane distillation, and then the whole recovery has been significantly increased to 98.8%. During the whole period of investigation, the PVDF membranes were found to be thermally stable and showed good separation characteristics.

Membrane fouling was investigated during the DCMD process. Feed flow decrease caused by the deposit clogging was the main reason for the reduction of module efficiency. A flow rate decrease would cause an unfavorable increase of the temperature polarization and lead to a reduction of the module efficiency. CaSO_4 would lead to a sharper module efficiency decline than CaCO_3 for their different structure and properties. Silica fouling was strongly influenced by the solution pH. Silica may co-precipitate with soluble metals (Ca^{2+} and Mg^{2+}) to form silicate

at alkaline solutions while colloid silica formed at acidic solutions. The influence of iron and manganese is not significant.

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