Fouling behavior and scaling mitigation strategy of CaSO$_4$ in submerged vacuum membrane distillation

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ABSTRACT

Fouling and scaling in membrane distillation (MD) is one of the major obstacles to its long term stability. Submerging the membrane directly into the feed is an alternative method to prevent flow channel blockage. The fouling behavior of CaSO$_4$ in submerged vacuum membrane distillation at varying experimental conditions was investigated. It presented a two-stage trend when the initial concentration of CaSO$_4$ was < 2700 mg/L. Dramatic flux decline occurred once the feed was concentrated to a critical level of saturation. A on-line periodically air backwash was applied to reduce CaSO$_4$ crystals deposition on the membrane surface or penetration in the membrane pores. While the role of air bubbles in affecting the fouling behavior of CaSO$_4$ largely depended on the crystal formation mechanism. The fouling rate was reduced by 54% with the help of air backwash when surface crystallization controlled the process while negligible effect was made when bulk crystallization played a more important role. The result could be explained by combining the experimental data with a first-order kinetic model proposed by Tansel. The off-line water cleaning suggested that the fouling layer could be removed effectively without additional chemical agent.

1. Introduction

Membrane distillation (MD) is a thermally driven technology using porous hydrophobic membrane as an unselective barrier to achieve distilled water production or aqueous solution concentration [1]. The nonvolatile components in feed solution can be rejected on one side of membrane while the vapor molecules are transported to the other side due to the vapor pressure difference. Besides the general advantages such as lower operating temperature than conventional distillation, lower operating hydrostatic pressure than pressure-driven processes and higher rejection factor of non-volatile solutes, the most prominent potential of MD technology lies in its unique ability to treat high salinity solutions [2,3]. Since water flux is not influenced by the osmotic pressure gradient, the process of MD can maintain relative sustainability without suffering from large permeate loss for the highly concentrated solution which is close to or even higher than the saturation point [4,5].

Despite the fact that MD has been increasingly studied over the last few years, membrane fouling, caused by accumulation of undesired materials on the membrane surface or in the membrane pores, is still an urgent issue which affects the long term stability of MD like all other membrane processes [1,6]. The existence of fouling layer not only adds additional heat and mass transfer resistances, but also increases the risk of pore blockage and membrane wetting, and finally results in deterioration of MD performance [7]. Therefore, it is necessary to understand the fouling behavior and find out effective fouling control techniques for specific pollutants. The types of pollutants existed in MD process can be mainly classified into inorganic pollutants, particulate pollutants and biological pollutants [8]. As most of the reverse osmosis retentate contains large amount of scaling ions, the research of inorganic fouling caused by sparingly soluble salts is of most concerned in literature [9,10].

Fouling in MD process is a complicated phenomenon which is significantly influenced by many factors, and the configuration of membrane module is one of them. It is worth noting that most of MD studies use conventional cross-flow hollow fiber module, which has strong inclination to fouling and is difficult for cleaning and maintenance [11]. This problem can potentially be minimized by submerging the membrane into the feed directly [12,13]. Fouling control techniques can influence fouling behavior as well, different strategies such as feed pretreatment [14,15], membrane surface modification [16,17] and chemical cleaning [18] have been studied to alleviate or eliminate the negative effect of fouling in varying degree. Bubble-assistant technology is considered as an effective way to remove deposition layer

from membrane surface especially for submerged membrane filtration process [19,20]. Recently, this method is gradually applied to MD process. Chen et al. reported that the scaling formation in direct contact membrane distillation could be alleviated by introducing gas bubbles when treating NaCl solution [21]. Ding et al. also found that intermittent gas bubbling reduced membrane fouling in concentrating traditional Chinese medicine [22]. However, opposite conclusion was made by Meng et al., *i.e.*, bubbles generated through air backwash increased salt deposition when feed solution contained sparingly soluble salts [13]. Therefore, further investigation is still needed to find out the role of air bubbles played in membrane fouling for specific pollutants.

In this paper, a self-made open membrane module was designed using polytetrafluoroethylene (PTFE) hollow fiber membranes. The submerged vacuum membrane distillation (SVMD) was used to reduce the risk of feed flow blockage and make it convenient for module cleaning. The main objective of this study was to investigate the effect of two different crystal formation mechanisms on the fouling behavior of $CaSO_4$ and the role of air backwash played in scaling mitigation in both cases. In addition, an empirical flux decline model was used to further explain the experiment results.

2. Experimental

2.1. Materials and membrane module

PTFE is a good candidate for MD due to its superior hydrophobicity, thermal stability, chemical resistance and mechanical strength [23,24]. Self-made microporous PTFE hollow fiber membranes [25] were used and sealed with an epoxy resin at both ends to fabricate a simplified open membrane module in this study. The characteristics of hydrophobic membranes and membrane module are listed in Table 1.

2.2. Feed solution

Calcium chloride and sodium sulfate were purchased from Tianjin Kemiou Chemical Reagent Company and used without further purification. The feed solution was prepared by mixing appropriate amount of fully dissolved $CaCl_2$ and Na_2SO_4 with deionized (DI) water as solvent.

Prior to all experiments, DI water was used as feed solution for 1 h to get initial pure water flux J_0.

2.3. Experimental design

The SVMD system was used in this study (Fig. 1). A curtain type of hollow fiber membrane module was simply submerged in a constant temperature feed tank, in which the outer surface of the hollow fiber membranes was contacted with hot feed solution directly. The volume of the initial feed solution was always 16 L. The feed temperature in this
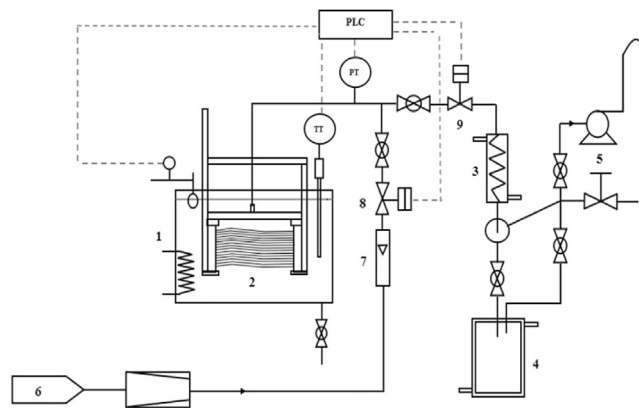

Fig. 1. Schematic of the SVMD setup.
1. Constant temperature feed tank. 2. Curtain type hollow fiber membrane module. 3. Condenser. 4. Permeate tank. 5. Circulating water vacuum pump. 6. Air compressor. 7. Air flow meter. 8. Intake valve. 9. Vacuum valve.

study was in the range of 70–80 °C and was controlled by a Pt-100 temperature sensor with accuracy of ± 0.5 °C. Vacuum pressure of the permeate was maintained at − 85 KPa (± 1.0 KPa) controlled a by vacuum valve. Both Pt-100 temperature sensor and vacuum pressure were connected to PLC system.

Permeate was collected in the permeate tank and its weight was measured by an electronic balance. Permeate flux was calculated using the equation as follows:

$$J \left[\frac{kg}{m^2 \cdot h} \right] = \frac{m}{A \cdot t} \tag{1}$$

where, m is the weight of permeate (kg), A is the effective area of membranes (m^2) and t is the operation time (h).

Permeate conductivity was continuously monitored by a conductivity meter. Salt rejection was calculated using the following equation:

$$R[\%] = \frac{C_f - C_p}{C_f} \times 100 \tag{2}$$

where, C_f and C_p is the conductivity of the feed and permeate, respectively.

The flux data were presented in terms of normalized flux ratio J/J_0 [26]. Where J is the instantaneous flux and J_0 is the initial flux when

Table 1
The characteristics of the PTFE hollow fiber membranes and membrane module.

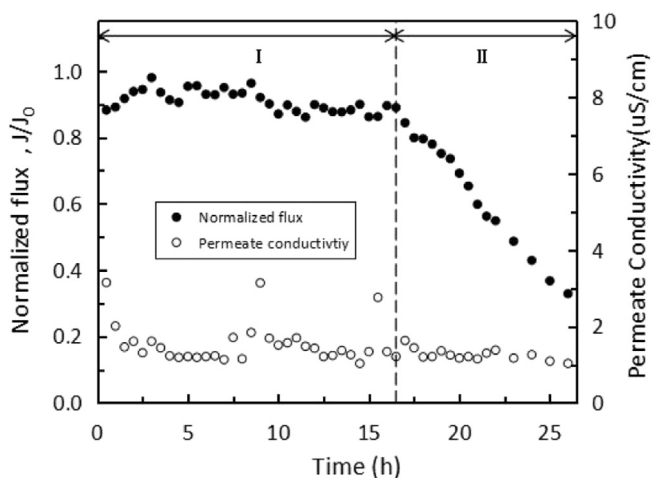| PTFE hollow fiber membrane properties	
Outer diameter (mm)	1.693
Inner diameter (mm)	0.862
Wall thickness (mm)	0.415
Porosity (%)	0.411
Mean pore diameter (μm)	0.186
Tortuosity	2.619
LEP_w (bar)	3.2
Membrane module for SVMD	
Effective length of membranes (cm)	23.2
No. of PTFE hollow fibers	55
Effective area of membranes (m^2)	0.068

Fig. 2. Normalized flux ratio and permeate conductivity as a function of operation time for concentrating 1800 mg/L $CaSO_4$ solution. The initial pure water flux was 4.2 kg/m^2·h. Experiment conditions: feed temperature 75 °C; vacuum pressure − 85 KPa.