



Adhesion of gypsum crystals to polymer membranes: Mechanisms and prediction



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ABSTRACT

In view of the scaling problem in the membrane water treatment process, the adhesion mechanism of gypsum crystals on different commercial microfiltration membranes in aqueous solution was firstly investigated using experimental methods and molecular dynamics simulations. The membrane chemistry has the most significant impact on its adhesion potential to gypsum crystals. Hydrophilic membranes have higher potential to scaling by the gypsum crystals compared to the hydrophobic membranes. The number of polar groups in the membrane molecules has higher effect on the adhesion energy than the variety of polar groups. The anti-adhering properties of the membranes increase with decreasing absolute adhesion energy. Physical structure of membranes was also crucial to its adhesion behavior under the condition that the adhesion energy of membranes was close to each other. The larger pore that exceeds a proper range leads to less adhesion mass. Subsequently, the membranes potentially used for membrane distillation were successfully predicted from the aspect of membrane chemistry in terms of their anti-scaling propensity using molecular dynamics simulations. This article provides an insight for the mechanism of gypsum scaling, and gives the prediction on the anti-scaling performance of the potential polymer membranes in membrane distillation.

1. Introduction

Desalination is becoming an important way to meet the increasing demand for fresh water due to population growth, industrial development, and water pollution. Nearly 19.8 billion gallons per day of fresh water is produced from the desalination plants installed worldwide, and 63.7% of the total capacity uses the membrane process [1,2]. Membrane distillation is a promising alternative technology to desalinate highly saline waters and for small scale plants in rural areas with many attractive features [3,4]. However, scaling is still a major challenge in membrane distillation process that operates at high temperatures and intermittent mode to a full-scale operation of plants [5–14].

In membrane distillation processes, water evaporation and temperature changes cause a super-saturated condition for sparingly soluble salts, and would eventually lead to nucleation and growth of crystals in the feed solution and on the membrane surface [15,16]. The most common sources of scalant are calcium sulfate, calcium carbonate which are inversely soluble at increased temperatures [17,18]. Calcium sulfate causes more severe scaling in direct contact membrane distillation process with seawater than calcium carbonate [4,16,19–21]

since the calcium carbonate can be removed by adding acids in pre-treating units. Scaling in membrane distillation causes wetting of membrane pores, reduces the permeate quality and flux rate, increases temperature and concentration polarization leading to greater energy consumption, membrane damage, chemical degradation and eventually increasing costs [11,22].

The scaling in membrane distillation usually involves two mechanisms: crystallization in the bulk (bulk crystallization or homogeneous crystallization) and nucleate on the membrane surface (surface crystallization or heterogeneous crystallization) [20].

Studies suggest that a supersaturated condition alone is not enough to start the crystallization of CaSO_4 on the membrane surface [19]. Though the solution characteristics and operating parameters play part of role, scaling can be initiated by membrane surfaces acting as nucleation sites [3]. Curcio et al. [23] found that the precipitation kinetics of CaCO_3 was significantly accelerated by the presence of microporous polypropylene hollow fibers which decrease the surface energy. Gryta [20] also found that gypsum crystals form mainly on the membrane surface and also penetrate into the pore interior which proves the existence of surface crystallization.

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The membrane material type difference was found to have a significant impact on scaling [11,12] besides their physical properties [24–28]. Guillen-Burrieza et al. and Cheng et al. [14,29] both found that PVDF membranes wet more and induces scaling easier, and finally have a greater population of internal salts crystals and a thicker salt layer on their surface compared to PTFE membranes in a direct contact membrane distillation system. In Cheng et al.'s work [29], the PTFE membrane has a higher distillate flux than that of PVDF at the same temperature, the concentration of feed solution and feed volume flow rate in the direct contact membrane distillation.

Membrane surface modification on hydrophobicity to enhance scale resistance of membrane distillation membranes has shown to have a dramatic effect in reducing scale formation [11,12]. Superhydrophobic fluorosilicone [16,17,30] coating on a polypropylene membrane surface reduced surface nucleation and particulate attachment and has been proven to eliminate membrane scaling by CaSO_4 in DCMD systems. Gryta [27] proved that hydrophobic polyethylene chlorinetrifluoroethylene (ECTFE) membrane exhibited the lower intensity of pore wetting and less scaling compared to PVDF membrane. Zhang et al. [31] fabricated a superhydrophobic PVDF flat-sheet membrane coated with a mixture of polydimethylsiloxane (PDMS) and hydrophobic SiO_2 nanoparticles showed a more stable flux after 4 h operation without particle deposition observed.

Though some results on membrane modification to enhance scaling resistance, an in-depth understanding on the relationship between the polymer chemistry and surface crystallization and its mechanism is still essential [11,12,32].

This research investigated the adhesion mechanism of gypsum on the different commercial microfiltration membranes, which was used to solve scale-adhering problem and improve the anti-adhering performance of the membranes in applications. The adhesion behavior of gypsum crystals on the membrane surfaces was firstly discussed from the chemical and physical properties of membranes using experimental methods and molecular dynamics simulations and the explanations for the adhesion mechanism were presented and discussed. Using the same simulation methods, further studies on several potential polymer sections for membrane distillation were evaluated for its anti-adhering performance. Our work provides a vision of the relationship between the membrane chemistry and the adhesion tendency of gypsum crystals to the membrane surface, giving guidance to the selection and synthesis of membrane species for membrane distillation process, as well as other membrane processes, from the view of scale inhibition.

2. Experimental

2.1. Materials

Commercial microfiltration membranes, polyvinylidene fluoride (PVDF) membrane, polyethylene (PE) membrane, polytetrafluoroethylene (PTFE) membrane, cellulose acetate (CA) membrane, Nylon6 membrane, polyethersulfone (PES) membrane, were all purchased from Shanghai Xingya Purification Material Factory (Shanghai, China). All the membranes purchased have the same average pore diameter of $0.22 \mu\text{m}$. CaCl_2 and Na_2SO_4 were purchased from the Chemical Reagent Plant (Tianjin, China).

2.2. The adhesion experiment

The crystals adhesion experiment was conducted in a vertical glass column (Inner diameter of 0.7 cm) with a membrane slide sticking tightly on the inner wall (Fig. 1). Commercially available microfiltration flat-sheet membrane types that usually used in membrane distillation [33,34] were chosen as the test membrane surfaces (Table 1). The surface wettability and morphology of the membranes were studied using Drop Shape Analyzer (KRUSS, DSA100) and Scanning Electron Microscopy (SEM) (FEL, Nova Nano SEM450), respectively.

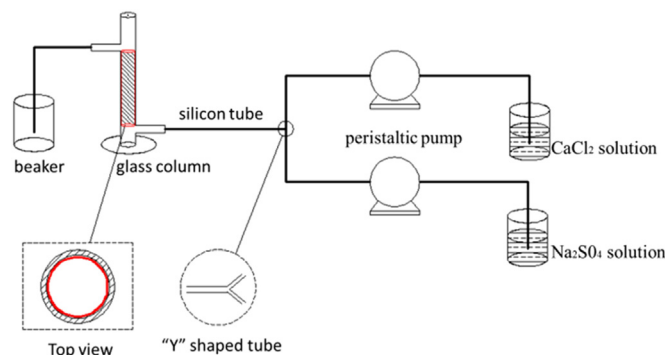


Fig. 1. Schematic of setup for adhesion experiment.

Table 1

The chemical structures of the repeating monomer units of the membranes used in the experiment and prediction.

Membranes used in experiment	Structure of repeated units	Membranes used in prediction	Structure of repeated units
PE		PVA	
PTFE		PVAC	
PVDF		PAA	
PES		PAN	
CA		SA	
Nylon6			

A membrane slide with a size of approximately $6.5 \text{ cm} \times 2.0 \text{ cm}$ as a test surface was firstly dried for one hour at 100°C in prior to the experiment and weighed m_1 . The drying here is to clear the influence of possible moisture during stock. Then, it was carefully stuck vertically on the inner wall of the glass column as the shadow section shown in Fig. 1.

Filtrated solutions of CaCl_2 and Na_2SO_4 with the same concentration were pumped and mixed at a "Y" shaped tube using separate peristaltic pumps (Longer Pump, BT100-2J) at a same flow rate of 0.18 mL/min , and then a supersaturated CaSO_4 solution was generated. The CaCl_2 solution was prepared with boiled distilled water aiming to drive out the CO_2 dissolved in the water and prevent the formation of the CaCO_3 . The volume of the inlet section (from Y-mixer to the bottom line of the membrane-attached section) of the glass device (Fig. 1) was 7.6 cm^3 , so the residence time of the mixed supersaturated solution before contacting to the membrane surface was 21.1 min .

The supersaturated CaSO_4 solution flowed in and out of the column continuously, which lasted for 5 h in each experiment. Then, the membrane was took out of the glass column using tweezers and a filter paper was used to sip up the solution on the membrane surface. After that, the membrane was dried under the same conditions as that before the experiment, and weighed m_2 . The apparent mass increment on the membrane surface was obtained by the equation, $\Delta m_1 = m_2 - m_1$.

To eliminate the influence of crystals possibly precipitated out in the process of drying, the blank test was carried out following the adhesion experiment. Firstly, a membrane slide with the same size was dried, and

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