

# Synergistic Effect of $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ Ions and Gypsum Scaling in Feed Solution on Forward Osmosis Boron Removal

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This paper investigates the synergistic effect of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions in feed solution on the forward osmosis (FO) removal of boron by a thin-film, composite membrane with embedded supports of polyester screens (TFC-ES). Specifically, water flux, reverse solute flux, boron flux and boron rejection rate were examined respectively to explore the influence of gypsum scaling on boron removal. The results indicate that gypsum scaling in the FO suppresses water flux and boron flux. After the surface of the polluted TFC-ES membrane was cleaned by deionized water, the membrane performance was recovered efficiently, as evidenced by the water flux recovery rate of 95.05%, and the boron rejection recovery rate of 94.21%. This research demonstrated the potential of the FO membrane in boron removal.

## 1. Introduction

Boron, existing in the form of boric acid or borate, is widespread in seawater, underground brine, and saline lakes in nature. Generally, the concentration of boron in the seawater ranges from 4 to 6 mg/L (Melnik et al., 2005). Boron is an essential trace element in the human body. However, excessive ingestion may cause such adverse effects as diseases in the reproductive, neural, digestive, and cardiovascular systems, and the deformity of the axial skeleton. According to the WHO Guidelines for Drinking-water Quality (2006), the boron content in drinking water should not exceed 0.5mg/L. In China, the Standards for Drinking Water Quality (GB5749-2006) also set a limit of 0.5mg/L on boron content (Wang, 2016). Similarly, boron removal is one of the important challenges to seawater desalination (Valladares Linares et al., 2014).

The beginning of 21st century marks the start of an era of energy and water crises due to the tremendous population growth across the globe (Alessia Viola, 2016, Cannistraro et al., 2015, Ciampi et al., 2015). In recent years, forward osmosis (FO) has emerged as a promising technology to extract potable water, thanks to its high salt rejection, low energy intensity and low membrane fouling propensity (Chung et al. 2012, Lau et al., 2015, Luo et al., 2014, Xie et al., 2016, Xie et al., 2015b, Zhao et al., 2012). The growing interest in seawater desalination and wastewater reclamation has added the importance to the FO removal efficiency for a broad spectrum of trace contaminants (Xie et al., 2012). However, very few studies have been performed on the removal of contaminants by the FO. Previous studies have demonstrated that  $\text{CaSO}_4$  scaling of cellulose triacetate (CTA) FO membrane is predominately affected by the feed solution composition and the deposition of bulk crystals (Liu and Mi, 2014). According to recent studies, the mechanism of reverse salt diffusion bears directly on the organic/biological fouling of the FO, as the fouling is intensified by the interaction between the foulants in the feed solution and the divalent ions in the draw solution that diffuse through the FO membrane (Zhang et al., 2014). So far, no detailed research has been done on the contaminant rejection rates under the synergistic effect of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions in feed solution.

In a previous study, the author studied boron transport through FO membranes and demonstrated that the draw solution-oriented active layer (AL-DS) has a much lower boron rejection rate than the feed solution-oriented active layer (AL-FW) because the AL-DS mode faces severer internal concentration polarization (ICP) of boron (Wang, 2016). Herein, the author focused on how the feed solution containing both  $\text{Ca}^{2+}$  and

$\text{SO}_4^{2-}$  ions affects water flux, boron flux and boron rejection rate before and after FO membrane scaling in the AL-FW mode, seeking to shed new light on gypsum scaling on boron removal in the FO.

## 2. Experimental

### 2.1 Materials

As shown in Figure 1, the experimental facilities contained a membrane module, a peristaltic pump, a feed solution container, a draw solution container and a data acquisition system consisting of an electronic balance and a computer. The circular flow of draw solution and feed solution was established on both sides of the membrane through the peristaltic pump, and the water molecules in the feed solution entered into the draw solution through the FO membrane in the circular flow. The data acquisition system automatically acquired the variation in feed solution quality based on the feedbacks from the electronic balance. NaCl solutions with different concentrations were used as the draw solutions and a digital balance was connected a computer to monitor weight change of the permeated water at 5 s intervals. DI water was used as the feed solutions and a conductivity meter was used to monitor the conductivity change at 30 s intervals for calculating the reverse solute flux of the membrane. Membranes were tested under two different modes: active layer facing draw solution (AL-DS) mode, and active layer facing feed solution (AL-FS) mode. Each test was conducted for 60 min in triplicate.

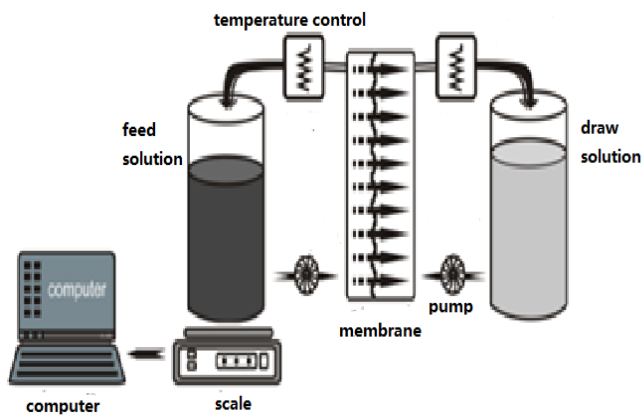
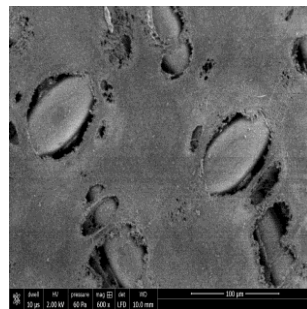
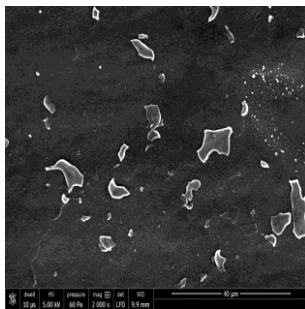


Figure 1: Schematic diagram of the FO experimental facility

### 2.2 Material

The FO membrane was produced by Hydration Technology Innovations (HTI) with an available area of  $47.57\text{cm}^2$ . The asymmetric membrane was denoted as the TFC-ES, for it is made up of a thin-film, composite (TFC) active layer, and a porous support layer with embedded supports (ES) of polyester screens. The material of the active layer was polyamide and that of the support layer was polysulfone and polyester. The TFC-ES membrane was about  $115\ \mu\text{m}$ -thick, and pH ranged from 2 to 11 (Wei et al., 2011a, Wei et al., 2011b).



(a) Active Layer of TFC-ES Membrane (b) Structure Layer of TFC-ES Membrane

Figure 2: The SEM images of three kinds of FO membranes

Figure 2 is the scanning electron microscopy (SEM) chart of the active layer and the support layer of the TFC-ES membrane. It can be seen that the membrane was porous and meshed in the support layer, but compact and non-porous on the top.

### 2.3 Measurement Index and Method.

Water flux is an important index representing the efficiency of forward osmosis, whose value exerts significant impact on the application popularization of osmosis water purification technology. In the forward osmosis process, pure water is permeated to the sides of draw solution from the feed solution, which leads to the decrease of feed solution quality. The quality of osmosis pure water is acquired by the real-time monitoring of quality change of feed solution by electronic balance and the water flux is calculated based on formula:  $J_w = \Delta m / \rho \Delta t$ . Apart from water flux, the solute concentration difference exists between the draw solution and feed solution in the process of forward osmosis, which causes small amount of draw solution solute may diffuse into the feed solution. This phenomenon is called reverse solute diffusion and its flux is called reverse solute flux. The researches indicate that on the one hand, this reverse solute flux will aggravate concentration polarization effect and membrane pollution, reducing the stability of forward osmosis system; on the other hand, it will accelerate the consumption of draw solution, adding processing costs. Multi-parameter water quality analyzer is used to measure the conductivity of feed solution after the experiment. The concentration of KCl can be calculated through the standard curve of concentration on conductivity of KCl. (Figure 3). The fitted equation of the standard curve of KCl concentration on conductivity is  $y = 1926.83251x + 8.1004$  and the degree of fitting is  $R^2 = 0.99973$ . The value of specific reverse solute flux was calculated by the ratio of reverse solute flux and water flux representing the efficiency of forward osmosis. The specific reverse solute flux calculation formula of forward osmosis is as follows:  $F_s = J_s / J_w$ , where  $F_s$  is specific reverse solute flux (mMol/L);  $J_s$  is solute flux (mmol/m<sup>2</sup> h); where  $J_w$  is the water flux (L/m<sup>2</sup> h) (Wang, 2016).

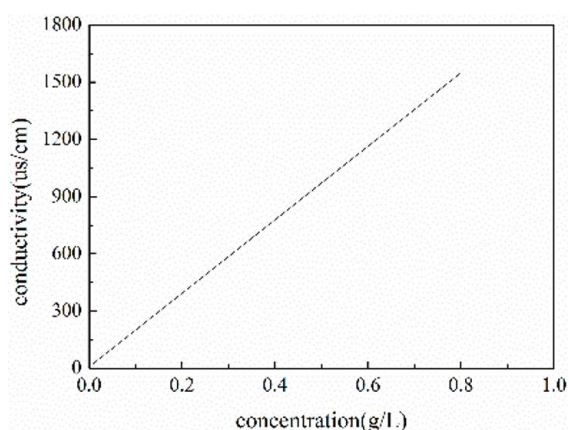


Figure 3: The standard curve of solution concentration about its conductivity, KCl.

## 3. Result and Discussion

### 3.1 Synergistic effect of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions on water flux

Figure 4a shows that, during the 960min running cycle, the water flux fell by 44.69% from 11.86LMH to 6.56LMH in the baseline test. The decline may be attributed to the net osmotic pressure reduction resulted from the dilution of the draw solution and the concentration of the feed solution. In the pollution test, the water flux decreased by 80.86% from 12.07LMH to 2.31 LMH, 36.17% more than the drop in the baseline test. The additional decline in water flux of the FO process is caused by gypsum scaling, a unique process in the pollution test other than the dilution of the draw solution and the concentration of the feed solution. To confirm this explanation, the active layer of the TFC-ES membrane after the pollution test was sampled and scanned by the SEM Figure 4b. Then, an element analysis was conducted based on the SEM chart and the membrane contamination of the active layer Figure 4c. The results show that there were three main elements: Ca (27.5%), S (25.67%) and O (46.59%), which signifies the existence of CaSO<sub>4</sub> crystals.

Moreover, the water flux decrease in the pollution test was roughly divided into two phases. The first phase lasted 270min from 500min to 770min, and the second phase lasted from 770min to the end of the test. The two-phase pollution phenomenon was observed by Xie et al. (2015a, 2013) in an organic pollution test. The following is a detailed description of the sharp decline in water flux. In the first phase, the feed solution was continuously enriched, causing the precipitation of CaSO<sub>4</sub> crystals; at 500min, the crystals began to appear

on the active layer, blocking the water passage through the membrane; then, the water flux gradually stabilized despite the further crystallization on the membrane surface. Under the action of water flux, the crystals precipitated in the feed solution continued to accumulate on the active layer, forming a compact layer of crystals as of 770min. The further pollution led to drastic drop in the water flux in the second phase.

In light of the high density and compactness of the active layer of FO membrane, the water flux decline was not triggered by film-hole plugging. To sum up, the pollution of the active layer had the following impacts on water flux: First, the existence of pollution layer hindered the reverse diffusion of the draw solute into the feed solution, exacerbating the concentration polarization; Second, the fouled layer increased the penetration resistance, i.e. the space resistance to the water flux, which indirectly lowered the driving force of the water flux.

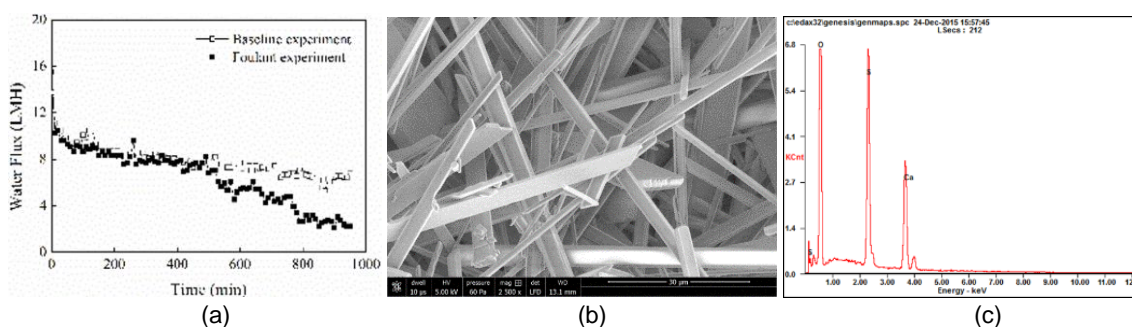


Figure 4: (a) Effects of coexistence of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in raw water on water flux, (b) SEM image of pollutants on the active layer surface of membrane after fouling, (c) EDS image of fouling layer

### 3.2 Synergistic effect of combined $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ion on Boron flux and Rejection

Table 1 shows that the baseline test of boron flux is  $20.69 \text{ mg/m}^2 \text{ h}$ , the corresponding pollution test boron flux is  $16.49 \text{ mg/m}^2 \text{ h}$ , illustrate the foulant test produced fouled layer of boron flux has certain effect. As mentioned previously, boron in feed solution in the forward osmosis process will pass through the active layer surface caused the enrichment of concentration polarization, but as a result of membrane fouling after the water flux fallen sharply, lead to weakened dramatically boron concentration degree, while pollution layer itself exacerbated boron concentration polarization, but due to water flux of the boron concentration degree decline, thus reducing boron concentration difference effectively, which reduced the boron flux. Although the baseline test boron flux was higher than the foulant test's, but the table 1 shows the baseline test boron intercept rate and the foulant test boron intercept rate similar to that of 47.58% and 49.02%, respectively, this is mainly due to the average of the baseline test water flux is greater than the average foulant test water flux, which leads to a more intense the dilution effect (Xie et al., 2016).

Table 1: Effects of coexistence of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in raw water on boron flux and rejection rate

Experiment	Boron Rejection %	Boron Flux $\text{mg}/(\text{m}^2 \cdot \text{h})$
Baseline	47.58	20.69
Foulant	49.02	16.49

### 3.3 Effects of interfacial polymerization reaction time on TFC membranes FO performance

Figure 5a shows that after cleaning the contaminated membrane at the beginning of the corresponding flux was  $11.44 \text{ LMH}$ , the new film at the beginning of the corresponding flux was  $14.04 \text{ LMH}$ , membrane flux is smaller in the early after cleaning. This is mainly due to the fault current cleaning cannot remove contaminants on the surface of the active layer completely, leading to positive after the start of the feed solution infiltration process cannot be fully formed on the surface activity of pure water in the membrane layer, thus leading to a lower initial flux. Figure 5b shows the membrane surface after cleaning residue contaminants on the surface of scanning electron microscopy (SEM), the figure shows that the crystalline structure of the crystal structure of pollutants loose than that before cleaning (Figure 4).

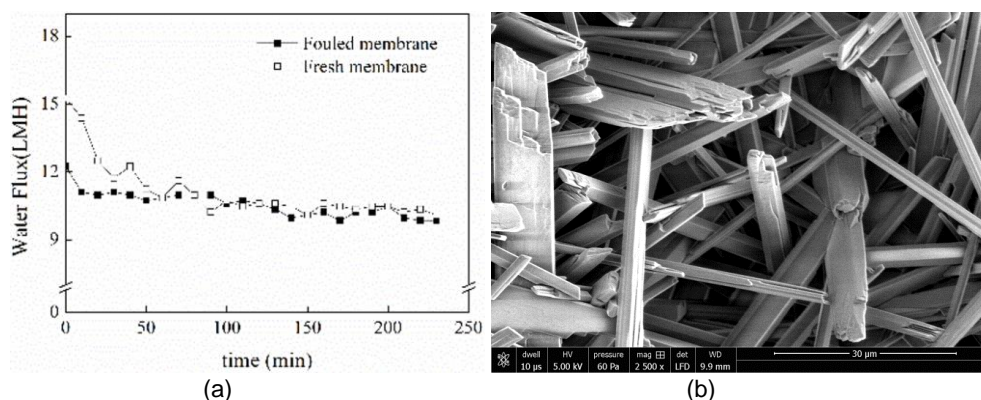


Figure 4: (a) Water flux recovery after cleaning, (b) SEM image of residual pollutants on the active layer surface of membrane after cleaning

Besides, the fouled membrane after cleaning exhibited a water flux of 10.57 LMH, the new film the corresponding average water flux was 11.12 LMH, indicates that the crystallization of fouled osmosis membrane water flux performance recovered well after cleaning, the recovery rate is 95.05%.

Table 2 shows the comparison of Boron rejection and product water Boron concentration of the fresh membrane and after cleaning membrane. The table shows that corresponding boron intercept contaminated membrane after cleaning rate was 57.74%, the new film the corresponding boron intercept rate was 61.29%, the recovery rate of 94.21%. This is mainly due to the fouled membrane cleaning after the corresponding new membrane water flux and the corresponding water flux gap was intense enough, didn't remove the contamination layer added boron concentration polarization, led to the boron intercept rate was less than the corresponding rate of boron intercept new film. In addition, the fouled membrane cleaning after the corresponding water production boron concentration was less than 0.5 mg/L, to China's "drinking water health standards" (GB5749-2006) of boron concentration is lower than 0.5 mg/L (Wang, 2016).

Table 2: Boron rejection rate recovery after cleaning

Membrane	Boron Rejection %	Product Water Boron Concentration mg/L
Fresh Membrane	61.29	0.3380
Fouled Membrane after cleaning	57.74	0.3540

#### 4. Conclusions

1. Boron flux and water flux by the effect of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  coexist in the feed solution. Gypsum scaling in the process of forward osmosis prevented water flux as well as the flux boron;
2. The fouled TFC - ES membrane was cleaned by DI water at the membrane surface and efficient performance obtained after cleaning, the water flux recovery rate was 95.05%, and the rate of boron intercept recovery rate was 94.21%, indicating a promising application of Forward Osmosis membrane in boron removal.

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