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Effects of pH and temperature on forward osmosis membrane flux using rainwater as the makeup for cooling water dilution

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HIGHLIGHTS

- The existence of NaOH flux promoted more CO_2 dissolved into the feed solution.
- pH in both feed and draw solutions had little direct effect on membrane flux.
- The membrane flux obtained at 50 °C was about 10 times higher than the value at 3 °C.
- Membrane structure showed notable effects on water flux at temperature below 30 °C.
- No membrane fouling or water flux decrease was observed during extended operation.

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ABSTRACT

Cooling water plays an important role in maintaining proper temperatures for many industrial processes. To compensate for water loss and to maintain proper cooling water quality, fresh water must be added to the circulating system. In this study, we evaluated the feasibility of forward osmosis using rainwater as the makeup water source for the cooling water. It was determined that the average water flux was 1.75 $L/(m^2 \cdot h)$ at 23 °C and decreased gradually to 0.65 $L/(m^2 \cdot h)$ after the draw solution was diluted 4 times. Although the changes in pH had a small direct effect on the water flux, the existence of sodium hydroxide would promote the dissolution of more carbon dioxide into the feed solution and thus inhibit the permeation process. However, the temperature showed a notable effect on the water flux. By increasing the temperature of the draw solution from 3 °C to 50 °C, the membrane flux increased approximately 10 times. During the extended operation, no decreases in flux were observed as a result of membrane fouling, even when 50 mg/L kaolin or 25 mg/L sodium alginate was added to the feed solution.

1. Introduction

Membrane technologies, such as ultrafiltration, nanofiltration, and reverse osmosis (RO) have been studied for approximately 50 years, and were considered to be the most viable processes in both water and wastewater treatments due to their high efficiency in removing suspended particles, colloids, and solutes [1,2]. The major drawback of these pressure-driven membrane processes, especially in nanofiltration and reverse osmosis desalination, is their high energy cost [3,4]. Extra pressure is needed to overcome the osmotic pressure caused by the concentration gradient of the two solutions that exist before and after the pressure-driven membrane [5]. In addition, fouling is inevitable in most pressure-driven membrane processes [1,6], and as a result, large amounts of chemical cleaning reagents are required [7,8].

In contrast to nanofiltration and reverse osmosis desalination, forward osmosis (FO) is an osmotic pressure driven filtration process [9]. Water naturally flows through the semi-permeable membrane due to the osmotic pressure differential between feed and draw solutions. The draw solution is then discarded or re-concentrated by removing the product water and recycled [10,11]. FO is usually performed with low or even without hydraulic pressure, can achieve high rejection of nearly all of the contaminants [12,13], and has a lower irreversible fouling potential [14]. However, after FO treatment, neither the feed solution nor the draw solution is purified water and thus cannot be

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used directly for drinking or irrigation purposes without additional treatment. Therefore, the application of FO in water and wastewater treatment is mainly dependent on the water quality and the reuse target of the treated water.

Cooling water is typically used to maintain proper temperatures inside buildings or certain production processes [15]. As water evaporates in a cooling tower system, dissolved solids remain behind and thus increase the impurities in the remaining cooling water. If the concentration of dissolved solids is too high, the heat exchange efficiency decreases as a result of scale formation or corrosion [16]. To compensate for water loss and to maintain consistent water quality, the concentrated water is partially removed via bled off events, and the volume is adjusted by adding municipal water [16,17]. From a water efficiency standpoint, controlling the salt content in the makeup water helps to extend the life of the circulated cooling water and reduce the frequency of bleed-off events. Rainwater is an important water source. However, its low pH and the presence of suspended contents, such as inorganic particles obtained during the initial rain and algae produced in the tank after a long storage period, cause serious pipe system corrosion and sediment problems. Therefore, rainwater cannot serve as the makeup water prior to pretreatment.

Past studies have demonstrated that anaerobic digester sludge, beverage products, brackish water, and seawater can effectively be treated with FO [18,19]. However, despite the great potential in treating waters with high salt contents, the application of FO with low salt solutions, such as cooling water, as the draw solution is rarely reported in the literature [20]. Meanwhile, both the temperature and pH of the cooling water are significantly higher than that of the brackish water and seawater, which may affect the water flux and even destruct the structure of the FO membrane. The present study evaluated the use of a bench scale FO system by treating rainwater as the feed solution (cooling water makeup water) and the concentrated cooling water as the draw solution. The objective of the study was to investigate the effects of temperature and pH on the FO membrane flux, to assess flux variations during extended operation, and to evaluate the overall feasibility of FO in the treatment and reuse of cooling water with rainwater as a makeup water source.

2. Materials and methods

2.1. Feed and draw solutions

The feed solution used in this experiment was rainwater collected on Oct. 15, 2012 from the rooftop of the Engineering Technology Laboratory at Pennsylvania State University — Harrisburg campus. Rainwater was stored in a 25 L barrel at room temperature. The cooling water used in the experiment was obtained from the steam plant at Pennsylvania State University — Harrisburg campus. The cooling water was used as the draw solution for the FO system. The water quality of both the rainwater and the cooling water was listed in Table 1.

2.2. Membrane

The cellulose acetate-based FO membrane was provided by Hydration Technologies, Inc. (Albany, OR). Its thickness was much less compared to the RO membranes, thus increasing the water flux at relatively low osmotic pressures. The structural properties of the FO membrane included a water permeability coefficient (A), mass transfer coefficient (K_f), and solute resistant coefficient (K) of 3.11×10^{-7} m/(s·atm), 1.74×10^{-5} m/s, and 2.67×10^5 s/m, respectively [21].

2.3. Forward osmosis cross flow setup

The bench-scale FO system for this study included a membrane permeation unit, a water circuiting system, and a data monitoring and recording system (Fig. 1). The membrane permeation unit was constructed with symmetrical flow channels on both sides of the membrane. A membrane coupon with an effective area of 20-cm^2 was put in the cell. The feed and draw solutions were continuously circulated between the storage tanks and the membrane cell with a speed of 100 mL/min. The cross-flow rate on each side of the membrane was the same and was fixed at 45 mL/min by a variable speed peristaltic pump (Cole-Parmer, Vernon Hills, IL). The changes in the weight of the feed solution or draw solution were recorded by a digital balance (TL2100, Mettler Toledo, Germany) to determine the membrane flux of the pure water. Other operational parameters such as water temperature, pH, and conductivity were monitored on-line with the corresponding sensors and were recorded using Logger Pro 3.8.6 software purchased from Vernier Software & Technology.

2.4. Forward osmosis experiment

The active layer of the FO membrane was in contact with the feed solution throughout the experiment. To examine the effect of pH on the water flux, 0.1 mol/L NaOH was added to the feed solution and gradually increased its pH from 5.6 to 9.2. Then, 0.1 mol/L HNO_3 was added to the feed solution and decreased its pH back to 5.6. The total run time was controlled at approximately 1.5 h. A similar experiment was conducted by changing the pH of the cooling water (draw solution) from 12.4 to 7.5 and then back to 12.4 by adding 0.1 mol/L HNO_3 and 0.1 mol/L NaOH sequentially. The temperatures of both the feed solution and the draw solution were maintained at approximately 23 °C for the pH experiment. To observe the effects of the water temperature on the water flux of the FO membrane, the temperatures of both the draw solution and the feed solution were adjusted between 3 and 50 °C in two constant-temperature incubators.

To assess the effects of membrane fouling on the water flux, a new membrane coupon was placed in the membrane cell. Then, 500 mL of rainwater and 500 mL of cooling water were added to the feed solution and the draw solution tanks, respectively. After a 30 min run, the sodium alginate and kaolin stock solution were added to the feed solution to achieve a final concentration of 25 mg/L alginate and 50 mg/L kaolin, respectively.

2.5. Water quality and membrane structure analysis methods

As described in Section 2.3, the parameters including pH, water temperature, and conductivity were monitored on-line using the Logger Pro 3.8.6 software and the corresponding sensors. Before the determination, all sensors were calibrated with standard solutions. TDS was measured according to the standard method 2540c (APHA, AWWA and WEF 2005). The acidity and alkalinity were measured using chemical titration according to the standard methods 2310b and 2320b, respectively (APHA, AWWA and WEF 2005). Elements including sodium, potassium,

Table 1
Rainwater and cooling water quality used in this experiment.

Type	pH	T (°C)	Cond. (μs/cm)	TDS (mg/L)	Mg^{2+} (mg/L)	Iron ions (mg/L)	Hardness (mg $CaCO_3$/L)	Alkalinity (mg $CaCO_3$/L)
Rainwater	5.5	15	9.1	4.5	0.7	ND	4.2	5.0
Cooling water	12.4	40	5090	2540	100	0.016	200	890