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Development of polyamide forward osmosis membrane for humic acid removal

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ABSTRACT

This paper presents synthesis and performance of polyamide forward osmosis (FO) membrane for humic acid (HA) removal. Three polyamide membranes were synthesized by reaction between m-phenylenediamine and trimesoyl chlorideat different reaction times (10, 30 and 60 s). Five different concentrations of sodium chloride draw solutions and 15 mg/L of HA solution as feed solution were tested in one hour to obtain water flux, reverse salt diffusion and HA removal. Reverse salt diffusion and HA removal were measured using conductivity and a UV–vis spectrometer, respectively. Overall, membranes modified for longer reaction times (30 and 60 s) exhibited good performance in term of moderate flux, higher HA removal and low reverse salt activity. In addition, it was found that higher concentration of draw solution leads to lower HA rejection and higher reverse salt diffusion, which indirectly represented overall membrane performance.

Keywords: Forward osmosis; Polyamide forward osmosis membrane; Water flux; Reverse salt; Humic acid removal

1. Introduction

The increase in the human population throughout the world is expected to increase the demand for basic human needs. Access to clean water for domestic and commercial use is one human need. The increase in the world population will increase the demand for clean water. Currently, water treatment is one of the most essential fields if we are to overcome this water shortages problem. As a result, intensive efforts in finding other potable water sources, such as seawater and wastewater reuse, have been made to ensure the reliable and continuous supply of fresh water. Osmosis is a physical separation process that has been explored by many researchers in various disciplines of sciences and engineering. Further development in this field of osmosis has led to a newer form of water treatment process known as forward osmosis (FO). FO consists of water transport across a selectively

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permeable membrane from a region of higher water chemical potential to a region of lower water chemical potential. Hydraulic pressure is not needed, unlike for reverse osmosis. Separation occurs using the osmotic pressure between the draw solution and the feed solution.

Previously, researchers have found that FO has a lower membrane fouling propensity [1]. Regardless, research interest in organic fouling has attracted a great deal of attention by researchers [2,3]. Flux behaviour of the membrane is affected by internal concentration polarization (ICP), where a higher draw solute concentration contributed to fouling accumulation [2]. In addition, ICP resulted in a decrease in permeate flux and reverse salt diffusion activity due to reduction in draw solution concentration in between the support and dense layers of the membrane [4]. Besides this, the formation of an organic fouling layer is also significantly governed by a few factors including calcium binding, permeation drag and hydrodynamic shear force [3]. Commercial FO membranes (cellulose tri-acetate, CTA and cellulose acetate, CA, both from Hydration Technologies Inc., HTI) have been used to investigate the organic fouling behaviour for different foulants (i.e. humic acid (HA), alginate, bovine serum albumin) [2,3]. In the last few years, polyamide thin-film composite (TFC) membrane has been developed for FO application and also promises good performance. For example, Wei et al. [5] investigated the effect of monomer concentrations (m-phenylenediamine (MPD) and trimesoyl chloride (TMC)) on the performance of polyamide FO membrane. However, experiments were limited to a salt solution as feed only. Therefore, this research aims to study the performance of a lab casted polyamide FO membrane for treatment of feed water containing organic substances (i.e. HA) and effect of reverse salt diffusion on overall FO performance.

2. Material and methods

2.1. Chemicals

Draw solutions were prepared by dissolving preweighted quantities of sodium chloride (NaCl) into pure water. The draw solution used in this study was from Fisher Sci (solid NaCl 95% purity). For feed solution, a diluted HA solution of 15 mg/L was used. HA was obtained from Fluka.

2.2. Preparation of membrane

Polyamide membrane was prepared by reaction between 2 wt% aqueous MPD solution and 0.15 wt% TMC in hexane solution through the interfacial polymerization method. Firstly, commercial polyethersulfone ultrafiltration membrane as support was immersed in MPD solution for 30 min before draining the excess MPD and then the membrane reacted with TMC solution at three different reaction times of 10, 30 and 60 s. The membrane was then dried overnight and soaked into distilled water before it was used.

2.3. Preparation of draw solution

NaCl solution was used as a draw solution because of the high performances shown in FO treatment processes [4]. NaCl solute was dissolved in pure water at five different concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 M.

2.4. Preparation of feed solution

A 15 mg/L HA solution was prepared to act as synthetic river water and used as the feed solution in FO experiments. Many researchers have used HA solution because of the large proportion of HA typically found in the natural organic matter present in surface or ground waters.

2.5. FO experiment

The feed solution of 15 mg/L of HA and the draw solution of 0.5 M NaCl were prepared in two different 1-L beakers. The feed solution containing HA was placed on an electronic balance to record mass changes during the experiment. The polyamide membrane was positioned vertically in a membrane cell between two compartments, one containing the draw

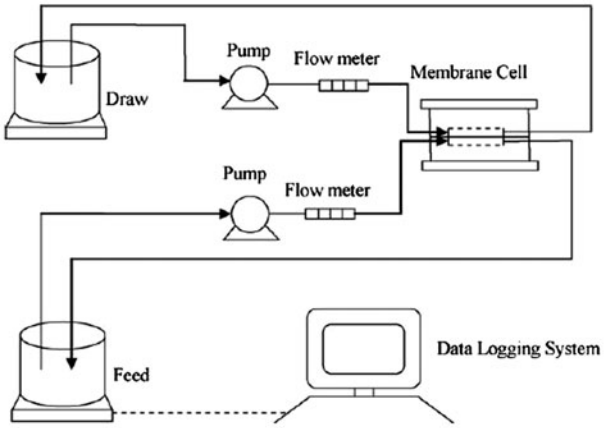

Fig. 1. The schematic diagram of lab-scale FO system [2].

solution and the other containing feed solution, as shown in Fig. 1. The membrane was oriented such that the polyamide layer of membrane was facing the feed solution compartment to increase the solute rejection and thus obtaining a higher water flux [5]. The initial mass of feed solution was measured and recorded and further recodings were made at time intervals of 5 min until the experiment was completed (1 h). The time taken for this FO process was fixed at 1 h for each concentration of draw solution. Temperature and pressure were maintained at ambient values. After 1 h of experiment, the mass of feed solution was recorded and measured. According to Mehrparvar et al., the method of calculating flux is derived using the following formula [6]:

$$J_{\mathrm{w}} = \frac{\Delta V}{A \Delta t} \tag{1}$$

where V is the volume of water which permeates through the membrane, Δt is the time taken in hours and A = effective area of the membrane. The mean of mass changes was converted into volume to obtain the water flux value using Eq. (1).

Next, the draw solution and feed solution were taken to a UV–vis spectrometer to check the concentration of HA which was present in the used draw solution. In order to get the concentration of HA in the draw solution and feed solution, a standard curve was constructed to derive the concentration value in terms of absorbance. Then the concentration value was inserted in Eq. (2) to calculate the HA rejection:

$$R = \left(1 - \frac{C_{\mathrm{a}}}{C_{\mathrm{b}}}\right) \times 100\% \tag{2}$$

where R is the HA rejection value in % in the FO process, C_{a} is the concentration of HA in the draw solution, while C_{b} is the bulk concentration of HA in the feed solution. The final conductivity of feed solution also was measured and recorded. The differences in conductivity between initial and final value recorded values showed the reverse salt diffusion process occuring in this study. These steps were repeated using other concentrations of draw solution (1.0, 1.5, 2.0 and 2.5 M).

3. Results and discussion

The water flux was obtained using Eq. (1) after experiments had been running for 1 h using five different concentrations of draw solution for each of the membranes (10, 30 and 60 s). Using the data obtained from the experiment, a series of flux was calculated to determine the performances of polyamide FO. The flux value for each draw solution can be seen in Fig. 2, a graph of flux of water through three different types of membranes against the concentration of draw solution.

By refering to Fig. 2, the water flux increased when concentration of draw solution was increased. This trend was supported by the findings of a previous study done by Arena et al. where they claimed the increase in the concentration of NaCl will increase the osmotic pressure thus promoting the increase in water flux in FO [7]. Osmotic pressure with a magnitude corresponding to the concentration of the draw solution will contribute to the movement of water from feed solution to draw solution to naturally balance the concentration of the solutions [8]. In term of membrane flux, at any draw solution concentration, the membrane modified for the shortest reaction time (10 s) showed the highest water flux reading compared to the other two membranes. It could be due to the polyamide layer formed on the top surface being incomplete as the time taken for reaction occur was too short (10 s). However, when longer reaction times were applied, the flux observed were reduced accordingly. Ji and Mehta reported that the growth of a thin film depends very much on the reactant concentration and reaction time [9]. As the reaction time was increased, the TFC layer was postulated to be thicker and thus resulted in a lower flux. In this study, longer reaction times would induce a thicker and denser thin-film layer on top of the polyethersulfone UF support leading to a lower flux obtained.

Other than water flux, this study also focuses on HA removal and reverse salt problems. From Fig. 3 it can be seen that HA rejection increased as reaction time for interfacial polymerization was increased. This supports our previous claim that the longer reaction time could produce a denser membrane and reject more HA molecules. Membranes modified with a reaction time of 60 s showed the highest HA rejection compared to the other two membranes which obtained 99% HA rejection at 2.5 M of draw solution, while 10 s of reaction time shows the lowest HA rejection by 95% at the same draw solution concentration. The modification made to the ordinary ultrafiltration membrane using interfacial polymerization method promotes a higher degree of crosslinking between polymers at the membrane surface that are responsible for a higher salt rejection [5]. Besides that, it was observed that HA rejection decreased with the increase in concentration of the draw solution. This phenomenon can be explained as follows: when a high concentration draw solution was applied, the osmotic

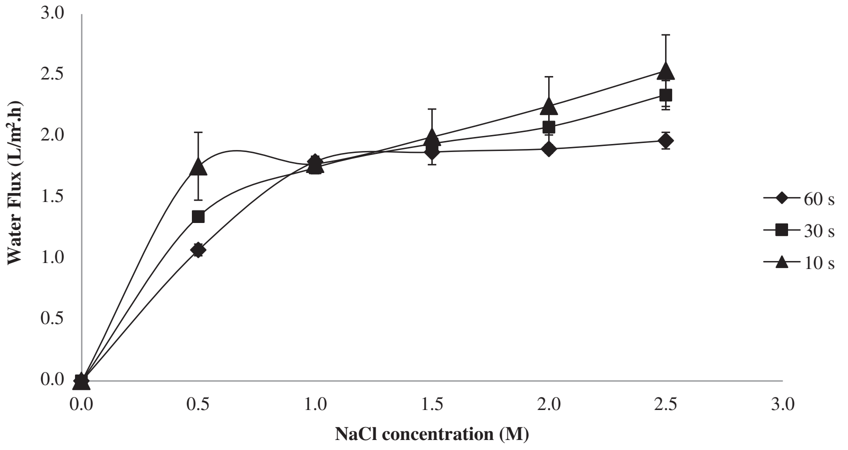

Fig. 2. Water flux against concentration of NaCl.

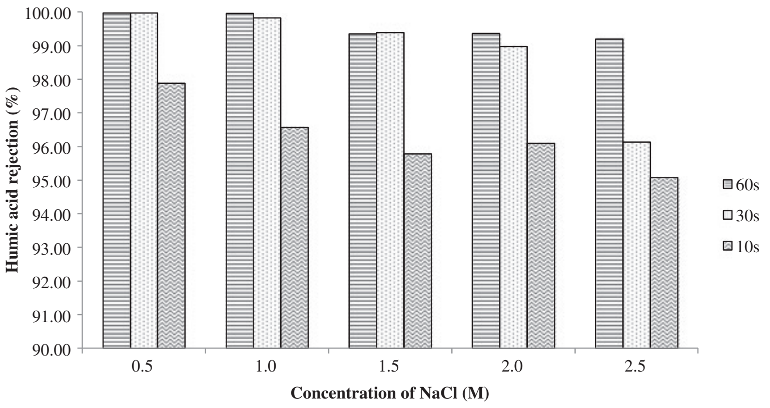

Fig. 3. HA rejection against concentration of draw solution.

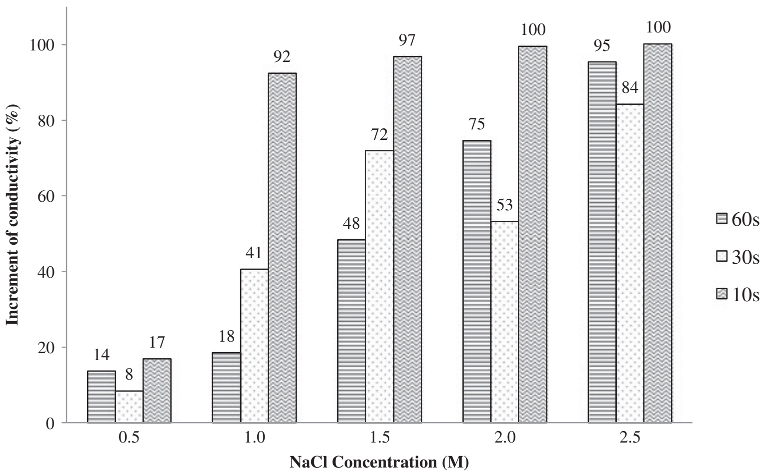

Fig. 4. Increment in conductivity against NaCl concentration.

pressure became high and this promoted more water molecules in feed side to diffuse to the draw solution side (the water flux increased) and at the same time helped some HA solute to permeate through the membrane into draw solution side [10].

Reverse salt diffusion was determined by the changes of conductivity value in HA solution after 1 h operation (as shown in Fig. 4). The result shows that increasing the concentration of draw solution leads to an increase in the differences of conductivity seen between the different membranes and indirectly represents a higher reverse salt diffusion at a higher concentration of draw solution. A similar trend was also observed by Chekli et al. where it was found that the increase in draw solution concentration will increase the amount of solute in the draw solution side. This will indirectly increase the possibility of solutes moving from the draw solution into the feed side of the system [11]. In general, membranes modified for longer reaction times (30 and 60 s), exhibited a lower reverse salt activity (shown by a lower % of conductivity increment) especially at moderate draw solution concentrations (1.0–2.0 M). However, at the highest concentration of draw solution (2.5 M), all modified membranes possess similar reverse salt activity. This shows that the optimum draw solution concentration is also an important factor to be considered for the best membrane performance (high flux, high HA removal and low reverse salt activity).

4. Conclusion

The performances of FO not only depend on the draw solution but also on the types of membrane used in FO. Higher water flux was obtained from the higher concentration of draw solution and membranes prepared with a short reaction time. In terms of HA removal and reverse salt diffusion, the higher the concentration of draw solution the lower the HA rejection and higher reverse salt diffusion. Membranes modified at longer reaction times (30 and 60 s) produced membranes with higher HA removal and lower reverse salt diffusion. On top of that, moderate draw solution concentration also plays an important role for minimizing reverse salt activity. These results may be useful in considering FO as one of the water treatment process and can assist in selection of draw solution and types of membranes used in the field of FO.

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List of symbols

J_w	—	forward osmosis water flux (L m^{-2} h^{-1})
A	—	effective membrane area (m^2)
Δt	—	operation time (h)
ΔV	—	volume changes of feed solution (L)
R	—	HA rejection (%)
C_a	—	salt concentration in the permeate volume (mol L^{-1})
C_b	—	salt concentration in the feed (mol L^{-1})

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