Effect of Operating Conditions on Forward Osmosis for Nutrient Rejection Using Magnesium Chloride as a Draw Solution

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Abstract—Advanced treatments such as forward osmosis (FO) can be used to separate or reject nutrients from secondary treated effluents. Forward osmosis uses the chemical potential across the membrane, which is the osmotic pressure gradient, to induce water to flow through the membrane from a feed solution (FS) into a draw solution (DS). The performance of FO is affected by the membrane characteristics, composition of the FS and DS, and operating conditions. The aim of this study was to investigate the optimum velocity and temperature for nutrient rejection and water flux performance in FO treatments. MgCl₂ was used as the DS in the FO process. The results showed that higher cross flow velocities yielded higher water fluxes. High rejection of nutrients was achieved by using a moderate cross flow velocity at 0.25 m/s. Nutrient rejection was insensitive to temperature variation, whereas water flux was significantly impacted by it. A temperature of 25°C was found to be good for nutrient rejection.

Keywords—Cross flow velocity, forward osmosis, magnesium chloride, temperature.

I. INTRODUCTION

FORWARD osmosis (FO) is a kind of physicochemical process that uses membranes and chemical potential to treat water. The FO process involves the transport of water across a selectively permeable membrane from a solution of higher water chemical potential or lower osmotic pressure, which is named as the feed solution or FS, to a solution of lower water chemical potential or higher osmotic pressure, which is named as the draw solution or DS [1]. In this study, the FS used was a secondary treated effluent that contained nutrients such as nitrogen (nitrite, nitrate, and ammonium) and phosphorus (phosphate). These nutrients can cause severe environmental problems such as eutrophication, oxygen deficiencies in water bodies, fish kills [2], and changes in the abundance and diversity of aquatic invertebrates, fish, and possibly even birds and mammals [3]. Additionally, elevated concentrations of un-ionized ammonia, nitrate, and nitrite in water may be toxic to humans and aquatic life. Thus, the removal of nutrients from treated effluents is highly desirable. For the DS, this study utilized MgCl₂ because of its relatively high osmotic pressure [4]. According to the findings of Achilli et al. (2010), MgCl₂ may be the best DS for most water and wastewater applications, but this still needs further investigation [5].

The performance of FO is affected by the membrane characteristics, composition of the FS and DS, and operating conditions. Hence, these factors should be optimized to increase the efficiency of the process and decrease concentration polarization or CP [6]. The CP is caused by the concentration difference between the FS and DS troughs across an FO membrane [7]. The CP arises because the water flux in FO is in the opposite direction to the reverse solute flux [8]. Since the effect of the membrane, DS, and operating conditions on the FO efficiency are closely related to each other, all these factors must be investigated.

During the osmotic process, mass transfer is critical for the FS and DS where CP will reduce water flux and induce fouling. The CP effect can be controlled with cross flow velocity and hydrodynamics [9]. When an asymmetric membrane is used, the boundary layer occurs within the support layer of the membrane, thus protecting it from the shear and turbulence associated with cross flow velocity along the membrane surface. This phenomenon affects the water flux. Lower FS cross flow velocities in FO may generate higher external CP [9]. A low velocity of cross flow will minimize reverse solute transport from DS to FS, but it may also reduce water flux by increasing the external CP and creating conditions conducive to membrane fouling. However, other studies have shown that different flows in FO did not change the water flux [10], [11]. This study investigated the effect of cross flow velocity specifically because of these various performances found in earlier FO studies.

In the FO process, increasing temperatures will increase the water flux because of the increase of DS osmotic pressure and the decrease in wastewater viscosity [9]. In wastewater applications using FO, an increase in temperature will concentrate the wastewater faster, but this may lead to greater fouling of the membrane [6]. Thus, the optimal temperature for the rejection of nutrients needs to be investigated.

Based on the aforementioned reasons, this study aims to investigate the optimum velocity and temperature for nutrient rejection and water flux performance in FO treatments using MgCl₂ as DS.

II. MATERIALS AND METHODS

A. Feed and Draw Solution

An actual sample of secondary treated effluent from the
Eastern Municipal Wastewater Treatment Plant in Ube City, Yamaguchi, Japan, was collected for analyses. The concentrations of nitrite (NO$_2^-$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), and phosphate (PO$_4^{3-}$) in the effluent were 0.1 mg/L, 11.4 mg/L, 3.4 mg/L, and 2.7 mg/L, respectively. Then, an artificial secondary treated effluent was prepared for use as the FS; this solution contained the same concentrations of nutrients that were determined for the actual secondary treated effluent. The raw materials added for nitrite, nitrate, ammonium, and phosphate were sodium nitrite (NaNO$_2$) at 0.03 mM, potassium nitrate (KNO$_3$) at 2.8 mM, ammonium chloride (NH$_4$Cl) at 0.85 mM, and potassium hydrogen phosphate (KH$_2$PO$_4$) at 0.3 mM, respectively. For the DS, magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O) was mixed with deionized (DI) water (SA 2100E Eylea Japan) to achieve a final concentration of 1 M. Different concentrations of the DS will have different viscosity values that need to be taken into consideration for the diffusion constant. The viscosity of the DS used in this study was measured by a viscometer (TVC-5 Toki Sangyo, Japan).

**B. Membrane**

Commercial non-woven flat sheet membranes from Hydration Technologies Inc. (HTI) were used in the experiments. The membrane chemistry is proprietary, though it is believed to consist of asymmetric cellulose triacetate (CTA) with a non-woven (NW) support layer. The contact angle for the CTA-NW membranes is 64° [12], and they are stable at a pH range of 3–8 [6].

**C. Forward Osmosis Cross Flow Set-up**

To investigate the effect of cross flow velocity and temperature, the experiment was set-up as shown in Fig. 1. Two peristaltic pumps equipped with a speed controller (Eylea, RP-2100) were used to recirculate the FS and DS. Three cross flow velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s were applied. The temperatures tested included 20°C, 25°C, and 30°C. A water bath and magnetic stirrer were used to maintain the temperature.

The temperature and pH were monitored intermittently with a pH meter/thermometer (Horiba D-13). Two rectangular sides with dimensions 135 mm long, 90 mm wide, and 4 mm deep, are permitted the FS and DS to flow to the membrane. The effective membrane area was 0.012 m$^2$. The active and support layers of the membrane were facing the FS and DS in the FO mode, respectively [4]. The water that permeated through the membrane into the DS was allowed to overflow into a beaker that was placed on a balance (PJI3000 Mettler-Toledo USA). The change of weight on the balance was recorded to calculate the water flux through the membrane. A 3.5 L flask was used to hold the artificial FS, and a 1 L flask was used to hold the DS. The time for conducting a single cross flow experiment was 8 hours [1] [13]. At the end of the cross flow process, permeates were collected and analyzed for nitrogen (NO$_2^-$-N, NO$_3^-$-N, and NH$_4^+$-N), and phosphorus (PO$_4^{3-}$-P).

Nutrient rejection was calculated by subtracting the initial concentration from the final concentration.

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**D. Cross Flow Velocity Determination**

In previous studies, FO cross flow velocity or flow rate and effective membrane area were varied. Holloway et al. (2007) used 1.5 L/min and 139 cm$^2$ [13], while Xue et al. (2015) used 8.3 cm/s and 60 cm$^2$ [14]. This experiment used a tube diameter of 7.94 mm, an effective membrane area of 120 cm$^2$, and various flow rates were achieved by adjusting the speed of the peristaltic pump according to the diagram shown in Fig. 2. The applied cross flow velocities investigated in this study are shown in Table I.

**To characterize different flow regimes within similar fluids, such as laminar or turbulent flow, one can use the Reynolds equation, which is:**

$$Re = \frac{uR}{\nu} = \frac{\rho uR}{\mu}$$  \hspace{1cm} (1)

where Re is Reynolds number, $u$ is the velocity of the object relative to the fluid (m/s), $R$ is the hydraulic diameter that can change with L, the traveled length of the fluid (m), $\mu$ is the dynamic viscosity (mPa·s or kg/(m·s)), $\nu$ is the kinematic viscosity (m$^2$/s), and $\rho$ is the density of the fluid (kg/m$^3$). The flow regimes, whether laminar or turbulent, determine the Sherwood number, which is related to the mass transfer coefficient.
E. Rejection of Nutrients

According to McCutcheon et al. (2006), nutrient rejection in the FS can be determined by collecting a sample of diluted DS after a complete FO run [9]. Based on the final concentration of the nutrients in the diluted DS and the initial concentration of the nutrients in the FS before the FO cross flow process, the percentage of rejection, R, is calculated as

\[ R = 100 \left(1 - \frac{C_2}{C_1}\right) \]  

where \( C_1 \) and \( C_2 \) are the final nutrient concentration in the diluted DS after the FO process and the initial nutrient concentration in the FS before the FO process, respectively. The nitrogen (NO\(_2\)-N, NO\(_3\)-N, and NH\(_4\)-N) and phosphorus (PO\(_4\)-P) contents of the FS and DS were determined according to standard methods [16] with a UV-Vis spectrophotometer (Hitachi U-1800). All samples were diluted to allow for measurements within the standard calibration range.

F. Water Flux Calculation

Osmosis leads to water flux from the FS to the DS across the FO membrane, and this results in increased weight of the DS. The water flux can be calculated using (3), where the change in weight of DS is converted to a volume and then the value is divided by the membrane area and time duration; this equation is as follows:

\[ J_w = \frac{W_e - W_i}{\rho A_m t} \]  

where \( J_w \) is the water flux (L/m\(^2\)·h), \( W_e \) is the final weight of the DS at the end of the FO process (g), \( W_i \) is the initial weight of the DS (g), \( \rho \) is the density of the fluid (kg/m\(^3\)), \( A_m \) is the membrane area (m\(^2\)), and \( t \) is the time duration (hour). The fluid at different concentrations has different viscosity values that need to be considered for the diffusion constant calculation. The diffusion constant can be expressed as

\[ D = \frac{k_B T}{6 \pi \eta r} \]  

where \( D \) is the diffusion constant, \( k_B \) is the Boltzmann constant (1.381 × 10\(^{-23}\) m\(^2\)·kg/s\(^2\)·K), \( T \) is the absolute temperature, \( \eta \) is the viscosity (mPa·s or kg/(m·s)), and \( r \) represents the radius of spherical particles (m).

III. RESULTS AND DISCUSSION

A. Effect of the Cross Flow Velocity

To elucidate the effects of the FO cross flow velocity on nutrient rejection and water flux, a series of FO processes were conducted at velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s. The same concentration of 1 M DS was applied to the CTA-NW membrane in these experiments. The effects of cross flow velocity on water flux are shown in Fig. 3. While a water flux of 6.3 L/m\(^2\)·h was achieved at a cross flow velocity of 0.17 m/s, the water flux was around 30% higher (i.e., 8.4 L/m\(^2\)·h) at a cross flow velocity of 0.34 m/s, the water flux increased again by 30% (i.e., 11.3 L/m\(^2\)·h). The boundary layer thickness would have been higher at lower cross flow velocities [17], and thus, CP likely occurred under those conditions. Notably, CP can adversely affect the water flux [9]. During the FO process, internal CP acts to diminish the driving force across the membrane and decrease water flux [18]. In this study, at the low cross flow velocity of 0.17 m/s, the water flux did not decrease substantially, which was probably a result of the short time used for the FO process.

As shown in Fig. 4, the rejection percentages for nitrogen (NO\(_2\)-N, NO\(_3\)-N, and NH\(_4\)-N) and phosphorus (PO\(_4\)-P) during FO differed for the different cross flow velocity conditions. Rejection percentages for NO\(_2\)-N, NO\(_3\)-N, NH\(_4\)-N, and PO\(_4\)-P at 0.17 m/s were 43.90%, 91.76%, 54.96%, and 85.88%, respectively, whereas for 0.25 m/s, the rejection percentages increased to 51.22%, 95.11%, 99.17%, and 97.03%, respectively. When the FO cross flow velocity was increased to 0.34 m/s, the rejection percentages slightly increased for NO\(_2\)-N (97.35%) and NH\(_4\)-N (99.72%), but the percentages decreased for NO\(_3\)-N (36.59%) and PO\(_4\)-P (88.36%). Given the varying levels of rejection for nutrients in this study, the cross flow velocity of 0.25 m/s was considered to be the optimal condition for mixing and mass transfer in the flow pipe and the membrane area of 0.012 m\(^2\).

The rejection of NO\(_2\)-N and NH\(_4\)-N was low when the effluent was treated with a low cross flow velocity because of the effect of small molecular weight compounds and hydrated ion diameters, which makes the transfer across the FO membrane easy in low mixing conditions. The NO\(_3\) molecular weight and hydrated ion diameter are 46.01 g/mole and 0.3 nm, respectively, whereas those of NH\(_4\) are 18.01 g/mole and 0.25 nm, respectively. Conversely, the higher molecular weights and hydrated ion diameters for NO\(_2\)-N (62.01 g/mole and 0.4 nm) and PO\(_4\) (94.97 g/mole and 0.4 nm) resulted in higher rejection rates owing to attenuated transfer across the membrane. The increased cross flow velocity at 0.25 m/s increased mixing and reduced nutrient transfer; therefore, the rejection percentages
were higher. The highest velocity of 0.34 m/s resulted in decreased rejection for some of the nutrients; thereby this value represents the limiting condition for this experiment given the flow pipe size and membrane dimension. Further increases in velocity might ruin the membrane. Ultimately, an operating velocity of 0.25 m/s is suggested for further experiments and applications. These findings agree with the selected velocity for the proposed FO methodology [19].

Mass transfer in cross flow filtration is largely an unknown parameter because of the variations that result from changing experimental circumstances such as the membrane channel and FS and DS flow rates. The cross flow velocity has a direct influence on the mixing and mass transfer in the flow channel [19]. To obtain reliable mass transfer coefficient relations directly from experimental data, one method that can be used is based on the variation in observed retention when cross flow velocity changes were applied [20]. Mass transfer coefficients also can be estimated from many different theoretical equations, correlations, and analogies that are functions of material properties, intensive properties, and flow regimes (laminar or turbulent flow). In this study, to help elucidate the effects of the FO cross flow velocity in the DS, pre-experiment measurements of the FS and the 1 M MgCl$_2$ DS were obtained and the observed dynamic viscosity ($\mu$ in mPa·s) values were 0.9 mPa·s = 0.9 × 10$^{-3}$ kg/m·s and 1.1 mPa·s = 1.1 × 10$^{-3}$ kg/m·s, respectively. To convert the dynamic viscosity ($\mu$ in mPa·s) into kinematic viscosity ($\nu$ in m$^2$/s), the dynamic viscosity is divided by the density of FS and MgCl$_2$, which are 1000 kg/m$^3$ and 1569 kg/m$^3$, respectively, thereby resulting in values of 9.0 × 10$^{-7}$ m$^2$/s and 7.01 × 10$^{-7}$ m$^2$/s, respectively. The hydraulic diameter for both sides by the FS and DS was 14.68 × 10$^{-3}$ m, and this was derived from dimensions of the rectangular membrane module with the assumption that the width of the channel is 90 mm and the height of flow is 4 mm. The velocity in rectangular membrane module for Reynolds number calculation was determined by dividing flow rate with hydraulic radius of rectangular membrane module. To determine the flow regime, whether it’s laminar or turbulent, Reynolds number was calculated using Eq. (1). The results are shown in Table II.

![Fig. 4 Rejection of nutrients by the CTA-NW membrane with a 1 M MgCl$_2$ DS at different velocities of 0.17 m/s, 0.25 m/s, and 0.34 m/s](image)

All of the flow regimes were seemingly low laminar referred to the low Reynolds number. The higher velocity that resulted higher flow rate will restrained nutrient transfer to the DS side, thereby increasing nutrient rejection. In higher flows and at high DS concentrations, the thickness of the boundary layer will be diminished, thus decreasing the severity of internal CP and increasing the water flux [21]. However, the mechanical strength of the membrane should be considered as one of the main limitations of high mixing that affect performance of nutrient rejection. Conversely, Park et al. (2011) concluded that development performance of the membrane might be the most efficient way to maximize FO performance, rather than through optimizing operation conditions such as FS and DS velocity [22].

**B. Effect of Temperature**

The effect of temperature on the rejection of nutrients by FO was investigated. Three sets of FO experiments using three temperatures of 20°C, 25°C, and 30°C on both the FS and DS sides were conducted. In all experiments, the same concentration of 1 M MgCl$_2$ DS was used and CTA-NW membranes were employed. Interestingly, the results showed that the rejection of ion nutrients was insensitive to temperature variations (Fig. 5). For example, the negative ion nitrate rejection amount only increased slightly with increases in temperature; specifically, the rejection percentages were 94.96%, 99.17%, and 99.51% at temperatures of 20°C, 25°C, and 30°C, respectively. However, the positive ion ammonium rejection amount did increase more pronouncedly with increases in temperature; specifically, the rejection percentages were 83.37%, 97.03%, and 97.38% at temperatures of 20°C, 25°C, and 30°C. Nevertheless, the inconsistent results indicate that temperature does not play a significant role in charged ion nutrient rejection. In aqueous solutions, charged ions are hydrated and the hydration of the charged ions results in size exclusion. In addition to size exclusion, negative membranes and electrostatic interactions can be important rejection mechanisms for charged ions or solutes [23], [24]. This finding is supported by previous study results that found that solution temperature and transmembrane temperature differences only exerted a small influence on the rejection of charged trace organic contaminants by CTA and thin film composite (TFC) membranes, whereas neutral trace organic contaminants were significantly affected by temperature [25].

<table>
<thead>
<tr>
<th>Flow rate (L/min)</th>
<th>Reynolds number for FS</th>
<th>Reynolds number for DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>375</td>
<td>482</td>
</tr>
<tr>
<td>0.75</td>
<td>538</td>
<td>691</td>
</tr>
<tr>
<td>1</td>
<td>767</td>
<td>984</td>
</tr>
</tbody>
</table>
In contrast to lack of effect on nutrient rejection, water flux was significantly impacted by temperature changes in the FS and DS. The increase of temperature in the FS enhanced the diffusivity of water molecules, thereby increasing the water flux. At the same time, the increase of DS temperature decreased DS viscosity and increased the DS diffusivity constant (4), thereby increasing the water flux [24], [25]. The viscosity is influenced by temperature and the concentration of the solution. Further experiments should be conducted to investigate the effects of DS concentration variations. The DS concentration must be eventually optimized as well because the water flux is non-linearly related to the concentration of DS [25]. A simple correlation statistical test (Table III) was conducted and the results showed that temperature had a stronger correlation with water flux (0.97) than with the rejection of nutrients (0.61–0.90).

TABLE III

<table>
<thead>
<tr>
<th>T</th>
<th>R NO2</th>
<th>R NO3</th>
<th>R NH4</th>
<th>R PO4</th>
<th>Water flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.61</td>
<td>1.00</td>
<td>0.86</td>
<td>0.93</td>
<td>1.00</td>
</tr>
<tr>
<td>R NO2</td>
<td>0.88</td>
<td>0.91</td>
<td>1.00</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td>R NO3</td>
<td>0.86</td>
<td>0.93</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>R NH4</td>
<td>0.90</td>
<td>0.90</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>R PO4</td>
<td>0.97</td>
<td>0.79</td>
<td>0.96</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td>Water flux</td>
<td>0.97</td>
<td>0.79</td>
<td>0.96</td>
<td>0.97</td>
<td>0.98</td>
</tr>
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</table>

IV. CONCLUSION

This study investigated the optimum velocity and temperature to use during FO treatments aimed at achieving high nutrient rejection rates. The DS was composed of 1 M MgCl₂, a water flux of 6.3 L/m²·h was achieved at a cross flow velocity of 0.17 m/s, and this increased to around 30% and 60% at cross flow velocities of 0.25 m/s and 0.34 m/s, respectively. Nutrient rejection was successfully achieved by a moderate velocity of cross flow at 0.25 m/s. The higher velocity that resulted higher flow rate will restrained nutrient transfer to the DS side, thereby increasing nutrient rejection. Temperature had less of an impact on nutrient rejection than the velocity, but temperature did have an effect on the water flux. A temperature of 25°C exhibited good nutrient rejection rates.

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REFERENCES


