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Forward osmosis as appropriate technology with starch-based draw agent

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ABSTRACT

The appropriate technology (AT) has been gaining attention for securing safe water resources in developing countries. Despite its promising energy-saving operation, forward osmosis (FO) system is a lack of suitable draw agent to be implemented as an AT. In this study, we propose a conceptual small-scale FO system with a starch-based draw agent. This FO system successfully produced about 17.3 L/m^2d of drinking water and achieved 95% of the arsenic removal rate using a starch paste combined with amylase as a draw agent. The osmotic pressure, which is necessary for producing permeate water, was generated by small molecules, such as maltose. These molecules were formed from the decomposition of starch by amylase. Because the draw agent used in this study is edible, the permeate water is directly drinkable without any further separation. In addition, diverse starch-containing foods such as flour, raw potatoes, raw sweet potatoes, and bananas were also confirmed as an alternative starch source for draw agent.

Keywords: Appropriate technology; Forward osmosis; Starch; Draw solution; Arsenic; Amylase

1. Introduction

Water shortage is a more severe problem in developing countries than industrialized countries [1]. Because there is a lack of capital for centralized water treatment systems in developing countries, appropriate technologies (ATs), which are small-sized, low cost, ecofriendly, and labor intensive technologies, are urgently required [2]. In this regard, disinfection and filtration systems as ATs have been well developed [3–8]; however, the systems are less effective to treat heavy metals in water, requiring new technology, such as membrane-based ATs [9]. Nanofiltration (NF) and reverse osmosis (RO) membrane systems are able to remove toxic metal ions [10–13], but both systems require high hydraulic pressure consuming a large amount of electricity, making them less favorable as ATs.

FO has been gaining attention as an energy-saving desalination process because it uses an osmotic pressure gradient between the feed solution and draw solution [14–16]. FO system is capable of removing

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various contaminants including bacteria, viruses, organic compounds, and heavy metals simultaneously with a one-step operation [17,18] In addition, FO was recently reported to treat arsenic, which is one of the major toxic heavy metals in ground water [17]. However, FO has had a limited choice in draw solution.

Draw solution as an AT should be low in cost, as well as have high osmotic pressure, non-toxicity, and easy recovery process. So far, many robust draw agents have been developed. Ammonium bicarbonate [14,19], the magnetic nanoparticles [20–22], the polymer hydrogel [23], the electrolyte polymer [24], and the polarity changeable polymer [25] were investigated as possible candidates. In addition, combined with NF/RO as a recovery process, various solutes including sucrose [26], organic salts [27], hexavalent phosphazene salts [28] were proposed. As separation-free draw solutions, sweet drink of Hydration Technology Innovations (HTI) [14] and fertilizers [29,30] was introduced. Nevertheless, the obstacle to the effective use of the reported draw agents for AT has still remained, given operational cost and local supplement.

Here, we propose a small-scale FO system with a starch-based draw agent as an AT. This system does not require a further separation step for its draw agent. Amylase was introduced with the intention of decomposing starch into small molecules which generate osmotic pressure for the production of permeate water. Arsenic was chosen as a representative toxic heavy metal.

2. Materials and methods

2.1. Materials and preparation of starch-based draw agents

A commercial FO membrane made of cellulose triacetate (CTA) (HTI, USA) was used in this study. The FO membrane was stored as flat sheets in deionized (DI) water at 4˚C prior to their use. H_3AsO_3 (As (III), arsenite) and extracted amylase powder were purchased from Sigma-Aldrich (Aldrich, St. Louis, MO) and used without further purification. Commercial cooked rice (HatBan, CJ, Korea) was mostly used as a starch source. Additional starch-containing foods such as flour, raw potatoes, raw sweet potatoes, and bananas were also used. Because flour is a dry powder, DI water was added to make a paste in concentration of 50 and 20 wt%. The water content of the starch-containing foods was analyzed by measuring the weight change after drying at 70˚C overnight, and their sugar contents were retrieved from the database of the United States Department of Agriculture (USDA) [31].

Starch-containing food (50 g) was mixed with a small amount of amylase solution (5 mL) at 25˚C for 30 min to make a starch paste draw agent. The mixing with amylase solution was intended to promote the decomposition of the starch to maltose. The concentrations of amylase solution were 100, 200, and 300 unit/mL. Note that one unit of amylase liberates 1.0 mg of maltose from starch in 3 min at pH 6.9 at 20˚C (Aldrich, St. Louis, MO). Human saliva (saliva of a 26 old) was tested as another alternative source of amylase.

The concentration of maltose in the starch paste draw agent was measured by High Performance Liquid Chromatography (HPLC) (Ultimate 3000, Dionex, USA). The sample was diluted with DI water and filtered with a 0.45 μm PVDF filter to be analyzed by HPLC.

2.2. FO performance test

Fig. 1 shows a conceptual laboratory-scale batch FO system employing a starch-based draw agent (cooked rice). The feed reservoir was filled with 150 mL of tap water (pH 7.2). The Korean tap water contains about 100 mg/L NaCl. The temperature was controlled with a thermostat (Lab. Companion, Korea). As shown in Fig. 1, the starch paste mixed with the amylase was filled in the draw reservoir. No water was added to the draw reservoir. As a control experiment, 50 g of water with 5 mL of 200 unit/mL amylase was also tested. The permeate flux was calculated by measuring the feed volume change. The permeate flux was measured for 30 min after stabilization. In addition, the permeate flux change was monitored for 24 h. The initial permeate fluxes were measured for 96 h, replacing the draw agent every 24 h. Unless otherwise specifically stated, the active layer of the FO membrane faced toward the draw side. The arsenic removal rate was examined with 300 μg/L of arsenic in both active layer facing draw side (AL-DS) and active layer facing feed side (AL-FS) (refer to Fig. S2). Vigorous stirring (400 rpm) was carried out in the feed side. The arsenic concentration was measured by Inductively Coupled Plasma Mass Spectrometer (Varian 820-MS, Varian, Australia).

2.3. Estimation of performance

J_w (water flux) can be found from Eq. (1) [14,32,33]. The osmotic pressure follows the Van't Hoff Eqn. in a low molar concentration (<0.1 M) [34]. It is assumed that the effect of external concentration polarization is negligible at low water flux.

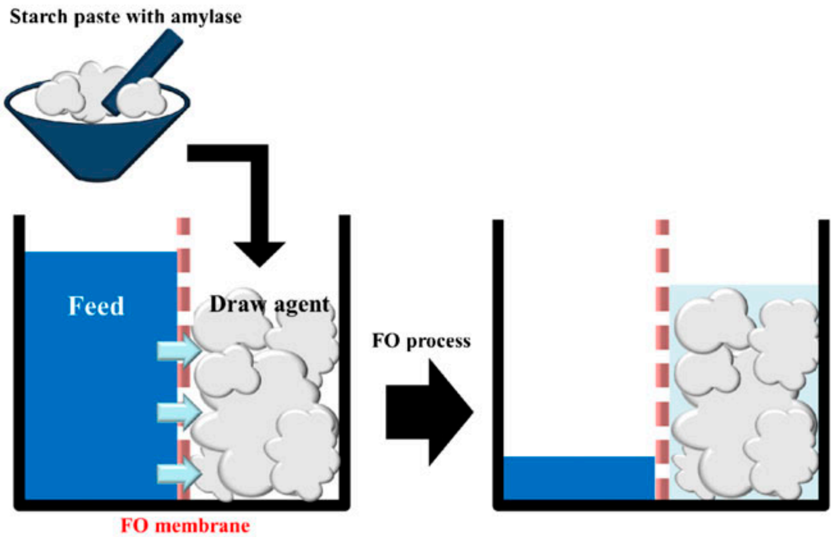

Fig. 1. Schematic diagram of a conceptual small-scale forward osmosis system with a cooked rice-based draw agent (effective membrane area: 4 × 7 cm^2, the volume of feed and draw reservoir: 150 mL, respectively).

$$J_W = A\left(\pi_{\text{draw}} - \pi_{\text{feed}} \exp(J_W K)\right) \quad (1)$$

$$K = \left(\frac{1}{J_W}\right) \text{In}\left(\frac{A\pi_{\text{draw}}}{J_W + A\pi_{\text{feed}}}\right) \quad (2)$$

$$K = \frac{S}{D} \quad (3)$$

where π_{draw}: osmotic pressure of draw agent at membrane surface (atm); π_{feed}: osmotic pressure of feed (atm); J_w: water permeate flux (L/m^2 h); A: water permeability (L/m^2 h atm); D: diffusion coefficient (m^2/s); S: structural parameter (m); K: the solute resistivity for diffusion within the porous support (s/m).

The value of A was 1.1 ± 0.1 LMH/atm when permeability was measured under 25–250 psi in the RO system. And 97.5% of NaCl was rejected with this FO membrane in RO system. The diffusion coefficient of 100 mg/L NaCl is obtained as 1.6×10^{-9} m^2/s [35]. The value of S was 477×10^{-6} m calculated from the water flux in AL-FO mode with 100 mg/L NaCl as feed solution and 0.1, 0.5, and 1 M of NaCl as draw solution. The lab-scale cross-flow RO system and FO system for finding these values were described in detail in our previous study [36].

3. Results and discussion

3.1. Effect of amylase

Fig. 2 shows the permeate flux of a small-scale forward osmosis (FO) system with different concentrations of amylase. As shown in Fig. 2, it is clear that water flux can be induced by the activity of amylase on the starch paste. In Fig. 2, negligible water permeate fluxes were observed both in the absence of starch (0.07 ± 0.04 LMH) and in the absence of amylase (0.09 ± 0.04 LMH). On the other hand, larger water fluxes were observed at higher amylase concentrations with starch. For example, the flux at 100 and 300 units/mL of amylase was 0.6 ± 0.1 LMH and 1.5 ± 0.2 LMH, respectively. It is explained that the amylase amplified the osmotic pressure of the starch draw agent. In addition,

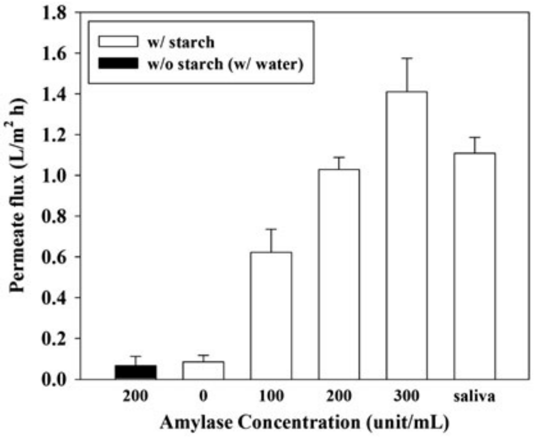

Fig. 2. The permeate flux of a FO system under several conditions of amylase concentration (feed solution: tap water; draw agent: 50 g of cooked rice paste or water with/without 5 mL of amylase solution; membrane orientation: active layer facing the draw agent; 25˚C).

1.1 ± 0.1 LMH of permeate flux was found even in the presence of human saliva which is readily obtainable as an amylase source. As another amylase source, malt powder is also available [37]. Furthermore, the starch paste draw agent is able to induce water flux from mild saline feed as 2,000 mg/L NaCl, not only from the tap water (details in Fig. S3).

Since the starch paste with amylase is edible, the product water is directly consumable without any further separation steps. The used paste is also edible. Cooked rice and saliva are readily obtainable, which is one of the most important prerequisites for ATs. Thus, the small-scale FO system with a starch-based draw agent as an AT proposed has advantages in terms of easy operation and local accessibility of the draw agent.

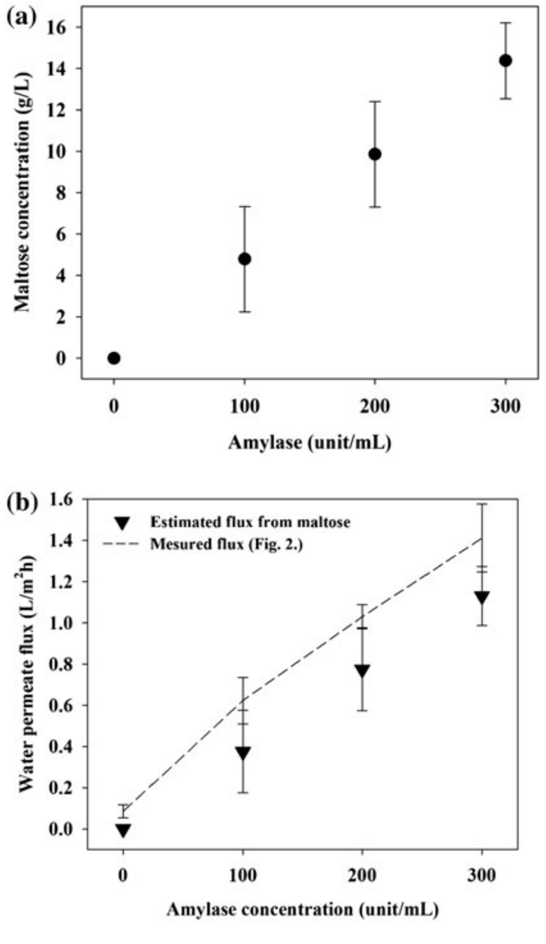

Fig. 3. (a) Maltose content generated from decomposition of cooked rice (b) and the water flux estimated from the maltose in the draw agent at several amylase concentrations (50 g of cooked rice paste with 5 mL of 0, 100, 200, and 300 units/mL amylase solution at 25℃). The permeate flux from the amylase concentration used in Fig. 2 was included for comparison purpose.

Fig. 3(a) and (b) show the maltose content in the starch paste draw agent and the water flux estimated from the maltose concentration at several amylase concentrations from Eq. (1). As shown in Fig. 3(a), larger maltose contents were measured with higher amylase concentrations. For example, maltose concentration was detected from 4.8 ± 2.5 g/L (14.0 ± 7.5 mM) at 100 unit/L of amylase to 14.4 ± 1.8 g/L (42.3 ± 5.4 mM) at 300 unit/mL. It is explained that the activity of amylase promotes the decomposition of the starch into small molecules such as maltose. In addition, note that the osmotic pressure estimated from the starch concentration itself is negligible, since the molecular weight of starch is about 10,000 times higher than that of maltose [38]. Higher content of small molecules such as maltose concentration contributed to enhancing the osmotic pressure of the draw agent, resulting in a higher permeate flux.

In Fig. 3(b), the measured permeate flux is higher than the expected value from the maltose concentration. For example, 1.4 ± 0.2 LMH was measured at 300 units/L of amylase in Fig. 2, on the other hand, 1.1 ± 0.2 LMH is estimated. It is explained that the presence of small molecules other than maltose contributes to additional osmotic pressure.

3.2. Permeate flux performance over time

Fig. 4(a) and (b) shows the variation of the permeate flux during 24 h of operation and initial fluxes for four repeated 24 h period of operation. The draw agents were replaced with new starch paste in each cycle for 96 h. As shown in Fig. 4(a), the permeate flux was relatively maintained above 0.5 LMH for 24 h despite the dilution of the draw agent by the product water. The total production of water was 17.3 L/m^2 for 24 h (note the shaded area below the curve of the permeate flux). From the result, more than 2 L of drinking water which is the daily recommended allowance (DRA) can be produced using two sets of this FO system commercial FO batch pack from HTI. The membrane area of this FO pack is about 0.07 m^2. In addition, a shorter replacement period for the draw agent is beneficial in enhancing the productivity, considering the variation of the permeate flux seen in Fig. 4(a). Furthermore, the flux was enhanced by 58% at 37℃, showing that operation in high temperature is beneficial to enhance the productivity (refer to Fig. S4). Fig. 4(b) shows the initial permeate fluxes induced by replacing the draw agent every 24 h over a 96 h period. The initial fluxes show a sustained water permeate flux exceeding 1.0 LMH as long as the draw agent is replaced within 24 h, thus enabling stable water production.

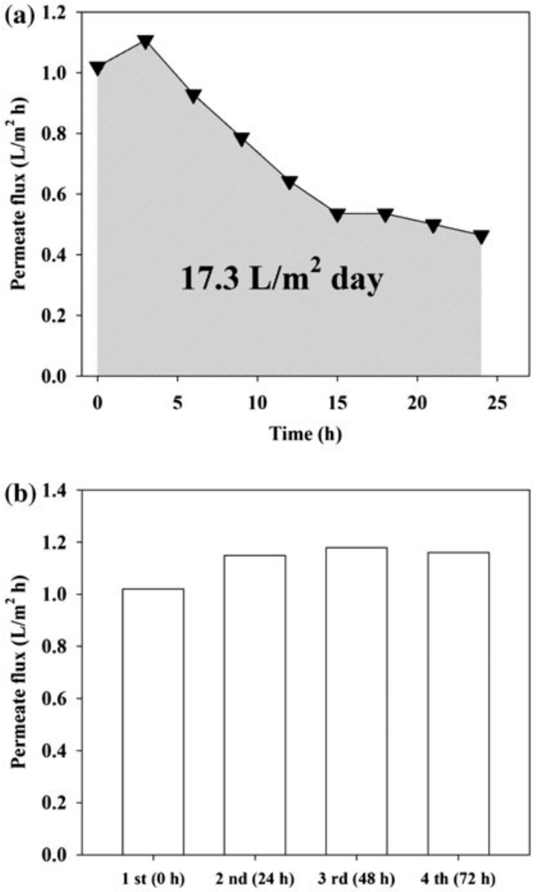

Fig. 4. The permeate flux of a small-scale FO osmosis system during 24 h of operation (a) and its initial fluxes for four repeated 24 h period of operation after replacing the draw agent (b) (feed solution: tap water; draw agent: 50 g of starch paste with 5 g of human amylase; active layer facing the draw agent; 25˚C).

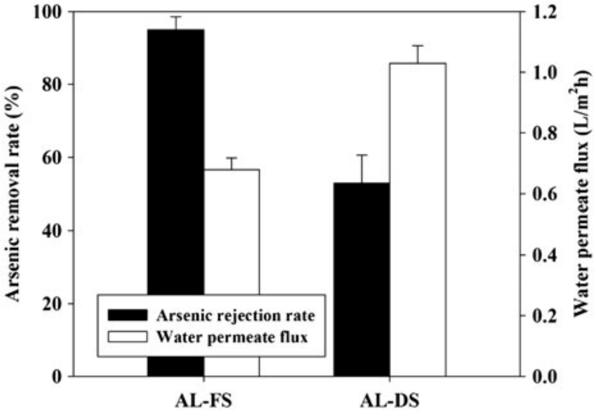

Fig. 5. Arsenic rejection and water permeate flux in a small-scale FO system with respect to the membrane orientation (feed solution: 300 μg/L of arsenic(As(III)) in tap water at pH 7; draw agent: 50 g of cooked rice paste with 5 g of human amylase solution; 25˚C).

3.3. Arsenic removal

Fig. 5 shows the arsenic removal rate and the water flux with respect to the membrane orientation (AL-DS and AL-FS). As shown in Fig. 5, the arsenic removal at the AL-FS was much better than that at the AL-DS, although the water flux in the AL-FS was lower than that in the AL-DS. For example, the arsenic removal rates were 95.0 ± 3.5% at the AL-FS and 52.9 ± 7.7% at the AL-DS. On the other hand, the water flux in the AL-FS was 66% lower than that in the AL-DS. The main reason for the low arsenic removal rate at the AL-DS compared to the AL-FS is that the arsenic in the feed side was concentrated in the support layer due to the ICP (refer to Fig. S2). The removal rate of arsenic(III) is less than that of charged ions such as NaCl is its neutral charge at pH 7 [39]. From the result in Fig. 5, AL-DS mode is recommended where the feed water contains large amount of arsenic (>20 μg/L).

3.4. Application of diverse starch-based draw agents

Table 1 presents the permeate flux of the FO system with various starch-containing foods as the tested draw agents. Several important observations from Table 1 can be made. First, various foods containing starch such as bananas, raw sweet potatoes, flour (50 and 20%), and raw potatoes also provide permeate flux ranging from 0.2 to 1.9 LMH, showing their efficacy as starch-based draw agents. From the result, it is confirmed that this FO system with starch-based draw agent is applicable in various countries as an AT, because people in the world has their native starch-containing food. Second, the permeate flux appears to be dependent on the water and sugar content in the food. For example, low water-containing foods, such as bananas, raw sweet potatoes, and flour (50%), achieved a relatively high water permeate exceeding 1 LMH compared to low permeate flux (about 0.3 LMH) from high water-containing foods, such as raw potatoes and flour (20%). It is explained that high water content in the food diluted the concentration of the starch and amylase, resulting in low osmotic pressure. Furthermore, a large amount of sugar which is smaller than maltose appeared to contribute in enhancing the water flux. For example, bananas with the highest sugar content achieved a notable water flux of 1.9 ± 0.5 LMH, compared with the 1.1 ± 0.2 LMH from the raw sweet potatoes and 1.0 ± 0.1 LMH from the flour (50%), which have a similar water content with the bananas. From this result, starch food with less

Table 1
Summary of content of various starches and measured water flux

	Water content (wt%)	Sugar content (wt%)[a]	Flux (LMH)[b]
Banana	54	12.2	1.9 ± 0.5
Raw sweet potato	48	4.2	1.1 ± 0.2
Flour (50%)	50	<1.0	1.0 ± 0.1
Flour (20%)	80	<1.0	0.3 ± 0.1
Raw potato	80	<1.0	0.2 ± 0.1

[a] Obtained from the USDA Nutrient Database [31].

[b] Measured under the following conditions: feed, tap water; draw agent, 50 g of pasted starch with 5 mL of amylase (200 units/mL); 25˚C; membrane orientation, active layer facing the draw agent.

water content and more sugar content is more beneficial to be applied as draw agent in this small-scale FO system.

4. Conclusion

A small-scale FO system with a starch-based draw agent was suggested as an AT. This FO system successfully produced about 17.3 L/m^{2}d of drinking water with cooked rice combined with amylase as the draw agent. Two liters of drinking water can be produced using two sets of the commercial FO batch pack from HTI (membrane active area is about 0.07 m^2). The osmotic pressure necessary for producing permeate water is generated by large amounts of small molecules formed because of the decomposition of starch by amylase. Because the draw agent used in this study is edible, the permeate water is directly drinkable without any further separation required. In addition, the FO membrane system effectively rejected arsenic up to 93% at the AL-DS. In addition, diverse starch-containing foods such as bananas, raw sweet potatoes, flour (50 and 20%), and raw potatoes were successfully used as starch-based draw agents.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1040268.

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