Estimation of Water Flux and Solute Movement during the Concentration Process of Hydrolysed Urine by Forward Osmosis

Benedicte Carolle Wind - Yam Nikiema, Ryusei Ito, Mokhtar Guizani, Naoyuki Funamizu

Original Article

ABSTRACT

Urine is rich in nutrients and can be applied as a fertilizer. The limitation on the application is the transportation cost for the farmlands. The cost estimation required 80% of the volume reduction for a feasible utilization of urine in the farmlands near urban areas. The volume reduction system by forward osmosis (FO) process was proposed to address this problem. In this study, the experiments on FO process with real and synthetic hydrolysed urine were performed to assess the FO performances, to evaluate the solute diffusion and to describe the water flux considering the activity of solutes. This study showed both real and synthetic urine can be concentrated to 2–5 times with 2–5 mol/L sodium chloride solution. High diffusivity of ammonia and carbonates were observed, but the diffusion of other solutes was low. The activities of the solutes in the non-ideal solution should be considered for estimation of the osmotic pressure of the solution which reflects the water flux. The software PHREEQC can be used for estimation of the activities in such high concentration solutions. The organic matter in real hydrolysed urine had a negligible effect on the osmotic pressure variations.

Keywords: osmotic pressure, activity, diffusion, membrane treatment

INTRODUCTION

The price volatility of fertilizer in 2008 had a negative influence on real income especially for smallholder farmers, then refracted to poor vulnerable consumers by increasing the food price [1]. A recycling system of nutrients should be considered to manage the crisis of the price volatility by decreasing the fertilizer costs. Some reports showed urine can work as a fertilizer for growing crops [2–4], because it is rich in nutrients which occupy 88 to 98% of the nitrogen (N), 65 to 71% of the potassium (K) and 67 to 68% of the phosphorous (P) in toilet wastewater [2]. Our previous case study in Pakistan [5] showed that 10 m³/ha of urine is required for the cultivation of cotton and must be transported for 40–60 km from a town, which is a main source of urine, to the farmlands. The transportation cost of urine was higher than the cost for chemical fertilizers because of bulky volume of urine, so that 80% of volume reduction was recommended for its feasible reuse.

To address this management limitation, different methods were developed to recover nutrients from source-separated urine, mainly as nitrogen and phosphorus. It can be achieved using evaporation [6], freeze drying [7] electro dialysis [8], and reverse osmosis [9]. However, all these technics are energy intensive processes resulting in high cost. We proposed forward osmosis (FO) method for a substantial urine volume reduction to reduce the energy cost. Forward osmosis is an osmotic process, where water molecules move across a semipermeable membrane from the low solute concentration solution to the high solute concentration solution under the effect of the osmotic pressure gradient. The advantages of FO are low fouling potential and small energy input [9–11]. It is adopted in the applications of desalination, food processing, nuclear wastewater treatment, landfill leachate treatment and emerging drinks among others [12–14].

The application of FO on urine concentration is quite recent. Urine can easily hydrolyse and increase the concentration of ammonia (NH₃) and inorganic carbon (IC) resulting in high osmotic pressure. Zhang et al. [13] evaluated the technical feasibility of synthetic urine concentration.
with a FO process and attempted to estimate water flux and nutrient rejections. However, their work ended up with underestimated water flux, and the solutes coupled diffusion phenomena in the FO process was assumed to be the reason of the imparity between the experimental and the simulated fluxes. Our preliminary experiments reported that fresh and hydrolysed urine respectively had 1.81 and 3.07 MPa of osmotic pressures, and they increased respectively to 8.16 and 11.62 MPa by 5 times the concentration. These are enough high pressures compared with 2 MPa of sea water for desalination [15]. The solutions with such a high osmotic pressure cannot be treated as ideal solutions, because the ion pairing or the solute-solute interactions contribute to give the lower osmotic pressure, resulting in solution concentrations not suitable for estimation [16]. Therefore, the consideration of the activity which is the product of the concentration and the activity coefficient of a solute can be introduced in the estimation of the water flux. From the viewpoint of applying FO to real urine concentration, the water flux should be estimated from the initial condition of the two solutions for developing the calculation model of FO process. Real hydrolysed urine (RHU) contains urea, inorganic ions, organic matter, such as creatinine, amino acids and carbohydrates [17], although most of the organic matter compounds are unknown. Synthetic hydrolysed urine (SHU) is mainly composed of inorganic matters. Since SHU provides stable and controllable urine conditions suitable for laboratory experiments and modelling purpose, it is worth investigating the effect of the solute on the calculation of water flux.

The aims of this research were to assess the FO performances that could be achieved with RHU and SHU, to evaluate the solute diffusion during the FO process, to assess the adequacy of the activity parameter for the calculation of water flux, and to identify the solutes that affect water flux estimation.

### MATERIAL AND METHODS

#### Preparation of solutions

The experimental conditions are summarized in Table 1. The FO performances for RHU and SHU concentration were assessed by estimating the water flux, volume and solute concentration factors in Run 1 and 2. The composition of synthetic urine followed the report of Wilsenach [18] and is presented in Table 2a. All agents were special grade from Wako Pure Chemical Industries (Osaka, Japan). The real urine was collected from 5 women and 10 men with ages between 21 and 27 years old, and then kept at 2°C. The solutions were hydrolysed by the addition of Jack bean urease (Wako Pure Chemical Industries, Osaka, Japan) and stored for 24 hours at room temperature. The solute concentrations of RHU and SHU are summarized in Table 2b.

For the draw solutions, 2, 3, 4 and 5 mol/L of the sodium chloride (NaCl) solutions were used and were prepared by dissolving NaCl (Wako Pure Chemical Industries, Osaka, Japan) in deionized water.

Run 3 was performed as a complementary experiment to investigate the effect of ion valence of NH\(_3\) on its diffusion during the FO process. An ammonium chloride (NH\(_4\)Cl) solution and 1.4 mol/L NH\(_3\)/NH\(_4\)Cl buffer solution with pH of 5.6 and 9.4, respectively, were prepared from NH\(_4\)Cl (Wako Pure Chemical Industries, Osaka, Japan) and concentrated NH\(_3\) solution (Wako Pure Chemical Industries, Osaka, Japan).

#### Experimental setup

Figure 1 shows a FO reactor operated in co-current mode. It was composed of two symmetric flow channels separated by a sheet of an asymmetric cellulose triacetate membrane, CTA-ES (Hydration Technology Innovations, Albany, USA), while the SEM images of the surface and cross section are shown in Fig. 2. The membrane is used by researchers in FO applications for modelling and parameter estimation.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Synthetic hydrolysed urine</td>
</tr>
<tr>
<td>Run 2</td>
<td>Real hydrolysed urine</td>
</tr>
<tr>
<td>Run 3</td>
<td>Pure water</td>
</tr>
</tbody>
</table>

Table 2 Compositions of urine solutions.

(a) Compositions of synthetic urine:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Calcium Chloride (CaCl$_2$·H$_2$O)</td>
<td>0.65</td>
</tr>
<tr>
<td>2. Magnesium Chloride (MgCl$_2$·6H$_2$O)</td>
<td>0.65</td>
</tr>
<tr>
<td>3. Sodium Chloride (NaCl)</td>
<td>4.60</td>
</tr>
<tr>
<td>4. Sodium Sulfate (Na$_2$SO$_4$)</td>
<td>2.30</td>
</tr>
<tr>
<td>5. Tri-Sodium Citrate (C$_6$H$_5$Na$_3$O$_7$·2H$_2$O)</td>
<td>0.65</td>
</tr>
<tr>
<td>6. Sodium Oxalate (Na$_2$(COO)$_2$)</td>
<td>0.02</td>
</tr>
<tr>
<td>7. Potassium Dihydrogen Phosphate (KH$_2$PO$_4$)</td>
<td>4.20</td>
</tr>
<tr>
<td>8. Potassium Chloride (KCl)</td>
<td>1.60</td>
</tr>
<tr>
<td>9. Ammonium Chloride (NH$_4$Cl)</td>
<td>1.00</td>
</tr>
<tr>
<td>10. Urea (NH$_2$CONH$_2$)</td>
<td>25</td>
</tr>
<tr>
<td>11. Creatinine (C$_4$H$_7$N$_3$O)</td>
<td>1.10</td>
</tr>
</tbody>
</table>

(b) Solute concentrations of the RHU and SHU:

<table>
<thead>
<tr>
<th>Solute</th>
<th>Synthetic fresh urine (mol/L)</th>
<th>SHU (mol/L)</th>
<th>RHU (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea-N</td>
<td>0.804</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium-N</td>
<td>0.02</td>
<td>0.82</td>
<td>0.73</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.14</td>
<td>0.14</td>
<td>0.21</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.14</td>
<td>0.11</td>
<td>0.16</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.00</td>
<td>0.48</td>
<td>0.37</td>
</tr>
<tr>
<td>Total Carbon</td>
<td>1.10</td>
<td>1.08</td>
<td>1.73</td>
</tr>
<tr>
<td>pH</td>
<td>5.6</td>
<td>9.43</td>
<td>9.60</td>
</tr>
</tbody>
</table>
The cross section of the channel was 0.2 cm² and the effective filtration area was 98.27 cm². Two glass bottles of 1 L capacity kept 500 ml of both the feed solution (FS) and draw solution (DS). The solutions were circulated by two peristaltic pumps through their respective bottles with a flow rate of 14 L/h to avoid the effect of external ion polarization by boundary layer. The weight increase of the DS was measured over time by an electrical balance OHAUS (OHAUS Corporation, Tokyo, Japan) connected to a computer with data collection software WINCT (A&D Company Limited, Tokyo, Japan). The membrane was soaked in pure water for 5 hours at room temperature before each test.

The experiments in Run 1 and 2 were carried out during 7 hours close to the equilibrium condition, while that for Run 3 was stopped at 3 hours. The concentrations of potassium (K), sodium (Na), and chloride (Cl) were measured with an ion chromatography system ICS-90 (DIONEX Corporation, California, USA). Ammonia (NH₃) and phosphate (PO₄) were measured with USEPA Hach Nessler method 8038 and Hach PhosVer (ascorbic acid) method 8048 with a spectrophotometer DR-2800 (Hach Company, Colorado, USA). The inorganic carbon (IC) and total organic carbon (TOC) were measured by a TOC-9000A analyser (Shimadzu Corporation, Kyoto, Japan).

The freezing point depression of a NaCl solution and a SHU were measured with a DSC-20 analyser (Shimadzu Corporation, Kyoto, Japan) to verify the activity calculation by equilibrium solver PHREEQC [19]. It assessed the activities of the NaCl solutions with a concentration range of 0.25 - 4.00 mol/L and SHU with concentration from 1 - 4 times.

The correlation between the total activity in the solution, \( A_T \) (mol/kg-water), and freezing point depression, \( T_f \) (K), is described according to equation (1),

\[
T_f = K_f A_T
\]

where \( K_f \) is the cryoscopic constant (K kg/mol) whose value is 1.853 for water [20]. The measurement of the freezing point depression for all samples was hardly realized so that PHREEQC calculated the activity from the molar concentrations of the solutes. It considers the acid-base reactions, complex formation reactions, solubility equilibria and charge balance [21]. The equations involved in the calculation of the activity coefficients are presented and explained in [22] while a table of typical data input in PHREEQC is shown in Table S1 in the supplementary materials.

Theoretical calculation

The experimental water flux through the membrane, \( J_{w,exp} \) (m/s), was calculated from the weight increase of the DS by equation (2),

\[
J_{w,exp} = \frac{V_{d,t} - V_{d,t+\Delta t}}{S \Delta t}
\]

where \( t \) and \( \Delta t \) are time and time difference (s), respectively; \( V_{d,t} \) and \( V_{d,t+\Delta t} \) are the volume of DS at \( t \) and \( t+\Delta t \) (m³), respectively; and \( S \) is the filtration area (m²). The volume concentration factor, \( C_1(\cdot) \), and concentration factor of each solute, \( C_r(\cdot) \), were calculated with equations (3) and (4).

![Fig. 2 SEM images of the CTA membrane on (a) surface at the support layer side and on (b) the cross section.](image-url)
where $V_{F,\text{ini}}$ and $V_{F,j}$ are the FS volumes at initial state and at 7 hours (m$^3$), respectively, while $C_{F,\text{ini}}$ and $C_{F,j}$ are the concentrations of solutes in FS at initial state and at 7 hours (mol/L), respectively.

It is known that the water flux is proportional to the osmotic pressure, $\Delta \pi$ (Pa), as described in equation (5),

$$J_w = K \Delta \pi$$

where $K$ is the water permeability through the membrane (m/s/Pa). The osmotic pressure can be calculated from the sum of the molar concentrations or activities of each solute as equations (6) or (7),

$$\Delta \pi = RT \left( \sum C_{i,\text{DS}} - \sum C_{i,\text{FS}} \right)$$

$$\Delta \pi = RT \left( \sum A_{i,\text{DS}} - \sum A_{i,\text{FS}} \right)$$

where $C_{i,\text{DS}}$ and $C_{i,\text{FS}}$ are the molar concentrations of the solute $i$ in DS and FS (mol/kg-water), respectively; $A_{i,\text{DS}}$ and $A_{i,\text{FS}}$ are the activities of the solute $i$ in the DS and FS (mol/kg-water), respectively; $R$ is the gas constant (J/K/mol); and $T$ is the temperature (K).

**RESULTS AND DISCUSSION**

**FO performances**

Figure 3 shows the time course of the water flux for Run 1 and 2. A gradual decrease of water fluxes was observed owing to the change of solute concentrations in both solutions by diluting the DS and concentrating the FS, resulting in lower osmotic pressure difference across the membrane. The water flux obtained in the RHU case is 15% lower compared to the SHU one. The volume reduction level increases exponentially with the DS concentration increase (Fig. 4 (a)). The maximum volume concentration factors reached by the system were 4.5 and 5 for RHU and SHU, respectively. The performance reduction for the SHU case could be explained by the slight variations between the synthetic and the real urine compositions presented in Table 2 (b). The overall concentrations of SHU and RHU are respectively 2.77 and 3.26 mol/L of which more than 42% are organic matter. The volume reduction of RHU and SHU to 1/5 of their initial volumes reduces the nutrient content of urine. Figure 4 (b) shows $K$ and PO$_4$ had a concentration factor of 4.41 and 4.61, respectively, which are close to the water concentration factor of 5, indicating a low diffusion of these solutes. However, the concentration factor of NH$_3$ was 2.84 and was low compared to the water concentration factor which indicated a high diffusion of the urine nitrogen. The
The nutrient content of urine was therefore reduced to 60%, 88% and 90% of its initial NH₃, PO₄ and K content, respectively. An optimization of the FO process is necessary to improve the nutrient recovery from hydrolysed urine.

**Solute diffusion through the membrane**

The mass balances of the solutes are illustrated in Fig. 5. The solutes diffused similarly for both RHU and SHU, and were categorized into 3 groups: 1) low diffusion of Na, Cl, PO₄ and TOC; 2) middle diffusion of K; and 3) high diffusion of NH₃ and IC. Around 7 to 15% for Na and Cl ions moved from the DS to urine side in 7 hours. The membrane in FO process showed very high retention of PO₄ superior to 90% and 80 − 90% for K ions. These values are similar to those obtained in other FO experiments [13,23,24]. Nearly 30% of the IC passed through the membrane. As for the TOC, low diffusion occurred in both RHU and SHU. Liu et al. [25], observed a TOC rejection of 98% in the case of fresh urine (pH = 6). About 60 to 65% of the NH₃ remained in the FS and is in agreement with the reports [13,26]. In FO concentration process, size exclusion and electrostatic effects have a substantial role in controlling the forward solute transport through the membrane [23,27]. The hydration radius of the ions are responsible for limiting the diffusion during the process, e.g. K ion which has a small hydration radius has a high diffusivity compared to PO₄, Na and Cl. **Figure 6** focuses on the diffusion of NH₃ during concentration process of NH₄Cl solution by FO at pH 5.6 and 9.4. The total ammonia is partitioned between the weak acid ammonium (NH₄⁺) and the molecule NH₃ by chemical equilibrium [28]. The increase in the NH₃ amount in FS was observed at the high pH, in contrast to a slight increase at the low pH. This phenomenon is also reported by another researcher [29] and is linked to the different diffusivity of the species. NH₃ with low diffusivity and NH₃ with higher diffusivity through the membrane are dominant at low and high pH, respectively. This is because the membrane let NH₃, which has similar chemical properties to H₂O molecule on molecule size and polarity, pass through the membrane.

**Water flux estimation**

**Figure 7** represents the correlation between the experimental water flux and the osmotic pressure difference calculated from the measured concentrations in the FS and DS. A negative osmotic pressure difference was obtained from the calculation with equation (6), which indicates a high concentration of FS compared to DS. Water flux is proportional to the osmotic pressure difference and water permeability coefficient of the membrane although positive water flux was obtained to present water movement from DS toward FS. This result suggests the consideration of only the concentration of the solutions like equation (6) is no longer able to estimate the osmotic pressure difference. Therefore, the activity was considered for the estimation of the osmotic pressure to consider the interactions of molecules for non-ideal solutions.

The software PHREEQC was used to calculate the activities of the inorganic solutes (Na, Cl, K, PO₄, NH₃, and IC) and the organic matter effect on the activity change was neglected by assuming that the activity coefficient is 1 for the TOC present in RHU and SHU. The software PHREEQC calculations were first verified by experimental measure-
Fig. 5 Amounts of solutes in feed and draw solutions for the case of RHU and SHU used with 5 mol/L NaCl solution. a) Na, b) Cl, c) K, d) PO$_4^{3-}$, e) NH$_3$, f) IC, and g) TOC. SHU and RHU Balance in each graph represent the sum of the solute amount in feed and draw solution.
ments with the freezing point depression method, to confirm it can calculate the activities of solutes in non-ideal solutions. The results are presented in Fig. S1 in the supplementary materials. Figure 8 shows the relationship between the experimental water flux and the osmotic pressure estimated by equation (7). The water flux was proportional to the osmotic pressure under 15 MPa, and the water permeability coefficient was estimated as 0.82 L/m²·h/MPa. No significant difference between RHU and SHU was observed. This suggests that the calculation of the osmotic pressure should consider the solute activities in non-ideal solutions; the inorganic solutes in SHU contribute to the osmotic pressure variation in contrast to the organic matter effect that is negligible and does not affect the water flux variations. Since SHU and RHU showed similar permeability during the concentration process, the unknown organic matter does not affect the FO

Fig. 6 Amount of NH₃ in feed and draw solutions. a) Case of 0.85 mol/L NH₄Cl draw solution at pH 5.6 and b) case of 1.4 mol/L NH₄Cl buffer draw solution at pH 9.4 using deionized water as feed solution. The sum of NH₃ amount in feed and draw solution is represented the Balance in each graph.

Fig. 7 Relationship between water flux and osmotic pressure difference calculated by Eq. (6).
short-term performances and SHU can be used as a substitute for RHU for further FO investigations such as modelling where precise and controlled compositions are required.

CONCLUSIONS

The volume reduction experiments of SHU and RHU by FO process with cellulose triacetate membrane were carried out to assess the concentration performances, assess solute diffusion, analyse the role of solute interactions on water flux estimation, and determine the effect of organic matter on water flux estimation. As a result, the volumes of both SHU and RHU were reduced to 1/2–1/5. Molecular NH$_3$ and IC had a high diffusivity through the membrane. The consideration of the activities for high concentration solutions showed good estimation on the water flux from the osmotic pressure. The organic matter in RHU had a negligible effect on the osmotic pressure variation, therefore, inorganic solutes have major effects on the flux calculation.

SUPPLEMENTARY MATERIALS

Supplementary Materials for this article are available at the journal website as separate file (s).
https://www.jstage.jst.go.jp/browse/jwet

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REFERENCES


