

Hydrolysed Urine Concentration by Forward Osmosis: Numerical Modelling of Water Flux and Nutrients Concentration

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Abstract

For the concentration of urine by forward osmosis process, many solutes move between the feed and draw solutions by diffusion and advection. This study proposed a numerical model for water flux and nutrients concentration estimation during hydrolysed urine concentration by forward osmosis, and evaluated the parameters for the simulation. As a result, the permeability of water through the membrane was proportional to the difference of sum of solute concentrations between the solutions, while Na, PO₄, K, Na, and Cl slightly diffused but NH₃ has high diffusivity. The diffusivities of the solutes were evaluated by fitting the simulated results with the experimental one. The model represents well the water flux. Ammonia concentration simulation was deviating from the experimental results. Further considerations should be included in the model for the improvement of NH₃ concentration estimations such as the NH₃ and NH₄ species concentrations variation in the feed and draw solution

Keywords: Osmotic pressure, Urine, Numerical model, Concentration

INTRODUCTION

Urine, the yellow water contributes to a large proportion of nutrients from the domestic wastewater 80% of nitrogen, 50% of phosphorous, and 55% potassium (Zhang et al., 2014), while is adopted for the reuse of nutrients as fertilizers. The urine is mainly produced in urban area to be transported to farmlands outside of the area. Masoom et al. (2011) estimated 80% of volume reduction of urine is required for feasible reuse of urine fertilizer in a farmland, where is 35 km away from the source. Here, urine is mainly recovered via the urine separation toilets, then stored in a tank, where the urine can be hydrolyzed by contamination of microorganisms. The hydrolyzed urine has high concentration of solute to give high osmotic pressure. Forward osmosis (FO) process is one of the possible candidate for concentration of high osmotic pressure solution.

FO is a membrane process with the difference of osmotic pressure between a feed solution (low solute concentration) and a draw solution (high solute concentration) as driving force. It can be engineered and adapted to treat many feed types with various application fields (Lutchmiah et al., 2014, Cath et al., 2006), although its application for urine concentration is quite recent (Zhang et al., 2014). The water flux can be predicted by current existing models which assumes a single component of solute with several factors related to the membrane structure, the concentrations of the draw and feed solutions (Zhang et al., 2014). Then, we are facing some new challenges related to the estimation of water flux and solute flux for each component in urine by diffusion and advection.

The objective of this research is to propose a numerical multi-component model for the estimation of water flux during hydrolyzed urine concentration taking account the diffusion of the solutes in urine and sodium chloride solution as draw solution through a cellulose triacetate (CTA)-FO membrane.

THEORY

The CTA-FO membrane is composed by an active layer which is a dense solute rejecting part and a porous layer playing the support role during the filtration process. The solutes move through the active layer by a diffusive flow, while they cross the support layer by advection and diffusion. The concentration difference across the active layer represents the driving force for water movement.

The water flux, J_w (L/m²/h), is calculated with the flux equation for FO given by the equation 1.

$$J_w = P * RT * \left(\sum_i^m C_{i,AL_SL} - \sum_i^n C_{i,Fi_AL} \right) \quad (1)$$

where, P is the water permeability through the active layer (m²), R the gas constant (J/mol/K) and T the absolute temperature (K), C_{i,AL_SL} is the concentration of component i at the surface of the active layer of the draw side (mol/m³) and C_{i,Fi_AL} is the concentration of i at the surface of the active layer of the feed solution side (mol/m³). Here, the product of R , T and difference of sum of concentrations in feed and draw solution is recognized as an osmotic pressure difference, $\Delta\pi$ (Pa), assuming single proportion to the difference of the sum of solute concentrations. The concentrations of i across the membrane were calculated considering the advection equations in active and support layers which are respectively represented by equations 2 and 3. These equations are second order linear partial differential equations (PDE) for multi component.

$$\frac{\partial C_i}{\partial t} = D_{Al,i} \frac{\partial^2 C_i}{\partial x^2} \quad (2)$$

$$\frac{\partial C_i}{\partial t} = D_{Sl,i} \frac{\partial^2 C_i}{\partial x^2} - J_w \frac{\partial C_i}{\partial x} \quad (3)$$

where, C_i is the concentration of a component i inside the layers (mol/m³), $D_{Al,i}$ and $D_{Sl,i}$ are respectively the diffusivities of i in the active layer and support layer, t is time (s) and x is the distance from the surface of the layer of feed solution side (m). Normally, water flows from the feed to draw solutions owing to the higher solute concentration in draw than that in feed, so the volume of the bulk solution in feed, V_{FS} (m³), decreases and that in draw, V_{DS} (m³), increases, simultaneously their solute concentrations varies. The volumes of feed and draw solution, V_{FS} and V_{DS} (m³), can be estimated as;

$$\frac{\partial V_{FS}}{\partial t} = -J_w S \quad (4)$$

$$\frac{\partial V_{DS}}{\partial t} = J_w S \quad (5)$$

where, S is the effective surface area (m²). The concentrations in bulk solutions, $C_{i,FS}$ and $C_{i,DS}$ (mol/m³), are calculated by consideration of the flux and volume change. The concentration variations of the bulk feed and the bulk draw solutions can be described by the equations as follow:

$$\frac{\partial C_{i,FS} V_{FS}}{\partial t} = -J_{s,i} \Big|_{at\ FS} = -J_w S C_i \Big|_{at\ FS} + S D_i \frac{\partial C_i}{\partial x} \Big|_{at\ FS} \quad (6)$$

$$\frac{\partial C_{i,DS} V_{DS}}{\partial t} = J_{s,i} \Big|_{at\ DS} = J_w S C_i \Big|_{at\ DS} - S D_i \frac{\partial C_i}{\partial x} \Big|_{at\ DS} \quad (7)$$

where, J_s is the molar flux of the solutes through the layers (mol/s/m²). The set of initial and boundary conditions for the simulation of the water flux and the solutes concentration is as follows:

Initial condition

$$C_i = 0 \text{ (at } t = 0, \text{ for any } x) \quad (8)$$

$$C_{i,FS} = C_{i,FS,0} \text{ (at } t = 0, \text{ for feed solution)} \quad (9)$$

$$C_{i,DS} = C_{i,DS,0} \text{ (at } t = 0, \text{ for draw solution)} \quad (10)$$

Boundary conditions

$$C_{i,0} = C_{i,FS} \text{ (feed solution)} \quad (11)$$

$$C_{i,n} = C_{i,DS} \text{ (draw solution)} \quad (12)$$

The finite difference approximation of the partial derivatives was applied for numerical solution of these PDEs, then the differential equations were discretized using Crank Nicholson. The obtained systematic non-linear equations were solved with the Newton-Raphson method in each time step.

MATERIAL AND METHODS

Figure 2 shows the illustration of a FO reactor operating in co-current mode. It was composed by a sinusoidal symmetric flow channel separated by a CTA-FO asymmetric membrane (CTA-ES, HTI innovation technologies), which has a porous layer and an active layer as shown in figure 3. This membrane has been used in several studies on modelling and parameters estimation experiments of FO (Elimelech et al, 2010 ; Zhang et al, 2014). The membranes were oriented with the active layer facing the feed solution and were soaked in pure water for 5 hours at room temperature before starting the tests. The cross section of the channel was 0.2 cm^2 , where the effective filtration area was 98.27 cm^2 . The solutions were circulated by two peristaltic pumps through their respective containers with a flow rate of 14 L/h . The weight increase of the draw solution was measured over time by an electrical balance (OHAUS from Technical Advantages Company) connected to a computer with a data collection software (WINCT, A&D).

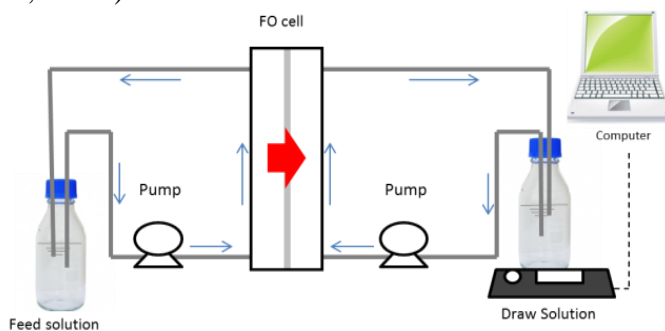


Figure 1. Forward osmosis experiment set up

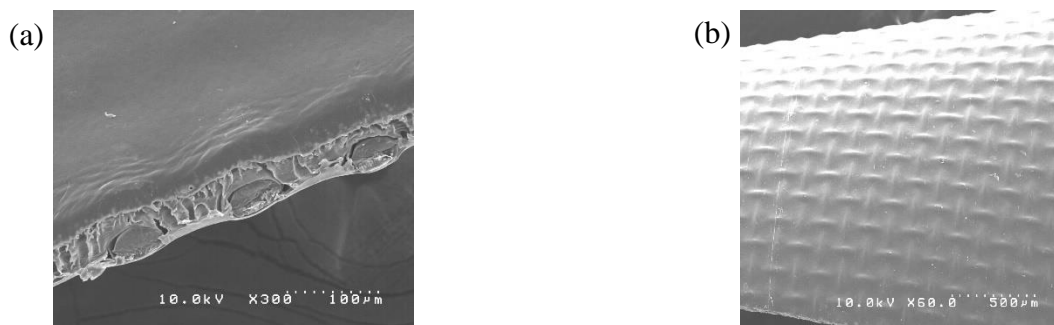


Figure 2. CTA-FO membrane SEM image (a) the cross section (b) the surface of support layer side

The experimental conditions are summarized in Table 1. Run 1 was performed for the permeability estimation of the membrane with several NaCl concentrations for draw solution and deionized water as feed solution. Run 2 was conducted for the diffusivity estimation of the ions of Na, Cl, PO_4 and K with

solutions of NaCl, NaH₂PO₄ and KCl, for draw solution and deionized water as feed solution. NH₃/NH₄Cl buffer solution prepared with 0.6 mol/l of NH₄Cl and 0.8 mol/l of NH₃ for NH₃-N diffusivity estimation. Run 3 was conducted with NaCl draw solution and hydrolyzed synthetic urine. The composition of the synthetic urine is given in the Table 2 (Wilsenach et al., 2007). The hydrolyzed urine was obtained by adding Jack Bean urease to the synthetic urine and keeping it during 24 hours before starting each experiment. All hydrolyzed urine concentration experiments were carried out during 7 hours close to the equilibrium condition. Two milliliter of feed and draw samples were collected every hour during each experiment for the estimation of NH₃, PO₄, K, Na, and Cl concentrations. The ions of K, Na, and Cl were measured with an Ion Chromatography System (ICS-90, DIONEX). NH₃ was measured using USEPA Nessler method and PO₄ was measured using a USEPA PhosVer (Ascorbic Acid) method, then the results were evaluated with a spectrophotometer (DR -2800, Hach).

Table 1. Experimental conditions

| | Draw solution | Feed solution | Membrane orientation | Cross flow velocity FS and DS |
|-------|---|-----------------|--|-------------------------------|
| Run 1 | NaCl (0.02M, 0.05M, 0.1M, 0.2M, 0.5 M) | Deionized water | (CTA)Active layer facing the draw solution | 19.44 cm/s |
| Run 2 | NaCl (0.50 M) | | | |
| | NH ₃ (0.8 M)/NH ₄ CL (0.6 M) | | | |
| | NaH ₂ PO ₄ (0.50 M) KCl (0.50 M) | | | |
| Run 3 | Hydrolyzed urine | NaCl (4M) | (CTA)Active layer facing the feed solution | 19.44 cm/s |

Table 2. Composition of human synthetic non hydrolysed urine

| | Component | Concentration (g/L) | mM |
|-----|---|---------------------|------|
| 1. | Calcium Chloride (CaCl ₂ .H ₂ O) | 0.65 | 4.4 |
| 2. | Magnesium Chloride (Mg Cl ₂ .6H ₂ O) | 0.65 | 3.2 |
| 3. | Sodium Chloride (NaCl) | 4.60 | 78.7 |
| 4. | Sodium Sulfate (Na ₂ SO ₄) | 2.30 | 16.2 |
| 5. | Tri-Sodium Citrate (Na ₃ citrate. 2H ₂ O) | 0.65 | 2.6 |
| 6. | Sodium Oxalate (Na ₂ -(COO) ₂) | 0.02 | 0.15 |
| 7. | Potassium Dihydrogen (KH ₂ PO ₄) | 4.20 | 30.9 |
| 8. | Potassium Chloride (KCl) | 1.60 | 21.5 |
| 9. | Ammonium Chloride (NH ₄ Cl) | 1.00 | 18.7 |
| 10. | Urea (NH ₂ CONH ₂) | 25 | 417 |
| 11 | Creatinine (C ₄ H ₇ N ₃ O) | 1.10 | 9.7 |

RESULTS AND DISCUSSION

Membrane water permeability

Figure 4 represents the water flux as a function of the osmotic pressure difference to determine the water permeability, which was estimated to 0.33 L/m².h.bar. This value is relatively low comparing to the one obtained in other studies 0.44 L/m².h.bar (Elimelech et al., 2010), and 0.94 L/m².h.bar (Zhang et al., 2012), because these coefficients were estimated under reverse osmosis conditions in contrast of our estimated permeability in forward osmosis mode.

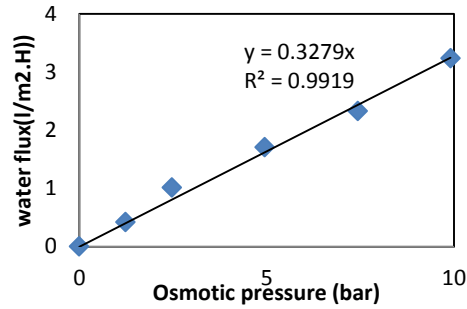


Figure 3. Water flux value over the osmotic pressure difference from run 1

Diffusion of solutes

The figures 5-8 respectively show the time course of water flux and the solute concentrations for the NaCl, KCl, NaH₂PO₄ and NH₄Cl tests. A decrease of the water flux was observed in all the cases owing to the progressive dilution of the draw solution and slight increase in concentrations in feed solution resulting in small osmotic pressure difference. From this data, the solute fluxes were estimated as shown in figures 9-12. The fluxes were almost constant for except NH₃. This may be because that the diffusion is driven by the concentration difference, although the advection flow from the feed to draw solutions inhibits the small mass transportation from the draw to feed side with low diffusivity. In contrast, NH₃ was strongly depends on the change in the concentrations which indicates the large mass transportation with high diffusivity.

The diffusivities of the solutes for the active and support layers were obtained with the experimental data for the cases to fit the water flux and ions concentrations as shown in figures 5-8. The simulation results were well fitted to experimental ones, while a slight deviation of NH₃ amount was observed in the feed solution. Our model considered a constant diffusivity coefficient of NH₃ and simulation results slightly deviate from the experimental trend. During the concentration the pH in varies from 9.4 to 8.73 in hydrolyzed urine and 6.7 to 9.75 in NaCl solution. In this pH range we have the presence of both NH₃ and NH₄⁺, while the pH variation contributes to the variation of the species concentrations in the solutions. The diffusivities obtained for the support layer side are 2.5×10^{-10} m²/s for Na and Cl, and 1.5×10^{-10} m²/s, 5.5×10^{-10} m²/s and 1.5×10^{-9} m²/s respectively for PO₄, K and NH₃. The diffusivity of the active layer side obtained were 2.75×10^{-12} m²/s for Na and Cl, and 1.85×10^{-12} m²/s, 2.85×10^{-12} m²/s and 5.75×10^{-12} m²/s respectively for PO₄, K and NH₃.

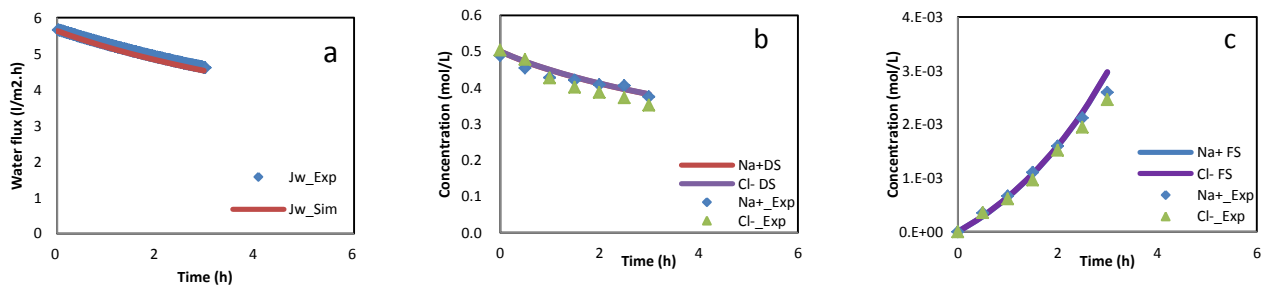


Figure 4. Simulation and fitting of Na and Cl concentration in (a) draw solution, (b) in feed solution and (c) time course of water flux

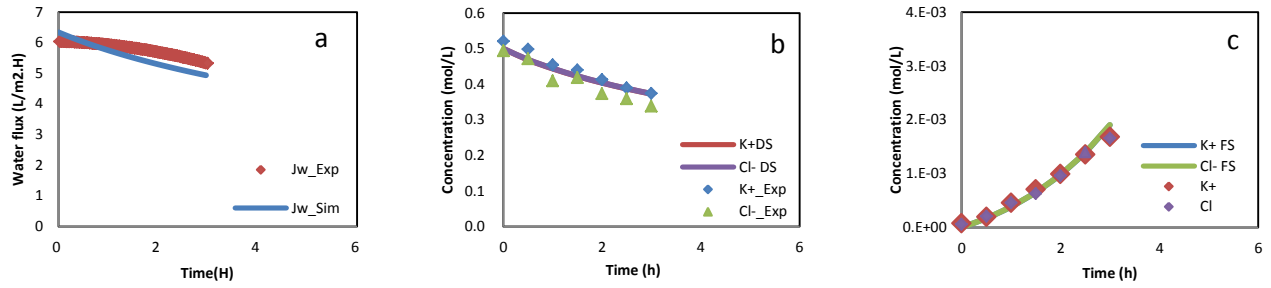


Figure 5. Simulation and fitting of K and Cl concentration in (a) draw solution, (b) in feed solution and (c) time course of water flux

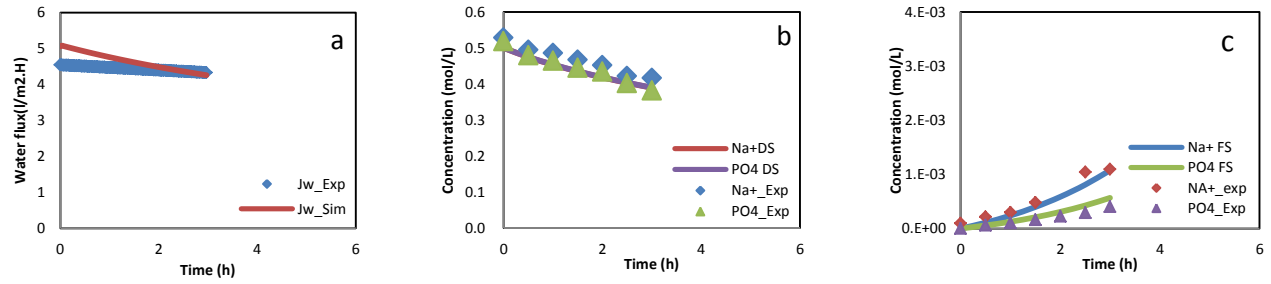


Figure 6. Simulation and fitting of PO₄ and Na concentration in (a) draw solution, (b) in feed solution and (c) time course of water flux

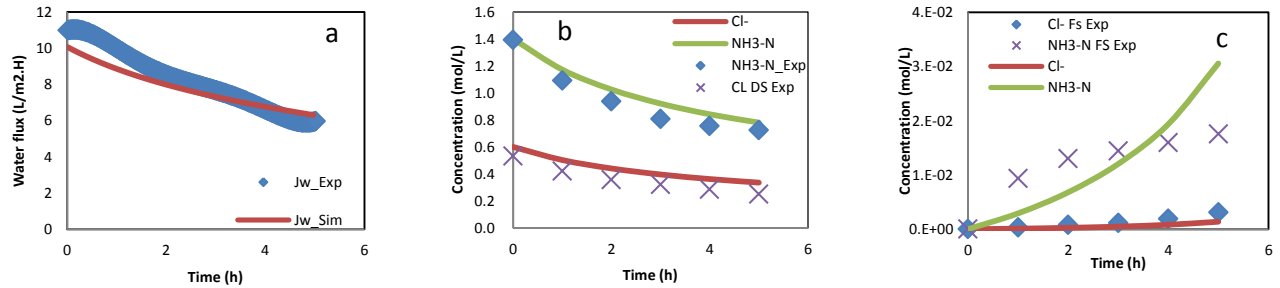


Figure 7. Simulation and fitting of NH₃ and Cl concentration in (a) draw solution, (b) in feed solution and (c) time course of water flux



Figure 8. Time course of solute flux of Na and Cl for NaCl experiment



Figure 9. Time course of solute flux of K and Cl for KCl experiment



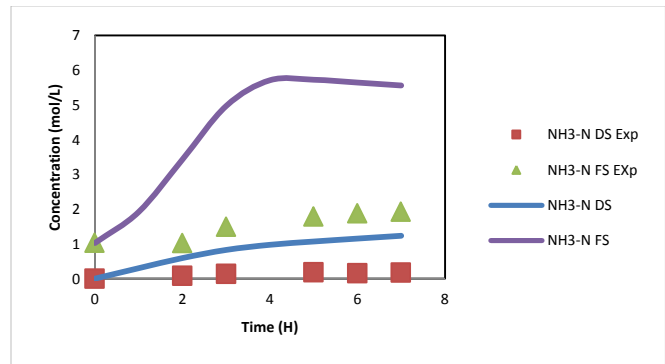
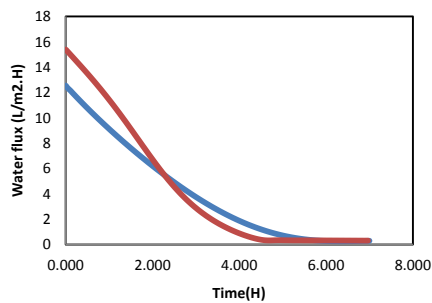
Figure 10. Time course of solute flux of Na and PO₄ for NaH₂PO₄ experiment



Figure 11. Time course of solute flux of (a) NH₃ and (b) Cl for NH₄Cl experiment

Concentration of hydrolyzed urine

Figure 13 represents the experimental and simulated data of the water flux and concentrations of major solutes of Na, Cl and NH₃ during hydrolyzed urine concentration by FO process. The NH₃ concentrations in feed and draw solutions increased. This is because NH₃ was only in feed solution which was concentrated by FO process at initial, then it diffused to draw solution to increase its concentration in the solution. The Na and Cl concentrations decreased in the feed solution because of the dilution by water movement, while their concentrations increased in the opposite side owing to the diffusion and the reduction of the volume. The simulation results agreed to the water flux and concentrations except NH₃ concentration with the permeability and diffusivities estimated above.



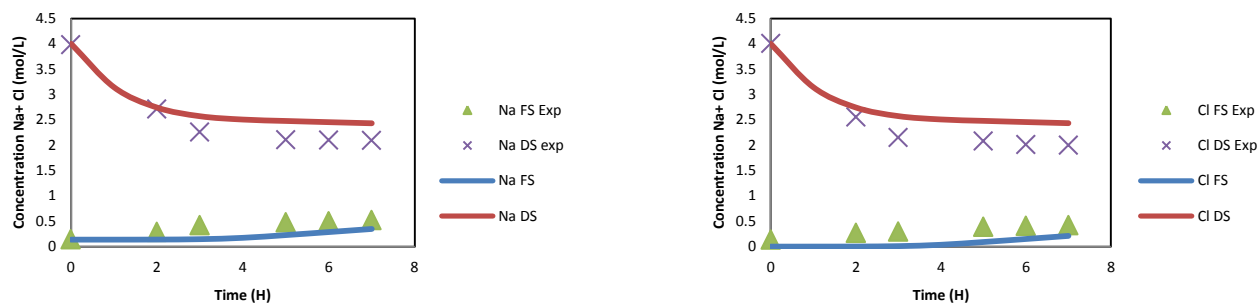


Figure 12. Time course of (a) the water flux, and concentrations of (b) NH_3 , (c) Na and (d) Cl in FS and DS during hydrolyzed urine concentration by FO

CONCLUSION

The FO process was performed to concentrate urine with high osmotic pressure solution. As a result, the water permeability as evaluated with deionized water as feed solution and NaCl solution as draw solution. The slight diffusion of Na, K, Cl and PO_4 was observed while NH_3 diffused through the CTA-FO membrane. Their diffusivities in the active and support layers were evaluated with a mathematical model proposed in this study, while the simulation results agreed to experimental data of the water flux and concentrations. The concentration of hydrolyzed urine was performed with FO process. The simulated results represent well the evolution of the water flux and concentrations of Na and K. However, the simulation of NH_3 concentrations in both solutions had a deviation from experimental one. Further considerations should be included in the model for the improvement of NH_3 concentration estimations such as the NH_3 and NH_4 species concentrations variation in the feed and draw solution.

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