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Development of a system for nutrients recovery from hydrolyzed urine by forward osmosis concentration

By

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

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RESUME

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2) B. C. W. Nikiema, R. Ito, M. Guizani, N. Funamizu, Numerical simulation of water flux and nutrients concentration during hydrolysed urine concentration by forward osmosis, Journal of Water Research (Submitted in June, 2017)

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B. C. W. Nikiema, R. Ito, M. Guizani, N. Funamizu : Design of a forward osmosis reactor for urine concentration and nutrients recovery , The 6th Maghreb Conference on Desalination and Water treatment, Hammamet, Tunisia, December 2017 (In preparation).

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« *Eternel, tu es mon Dieu; je proclamerai ta grandeur, je célèbrerai ton nom car tu as accompli des merveilles* » *Esaïe 25-1*

ABSTRACT

Development of a system for nutrients recovery from hydrolyzed urine by forward osmosis concentration

Human urine is nutrients-rich resource as it contains the major part of nutrients e.g. nitrogen, phosphate, potassium found in domestic wastewater therefore, urine has the potential to be reused in agriculture as a liquid fertilizer. Large quantities of urine are produced continuously, especially in populated areas, making available a continuous supply of nutrients. However, urine contains 95% of water giving bulky volume and low concentration of nutrients. So, urine storage and transport prior to application in farmland is non-economically competitive with chemical fertilizers and renders its reuse challenging. Hence, urine volume reduction and nutrients concentration appear to be necessary. Earlier studies suggested 80% volume reduction as a minimum requirement to be cost effective. Several volume reduction techniques were reported in the literature. However, they are all energy demanding processes, making the concentration of urine non-advantageous. Forward osmosis process is an emerging technology used in several applications for volume reduction and concentration and is reported to consume less energy than other concentration alternatives e.g. reverse osmosis, evaporation... In this study, we propose a nutrients recovery system with urine volume reduction by forward osmosis process. The FO volume reduction technic is an osmotic pressure driven process where water molecules move across a semipermeable membrane from a feed solution of low solute concentration to a draw solution of high solute concentration. Moreover, solutes in the solutions can diffuse from one compartment to another by their concentration differences. The objectives of this research were to develop a mathematical model for water and solutes flux estimation during urine volume reduction and to design a nutrient recovery system with forward osmosis concentration process.

In chapter 1, the problems on sanitation all over the world, potential of urine as a fertilizer, crisis of natural resources, resource oriented sanitation, forward osmosis applications and the phenomena involved in the membrane separation process were reviewed. The issues that should be assessed were identified and the objectives of the thesis were summarized.

In chapter 2, the phenomena that occur during forward osmosis process were studied. Experiments were carried out 1) to assess water flux performances of real and synthetic hydrolyzed urine, 2) to evaluate solutes diffusion, 3) to assess the adequacy of solutes activity for the calculation of water flux, and 4) to identify the major solutes for water flux estimation during the volume reduction process. Hydrolyzed synthetic urine and hydrolyzed real urine were used as feed solutions, and sodium chloride solution with concentration range of 3-5 mol/L was used as draw solution. The solutes activities were calculated with PHREEQC from the molar concentrations. As a result, it was found that: 1) the volumes of real and synthetic hydrolyzed urine could be concentrated to 2-5 times with 3-5 mol/L sodium chloride solution, 2) ammonia and the inorganic carbon in urine easily diffused to draw solution through the membrane, 3) solute activities in the feed and the draw solutions were suitable for the estimation of the osmotic pressure, and 4) the organic matter presented in real hydrolyzed urine had a negligible effect on the osmotic pressure

variation.

In chapter 3, a multicomponent mathematical model was developed to describe the phenomena occurring during forward osmosis process. The model considered the advection, diffusion and activities of the solutes in feed and draw solutions through a semi-permeable membrane. Partial differential equations were established to estimate the concentration variation across the membrane and in the bulk solutions. The finite difference approximation of the partial derivatives was applied to numerically solve these equations, then the differential equations were discretized with Crank Nicholson scheme. The obtained systematic non-linear equations were solved with the Newton-Raphson method at each time step. The solutes diffusivities and pure water permeability of the membrane were required for the simulation. These parameters were calibrated by the experimental data with single salt solutions as draw solutions and pure water as feed solution. The experimental conditions were simulated and compared with the experimental results. Least square method with Nelder mead algorithm was used to find the best fit of the volume and concentration curves for the diffusivities estimation. The model was later validated by comparing simulated and other forward osmosis experiments results using synthetic hydrolyzed urine and sodium chloride draw solution. The important outcomes of this research are that: 1) the simulation of the model was succeeded to estimate the evolution of volume and solute concentrations in both solution, 2) ammonia can diffuse from urine to draw solution and presented a lower concentration factor than feed solution volume reduction factor, and 3) the nutrients concentration profile inside the membrane was calculated to show the effect of the internal concentration polarization which reduced the osmotic pressure at the active layer surface to 35% of its initial value.

In chapter 4, a forward osmosis unit to be implemented for urine concentration was designed. The developed model was used to evaluate the required membrane area to concentrate hydrolyzed urine into 1/5 of its initial volume. To propose the design parameters the following points were assessed: 1) the required membrane area decreases with the increase of the initial draw solution concentration however this effect becomes negligible when the initial draw solution volume set exceeds urine initial volume, 2) the effect of initial osmotic pressure variation on ammonia concentration factor and recovery percentage, 3) the effect of the membrane area variation on ammonia concentration factor and recovery percentage. The results show that: 1) the required membrane area decreases with the increase of the initial draw solution concentration and volume. 2) Ammonia concentration factor slightly increase with the importance of the initial draw solution concentration. At 5 times volume reduction levels of urine, 1.1 to 1.4 concentration factor of ammonia were obtained and 22.7 - 27.5% of ammonia could be recovered with 300 cm^2 membrane areas. 3) The reduction of the area from 342 to 56 cm^2 enhanced the concentration factor of ammonia that increased from 1.4 to 3.9. To reduce 5 liters of urine to 1/5 in 12 hours operation we suggested a membrane area of 280 cm^2 and a draw solution volume of 5 L with the osmotic pressure of 32.6 MPa.

In chapter 5, the main findings and recommendations related to the application of forward osmosis process for a concentration of urine liquid fertilizer in agriculture were summarized.

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CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

The world population has increased within the last century and the societies across the world have observed significant urbanization. To improve the living and sanitary conditions technologies and wastewater infrastructures have been widely developed. Sewage collection systems were developed to convey and treat the wastewater in centralized treatment sites, clusters and onsite septic systems were adopted in areas where centralized systems were not feasible. With the growing pollution concerns, high load of nutrients pollution through infiltration and uncontrolled discharge was found to have harmful ecological effect of uncontrolled nutrient pollution in water bodies. Nutrients removal and recovery at wastewater treatment plants is therefore gaining significant attention however they require high energy for nitrogen conversion into less hazardous or gaseous form to protect the environment. At the same time the wastewater are important source of nutrients and these nutrients could be use as fertilizer.

The total fertilizer nutrient consumption is estimated at 183 200 000 tons in 2013 and is expected to reach 200 500 000 tons by the end of 2018 (FAO, 2016). Fertilizer production requires high energy for the processing and the conversion of nitrogen phosphorous and potassium into plant available forms. In the world about 70.000 kilojoules are required to produce one pound of nitrogen fertilizer which is 4.5 times higher than that of phosphate and 5.7 times than potash (Gellings and Parmenter, 2004 in Kabore et al., 2016). Another concern is the global peak of phosphorus production which is forecasted to occur around 2030; and once the maximum reached the production will drop down, creating a widening gap between supply and demand (Cordell, 2008, Sen et al., 2013). Effort should be made to utilize nutrient containing waste as efficiently as possible.

Alternatives to link agriculture and sanitation represent sustainable strategies for nutrients recycling and waste management. The On-Site Wastewater Differentiable Treatment Systems (OWDTS) which is based on the concept "don't collect" and "don't mixed" is a promising decentralized treatments system adapted for both develop and developing countries because of its low cost, no energy requirement and easy to operate and maintain (Lopez et al. 2002, Sen et al., 2012). Figure 1 shows the schematic illustration of OWDTS. In this system, wastewater streams (feces, urine and gray water) are collected and treated separately at household level, thus saving cost of sewerage pipelines. Among the wastewater streams, urine is the fraction that contains the major amount of nutrients. It contributes to approximately 80% of the nitrogen, 55% of phosphorous and 60% of potassium (Jönsson et al., 2000). Thus it is possible to collect relatively high concentrated fertilizer by diverting urine from the wastewater. The valued resources like compost or urine can be directly sell to the farmers as fertilizer or contribute to growth some vegetable in the household's garden which is a great source of income and food for the families.
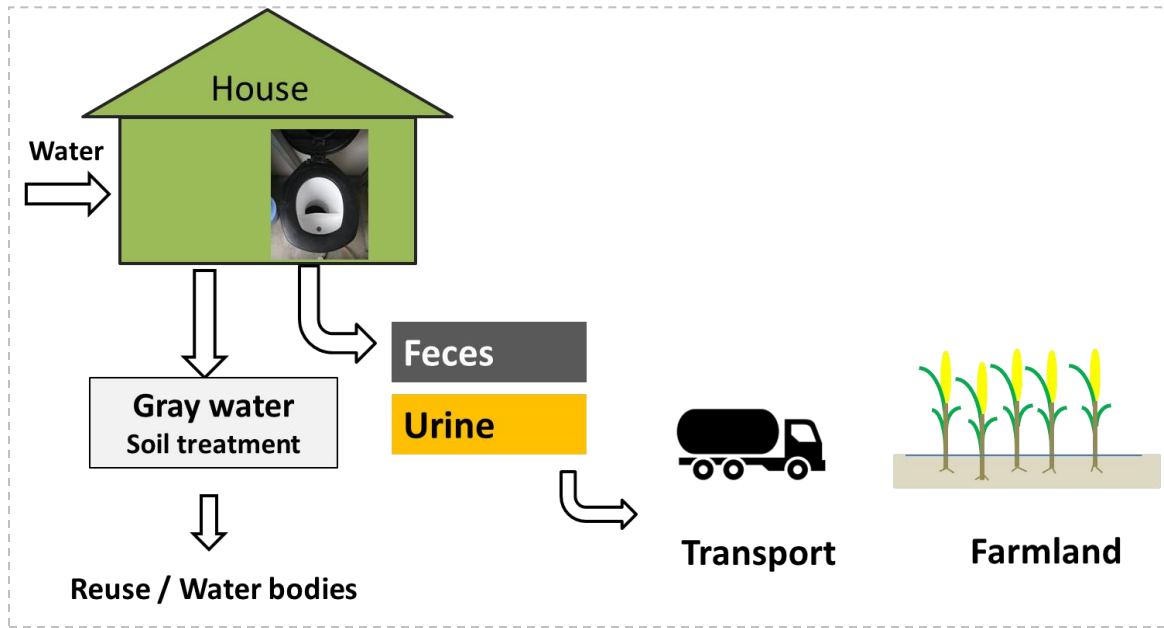
Figure 1 Onsite wastewater differential treatment system

1.2 VALUE OF URINE AS FERTILIZER

Urine contains high concentrations of sodium, chloride, urea, phosphate and potassium, and trace levels of calcium, sulfate and magnesium (Larsen and Gujer, 1996a). The pH value of fresh urine ranges 5.6 - 6.8 (Fittschen and Hahn, 1998, Liu et al., 2008). It contains the major portion of nutrients in the household wastewater fraction and represents only 1% of the total volume of wastewater (Maurer et al., 2006, Karak and Bhattacharyya, 2011).

Undiluted fresh urine contains 0.20 - 0.21 g/L of phosphorous and about 95% to 100% of phosphorous is bound as dissolved phosphate. The potassium amount ranges 0.9 - 1.1g/L as for the total nitrogen concentration $7 - 9$ g/L in which the sum of urea nitrogen, ammonia, and uric acid nitrogen amounts of 90 - 95 % of it (Gyuton 1986, Geiby Scientific Table 1981, Pahore, 2011). Urea accounts for 90% of the total N and can easily hydrolysed into ammonia. During separation, storage and transportation, urine is subject to several spontaneous processes such as urea hydrolysis, precipitation, or volatilization which change urine composition significantly. Furthermore, urease from eucaryotic and procaryotic organisms can hydrolyze urea as follows (Mobley and Hausinger, 1989):

$$NH_2(CO)NH_2 + 2\ H_2O \rightarrow 2\ NH_4^+ + CO_3^{2-} \tag{1}$$

The pH value may elevate up to a pH of 9.4, ammonia concentration increases, leading to changes in PO_4^{3-}-P concentration following hydrolysis of urea (Kirchmann and Pettersson, 1995; Fittschen and Hahn, 1998; Udert et al., 2003). Urea could be completely hydrolyzed in, the collection tank in one day if urease was added with sufficient mixing and the hydrolysis temperature was maintained at 25°Celcius (Liu et al., 2008).

Nutrients in urine are readily available to crop, since the major portion (90 - 100% of nitrogen, phosphorous and potassium (NPK) contents in urine) is present in inorganic form (Kirchmann and Pettersson, 1994). Therefore the use of urine in agriculture field presents a high potential in a viewpoint of agronomic value. However there are many challenges related to urine fertilizer application. Large volumes of urine are needed to fertilize farmland and there are problems related to the collection and transportation of these larger quantities (Lind et al., 2001). A decrease of urine solution volumes would also be beneficial for the utilization of urine in agriculture.

1.3 URINE VOLUME REDUCTION TECHNICS

Some volume reduction techniques such as reverse osmosis, electro dialysis, freezing thawing and thermal drying system, onsite volume reduction system (OVRS) have been tested

1.3.1   Onsite volume reduction system (OVRS)

The onsite volume reduction system (OVRS) is a human urine concentration system process that was conceived based on the drying theory and the atmospheric energy. Water contained in urine moves by capillarity pressure through a vertical sheet where air evaporation takes place. The OVRS was shown to be a feasible technic under cold, arid, tropical and temperate climates. 80% of 10L volume reduction could be achieved after 12 hours of laboratory experiment (Pahore et al., 2011). The application of the OVRS to urine concentration presents some limits mainly linked to urea hydrolysis which generate bad odors problems and ammonia loss in the air (Pahore et al., 2012). Moreover the performances depend strongly on the climate condition that contribute to make its application challenging.

1.3.2   Freezing thaw

The freezing thawing method was studies by Lind et al., 2001 and is based on a freezing and melting process controlled by a sodium chloride (NaCl) bath. With this method 80% of both nitrogen and phosphorous could be concentrated in 25 % of the volume. The energetic cost study carried out by Gulyas et al., 2004 shows that a centralized urine collection system is appropriate for a sustainable operation of the freezing concentrators. The annual energy consumption per capita was estimated to 38.1, 9.1 and 17.3 kWh respectively for the conventional sanitation, the ecological sanitation without freezing concentration and the ecological sanitation with freezing concentration for 584,000 habitants.

1.3.3   Vacuum membrane distillation

The vacuum membrane distillation (VMD) is gaining high interest owing its low cost, high efficiency and the energy saving advantages it presents. Water regeneration from the human

urine by a VMD process was evaluated using a polytetrafluoroethylene (PTFE) microporous plate membrane (Zhao et al., 2013). This research showed yields of water ranging 31.9 – 48.6 and high removal of COD between 99.3 to 99.5%. However ammonia nitrogen was fairly retained 40-75.1%. Efficient conditions such as relatively low temperature, sufficient membrane area and short heating time was therefore suggested to avoid the decomposition of urea and for the improvement of the recovered water quality.

1.3.4   Reverse osmosis

Reverse osmosis process was used to concentrate human urine at pH 7.1 and 50 bar of pressure could concentrate urine to 1/5 of its initial volume with a nutrients recovery of 70%, 73% and 71% respectively for ammonium, phosphate and potassium. Other application of RO on manure concentration showed similar results (Thörneby et al., 1999). However reverse osmosis membrane was prone to fouling caused by the precipitation of salts on the membrane surface which contribute to drastically reduce the performances.

The application of the technics presented may be challenging owing to high energy requirement, the operation and maintenances cost that can be significantly high and the climate conditions that may affect the performances. A promising technic which is independent to climate factors and consume low or no energy that could be used to reduce urine volume is Forward Osmosis (FO) process.

1.4 FORWARD OSMOSIS

Osmosis is one of the most fundamental phenomena found in chemical systems which arise when two aqueous solutions at different concentrations are separated by a membrane permeable to water (Hamdan et al., 2015). Osmosis is describe as the natural diffusion of water through a semi-permeable membrane from a solution containing lower salt concentration to a solution containing higher salt concentration (Cath et al., 2006).The generated chemical potential across the membrane gives rise to the osmotic pressure (π). The value of the osmotic pressure represents the minimum hydrostatic pressure that must be applied to on the higher concentration solution in order to stop the solvent (Linares et al., 2014, Hamdan et al., 2015). The osmotic pressure is a function of solute concentration; the number of species formed by dissociation in the solution. The common equation used for osmotic pressure (π) estimation is the Van't Hoff equation,

$$\pi = nMRT$$

where n is the Van't Hoff factor (accounts for the number of individual particles of compounds dissolved in the solution, M is the molar concentration (molarity) of the solution, R is the gas constant (R=0.0821 L·atm.mol^{-1}.K^{-1}) and T the absolute temperature (K). However the Van't Hoff equation is applicable only to ideal and dilute solutions where ions behave independently of one another (Phuntsho et al., 2014). At high ionic concentrations, the electrostatic interactions between the ions increase and it becomes a non-ideal solution. This ultimately reduces the activity coefficient of each ion and the

osmotic pressure of the solution (Snoeyink and Jenkins, 1980, Phuntsho et al., 2011)

Forward Osmosis (FO) process is an engineered osmotic process in which an high concentrated solution, termed a draw solution (DS), is used on one side of the semi-permeable membrane and the water to be treated is on the other side of the same membrane (Phuntsho et al., 2011). The general equation describing water transport in FO is as follow:

$$J_w = A.\Delta\pi$$

Where, Jw is the water flux, A is the water permeability constant of the membrane. Forward osmosis does not require hydraulic pressure therefore the less energy is required for the operation (Elimelech and Phillip, 2011). The absence of the hydraulic pressure reduce the severity of the membrane fouling compared to reverse osmosis where fouling is a major issue. Fouling in the FO process is observed to be physically reversible; hence, chemical cleaning may be only seldom required in the FO process (Lee et al., 2010; Mi and Elimelech, 2010; Zou et al., 2011). Depending on the properties of the membranes used, FO offers similar advantages to RO desalination in processing the rejection of a wide range of contaminants. FO is gaining process interest and has been studied for a large range of application in waste water treatment. It has been applied in complex industrial streams waste water treatment (Anderson, 1977, Coday et al., 2014, Zhang et al., 2014), for activated sludge treatment (Cornelissen et al., 2011), wastewater effluent from municipal sources treatment (Lutchmiah et al., 2011, Linares et al., 2013), Nuclear wastewaters treatment (Zhao et al., 2012), for sea water and brackish water desalination.

1.4.1   Draw solutions and reverse diffusion of draw solution solute

A draw solution (DS) is any aqueous solution which exhibits a high osmotic pressure. Its osmotic pressure should be higher than the feed solution osmotic pressure, to provide a drive force during the FO process. As described by the Van't Hoff equation, the osmotic pressure depends on the solute concentration, the number of species formed by dissociation in the solution, the molecular weight of the solute and the temperature of the solution. DS are generally classified as inorganic-based DS, organic-based DS and other compounds such as magnetic nanoparticles. The sub-classification includes electrolyte (ionic) solutions and non-electrolyte (non-ionic) solutions depending on whether the solution is made up of charged ions or neutral/non-charged solutes respectively (Phuntsho, 2011).

Inorganic based DS are mainly composed of electrolyte solutions, although non-electrolyte solutions are also possible. Numerous studies have used sodium chloride as the DS in a wide range of applications. The main reason that NaCl is used as the DS for many FO studies is that saline water is abundant on earth, making seawater a natural and cheap source of DS. Moreover, the thermodynamic properties of NaCl have been widely investigated, making it easier to study. Organic DS usually consists of non-electrolyte compounds; they have the potential to generate high osmotic pressure as they generally exhibit high solubility (Ng and Tang, 2006). Nanoparticle research is currently an area of

intense scientific interest due to a wide variety of biomedical applications such as biocatalysis and drug delivery.

The performance of the FO process also depends on the selection of suitable draw solutes because it is the main driving force in this process. Several parameters should be considered before the selection of an effective draw solution such as the diffusivity, the pH and the temperature. The main criterion is to assure that the draw solution has a high osmotic potential than the feed solution. The DS should have a low reverse leakage, be non-toxic and easily recoverable in the reconcentration system (Lutchmiah et al., 2014) and should exhibit minimized internal concentration polarization (ICP) in the FO processes (Zhao et al., 2012).

1.4.2   Membranes and concentration polarization

In forward osmosis the membrane is the part that allows the passage of solvent and retains the solutes. Any dense membrane can be used for the osmotic process (Cath et al., 2006). The semi-permeable membrane, usually made from polymeric materials, acts as a barrier that allows small molecules such as water to pass through while blocking larger molecules such as salts, sugars, starches, proteins, viruses, bacteria, and parasites (Xu et al., 2010). Different types of membranes were used for FO processes. Reverse osmosis membrane was used at the early stage of FO studies (Loeb et al., 1997, Cath et al., 2006), the researchers reported low fluxes even though the theoretical osmotic pressure gradient was very high when a DS containing very high concentration was used (Cath et al., 2006; Ng et al., 2006). The first FO membrane was developed by the Hydration Technologies Inc. (HTI) in the 1990s. It is an asymmetric cellulose triacetate (CTA) membranes presenting a thin overall thickness comprise ~50 µm and was widely used in several FO applications (McCutcheon et al., 2005, Zhao et al., 2012).

With the development of FO, asymmetric membranes are now used for FO application and are subject to internal concentration polarization between the two layers and to the external concentration polarization at the interface between the active layer and the solution in contact. Figure 2 (a) shows the illustration of the concentration polarization in an asymmetric membrane when the active layer of the membrane is placed against the feed solution termed the FO mode. The convective water flow drags solute from the bulk solution to the surface of the rejecting active layer. Water permeates this layer leaving the solute behind in higher concentrations called external concentration polarization. The draw solution is diluted within the support layer creating a phenomenon called internal concentration polarization (ICP). The driving force must therefore overcome this increased concentration in order for water flux to occur (McCutcheon and Elimelech, 2006, Mccutcheon and Elimelech, 2007). In Figure 2 (b) the membrane active layer of the membrane faces the DS termed as pressure retarded osmosis (PRO) mode. With this orientation, the salts are rejected by the membrane active layer, and their concentration in the support layer increase. The back diffusion of the concentrated salt on the membrane surface is restricted by the presence of the membrane support layer, which enhances the salt concentration. This phenomenon is known as concentrative ICP (Gray et al., 2006; McCutcheon and Elimelech, 2006, Phuntsho, 2011).
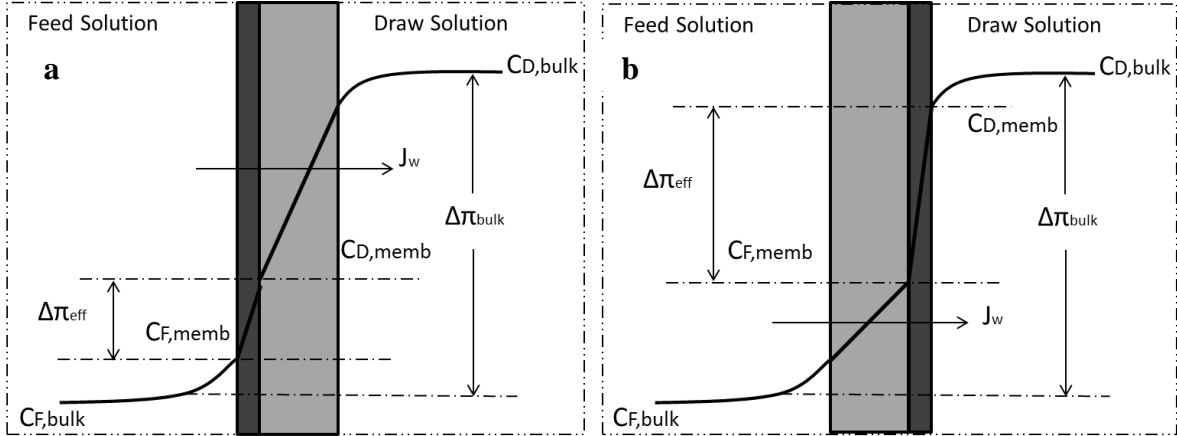
Figure 2 (a) Dilutive Internal Concentration Polarization, (b) Concentrative Internal Concentration Polarization

The CP phenomena are the primary causes of the lower-than-expected water flux because they lead to a reduction in the net driving force across the membrane. The effect of the ECP can be easily controlled in forward osmosis process by shear force. However the internal concentration polarization effect cannot be mitigated because it occurs within the membrane active and porous layer. The CTA in reviews studies have presented higher fluxes than RO membranes, a reduced internal concentration polarization (ICP) and presented to be resistant to chlorine, unsusceptible to adsorption of mineral, less sensitive to thermal chemical and biological degradation and hydrolysis in alkaline conditions (Lior, 2012, Mulder, 2012, Lutchmiah et al., 2014).

1.4.3 Forward osmosis in desalination and wastewater treatment process

Several studies have been done on sea water and brackish water desalination using forward osmosis process. With the development of FO Cellulose Triacetate and Thin Film Composite (TFC) membranes, other types of draw waters have been tested. A Bench-scale FO data demonstrates that the ammonia–carbon dioxide FO process with a recovery system is a viable desalination process. Salt rejections greater than 95% and fluxes as high as 25 L/m^2.H were achieved with a FO CTA membrane and a calculated driving force of more than 200 bar (Cath et al., 2006). Sherub et al., 2011 explored a new concept of desalination of saline water using fertilizer as draw solution followed by a direct application of the diluted fertilizer. They achieved fluxes between 1.06 L/m/H and 0.49 L/m/H using a cellulose acetate membrane embedded in a polyester woven mesh. However the rejection rates of salt and the effect of the pH of the draw solution on the membrane performance are still unknown.

The concentration of urine presents some challenges owing to urea and ammonia loss that are also related to urine pH. Zhang et al. (2014) have tested the application of FO process

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for synthetic fresh urine, hydrolyzed stale urine and treated stale urine dewatering. They achieved relatively high rejection of phosphate (97 - 99%), potassium (79 - 97%) and ammonium (31 - 91%) and water flux around $9 - 18$ L/m^2/H. They have also reported low rejection < 50 % of urea molecules. The experimental flux achieved was lower than the calculated one which leads to them to suggest further researches about the system condition which affect water flux. Therefore the phenomena affecting the performances remain unclear especially when the FO system is operated under high osmotic pressure conditions.

1.5 RESEARCH OBJECTIVES

The general objective of the research is design a forward osmosis unit for concentrated urine fertilizer production. The general concept of the system where urine will be collected at household level via urine diverting toilet, pass in the FO unit were it will be concentrated before its transportation and application as a liquid fertilizer.

To reach the general goal, the research was divided in three main parts with the objectives:

- To understand the phenomena occurring during urine concentration by forward osmosis process. Experiments were carried out 1) to assess the water flux performances of real and synthetic hydrolyzed urine, 2) to evaluate the solute diffusion, 3) to assess the adequacy of the solute activity for the calculation of water flux, and 4) to identify the major solutes for water flux estimation during the volume reduction process.

- To develop a numerical model for water flux and nutrients concentration estimation taking account the phenomena influencing the performances. To reach this objective the advection, diffusion theory was used to establish equations describing the concentration inside the membrane and in the bulk solutions.

- To propose a design of a FO unit to be implemented for hydrolyzed urine concentration. The developed model was used to evaluate the required membrane area and volume of draw solution to concentrate hydrolyzed urine to 1/5 of its initial volume and recover the nutrients.

1.6 REFERENCES

Anderson, D.K., 1977. Concentration of dilute industrial wastes by direct osmosis. University of Rhode Island.

Cath, T.Y., Childress, A.E., Elimelech, M., 2006. Forward osmosis: Principles, applications, and recent developments. J. Membr. Sci. 281, 70–87.

Coday, B.D., Xu, P., Beaudry, E.G., Herron, J., Lampi, K., Hancock, N.T., Cath, T.Y., 2014. The sweet spot of forward osmosis: treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. Desalination 333, 23–35.

Cordell, D., 2008. The Story of Phosphorus: missing global governance of a critical resource. Paper prepared for SENSE Earth Systems Governance, Amsterdam, 24th-1stAugust.

Cornelissen, E.R., Harmsen, D., Beerendonk, E.F., Qin, J.J., Oo, H., De Korte, K.F., Kappelhof, J., 2011. The innovative osmotic membrane bioreactor (OMBR) for reuse of wastewater. Water Sci. Technol. 63, 1557–1565.

Elimelech, M. and W. A. Phillip., 2011. The Future of Seawater Desalination: Energy, Technology, and the Environment. Science 333(6043): 712-717.

Fittschen, I., Hahn, H.H., 1998. Human urine-water pollutant or possible resource? Water Sci. Technol. 38, 9–16.

Gulyas, H., Bruhn, P., Furmanska, M., Hartrampf, K., Kot, K., Luttenberg, B., Mahmood, Z., Stelmaszewska, K., Otterpohl, R., 2004. Freeze concentration for enrichment of nutrients in yellow water from no-mix toilets. Water Sci. Technol. 50, 61–68.

Hamdan, M., Sharif, A.O., Derwish, G., Al-Aibi, S., Altaee, A., 2015. Draw solutions for Forward Osmosis process: Osmotic pressure of binary and ternary aqueous solutions of magnesium chloride, sodium chloride, sucrose and maltose. J. Food Eng. 155, 10–15. doi:10.1016/j.jfoodeng.2015.01.010

Hellström, D., Johansson, E., Grennberg, K., 1999. Storage of human urine: acidification as a method to inhibit decomposition of urea. Ecol. Eng. 12, 253–269.

Jenssen, P.D., Etnier, C., 1996. Ecological engineering for wastewater and organic waste treatment in urban areas: An overview, in: Conference" Water Saving Strategies in Urban Renewal", European Academy of the Urban Environment, Wien 1-2 February 1996.

Jönsson, H., Vinnera as, B., Höglund, C., Stenström, T.A., Dalhammar, G., Kirchmann, H., 2000. Recycling source separated human urine. VA-Forsk Rep. 1.

Kabore, S., Ito, R., Funamizu, N., 2016. Effect of Urea/Formaldehyde ratio on the production process of methylene urea from human urine, Journal of Water and Environmental Technology Vol.14 (2) 47–56

Karak, T., Bhattacharyya, P., 2011. Human urine as a source of alternative natural fertilizer in agriculture: A flight of fancy or an achievable reality. Resour. Conserv. Recycl. 55, 400–408.

Kirchmann, H., Pettersson, S., 1994. Human urine - Chemical composition and fertilizer use efficiency. Fertil. Res. 40, 149–154. doi:10.1007/BF00750100

Larsen, T.A., Gujer, W., 1996. Separate management of anthropogenic nutrient solutions (human urine). Water Sci. Technol. 34, 87–94.

Lee, S., C. Boo, M. Elimelech and S. Hong., 2010. Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). Journal of Membrane Science 365(1-2): 34-39

Linares, R.V., Li, Z., Abu-Ghdaib, M., Wei, C.-H., Amy, G., Vrouwenvelder, J.S., 2013. Water harvesting from municipal wastewater via osmotic gradient: an evaluation of process performance. J. Membr. Sci. 447, 50–56.

Lind, B.-B., Ban, Z., Bydén, S., 2001a. Volume reduction and concentration of nutrients in human urine. Ecol. Eng. 16, 561–566. doi:10.1016/S0925-8574(00)00107-5

Lior, N., 2012. Advances in water desalination. John Wiley & Sons.

Liu, Z., Zhao, Q., Wang, K., Lee, D., Qiu, W., Wang, J., 2008. Urea hydrolysis and recovery of nitrogen and phosphorous as MAP from stale human urine. J. Environ. Sci. 20, 1018–1024. doi:10.1016/S1001-0742(08)62202-0

Loeb, S., L. Titelman, E. Korngold and J. Freiman., 1997. Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane. Journal of Membrane Science 129(2): 243-249.

Lopez ZMA, Funamizu N., Takakuwa T., 2000. Onsite wastewater differential treatment system: modelling approach. Water Science Technology Vol. 46 No 6-7 pp317-324.

Lutchmiah, K., Cornelissen, E.R., Harmsen, D.J., Post, J.W., Lampi, K., Ramaekers, H., Rietveld, L.C., Roest, K., 2011. Water recovery from sewage using forward osmosis. Water Sci. Technol. 64, 1443–1449.

Lutchmiah, K., Verliefde, A.R.D., Roest, K., Rietveld, L.C., Cornelissen, E.R., 2014. Forward osmosis for application in wastewater treatment: A review. Water Res. 58,

179–197. doi:10.1016/j.watres.2014.03.045

Maurer, M., Pronk, W., Larsen, T.A., 2006. Treatment processes for source-separated urine. Water Res. 40, 3151–3166.

McCutcheon, J.R., Elimelech, M., 2006. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. J. Membr. Sci. 284, 237–247.

Mccutcheon, J.R., Elimelech, M., 2007. Modeling water flux in forward osmosis: Implications for improved membrane design. AIChE J. 53, 1736–1744. doi:10.1002/aic.11197

McCutcheon, J.R., McGinnis, R.L., Elimelech, M., 2005. A novel ammonia—carbon dioxide forward (direct) osmosis desalination process. Desalination 174, 1–11.

Mi, B. and M. Elimelech., 2010. Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents. Journal of Membrane Science 348(1-2): 337-345.

Mobley, H.L., Hausinger, R.P., 1989. Microbial ureases: significance, regulation, and molecular characterization. Microbiol. Rev. 53, 85–108.

Mulder, J., 2012. Basic principles of membrane technology. Springer Science & Business Media.

Ng, H. Y., W. Tang and W. S. Wong., 2006. Performance of Forward (Direct) Osmosis Process: Membrane Structure and Transport Phenomenon. Environmental Science & Technology 40(7): 2408-2413

Pahore, M.M., Ito, R., Funamizu, N., 2011. Performance evaluation of an on-site volume reduction system with synthetic urine using a water transport model. Environ. Technol. 32, 953–970.

Phuntsho, S., Lotfi, F., Hong, S., Shaffer, D.L., Elimelech, M., Shon, H.K., 2014. Membrane scaling and flux decline during fertiliser-drawn forward osmosis desalination of brackish groundwater. Water Res. 57, 172–182.

Phuntsho, S., Shon, H.K., Hong, S., Lee, S., Vigneswaran, S., 2011. A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: evaluating the performance of fertilizer draw solutions. J. Membr. Sci. 375, 172–181.

Sen, M., Hijikata, N., Ushijima, K., Funamizu, N., 2013 b. Effects of Continuous application of extra human urine volume on plant and soil. International Journal of Agricultural Science and Research, 3, 75-90

Snoeyink, V. L. and D. Jenkins, 1980. Water chemistry. John Wiley & Sons.

Thörneby, L., Persson, K., Träg\a ardh, G., 1999. Treatment of liquid effluents from dairy cattle and pigs using reverse osmosis. J. Agric. Eng. Res. 73, 159–170.

Udert, K.M., Fux, C., Münster, M., Larsen, T.A., Siegrist, H., Gujer, W., 2003. Nitrification and autotrophic denitrification of source-separated urine. Water Sci. Technol. 48, 119–130.

Xu, Y., X. Peng, C. Y. Tang, Q. S. Fu and S. Nie., 2010. Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis 335 performance in a spiral wound module. Journal of Membrane Science 348(1-2): 298-309.

Zhang, S., Wang, P., Fu, X., Chung, T.-S., 2014. Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD). Water Res. 52, 112–121.

Zhao, S., Zou, L., Tang, C.Y., Mulcahy, D., 2012. Recent developments in forward osmosis: opportunities and challenges. J. Membr. Sci. 396, 1–21.

Zhao, Z.-P., Xu, L., Shang, X., Chen, K., 2013. Water regeneration from human urine by vacuum membrane distillation and analysis of membrane fouling characteristics. Sep. Purif. Technol. 118, 369–376.

Zou, S., Y. Gu, D. Xiao and C. Y. Tang., 2011. The role of physical and chemical parameters on forward osmosis membrane fouling during algae separation. Journal of Membrane Science 366(1-2): 356-362

CHAPTER 2
ESTIMATION OF WATER FLUX AND SOLUTE MOVEMENT DURING THE CONCENTRATION PROCESS OF HYDROLYZED URINE BY FORWARD OSMOSIS

2.1 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 (FAO, 2015). A recycling system of nutrients should be considered to manage the crisis of the price volatility by decreasing the fertilizer costs. Some reports showed that urine can be used as a fertilizer for growing crops (EcoSanRes, 2016; WHO, 2006), because it is rich in nutrients which occupies 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 (EcoSanRes, 2004). Our previous case study in Pakistan (Pahore et al., 2010) showed that 10 m^3/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 (Pahore et al., 2010), freeze drying (Lind et al., 2001), electro dialysis (Pronk et al., 2006), and reverse osmosis (Ek et al., 2006). However, all these technics are energy intensive processes resulting in high cost. We proposed forward osmosis (FO) method for a substantial urine volume reduction and 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 (Lee et al., 2010; Cath et al., 2006)). It is adopted in the applications of desalination, food processing, nuclear wastewater treatment, landfill leachate treatment and emerging drinks among others (Lutchmiah et al., 2014; Zhang et al., 2014; Zhao et al., 2012).

The application of FO on urine concentration is quite recent. Urine can easily hydrolyze and increase the concentration of ammonia (NH_3) and inorganic carbon (IC) resulting in high osmotic pressure. Zhang et al. (2014) 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 hydrolyzed 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 concentration. These are enough high pressures compared with 2 MPa of sea water for desalination (Post et al., 2007). 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 (Yong et al., 2012). 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 hydrolyzed urine (RHU) contains urea, inorganic ions, organic matter, such as creatinine, amino acids and carbohydrates (Udert et al., 2006), although most of the organic matter compounds are unknown. Synthetic hydrolyzed 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.

2.2 MATERIAL AND METHODS

2.2.1 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 (2007) and is presented in Table 2.a. All agents were special grade from Wako Pure Chemical Industries, 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 hydrolyzed by the addition of Jack bean urease (1st grade, Wako Pure Chemical Industries, Japan) and stored for 24 hours at room temperature. The solute concentrations of RHU and SHU are summarized in Table 2.b. 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 (special grade, Wako Pure Chemical Industries, Japan) in deionized water.

Table 1 Experimental conditions

	Feed solution	Draw solution	Membrane orientation
Run 1	Synthetic hydrolyzed urine	(NaCl) 2M, 3M, 4M, 5M	(CTA) Active layer facing the feed solution
Run 2	Real hydrolyzed urine	(NaCl) 4M, 5M	
Run 3	Pure water	NH_4Cl (0.85M, pH 5.6) NH_4Cl (1.4 M, pH 9.4)	(CTA) Active layer facing the draw solution

Table 2 (a) Compositions of synthetic urine

	Component	Concentration (g/L)
1.	Calcium Chloride ($CaCl_2.H_2O$)	0.65
2.	Magnesium Chloride ($MgCl_2 .6H_2O$)	0.65
3.	Sodium Chloride (NaCl)	4.60
4.	Sodium Sulfate (Na_2SO_4)	2.30
5.	Tri-Sodium Citrate ($C_6H_5Na_3O_7.2H_2O$)	0.65
6.	Sodium Oxalate ($Na_2(COO)_2$)	0.02
7.	Potassium Dihydrogen Phosphate ($KH_2 PO_4$)	4.20
8.	Potassium Chloride (KCl)	1.60
9.	Ammonium Chloride (NH_4Cl)	1.00
10.	Urea (NH_2CONH_2)	25
11	Creatinine ($C_4H_7N_3O$)	1.10

Table 2 (b) Solute concentrations of the real and synthetic hydrolyzed urine

Solute	Synthetic fresh urine (mol/L)	SHU (mol/L)	RHU(mol/L)
Urea-N	0.804	-	-
Ammonium-N	0.02	0.82	0.73
Phosphate	0.03	0.02	0.01
Potassium	0.05	0.05	0.04
Sodium	0.14	0.14	0.21
Chloride	0.14	0.11	0.16
Sulphate	0.02	0.02	0.01
Calcium	0.01	-	-
Magnesium	0.01	0.00	0.00
Carbonate	0.00	0.48	0.37
TC	1.10	1.08	1.73
pH	5.6	9.43	9.60

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_4Cl) solution and 1.4 mol/L NH_3/NH_4Cl buffer solution with pH of 5.6 and 9.4, respectively, were prepared from NH_4Cl (special grade, Wako Pure Chemical Industries, Japan) and concentrated NH_3 solution (special grade, Wako Pure Chemical Industries, Japan).

2.2.2 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 asymmetric cellulose triacetate membrane (CTA-ES, Hydration Technology Innovations, USA), while the SEM images of the surface and cross section are shown in Figure 2. The membrane is used by researchers in FO applications for modelling and parameter estimation experiments (Ek et al., 2006; Lee et al., 2010; Lutchmiah et al., 2014; Yong et al., 2012). The cross section of the channel was 0.2 cm^2 and the effective filtration area was 98.27 cm^2. 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, Technical Advantages Company, USA) connected to a computer with a data collection software (WINCT, A&D Company, Japan). The membrane was soaked in pure water for 5 hours at room temperature before each test.
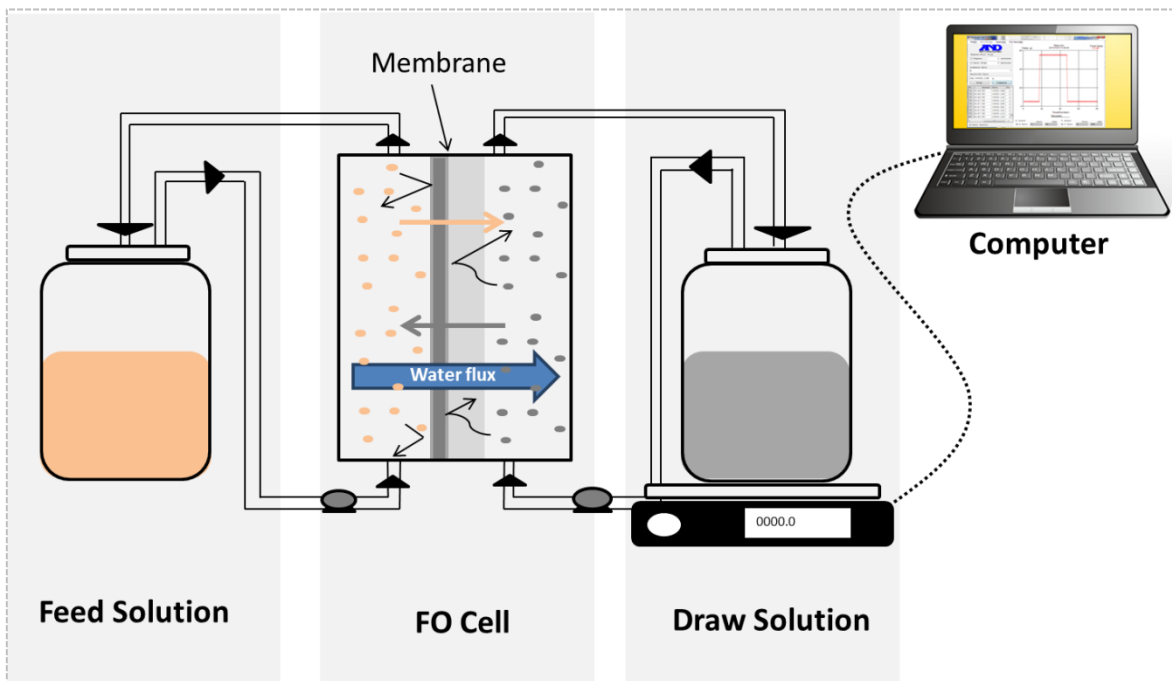
Figure 1 Forward osmosis experimental setup
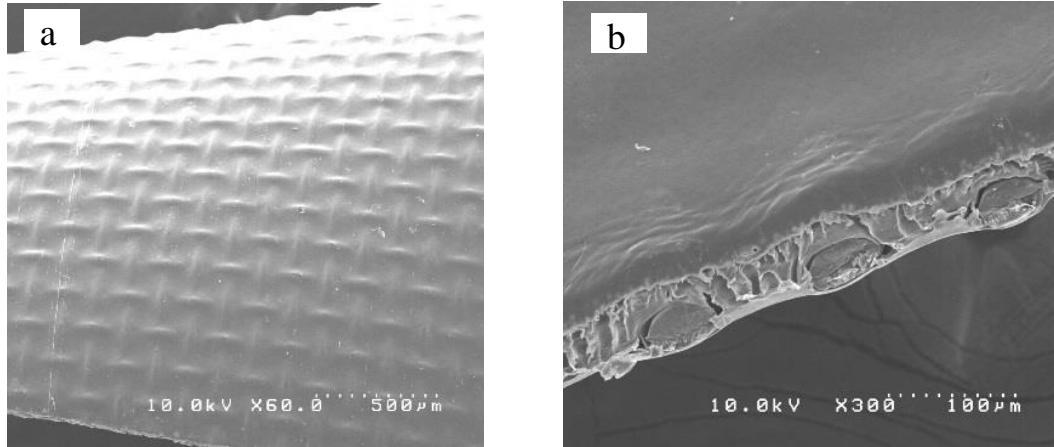
Figure 2 SEM images of the CTA membrane on (a) surface at the support layer side and on (b) the cross section

The experiments in Run 1 and 2 were carried out during 7 hours, while that for Run 3 was stopped at 3 hours. The concentrations of K, sodium (Na), and chloride (Cl) were measured with an ion chromatography system (ICS-90, DIONEX Corporation, USA). NH_3 and phosphate (PO_4) were measured with USEPA HACH Nessler method 8038 and HACH PhosVer (ascorbic acid) method 8048 with a spectrophotometer (DR-2800, HACH, USA). The inorganic carbon (IC) and total organic carbon (TOC) were measured by a TOC analyzer (TOC-9000A, Shimadzu, Japan).

2.2.3   Activity calculation

The freezing point depression of a NaCl solution and a SHU were measured with a DSC analyzer (DSC-20, Shimadzu, Japan) to verify the activity calculation by equilibrium solver Phreeqc (Phreeqc, 2016). 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)

$$T_f = K_f A_T \qquad\qquad (1)$$

where K_f is the cryoscopic constant (K kg/mol) whose value is 1.853 for water (Robinson and Stokes, 1965). 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 (Udert et al., 2003). The equations involved in the calculation of the activity coefficients are presented and explained in (Appelo et al., 2014) while a table of typical data input in Phreeqc is shown in Table S1 in the supplementary materials.

2.2.4 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),

$$J_{w,exp} = \frac{V_{d,t+\Delta t} - V_{d,t}}{S\Delta t} \qquad (2)$$

where t and Δt are time and time difference (s), respectively; $V_{d,t}$ and $V_{d,t+\Delta t}$ are the volume of DS at t and $t + \Delta t$ (m^3), respectively; and S is the filtration area (m^2). The volume concentration level, C_l (-), and concentration factor of each solute, C_f (-), were calculated with equations (3) and (4).

$$C_l = \frac{V_{F,ini}}{V_{F,t}} \qquad (3)$$

$$C_f = \frac{C_{F,t}}{C_{F,ini}} \qquad (4)$$

where $V_{F,ini}$ and $V_{F,t}$ are the FS volumes at initial state and at 7 hours (m^3), respectively, while $C_{F,ini}$ and $C_{F,t}$ 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),

$$J_w = K\Delta\pi \qquad (5)$$

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),

$$\Delta\pi = RT\left(\sum_i C_{i,\,DS} - \sum_i C_{i,\,FS}\right) \qquad (6)$$

$$\Delta\pi = RT\left(\sum_i A_{i,\,DS} - \sum_i A_{i,\,FS}\right) \qquad (7)$$

where $C_{i,\,DS}$ and $C_{i,\,FS}$ are the molar concentrations of the solute i in DS and FS (mol/kg-water), respectively; $A_{i,\,DS}$ and $A_{i,\,FS}$ 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).

2.3 RESULTS AND DISCUSSION

2.3.1   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 (Figure 4 (a)). The maximum volume reduction levels 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 level 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 level which indicated a high diffusion of the urine nitrogen. The nutrient content of urine was therefore reduced to 60%, 88% and 90% of its initial NH_3, PO_4 and K content, respectively. An optimization of the FO process is necessary to improve the nutrient recovery from hydrolyzed urine.
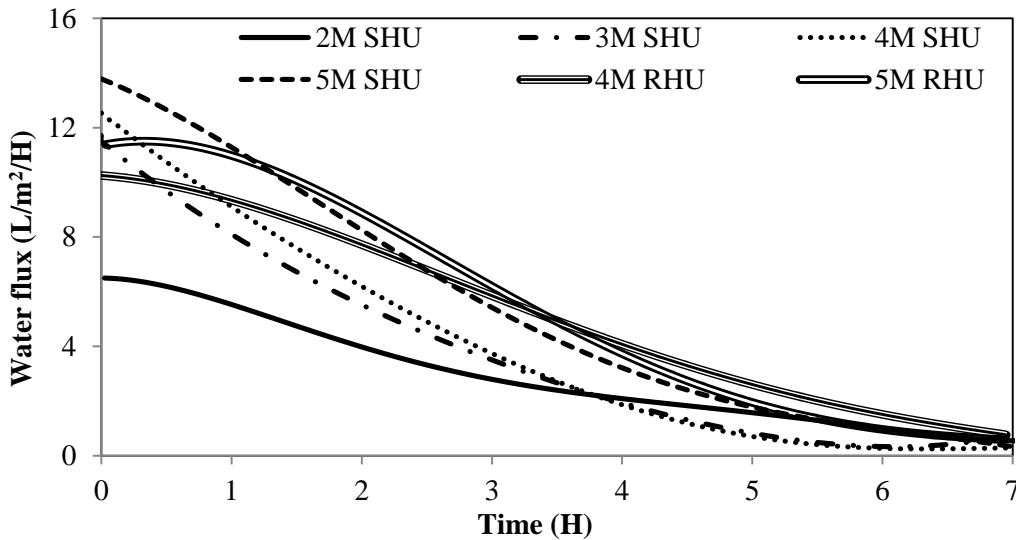
Figure 3 Time course of water flux during concentration process of SHU and RHU
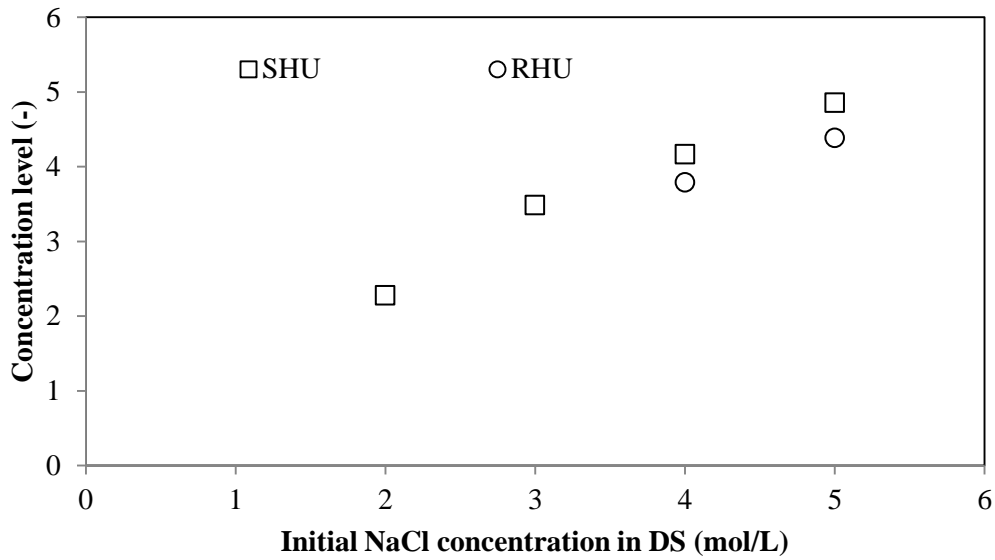
Figure 4 (a) SHU and RHU volume concentration factors versus the initial NaCl concentration
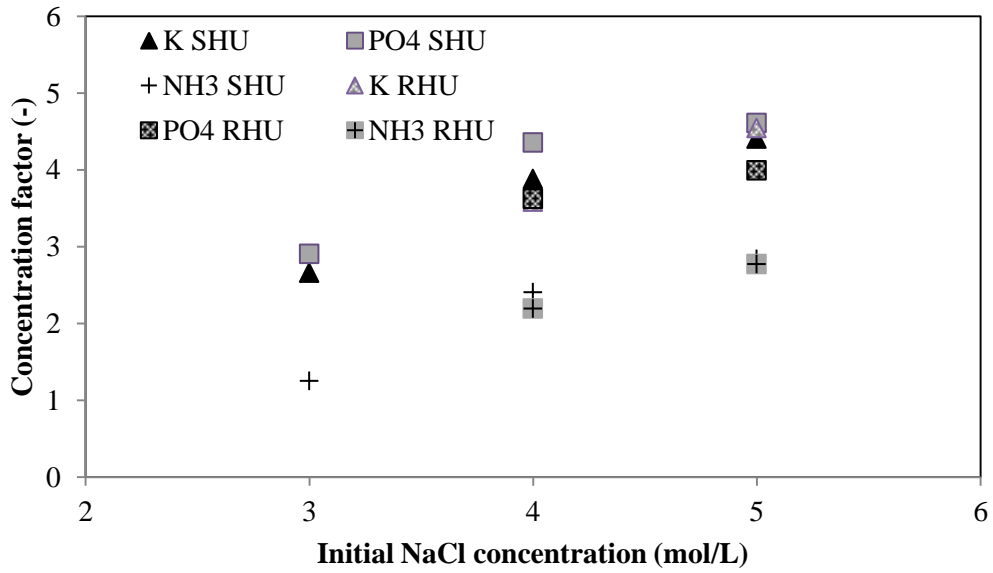
Figure 4 (b) SHU and RHU nutrient concentration factors versus the initial NaCl concentration

2.3.2 Solute diffusion through the membrane

The mass balances of the solutes are illustrated in Figure 5. The solutes diffused similarly for both RHU and SHU, and were categorized into 3 groups: 1) low diffusion of Na, Cl, PO_4 and TOC; 2) middle diffusion of K; and 3) high diffusion of NH_3 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 PO_4 superior to 90% and 80-90% for K ions. These values are similar to those obtained in other FO experiments (Zhang et al., 2014; Xie et al., 2013; Xue et al., 2015). Nearly 30% of the IC passed through the membrane. As for the TOC, low diffusion occurred in both RHU and SHU. Liu et al., 2016 observed a TOC rejection of 98% in the case of fresh urine (pH = 6). About 60 to 65% of the NH_3 remained in the FS and is in agreement with the reports (Zhang et al., 2014; Xie et al., 2014). In FO concentration process, size exclusion and electrostatic effects have a substantial role in controlling the forward solute transport through the membrane (Xie et al., 2013; Hancock and Cath, 2009). 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 PO_4, Na and Cl.
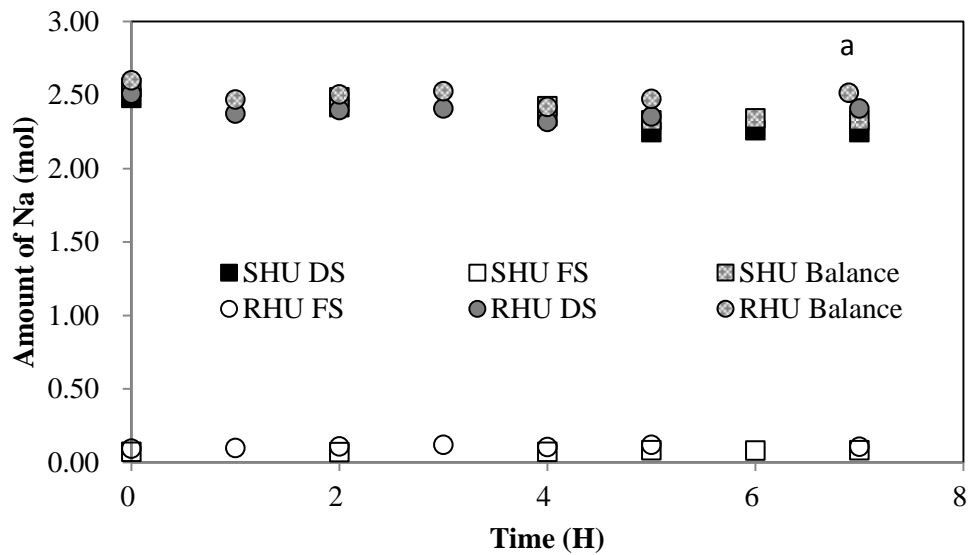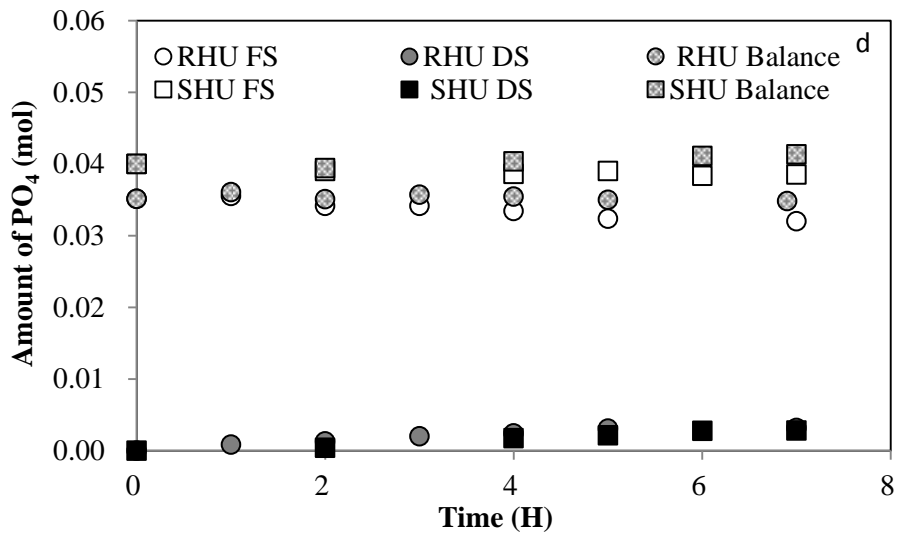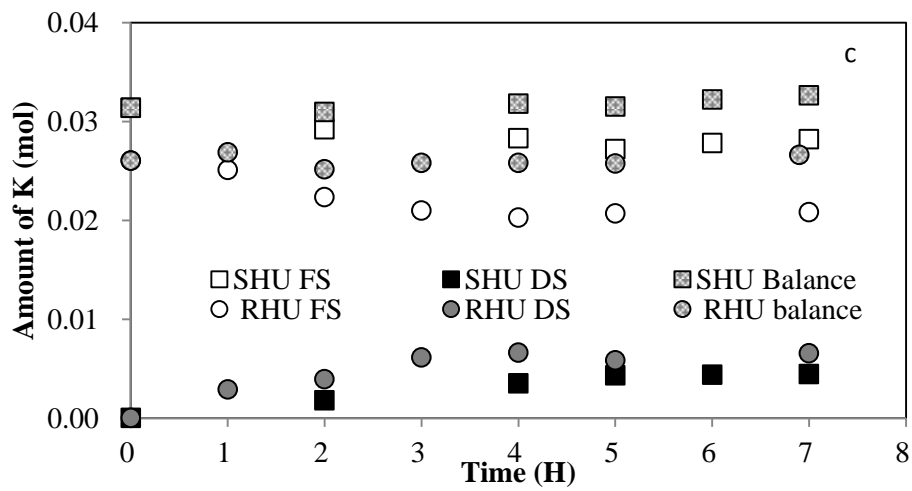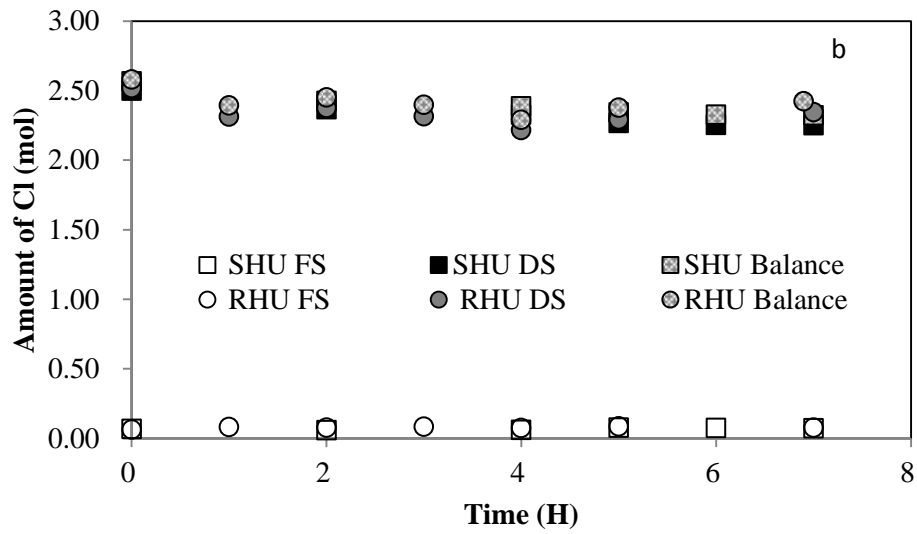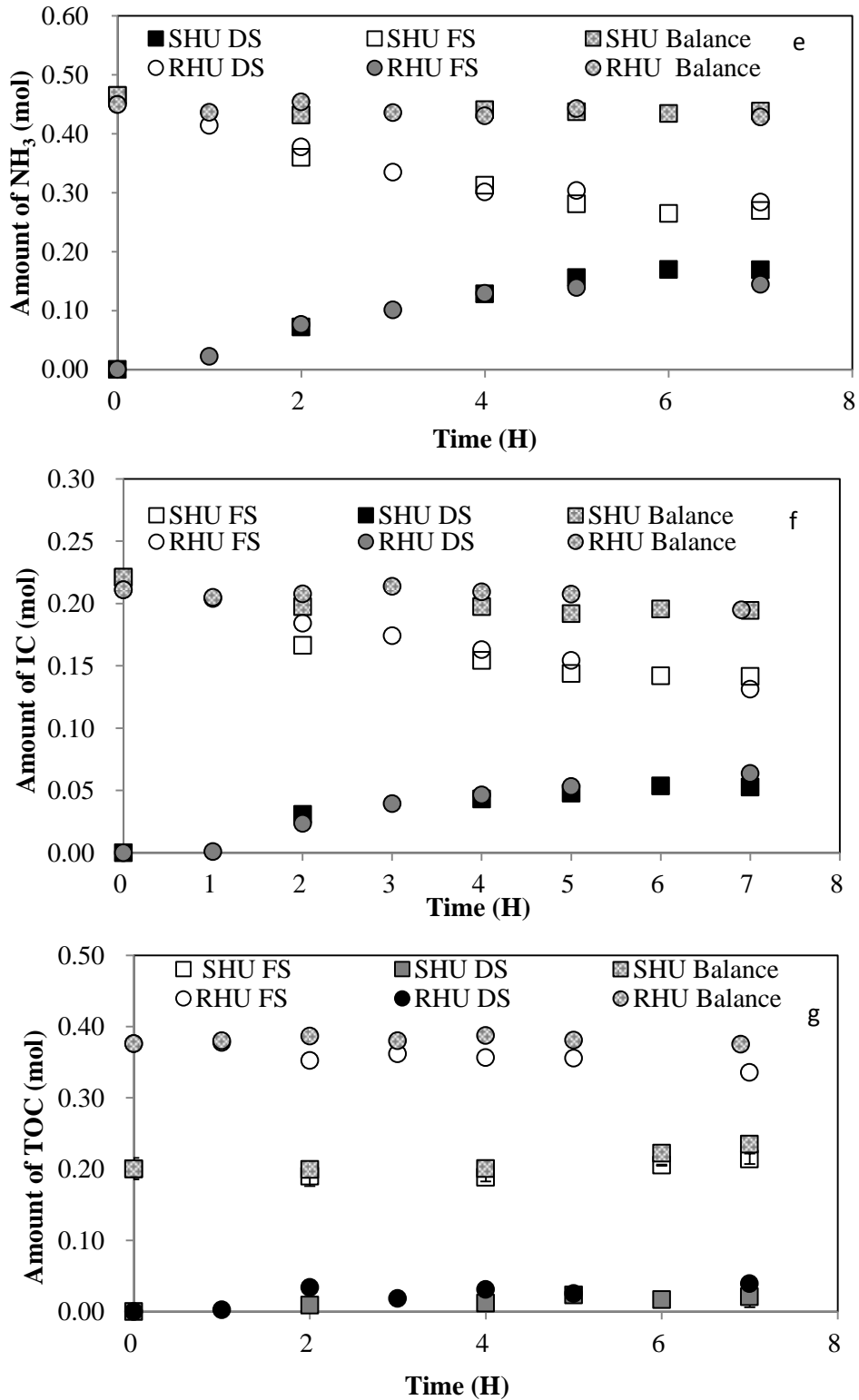
Figure 5 Amount of solute in feed and draw solution for the case of RHU and SHU used with 5mol/L NaCl solution: (a) Na, (b) Cl, (c) K, (d) PO$_4$, (e) NH$_3$, (f) IC, (g) TOC

Figure 6 focuses on the diffusion of NH_3 during concentration process of NH_4Cl solution by FO at pH 5.6 and 9.4. The total ammonia is partitioned between the weak acid ammonium (NH_4) and the molecule NH_3 by chemical equilibrium (Masse et al., 2007). The increase in the NH_3 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 (Cancino-Madariaga et al., 2011) and is linked to the different diffusivity of the species. NH_4 with low diffusivity and NH_3 with higher diffusivity through the membrane are dominant at low and high pH, respectively. This is because the membrane let NH_3, which has similar chemical properties to H_2O molecule on molecule size and polarity, pass through the membrane.
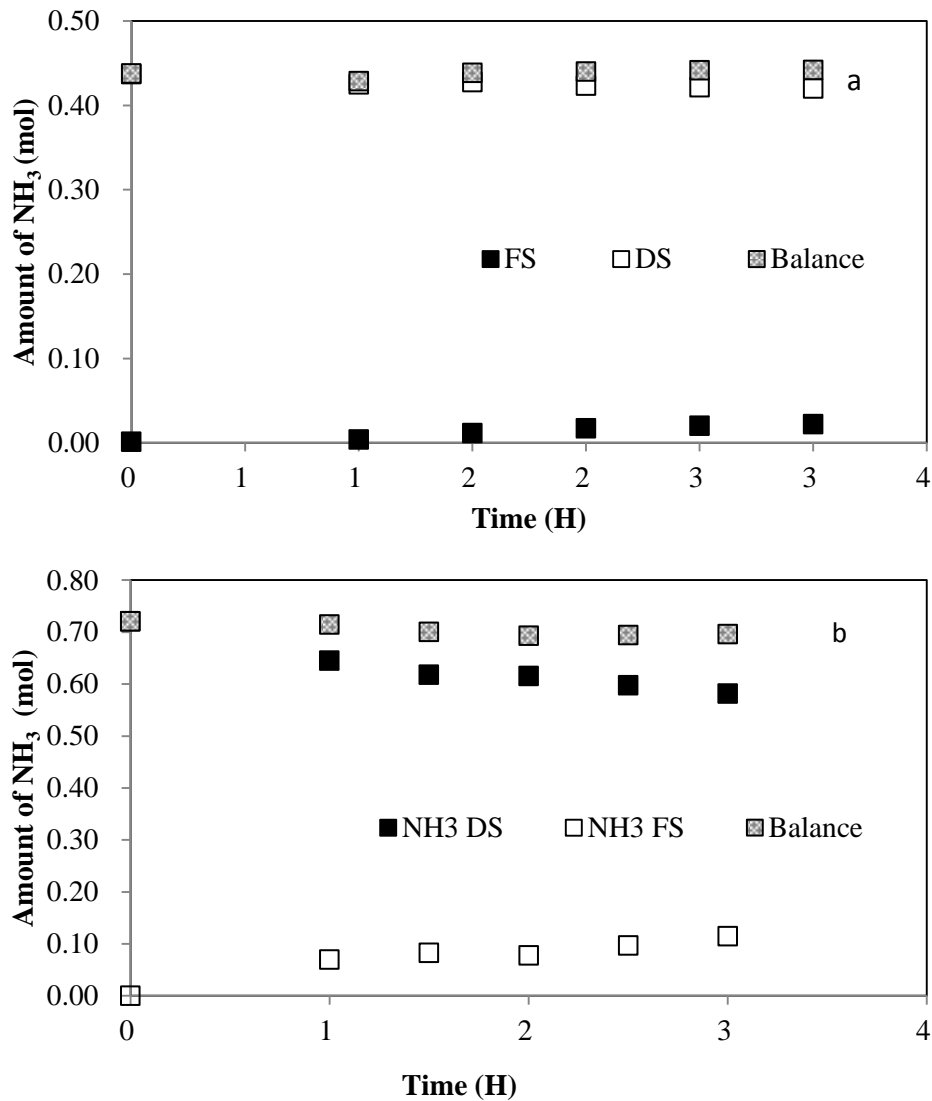
Figure 6 (a) Mass balance of ammonia for pH 5.6, (b) Mass balance of ammonia for pH 9.4

2.3.3   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.
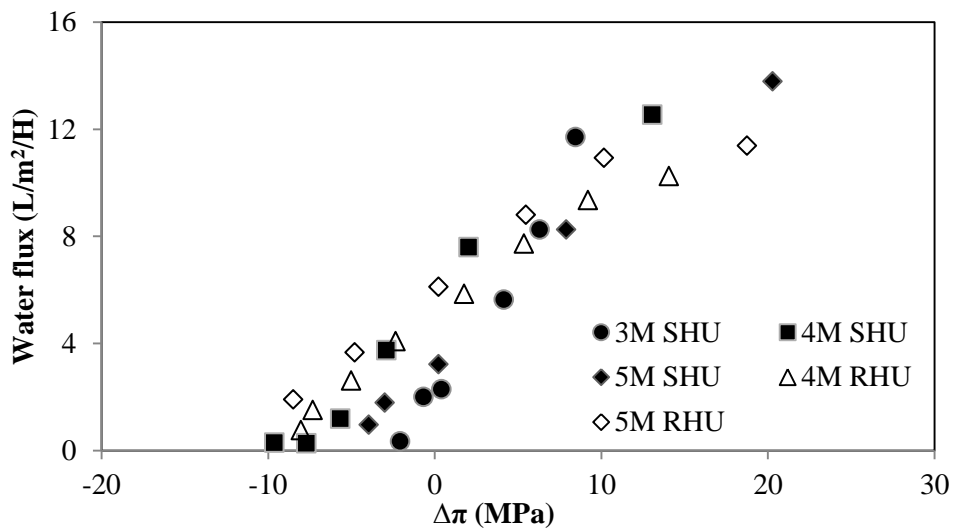
Figure 7 Relationship between water flux and osmotic pressure difference calculated by Equation. (6)

The software Phreeqc was used to calculate the activities of the inorganic solutes (Na, Cl, K, PO_4, NH_3, 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 measurements with the freezing point depression method, to confirm it can calculate the activities of solutes in non-ideal solutions. The results are presented in Figure S1 in the supplementary materials.
Figure 8 shows the relationship between the experimental water flux and the osmotic pressure estimated by equation (7). The relationship between water flux and the osmotic pressure is linear for pressure lower than 15 MPa and start decreasing with high pressure. That might be linked to the effect of the Internal concentration polarization occurring within the support layer of the CTA membrane and reduce the osmotic pressure difference. 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 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.
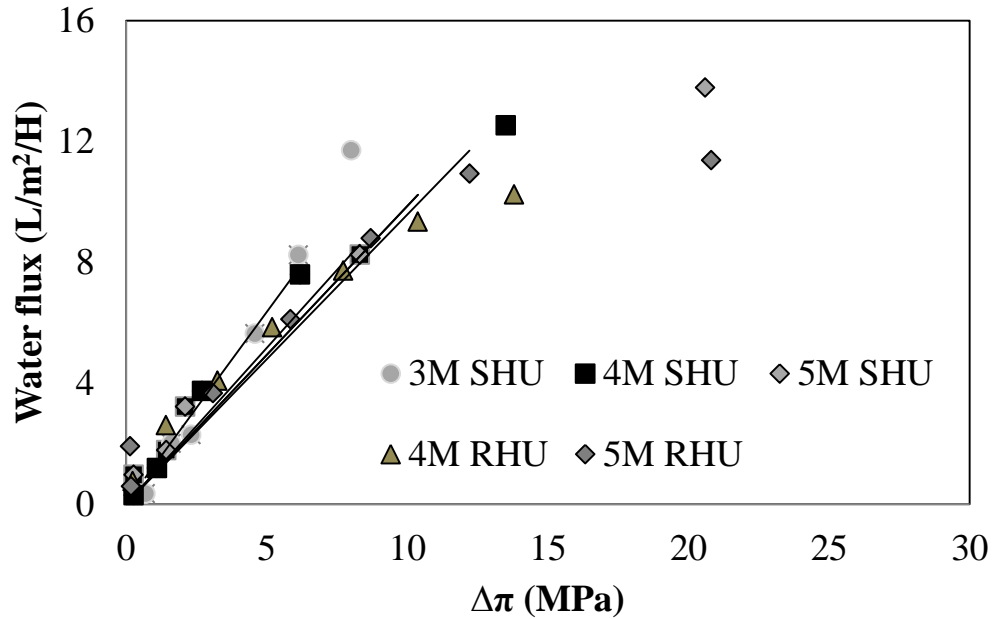
Figure 8 Relationship between water flux and osmotic pressure difference calculated by Equation (7)

2.4 CONCLUSIONS

The volume reduction experiments of synthetic and real hydrolyzed urine by FO process with cellulose triacetate membrane were carried out to assess the concentration performances, assess solute diffusion, analyze 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 synthetic and real hydrolyzed urine 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 real hydrolyzed urine had a negligible effect on the osmotic pressure variation; therefore, inorganic solutes have major effects on the flux calculation.

2.5 REFERENCES

Appelo, C. A. J., Parkhurst, D. L., and Post, V. E. A.: Equations for calculating hydrogeochemical reactions of minerals and gases such as CO_2 at high pressures and temperatures. Geochim. Cosmochim. Acta, 125, 49–67, 2014.

Cancino-Madariaga, B., Hurtado, C. F., and Ruby, R.: Effect of pressure and pH in ammonium retention for nanofiltration and reverse osmosis membranes to be used in recirculation aquaculture systems (RAS). Aquac. Eng., 45(3), 103–108, 2011.

Cath, T. Y., Childress, A. E., and Elimelech, M.: Forward osmosis: Principles, applications, and recent developments. J. Membr. Sci., 281(1–2), 70–87, 2006.

EcoSanRes Programme: Guidelines on the Safe Use of Urine and Faeces in Ecological Sanitation Systems, 2004. http: //www.ecosan.at/ssp. [Accessed: 19 Aug 2016].

EcoSanRes Programme: Use of Urine issue 3, 2004. http://www.ecosan.at/ssp/issue-03-use-of-urine. [Accessed: 19 Aug 2016].

Ek, M., Bergström, R., Bjurhem, J.-E., Björlenius, B., Hellström, D.: Concentration of nutrients from urine and reject water from anaerobically digested sludge. J. Water Sci. Technol., 54(11–12), 437– 444, 2006.

Food and Agriculture Organization of the United Nations: The State of Food Insecurity in the World, 2015.

Hancock, N. T. and Cath, T. Y.: Solute coupled diffusion in osmotically driven membrane processes. Environ. Sci. Technol, 43(17), 6769–6775, 2009.

Lee, S., Boo, C., Elimelech, M., and Hong, S.: Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). J. Membr. Sci., 365(1), 34–39, 2010.

Lind, B.-B., Ban, Z., Bydén, S.: Volume reduction and concentration of nutrients in human urine. J. Ecol. Eng., 16(4), 561–566, 2001.

Liu, Q., Liu, C., Zhao, L., Ma, W., Liu, H., and Ma, J.: Integrated forward osmosis-membrane distillation process for human urine treatment. Water Res., 91, 45–54, 2016.

Lutchmiah, K., Verliefde, A. R. D., Roest, K., Rietveld, L. C., and Cornelissen, E. R.: Forward osmosis for application in wastewater treatment: A review. J. Water Res.. 58, 179– 197, 2014.

Masse, L., Massé, D. I., and Pellerin, Y.: The use of membranes for the treatment of manure: a critical literature review. Biosyst. Eng., 98(4), 371–380, 2007.

Pahore, M. M., Ito, R., Funamizu, N.: Rational design of an onsite volume reduction system for source separated urine. J. Environ. Technol., 31(4), 399–408, 2010.

Pahore,M. M., Ito, R., Funamizu, N.: Performance evaluation of an on-site volume reduction system with synthetic urine using a water transport model. J. Environ. Technol., 32(9), 953–970, 2011.

PHREEQC: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.[Accessed: 22 Aug 2016].

Post, J. W., Veerman, J., Hameers, H.V.M., Euverink,G.J.W. Metz, S.J., Nymeijer, K., Buisman, C.J.N.: Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis. J. Membr. Sci., 288(1–2), 218–230, 2007.

Pronk, W., Biebow, M., Boller, M.: Treatment of source-separated urine by a combination of bipolar electrodialysis and a gas transfer membrane. J. Water Sci. Technol., 53(3), 139–146, 2006.

Robinson, R. A. and Stokes, R. H.: Electrolyte Solutions (2nd revised edn.) Butterworths. London, 1965.

Udert, K. M., Larsen, T. A. and Gujer, W.: Fate of major compounds in source separated urine. J. Water Science and Technology, 54 (11-12), 413-420, 2006

Udert, K. M., Larsen, T. A., M, Biebow, Gujer, W.: Urea hydrolysis and precipitation dynamics in a urine-collecting system. J. Water Res., 37 (11), 2571–2582, 2003.

Wilsenach, J. A., Schuurbiers, C. A. H., van Loosdrecht, M. C. M.: Phosphate and potassium recovery from source separated urine through struvite precipitation. J. Water Res., 41(2), 458–466, 2007.

World Health Organization: Guidelines for the Safe Use of Wastewater, Excreta and Greywater, 2006.

Xie, M. Nghiem, L. D., Price, W. E., and Elimelech, M.: Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–membrane distillation process. Environ. Sci. Technol. Lett., 1(2), 191–195, 2014.

Xie, M., Nghiem, L. D., Price, W. E., and M. Elimelech: A forward osmosis–membrane distillation hybrid process for direct sewer mining: system performance and limitations. Environ. Sci. Technol., 47(23), 13486–13493, 2013.

Xue, W., Tobino, T., Nakajima, F., and Yamamoto, K.: Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: Effect of membrane properties and feed solution chemistry. Water Res., 69, 120–130, 2015.

Yong, J. S., Phillip, W. A., and Elimelech, M.: Reverse permeation of weak electrolyte draw solutes in forward osmosis. Ind. Eng. Chem. Res., 51(41), 13463–13472, 2012.

Zhang, J., She, Q., Chang, V. W., Tang, C. Y., R. D. Webster: Mining Nutrients (N, K, P) from Urban Source-Separated Urine by Forward Osmosis Dewatering. J. Environ. Sci. Technol., 48(6), 3386–3394, 2014.

Zhao, S., Zou, L., Tang, C. Y., Mulcahy, D.: Recent developments in forward osmosis: opportunities and challenges. J. Membr. Sci., 396, 1–21, 2012.

CHAPTER 3
DEVELOPMENTOF A MODEL FOR URINE CONCENTRATION WITH ADVECTION AND BIDIRECTIONAL MULTICOMPENENT DIFFUSION

3.1 INTRODUCTION

Human urine is an important resource of fertilizer and several works proved it to be an effective fertilizer particularly for crops (EcoSan Club, 2010; WHO, 2006). Indeed, it takes up 80% of nitrogen, 50% of phosphorous, and 55% potassium in domestic wastewater which are the major nutrients for crops growth (Jönsson et al., 2000, Zhang et al., 2014a). It is mainly produced in high population density areas via the urine separation toilets; therefore, it should be transported to the farmlands and spread as a liquid fertilizer. The transportation cost was identified as the major issues which weaken the feasibility of urine liquid fertilizer utilization comparing with the chemical fertilizer (Larsen and Gujer, 1996; Lind et al., 2000, Dutta, 2012). The volume reduction of the collected urine is a solution to reduce the costs. Concentration technics such as evaporation (Pahore et al., 2011, Pahore et al., 2012), freeze drying (Lind et al., 2001, Gulyas et al., 2004), electro dialysis (Pronk et al., 2006), and reverse osmosis (Thörneby et al., 1999, Ek et al., 2006) among others were tested. All these volume reduction technics are energy intensive processes requiring and a more economic option is required. A process of forward osmosis (FO) emerges as an alternative for urine volume reduction since it is expected to be less energy consuming. FO is an osmotic process, where water molecules move across a semi-permeable membrane from the low solute concentration solution to the high solute concentration solution under the effect of the osmotic pressure gradient through the membrane. It has been studied for a large range of application such as: complex industrial streams waste water treatment (Anderson, 1977, Coday et al., 2014, Zhang et al., 2014), for activated sludge treatment (Cornelissen et al., 2011), wastewater effluent from municipal sources treatment (Lutchmiah et al., 2011, Linares et al., 2013) and recently on urine concentration (Zhang et al., 2014, Liu et al., 2016).

The performances of the FO process are commonly assessed by the water flux and solute flux passing through the membrane. Various mathematical models were developed to simulate the performances of the FO processes for applications in different fields such as desalination, wastewater treatment and urine concentration (Zhang et al., 2014b). Loeb, 1997 developed a model for water and solute flux estimation based on the internal concentration polarization (ICP) and assuming only draw solutes diffuse during the process. Mccutcheon and Elimelech, 2007 proposed a model for water flux estimation taking account the ICP and the external concentration polarization (ECP) effects under the assumption of a complete rejection of the feed and draw solutes. Suh et al., 2013 assumed one type of solute in the FO system and proportionality between the solute concentration and the osmotic pressure to predict the solute flux. In general, the proposed models consider the draw solutes diffusions and the ICP and ECP as having the most important role for estimation of the FO performance. These considerations are mainly related to the fact that the existing models were principally developed for performance assessment of desalination plants, and the models were adapted to other FO applications. The application to urine concentration involves several phenomena affecting the performances. Some

papers reported that the fast diffusion of ammonia occurs during the concentration process. This suggests that the diffusion of solutes is a considerable phenomenon in terms on the nutrient recovery. Moreover, urine and high concentration solutions cannot act as ideal solution because of intermolecular interactions. So, the activities of the solutes instead of the concentration were suitable for water flux estimation under high osmotic pressure operations (Nikiema et al., 2017), therefore, a mathematical model should consider diffusion and activity of each component to estimate the water flux and urine nutrients flux during the FO concentration process.

The objectives of this research are to develop a numerical multi-component model describing the phenomena of forward osmosis process for the performance estimation during volume reduction of urine taking into account the diffusion of the solutes in urine and draw solution through a semi-permeable membrane and activities of solutes, and to estimate the parameters for the model.

3.2 THEORY

A cellulose triacetate (CTA)-FO membrane is composed by an active layer which is a dense solute rejecting part and a porous mesh playing the support role. According to the diffusion theory, the water movement is driven by the difference of activities representing the thermodynamical concentration of each solute in real solutions across the active layer (Lonsdale et al., 1965). The water flux, J_w (m/s), is calculated with the flux equation for FO given by equation 1.

$$J_w = P * RT * (\sum_{i}^{m} A_{i,AL\_SL} - \sum_{i}^{n} A_{i,Fi\_AL})$$

(1)

where, P is the water permeability through the active layer (m/s/Pa), R is the gas constant (J/mol/K), T the absolute temperature (K), A_{i,AL_SL} is the activity of component i at the surface of the active layer of the draw side (mol/m^3) and A_{i,Fi_AL} is the activity of i at the surface of the active layer of the feed solution side (mol/m^3). 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 activities. The activity is a function of the concentration, C_i (mol/m^3), of i inside the layers, and activity coefficient, a_i (-), of i described as equation 2:

$$A_i = a_i C_i$$

(2)

The activity coefficient is calculated by Phreeqc software (Appelo et al., 2014) from the composition of solutes in the solution. 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 for multi component.

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

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

where, $D_{Al,i}$ and $D_{sl,i}$ are respectively the diffusivities of i in the active layer and support layer (m^2/s), 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. The volumes of feed and draw solution, V_{FS} and V_{DS} (m^3), can be estimated as;

$$\frac{\partial V_{FS}}{\partial t} = -J_w S \tag{4}$$

$$\frac{\partial V_{DS}}{\partial t} = J_w S \tag{5}$$

where, S is the effective surface area (m^2). The concentrations in bulk solutions, $C_{i,FS}$ and $C_{i,DS}$ (mol/m^3), 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 follows:

$$\frac{\partial C_{i,FS} V_{FS}}{\partial t} = -J_{s,i}\big|_{at\ FS} = -J_w S C_i\big|_{at\ FS} + S D_i \frac{\partial C_i}{\partial x}\bigg|_{at\ FS} \tag{6}$$

$$\frac{\partial C_{i,DS} V_{DS}}{\partial t} = J_{s,i}\big|_{at\ DS} = J_w S C_i\big|_{at\ DS} - S D_i \frac{\partial C_i}{\partial x}\bigg|_{at\ DS} \tag{7}$$

where, J_s is the molar flux of the solutes through the layers ($mol/s/m^2$). The set of initial and boundary conditions for the simulation of the water flux and the solutes concentration is as follows:

Initial conditions:

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

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

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

Boundary conditions:

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

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

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

To calibrate the model, equation (1) requires that we know the membrane pure water permeability, and equations (2), (3), (6) and (7) require solutes diffusivities. These parameters were calibrated from the experimental data. The experimental conditions were simulated and compared with the experimental results. Least square method with Nelder mead algorithm was used to find the best fit of the volume and concentration curves for the diffusivities estimation. The model was later validated by comparing simulated and other experiments results.

3.3 MATERIALS AND METHODS

3.3.1   Experimental set up

FO bench scale experiments were performed to estimate the physical parameters of the membrane, solute diffusivities, and to validate the model. The experimental set up used in this study is illustrated by the Figure 1 in Chapter 2. It was composed by a symmetric flow channel separated by CTA FO asymmetric flat sheet membrane (FTSH2O, Fluid Technology Solutions Inc.). 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, while 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 which gives 19.44 cm/s of cross flow velocity on the membrane surface. The weight increase of the draw solution was measured over time by an electrical balance (OHAUS, Technical Advantages Company) connected to a computer with a data collection software (WINCT, A&D). The solutions used in this paper were prepared with dissolving $NaCl$, NH_4Cl, NaH_2PO_4 and KCl into deionized water. NH_3/NH_4Cl buffer solution were prepared by dissolving 0.35 mol of NH_4Cl and 0.50 mol of NH_3 solution in to deionized water and then diluting to 1 L. Synthetic urine was prepared following the same procedure as Wilsenach et al., 2007, Pahore et al., 2011 and Kabore et al., 2016. All the chemicals were special grade from Wako Pure Chemical Industries, Japan. The synthetic urine was hydrolyzed by adding Jack Bean urease (Wako Pure Chemical Industries, Japan) and keeping it during 24 hours before starting experiment.

3.3.2 Experimental procedure

The experimental conditions are summarized in **Table 1**. The experiments in Run 1 were performed to estimate the CTA membrane pure water permeability with NaCl solutions as draw solution and deionized water as feed solution. The permeability was obtained as the slope of the correlation of the water flux to the initial osmotic pressure difference. Run 2 was conducted to estimate the diffusivities in active and support layers of major main solutes in urine: PO_4, K, NH_3, Cl and inorganic carbon (IC). The diffusivities were estimated by finding the minimum least square of error between experiment and simulation data of the water flux, feed solute concentration and draw solute concentration. Run 3 was conducted to validate the simulation results of water flux and solute concentrations in both draw and feed solutions. Additional data of run 1 and run 2 shown in chapter 2, Table 1 were used to validate the effect of ICP on the relationship between water flux and the osmotic pressure difference. NaCl solution and synthetic hydrolyzed urine (SHU) respectively used as draw solution feed solution. Two milliliters of feed and draw solutions were sampled every hour during each experiment for the estimation of solute concentrations.

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 .3 M)			
Run 2	NaCl (0.50 M)	Deionized water	Active layer facing the draw solution	19.44 cm/s
	NH_3 (0.5 M)/NH_4CL (0.35 M)			
	NaH_2PO_4 (0.50 M)			
	KCl (0.50 M)			
	NaH_2CO_3 (0.5M)			
Run 3	NaCl (5M)	Hydrolyzed urine	Active layer facing the feed solution	19.44 cm/s

The concentrations of K, Na, and Cl were measured with an ion-chromatography system (ICS-90, DIONEX Corporation, USA). NH_3 and PO_4 were analyzed by USEPA HACH Nessler method 8038 and HACH PhosVer (ascorbic acid) method 8048 with a spectrophotometer (DR -2800, HACH, USA), respectively. IC was measured by a total organic carbon analyzer (TOC-9000A, Shimadzu, Japan). The new membrane was soaked in deionized water for 30 minutes and dried a room temperature for 24 hours. The surface and the cross section of the membrane were observed with a scanning electron microscope (SEM S4800, Hitachi Corporation).

3.4 RESULTS AND DISCUSSIONS

3.4.1 Water permeability and solute diffusivities

Figure 1a represents the water flux as a function of the osmotic pressure difference with several concentrations of NaCl solutions. The water flux was proportional to the osmotic pressure difference, while the water permeability was estimated to 9.19×10^{-13} L/m^2 s Pa. Figure 1b shows the cross section of the CTA ES flat sheet membrane observed by SEM. It is composed by a dense rejecting layer (active layer) ≈ 10 μm and a mesh layer which plays a mechanical role (supporting layer) ≈ 30 μm. The parameters used for the simulation and the diffusivities estimation were summarized in Table 1. Figures 2-6 show the results of the water flux and solutes concentrations of the experiments carried out in run 2 and simulations performed. The time course of the water flux simultaneously decreased with decrease of the feed and increase of the draw solute concentrations, while they were well fitted with the simulation. The diffusivities values obtained are summarized in **Table 2**. With the good fitting results obtained, the diffusivities values were used for the further simulation of FO process for SHU concentration.
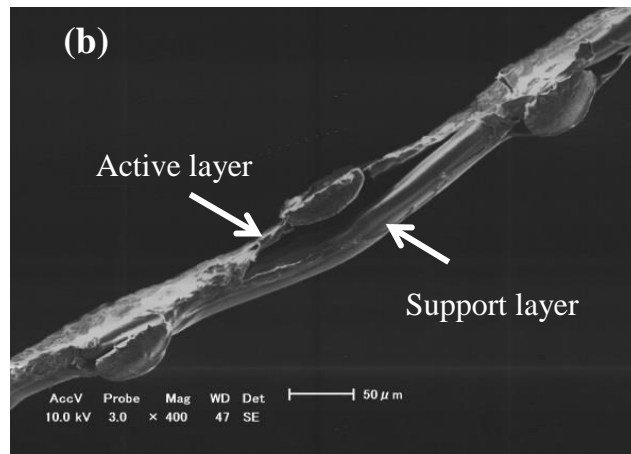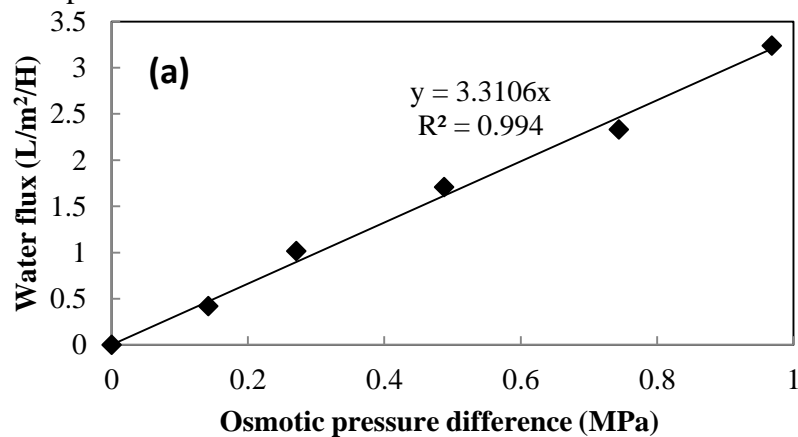
Figure 1 (a) Water flux as a function of the osmotic pressure difference of bulk solutions,

(b) Scanning electron microscopy image of the cross section of cellulose triacetate FO membrane.
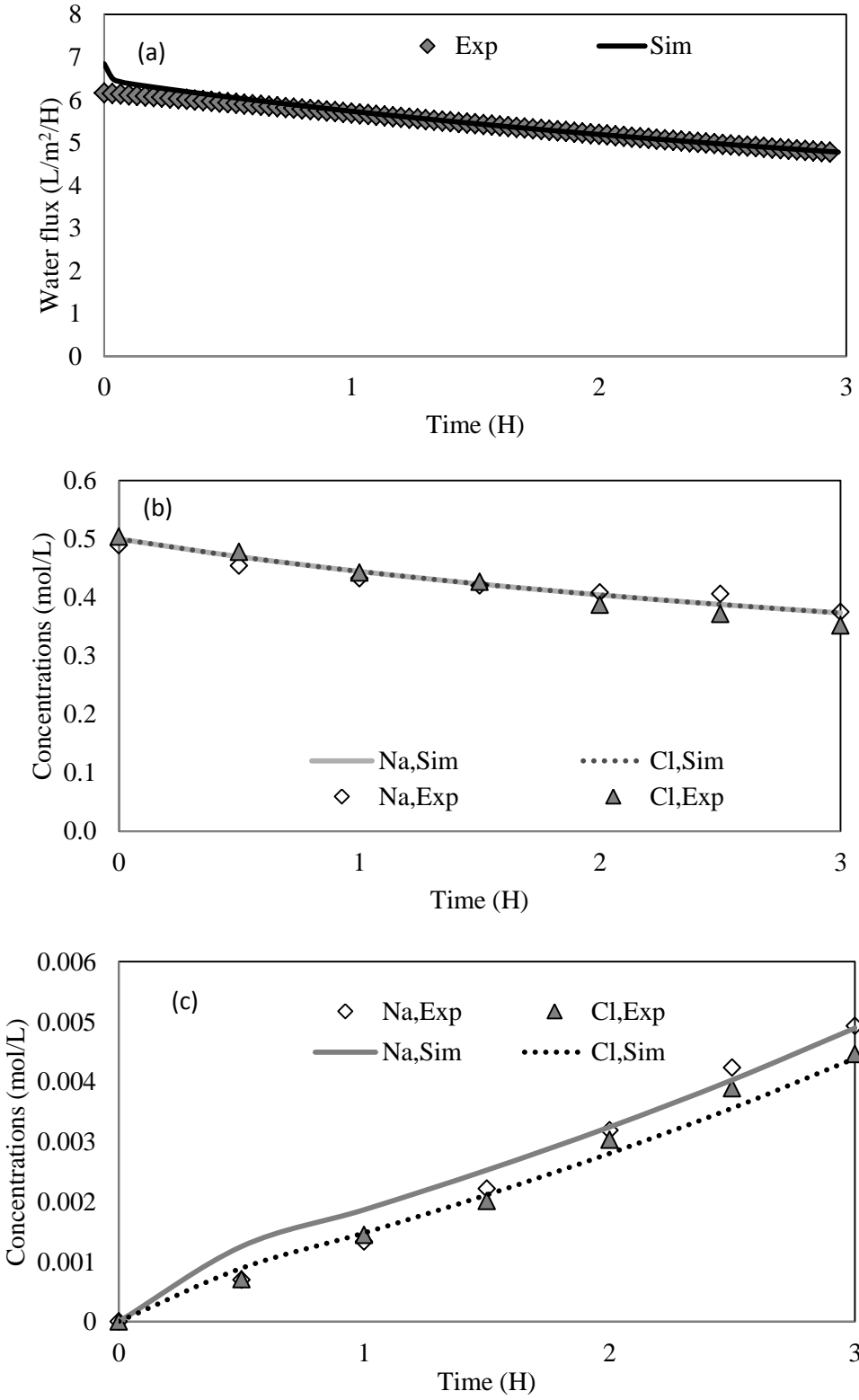
Figure 2 Experimental and fitted simulation results: (a) Time course of water flux, (b) draw solution concentration of Na and Cl, and (c) feed solution concentrations of Na and Cl
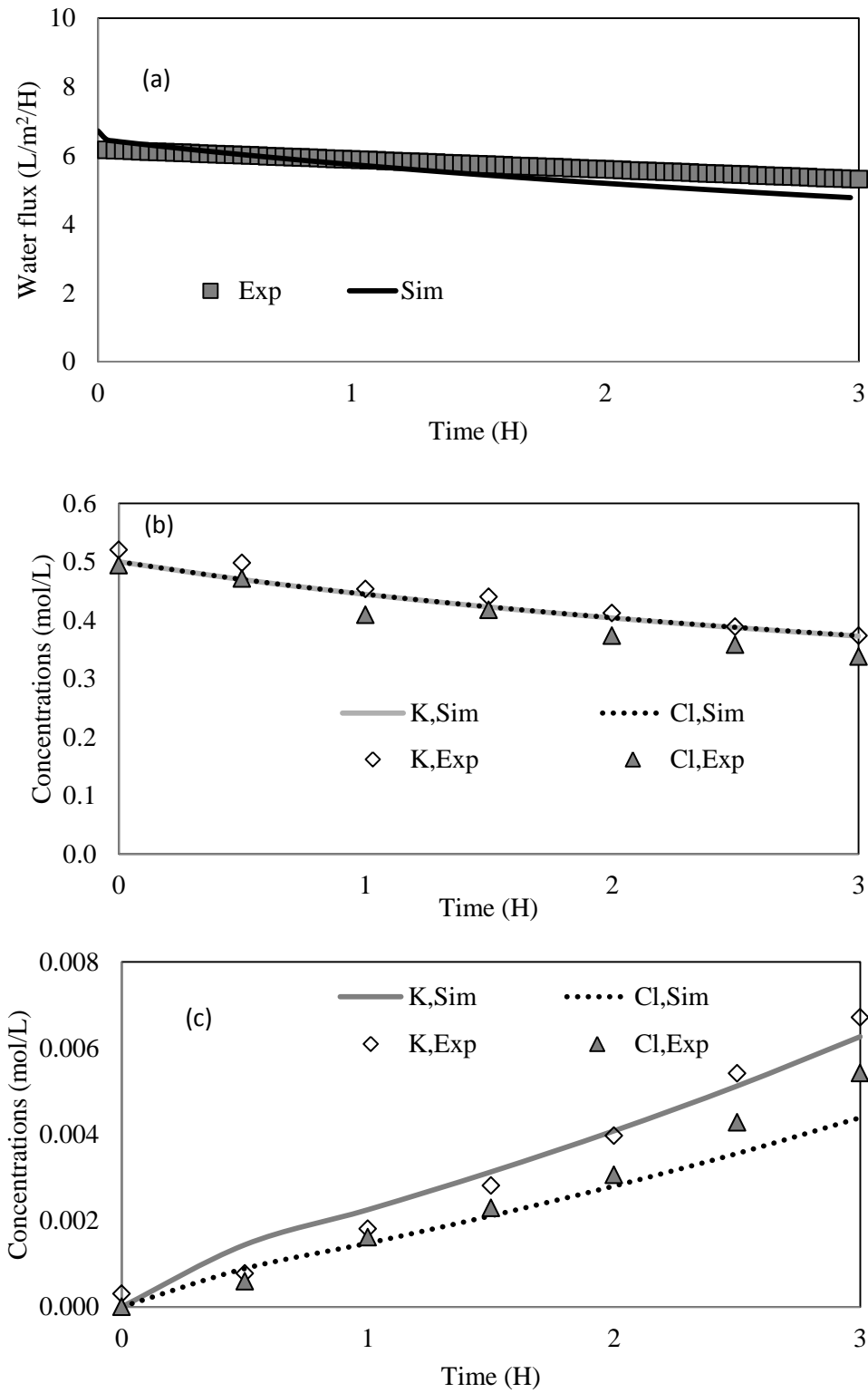
Figure 3 Experimental and fitted simulation results: (a) Time course of water flux, (b) draw

solution concentration of K and Cl, and (c) feed solution concentrations of K and Cl
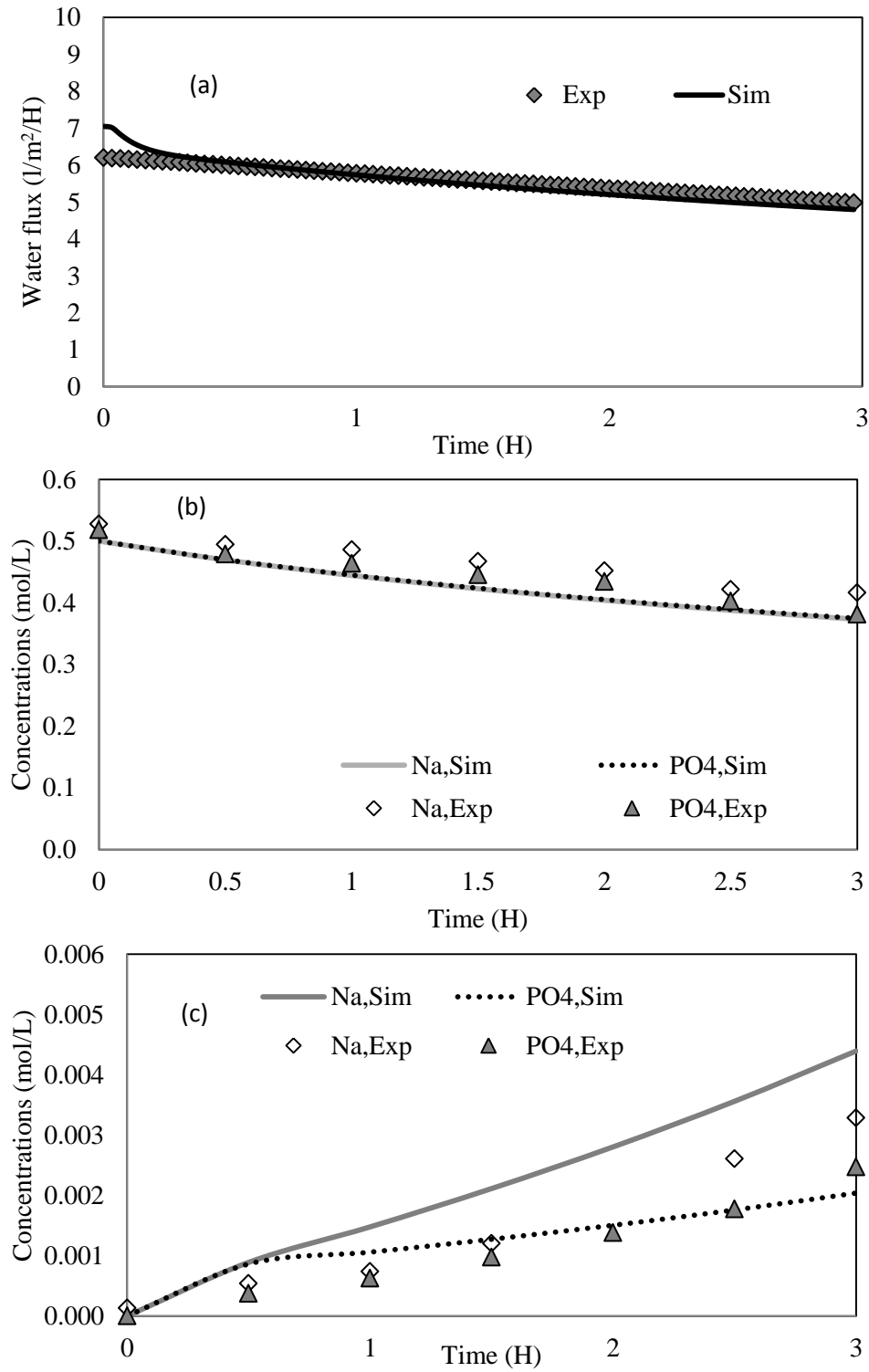
Figure 4 Experimental and fitted simulation results: (a) Time course of water flux, (b) draw

solution concentration of Na and PO4, and (c) feed solution concentrations of Na and PO4
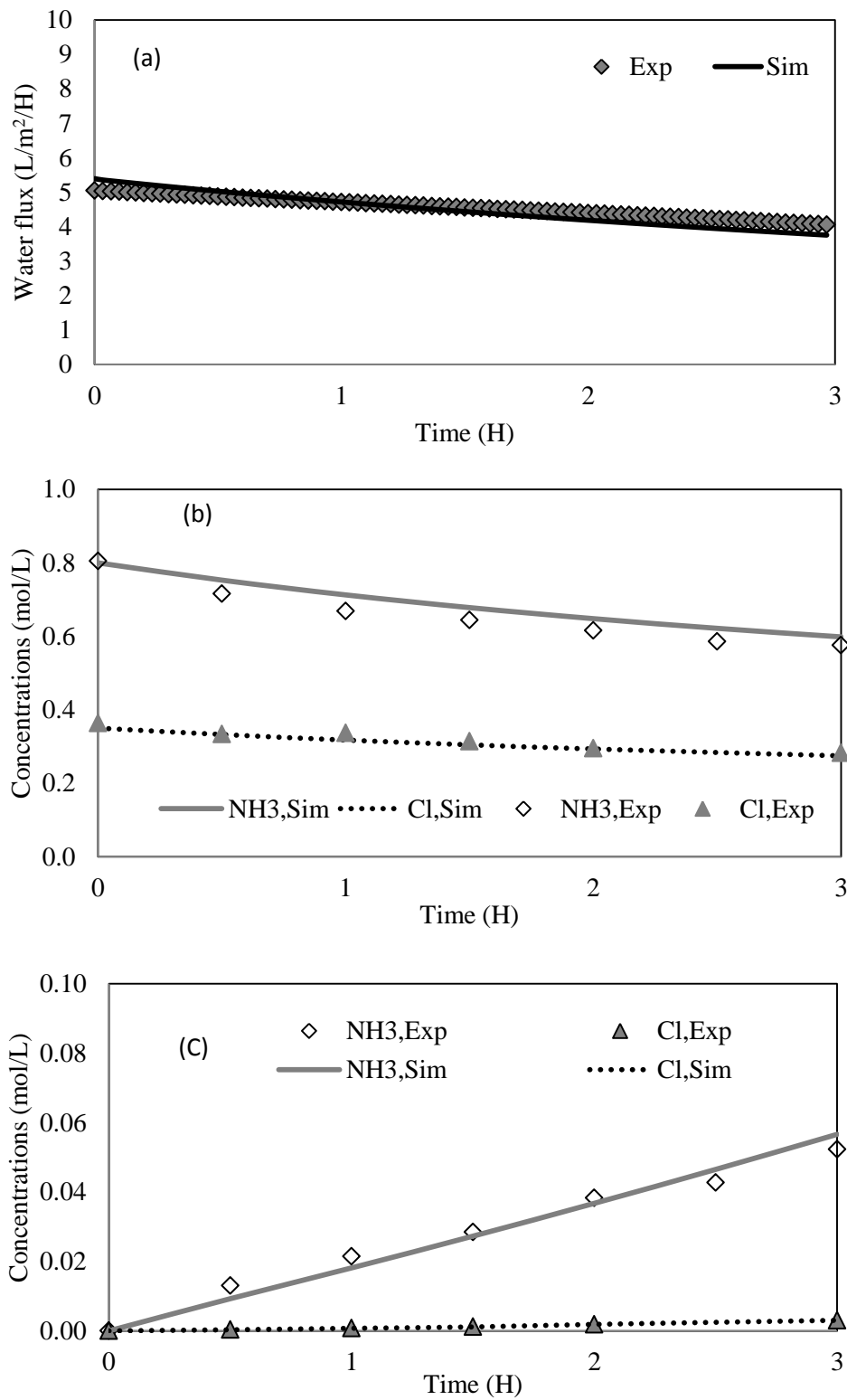
Figure 5 Experimental and fitted simulation results: (a) Time course of water flux, (b) draw

solution concentration of NH$_3$ and Cl, and (c) feed solution concentrations of NH$_3$ and Cl
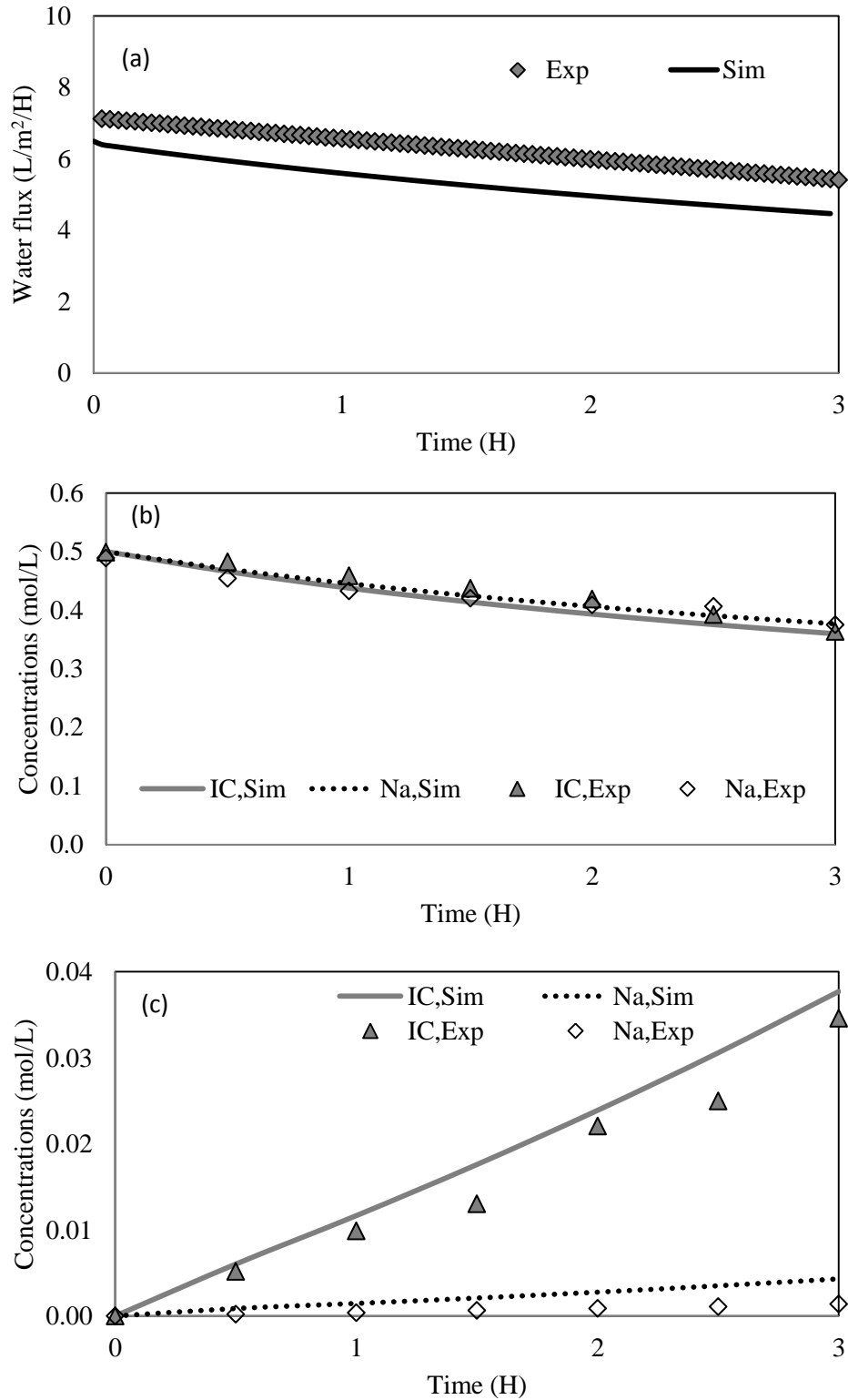
Figure 6 Experimental and fitted simulation results: (a) Time course of water flux, (b) draw

solution concentrations of Na and CO_3, and (c) feed solution concentration of Na and CO_3

Table 2 Summary of the solute diffusivities in the active and support layer

Solute	Diffusivity value in the active layer (m^2/s)	Diffusivity value in the support layer (m^2/s)
Na , Cl	2.85×10^{-13}	1.41×10^{-10}
NH$_3$	4.93×10^{-12}	4.35×10^{-11}
K	3.86×10^{-13}	2.34×10^{-10}
PO$_4$	7.46×10^{-14}	4.49×10^{-11}
IC	2.98×10^{-12}	5.1×10^{-10}

3.4.2 Model validation

3.4.2.1 Simulation of water flux and solute diffusion

Figure 7a represents the experimental and simulated data of the water flux during FO process for SHU concentration. The simulated results successfully estimated the evolution of water flux and show a rapid decreasing rate from 0 to 10 hours and slow decrease from 10 to 24 hours. Figure 7b shows the results of the simulation and experimental feed and draw solution volumes within 10 hours SHU volume was reduce to more than 80% of its initial volume and slightly increase from 10 to 24 hours which reflects the results of the simulated and the experimental water fluxes. Figure 7c and d shows the nutrients concentration variation in the feed and the draw solution. The K and PO$_4$ concentrations increased during the volume reduction process however NH$_3$ presents a different pattern which shows a peak of concentration at 5.9 hours of FO process. This result of NH$_3$ solute concentration can be explained by rapid water transportation from urine to draw solution within 5.9 hours which increases the concentration despite the diffusion of the solute. After 5.9 hours water flux decreases as well as the NH$_3$ concentration in SHU owing to its high diffusion and finally reached to equal of that in draw solution. The developed model showed good agreement to the concentrations of the PO$_4$, K and NH$_3$ obtained in the experiment.
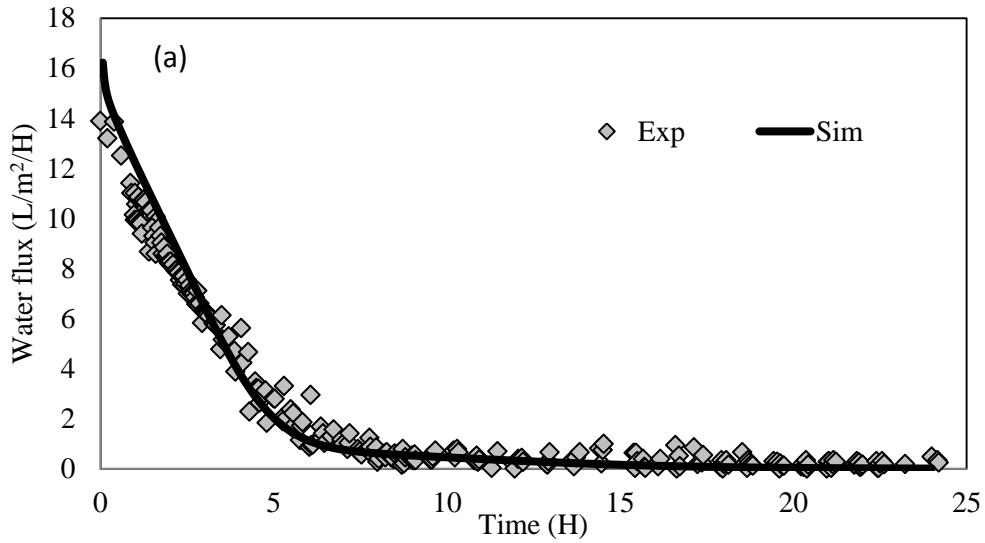
Figure 7 (a) Validation of the water flux estimation using time course of experimental and simulated water flux
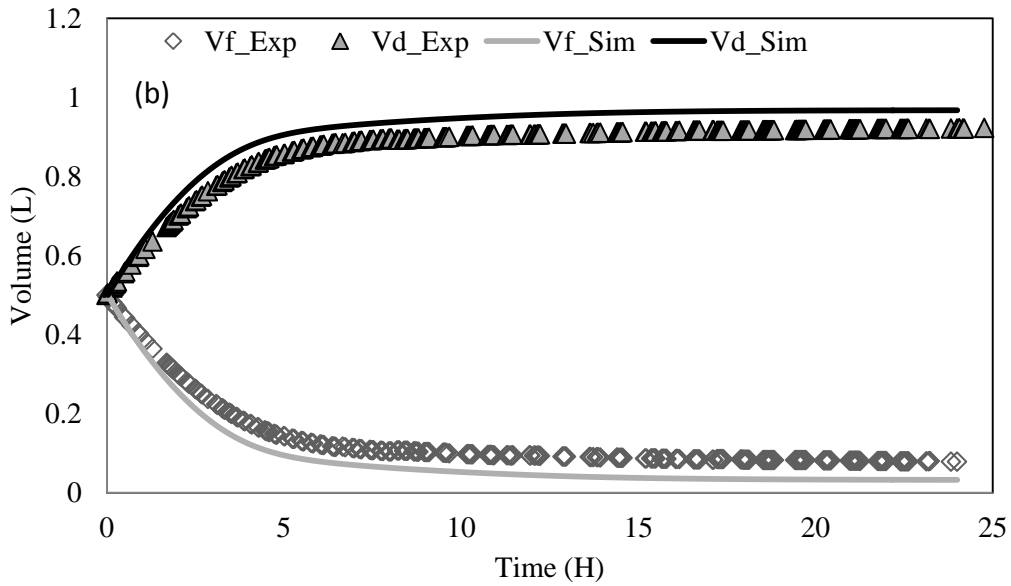
Figure 7 (b) Validation of feed and draw solution estimation using the time courses of experimental and simulated volumes
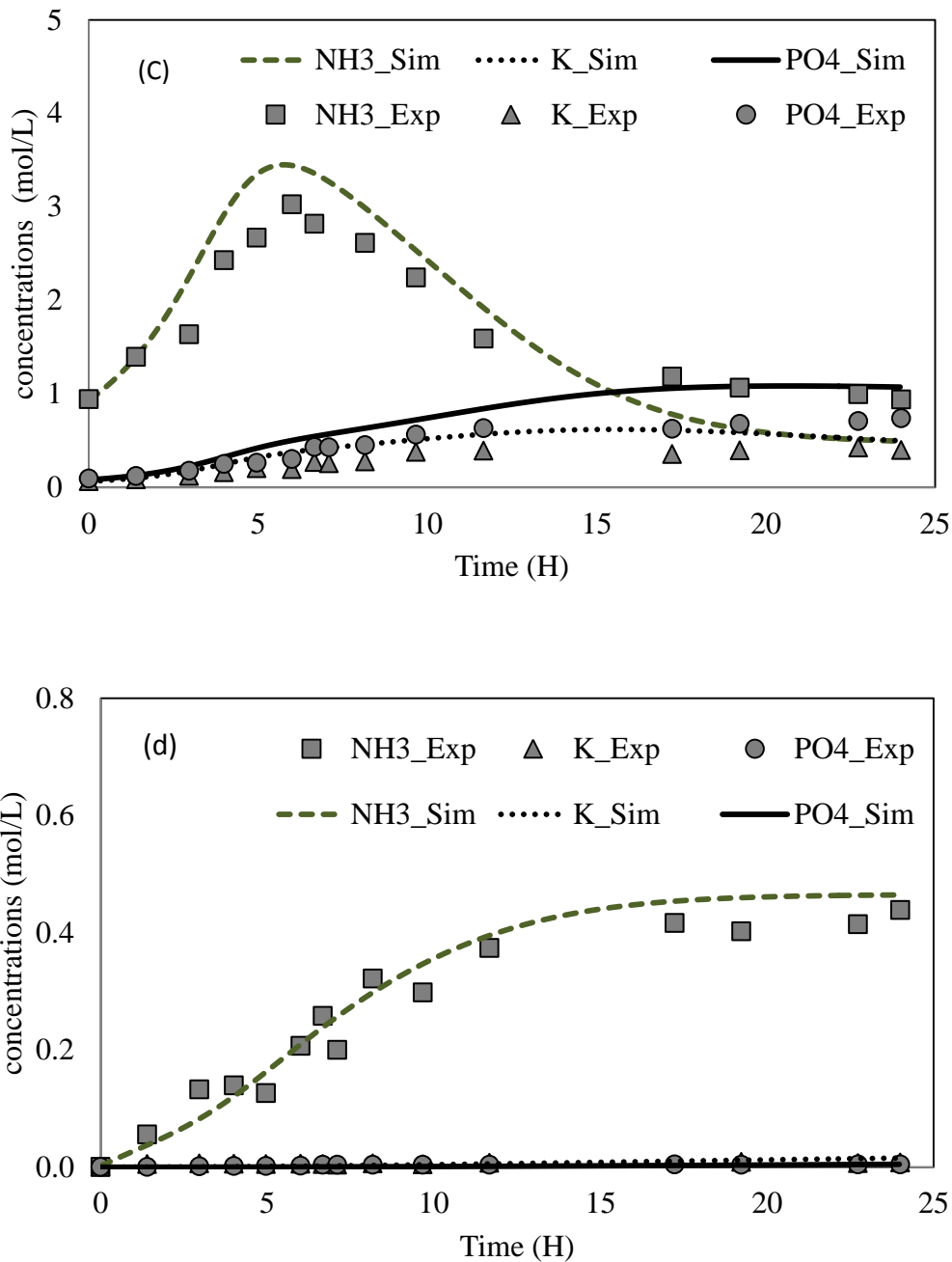
Figure 7 Validation of concentrations estimation: (c) time course of nutrients (NH$_3$, K, PO$_4$) concentrations in feed solution, (d) time course of nutrients (NH$_3$, K, PO$_4$) concentrations in draw solution.

Figures 8a to 8e show the time course of nutrients (NH$_3$, PO$_4$, K) amounts and NaCl which were initially present in SHU and draw solution in this study. Na, Cl, PO$_4$ and K have low diffusion coefficients through the CTA ES membrane showing slow transport between the SHU and draw solution so, the amounts of these elements were not changed much. NH$_3$

showed fast diffusion and its amount decreases up to 24 hours. The simulation results showed very well the diffusion trend of SHU nutrients and 83% of PO_4, 90% of K and 76% of NH_3 could be recovered at 5.9 hours.
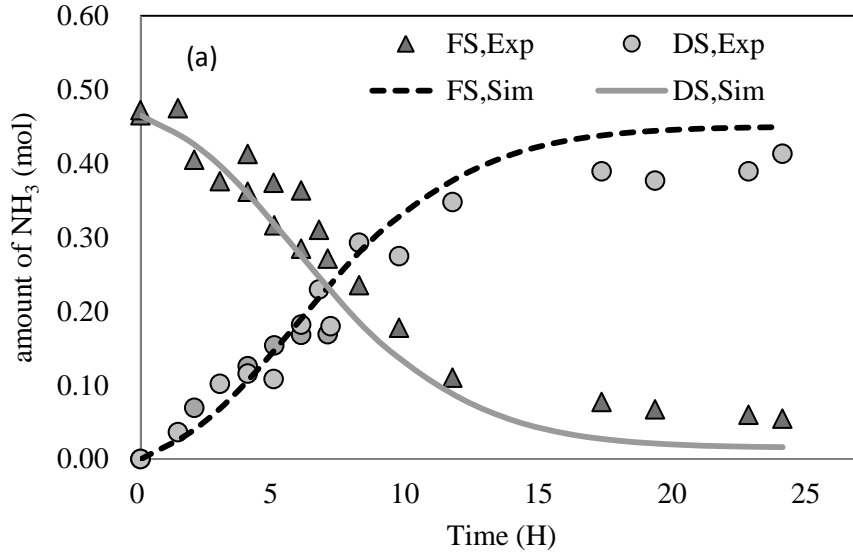
Figure 8 (a) Time course of NH_3 amount during synthetic hydrolyzed urine concentration with 5 mol/L NaCl draw solution
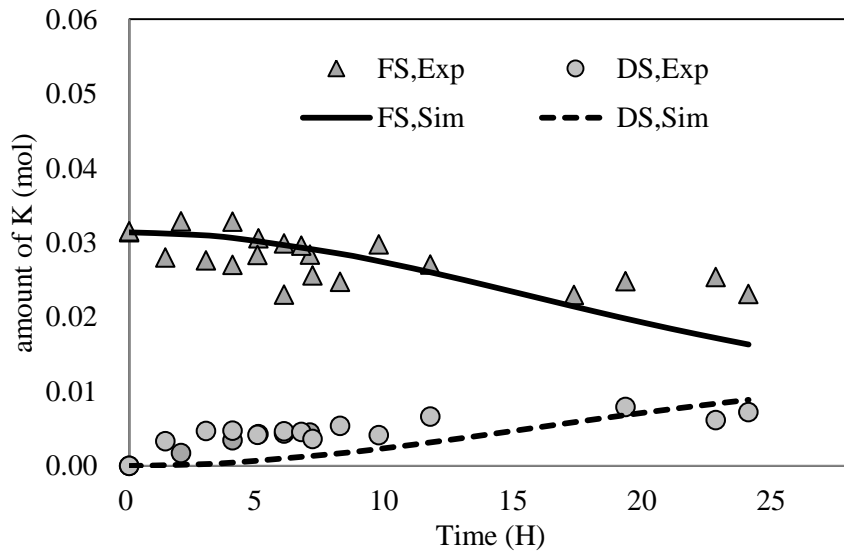
Figure 8 (b) Time course of K amount during synthetic hydrolyzed urine concentration with 5 mol/L NaCl draw solution
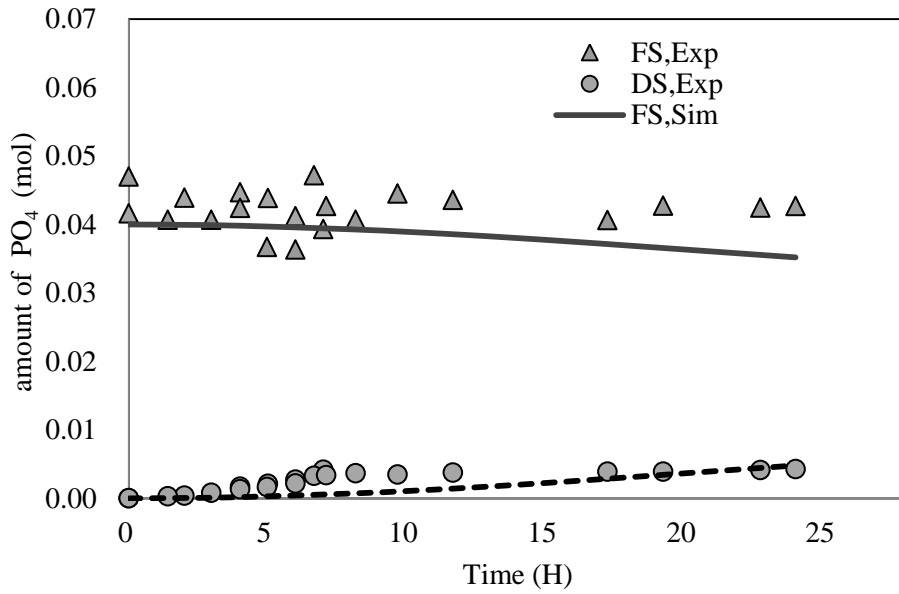
Figure 8 (c) Time course of PO$_4$ amount during synthetic hydrolyzed urine concentration with 5 mol/L NaCl draw solution
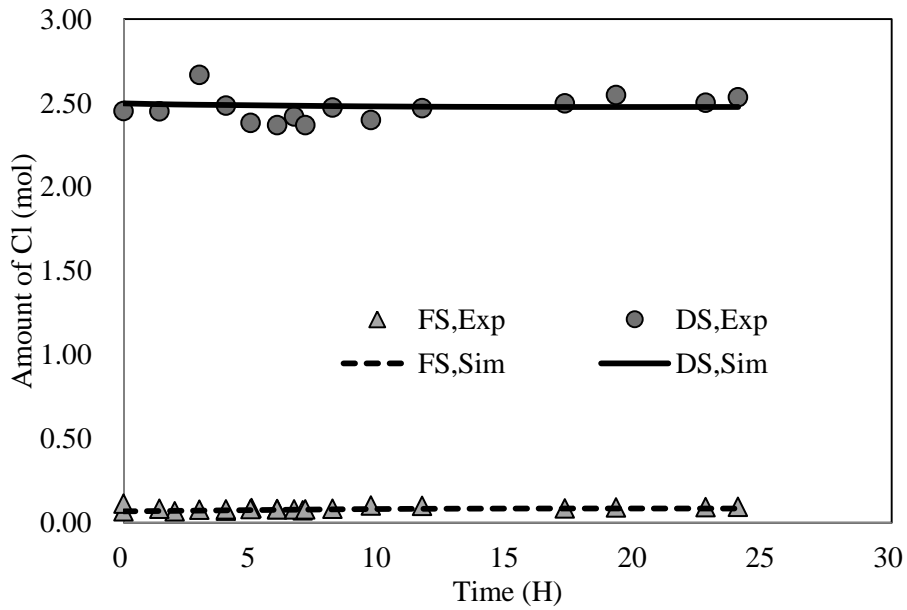
Figure 8 (d) Time course of Cl amount during synthetic hydrolyzed urine concentration with 5 mol/L NaCl draw solution
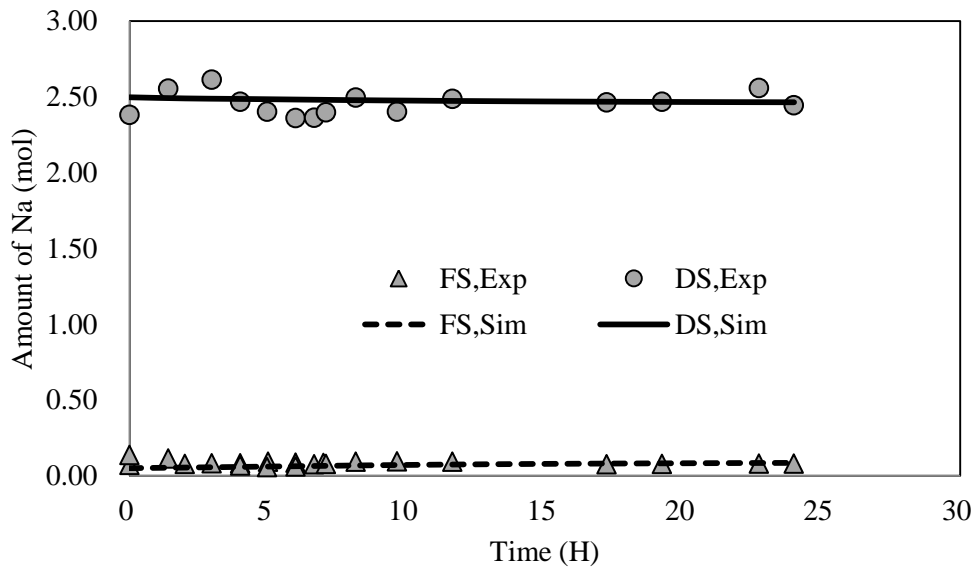
Figure 8 (e) Time course of Na amount during synthetic hydrolyzed urine concentration with 5 mol/L NaCl draw solution

3.4.2.2 Simulation of the Internal Concentration Polarization effect

The simulation model involves the calculation of the concentration profile inside the membrane layers. The relationships of the water flux and osmotic pressure obtained from Figures 3 and 6 were shown in Figure 9a. The water fluxes for both experiments were proportional to the osmotic pressure. The slope for NaCl experiment was similar to that obtained from Figure 3, while the slope for NH_4Cl was much lower than the others. This fact suggests that the osmotic pressure difference in bulk draw and feed solutions no longer is able to use calculation of the water flux. The simulation revived the experimental water flux. So, the detailed analysis of the simulation result was performed. Figure 9b shows the typical concentration profiles of NaCl and NH_4Cl cases. The boundaries between draw solution and active layer, active layer and support layer, and support layer and feed solution are respectively at 0, 10, and 40 μm. The concentration profile of both experiments showed decrease in concentrations of solutes with distance from draw solution. The concentration of Na and Cl at the boundary between active and support layer was almost zero because of very slow diffusion through the active layer. In contrast, the NH_3 concentration at the boundary was higher value than Na and Cl, and then concentration slope in support layer was observed.
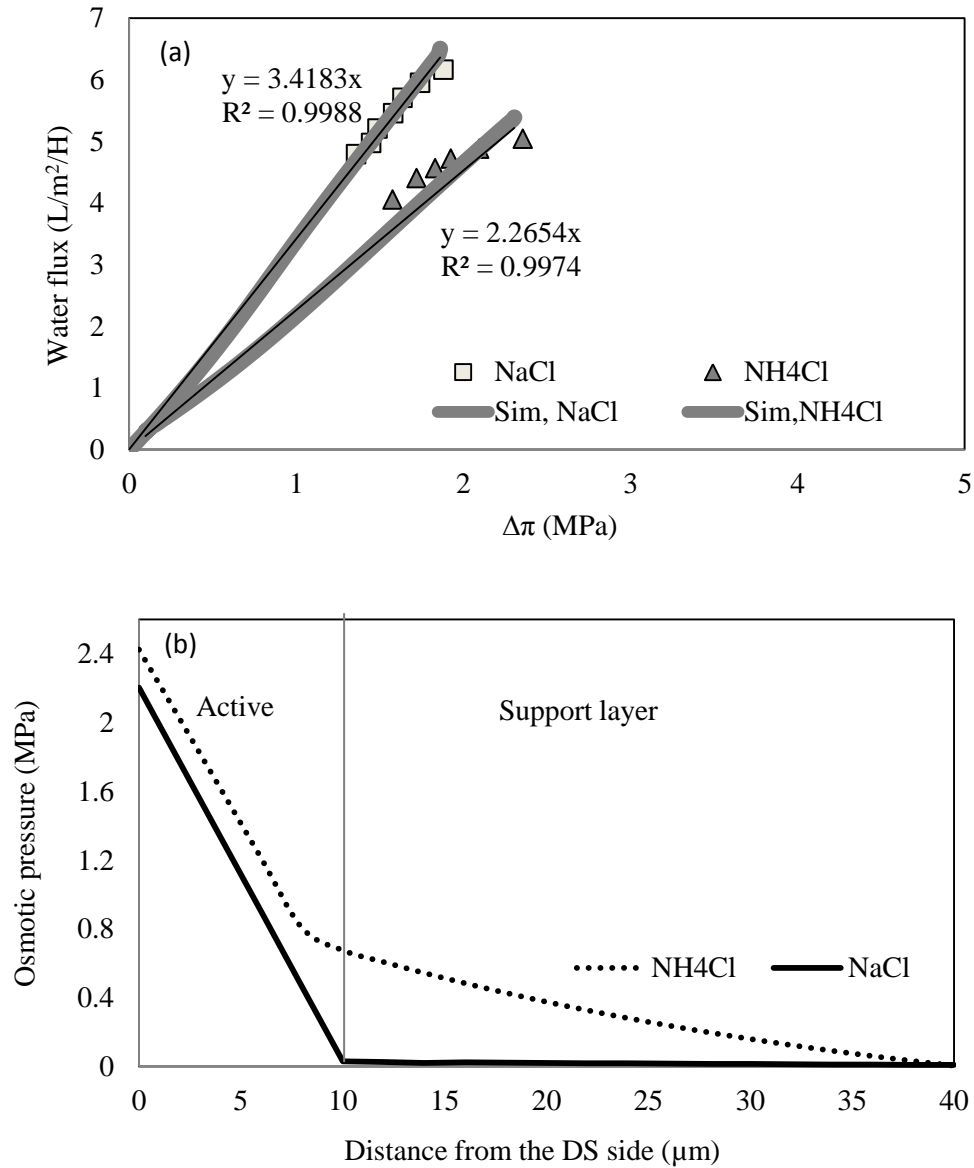
Figure 9 (a) Relationship of osmotic pressure difference and water flux, (b) simulated osmotic pressure profile of NaCl and NH$_4$Cl

Figure 10a shows the correlation of the water flux with the osmotic pressure between the bulk draw and feed solutions plotted with the experimental results of run 1 and run2 in chapter 2, Table1 and run3 in this chapter, Table1. The synthetic and real urine were used as feed solutions, while 2-5 mol/L NaCl solutions were used as draw solutions. The slope was lower than that in case of NaCl-deionized water to indicate heavily ICP occurs. The simulation performed for 4 and 5 mol/L draw solutions cases concentration showed good agreement to the experimental data by consideration of ICP. The osmotic pressure profile in the membrane is shown in Figure 10b. The positions of the boundary are same as figure

10b. Here, the draw solution had higher osmotic pressure than feed solution. The osmotic pressure drops in support layer to give the low osmotic pressure difference between active layer surfaces. The reason for this is as follows: the water flow was from the feed to draw solution. Na and Cl ions which were main source of osmotic pressure were swept by the water flow, less transported from feed solution through the active layer because of its low diffusivity and diffused from draw solution against the water flow. So that, the model proposed in this paper describes the phenomenon of the forward osmosis process very well.
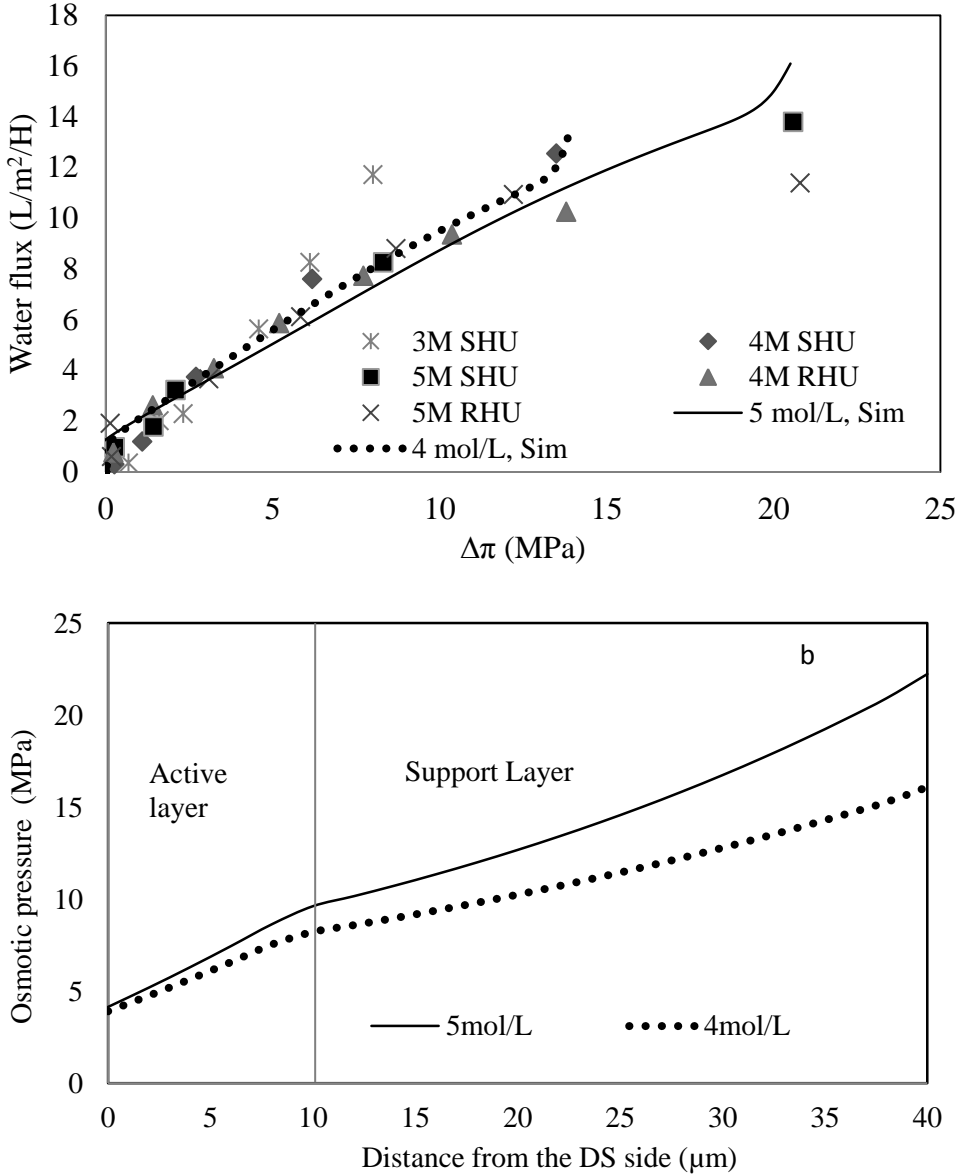
Figure 10 Effect of the internal concentration polarization: (a) Relationship of water flux and osmotic pressure difference, (b) Simulated osmotic pressure profile during synthetic hydrolyzed urine concentration with 5 mol/L and 4mol/L NaCl draw solution.

3.5 CONCLUSIONS

In this study, a new model was proposed for water flux and solution concentration estimation taking into account solute multicomponent diffusion, solutes activities and the effect of internal concentration polarization. The model relied on experimental determination of the water permeability evaluated with deionized water as feed solution and NaCl solution as draw solution and the diffusivities of Na, Cl, NH_3, K, PO_4 and IC in the active and support layers were evaluated with a mathematical model. The simulated results represent well the evolution of the water flux and the volume change and the feed and draw solutions. The diffusion of SHU nutrients (NH_3, K, and PO_4) was well estimated from up to 24 hours experiment. The simulation revealed that the lower water permeability for NH_4Cl than that for NaCl is caused by internal concentration polarization resulted from diffusion of NH_4 through the membrane. This mechanism also caused the permeability drop on SHU volume reduction. The model developed in this study can substantially help to predict the flux variation under different system conditions at high osmotic pressure difference conditions and therefore help to optimize the performances and to propose new designs for FO applications to urine concentration.

3.6 REFERENCES

Anderson, D.K., 1977. Concentration of dilute industrial wastes by direct osmosis. University of Rhode Island.

Appelo, C.A.J., Parkhurst, D.L., Post, V.E.A., 2014. Equations for calculating hydrogeochemical reactions of minerals and gases such as CO2 at high pressures and temperatures. Geochim. Cosmochim. Acta 125, 49–67.

Cath, T.Y., Childress, A.E., Elimelech, M., 2006. Forward osmosis: Principles, applications, and recent developments. Journal of Membrane Science 281, 70–87

Coday, B.D., Xu, P., Beaudry, E.G., Herron, J., Lampi, K., Hancock, N.T., Cath, T.Y., 2014. The sweet spot of forward osmosis: treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. Desalination 333, 23–35.

Cornelissen, E.R., Harmsen, D., Beerendonk, E.F., Qin, J.J., Oo, H., De Korte, K.F., Kappelhof, J., 2011. The innovative osmotic membrane bioreactor (OMBR) for reuse of wastewater. Water Sci. Technol. 63, 1557–1565.

EcoSanRes Programme: Use of urine issue 3, 2004. http://www.ecosan.at/ssp/issue-03-use-of-urine. [Accessed: 19 Aug 2016]

Ek, M., Bergström, R., Bjurhem, J.-E., Björlenius, B., Hellström, D., 2006. Concentration of nutrients from urine and reject water from anaerobically digested sludge. Water Sci. Technol. 54, 437–444.

Gray, G.T., McCutcheon, J.R., Elimelech, M., 2006. Internal concentration polarization in forward osmosis: role of membrane orientation. Desalination 197, 1–8.

Gulyas, H., Bruhn, P., Furmanska, M., Hartrampf, K., Kot, K., Luttenberg, B., Mahmood, Z., Stelmaszewska, K., Otterpohl, R., 2004. Freeze concentration for enrichment of nutrients in yellow water from no-mix toilets. Water Sci. Technol. 50, 61–68.

Jönsson, H., Vinner\a as, B., Höglund, C., Stenström, T.A., Dalhammar, G., Kirchmann, H., 2000. Recycling source separated human urine. VA-Forsk Rep. 1.

Kabore, S., Ito, R., Funamizu, N., 2016 .Effect of Urea/Formaldehyde ratio on the production process of methylene urea from human urine, Journal of Water and Environmental Technol. 2 ,47–56

Larsen, T.A., Gujer, W., 1996. Separate management of anthropogenic nutrient solutions (human urine). Water Sci. Technol. 34, 87–94.

Linares, R.V., Li, Z., Abu-Ghdaib, M., Wei, C.-H., Amy, G., Vrouwenvelder, J.S., 2013. Water harvesting from municipal wastewater via osmotic gradient: an evaluation of process performance. J. Membr. Sci. 447, 50–56.

Lind, B.-B., Ban, Z., Bydén, S., 2000. Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. Bioresour. Technol. 73, 169–174.

Lind, B.-B., Ban, Z., Bydén, S., 2001. Volume reduction and concentration of nutrients in human urine. Ecol. Eng. 16, 561–566.

Loeb, S., 1997. Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane. J. Membr. Sci. 129, 243–249.

Lonsdale, H., Merten, U., and Riley, R., 1965. Transport properties of cellulose acetate osmotic membranes. Journal of Applied Polymer Science, 9, 1341

Lutchmiah, K., Cornelissen, E.R., Harmsen, D.J., Post, J.W., Lampi, K., Ramaekers, H., Rietveld, L.C., Roest, K., 2011. Water recovery from sewage using forward osmosis. Water Sci. Technol. 64, 1443–1449.

McCutcheon, J.R., Elimelech, M., 2006. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. Journal of Membrane Science. 284, 237–247

Mccutcheon, J.R., Elimelech, M., 2007. Modeling water flux in forward osmosis: Implications for improved membrane design. AIChE J. 53, 1736–1744.

Nikiema, B. C.W., Ito, R., Guizani, M. and Funamizu, N., 2017. Estimation of water flux and solute movement during the concentration process of hydrolyzed urine by forward osmosis Journal of Water and Environmental Technology (In press)

Pahore, M.M., Ito, R., Funamizu, N., 2011. Performance evaluation of an on-site volume reduction system with synthetic urine using a water transport model. Environ. Technol. 32, 953–970.

Pahore, M.M., Ushijima, K., Ito, R., Funamizu, N., 2012. Fate of nitrogen during volume reduction of human urine using an on-site volume reduction system. Environ. Technol. 33, 229–235.

Pronk, W., Biebow, M., Boller, M., 2006. Treatment of source-separated urine by a combination of bipolar electrodialysis and a gas transfer membrane. Water Sci. Technol. 53, 139–146.

Liu, Q., Liu, C., Zhao, L., Ma, W., Liu, H., Ma, J., 2016. Integrated forward osmosis-membrane distillation process for human urine treatment. Water Res., 91, 45–54.

Suh, C., Lee, S., Cho, J., 2013. Investigation of the effects of membrane fouling control strategies with the integrated membrane bioreactor model. J. Membr. Sci. 429, 268–281.

Thörneby, L., Persson, K., Trägardh, G., 1999. Treatment of liquid effluents from dairy cattle and pigs using reverse osmosis. J. Agric. Eng. Res. 73, 159–170.

Wilsenach, J.A., Schuurbiers, C.A.H., Van Loosdrecht, M.C.M., 2007. Phosphate and potassium recovery from source separated urine through struvite precipitation. Water Res. 41, 458–466.

World Health Organization: Guidelines for the Safe Use of Wastewater, Excreta and Greywater, 2006

Zhang, J., She, Q., Chang, V.W., Tang, C.Y., Webster, R.D., 2014. Mining Nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering. Environmental Science and Technology 48, 3386–3394

Zhang, S., Wang, P., Fu, X., Chung, T. S., 2014. Sustainable water recovery from oily wastewater via forward osmosis-membrane distillation (FO-MD). Water Res. 52, 112–121.

CHAPTER 4

DESIGN OF A FORWARD OSMOSIS REACTOR FOR URINE CONCENTRATION AND NUTRIENT RECOVERY

4.1 INTRODUCTION

Wastewater treatment methods are moving toward water reuse and nutrient recovery due to the natural resources depletion and water crisis. Human urine contributes to a large proportion of nutrients from the domestic wastewater which was evaluated to 80% of nitrogen, 50% of phosphorous, and 55% of the potassium (Zhang et al., 2014). Undiluted fresh urine contains 0.20 - 0.21 g/L of phosphorous, 0.9 - 1.1g/L of potassium and 7 - 9g/L of nitrogen (Pahore et al., 2011), therefore the use of urine fertilizer in agriculture field presents a high potential in a viewpoint of agronomic value. Thus, urine source-separation systems been proposed to enhance nutrient recovery, however an extended use of these infrastructures will result in an increased amount urine solution to manage (Nybrant et al., 1996). B.B. Lind reported that large volumes of urine are needed to fertilize farmland and there are problems related to the collection and transportation of these large quantities (Lind et al, 2001). The main problems regarding the efficiency are related to management the storage and transportation of urine (Lind et al, 2001; Hellstrom, 1998). Therefore forward osmosis (FO) that appears to be a promising technic for solution concentration was proposed to concentrate urine. Forward osmosis (FO) process is an engineered osmotic process in which a concentrated solution, termed a draw solution (DS), is used on one side of the semi-permeable membrane and the water to be treated is on the other side of the same membrane (Phuntsho et al., 2011).

The general goal of this research is to propose a design of a unit that could be implemented at household level for urine concentration. Figure 1 shows the concept of urine concentration and an enlarged image of the FO unit. Urine should be collected at household level, concentrated with a FO unit before its transportation and application as a liquid fertilizer. The performances that could be reach by FO concentration are linked to the draw solution concentration that will be used to generate a high osmotic pressure difference, the membrane area through which water moves, the draw solution volume that should be high enough to sustain the osmotic pressure in order to reach the concentration target of urine in a specific required time.

Laboratory experiments on forward osmosis are generally carried out with small volumes of feed and draw solutions, small membrane areas, and the results to predict the FO performances within a large scale process were limited. Model based simulation; design provides valuable methods and tools to enhance the engineering and the economic performances of FO processes. A numerical model was proposed in our previous research and succeeded to simulate water flux and nutrients concentrations under various operating conditions. In this chapter numerical simulation using this model were performed to propose the membrane area, the draw solution concentration and volume for a design of a FO system using hydrolyzed urine. To achieve this objective the following points were

assessed from simulations 1) the relationship among the draw solution volume, the concentration and the membrane area, 2) the effect of draw solution initial osmotic pressure on water and ammonia concentration factor and 3) the membrane area variation effect on the water and ammonia concentration factor.
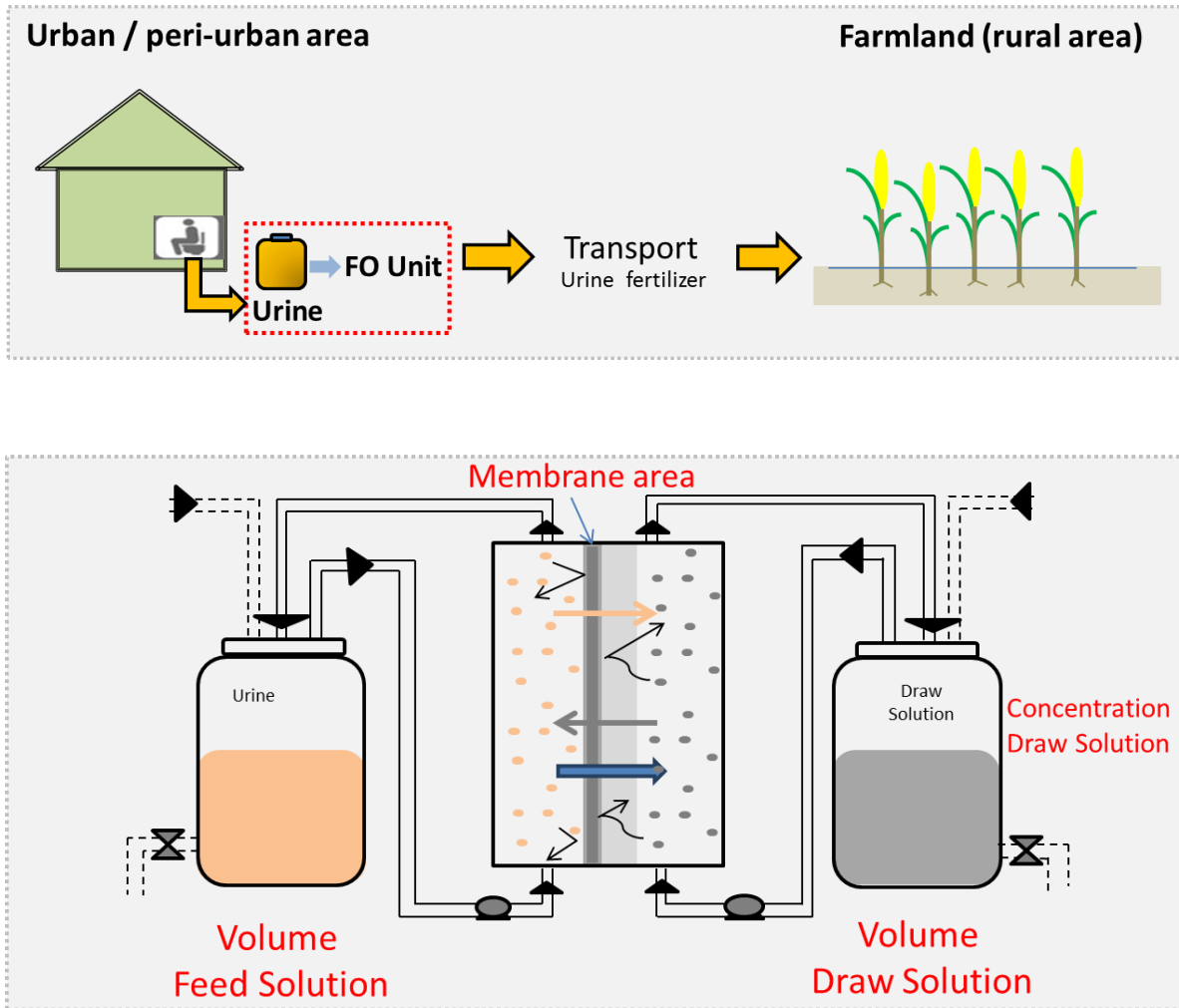
Figure 1 General concept of the concentration of urine by forward osmosis process

4.2 MATERIALS AND METHODS

The design of the FO reactor was proposed based on different draw solutions concentrations, volumes, and a daily urine load of 1 L as an example and later extended to 5 L case. The numerical model developed and validated in the chapter 3 was used for the estimation of the FO membrane area and the estimation of nutrients and water concentration factors.

4.2.1 Setting the volume reduction target

It is important to set urine volume reduction target by FO process. In order to provide financial incentives to farmers to use urine instead of the commercially available fertilizer 80% that is equivalent to 1/5 volume reduction was proposed (Massoom, 2012) in a configuration were urine should be transported toward farmlands for its application. A daily urine load of 1l was used as an example for the calculation of the membrane area and the performances. From the FO concentration results in chapter 2, 0.5 L could be concentrated to 80% in 7 hours operations therefore we proposed a volume reduction target time of 12 hours to concentrate 1 L of urine.

4.2.2 Simulation input data and design parameters

The model involves the diffusion of urine and draw solutes. The same diffusivities values obtained in the previous study (Chapter 3) as well as the permeability (A), the time step (Δt), the division step of the membrane (Δx), were used in the current simulation. The input concentrations of the synthetic hydrolyzed urine, NaCl draw solution osmotic pressure are respectively summarized in Table 1 and Table 2.

Table 1 Synthetic hydrolyzed urine concentration

Solute	Activity (mol/L)
Na	0.108
Cl	0.082
NH_3	0.685
IC	0.255
K	0.037
PO_4	0.016

Table 2 Combination of draw solution volume and concentrations used as the simulations initial conditions

Concentrations DS (mol/L)	DS (MPa)	Draw solution volumes (L)							
		0.15	0.20	0.25	0.5	1	2	4	5
2	6.96	C2, V0.15	C2,V0.2	C2,V0.25	C2,V0.5	C2,V1	C2,V2	C2,V4	C2,V5
3	11.40	C3, V0.15	C3,V0.2	C3,V0.25	C3,V0.5	C3,V1	C3,V2	C3,V4	C3,V5
4	16.93	C4, V0.15	C4,V0.2	C4,V0.25	C4,V0.5	C4,V1	C4,V2	C4,V4	C4,V5
5	23.87	C5, V0.15	C5,V0.2	C5,V0.25	C5,V0.5	C5,V1	C5,V2	C5,V4	C5,V5
6	32.60	C6, V0.15	C6,V0.2	C6,V0.25	C6,V0.5	C6,V1	C6,V2	C6,V4	C6,V5

4.2.3 Estimation of the required membrane area

Numerical simulations were performed to estimate the required membrane area to concentrate 1 liter of hydrolyzed urine to 1/5 of its initial volume in 12 hours. A combination of initial draw solution concentration and draw solution volume were set as initial condition for each simulation. Table 2 shows the 40 combinations used as initial conditions of the simulation. An iterative simulation was then performed for each combination to reach the target concentration factor of 5 in 12 hours. For this purpose an initial membrane area of 800 cm^2 was inputted in the program and was iteratively decreased according the equation 1 until the simulation results reached the target time and concentration.

$$A_{n+1} = A_n * \frac{t_n}{t_{12h}} \tag{1}$$

Where A_n and t_n are respectively the area and time used the reach 1/5 concentration of the current calculation, A_{n+1} the area of the next calculation and t_{12h} the target time that should be reached,

4.2.4 Calculation of the FO performances

The recovery percentage of NH_3, K and PO_4 was estimated from simulation results using the following equation (2):

$$R\ (\%) = \frac{C_{i_{ft}} * V_{ft}}{C_{i_{initial}} * V_{initial}} * 100 \qquad (2)$$

Where, $C_{i_{ft}}$ is the final concentration of the nutrient i, V_{ft} is the feed solution volume at the time t, $C_{i_{initial}}$ the initial concentration of the nutrient i and $V_{initial}$ the initial feed solution volume.

The volume concentration level, C_l (-), and concentration factor of each solute, C_f (-), were calculated with equations (3) and (4).

$$C_l = \frac{V_{F,ini}}{V_{F,t}} \qquad (3)$$

$$C_f = \frac{C_{F,t}}{C_{F,ini}} \qquad (4)$$

where $V_{F,ini}$ and $V_{F,t}$ are the feed solution volumes at initial state and at time t (m^3), respectively, while $C_{F,ini}$ and $C_{F,t}$ are the concentrations of solutes in feed solution at initial state and at time t (mol/L), respectively.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Relationship among the draw solution volume, concentration and the membrane area

Figure 2 shows the required membrane area to concentrate 1L of urine to 1/5 of its initial volume in 12 hours, plotted using the results obtained from the simulations conditions presented in Table 2. Low initial DS concentrations conditions require large draw solution volumes to reach 80% urine concentration owing to the low water flux that is generated. The required membrane area to reach the concentration target decreases with the increase of the initial draw solution concentration and volume. However this effect becomes negligible when the volume is higher than 1 L. From an economic point of view large membranes areas, high DS concentration and volume imply high implementation cost of the FO system. Since up to a certain DS volume the membrane variation is low is will be suitable to concentrate urine with a volume less or equal to 1L.
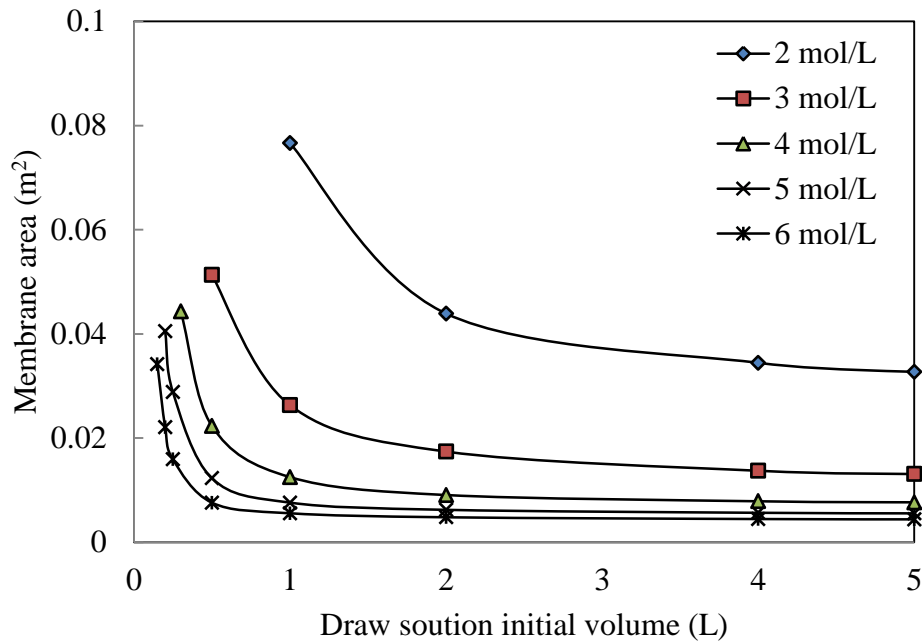
Figure 2 Relationship between the draw solution volume, concentration and the required membrane area

4.3.2 Effect of the initial osmotic pressure variation on ammonia concentration factor and recovery percentage

Figure 3 shows the time course of NH_3 concentration factor and urine volume concentration level plotted using the output results of the numerical simulation for a membrane area of 300 cm^2. Urine volume concentration level increases gradually and reaches a factor of 5 at 12 hours of volume reduction operation. NH_3 concentration factor shows an increasing pattern which reaches a peak value and decreases. This can be explained by the fact that during the FO process high water flux generates a rapid feed volume reduction which increases the NH_3 concentration at low water flux stage NH_3 concentration decreases owing to its high diffusion. Since the target of the FO design is to concentrate the volume to 1/5, the concentration factors values obtained when the volume was reduced by 1/5 were considered. At 5 times volume reduction level, NH_3 concentration factors of 1.1, 1.2, 1.2, 1.3 and 1.4 were obtained respectively for 2, 3, 4, 5 and 6 mol/L. Figure 4 shows the recovery percentage of NH_3 that was estimated to 22.7, 24.8, 24, 25 and 27.5% respectively for 1, 2, 3, 4, 5 and 6 mol/L DS. NH_3 concentration factor increases with an importance of the initial draw solution osmotic pressures and 6 mol/L DS concentration reaches high amount of NH_3 during the volume reduction process.
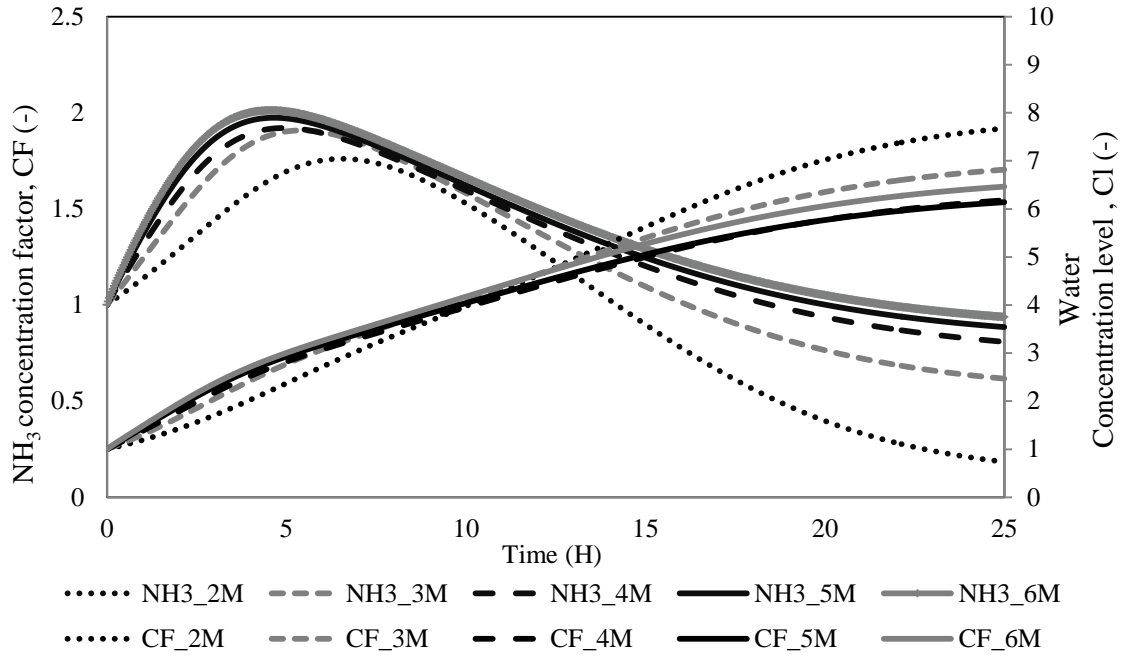
Figure 3 Time course of NH$_3$ concentration and the volume concentration level, case of 300 cm^2 membrane area

	2	3	4	5	6
NH3_DS	77.3	75.2	76.0	74.7	72.5
NH3_FS	22.7	24.8	24.0	25.3	27.5
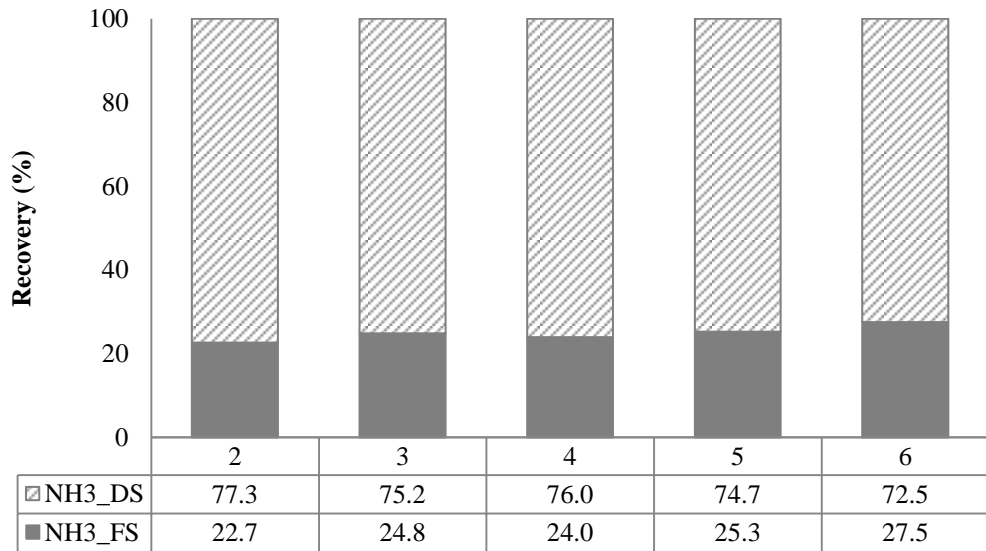
Figure 4 Recovery percentage of NH$_3$ corresponding to 1/5 volume reduction, case of 300 cm^2 membrane area

4.3.3 Effect of the membrane area variation on ammonia concentration factor and recovery percentage

From the analysis on the relationship between the DS volume and membrane area and knowing high DS concentration is suitable to recover high NH_3 amount, the analysis of the effect of the membrane area variation on NH_3 recovery was done using the output results of the numerical simulation for 6 mol/L DS concentration and 6 selected membrane areas values of 56, 76, 104, 160, 221, and 342 cm^2 that correspond respectively to DS volumes of 1, 0.5, 0.37, 0.25, 0.20, and 0.15L. Figure 5 shows that large membrane areas generate a rapid decrease of water flux that is owing to a fast dilution of the DS. A decrease of the area lead to a decrease of the amount of water that pass through the membrane therefore the decreasing rate of water flux is low. In Figure 6 NH_3 concentration factor significantly increases with the decrease of the membrane area and the concentration factor increase from 1.4 to 3.9 could be reached at five times volume reduction level. Moreover NH_3 recovery percentage could be improved from 28% to 79 % by decreasing the membrane area from 342 to 56 cm^2 (Figure 7).
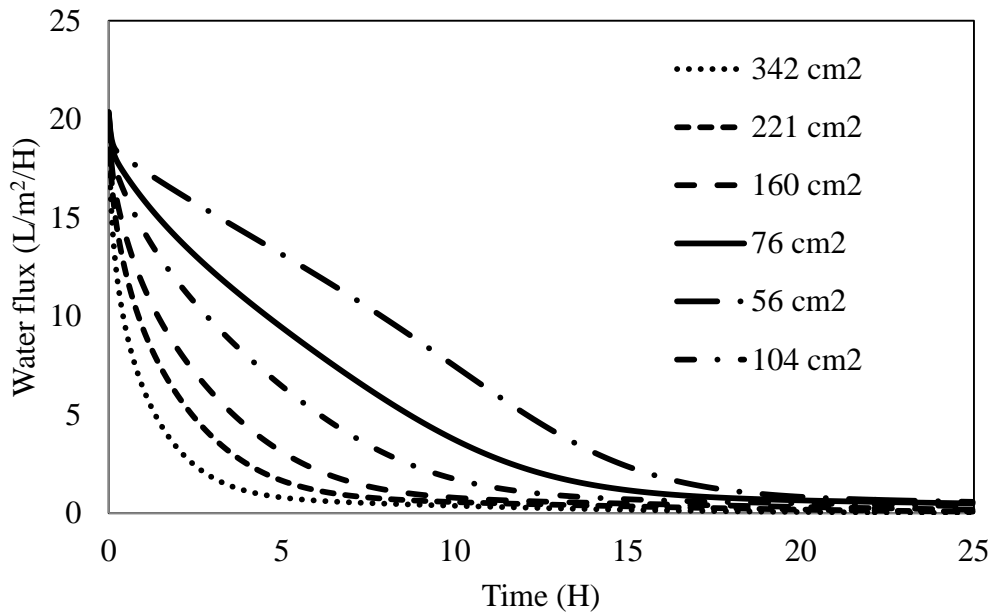
Figure 5 Time course of water flux calculated with variable membrane areas (342 - 56 cm^2)
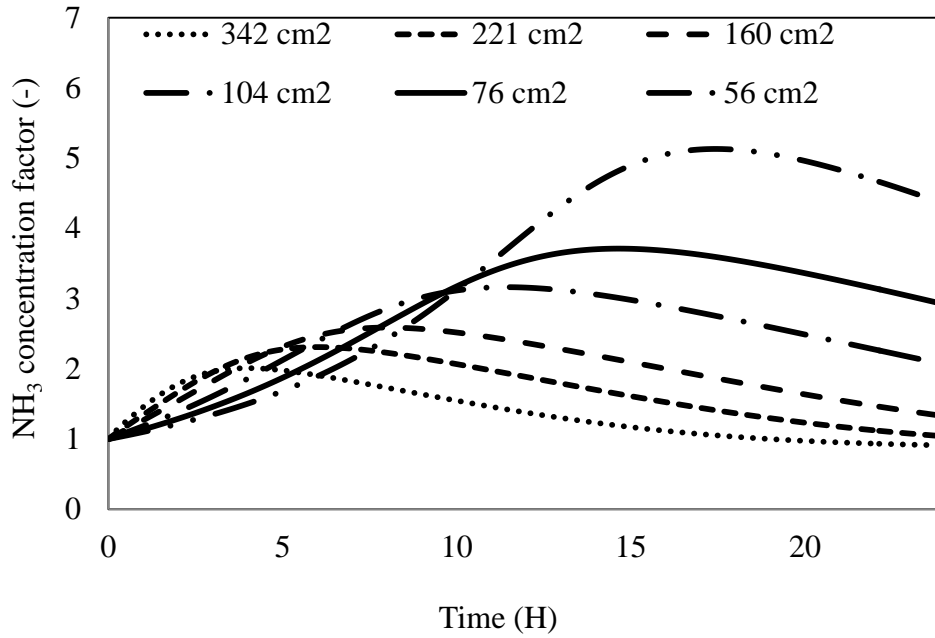
Figure 6 Time course of NH_3 concentration factor calculated with variable membrane areas (342 - 56 cm^2)

	342	221	160	104	76	56
☒ NH3 FS	72	62	53	37	29	21
■ NH3 FS	28	38	47	63	71	79
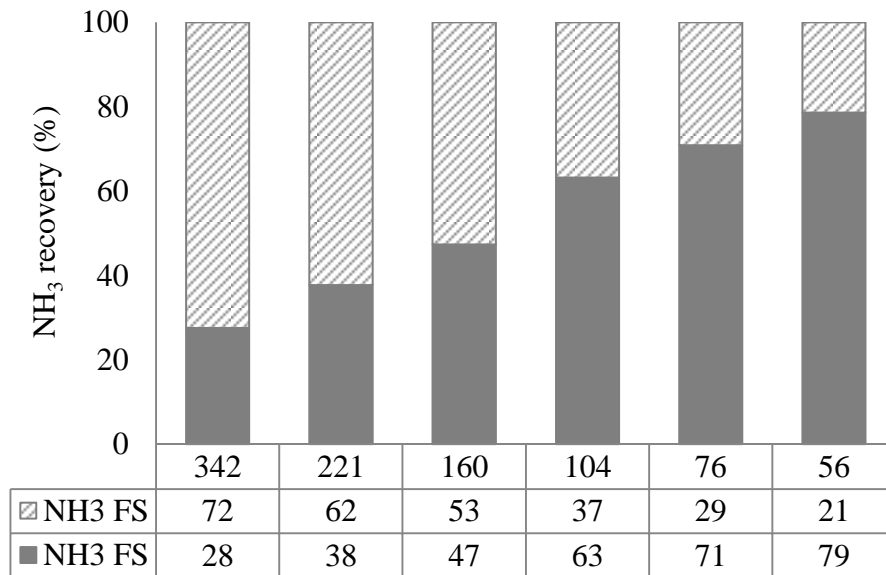
Figure 7 Recovery percentage of NH_3 corresponding to 1/5 volume reduction, case of variable membrane areas

4.3.4 Proposed design parameters for the FO unit

The design parameters were proposed based on the analysis of the draw solution initial concentration and the membrane area effect on urine volume reduction level and NH_3 concentration factor. To reduce 1 liter of urine to 1/5 in 12 hours operation we suggested a membrane area of 56 cm^2 and DS volume of 1 L with the 6 mol/L DS concentration. For a household of 5 persons and assuming that each member produce 1L of urine per day, the daily load of urine to concentrate was estimated to 5L. Therefore 280 cm^2 membrane area and 5 L of DS volume that are 5 times higher than the condition proposed for 1L case are required to reach 1/5 concentration in 12 hours. The FO performances that could be reached with the proposed parameters for a household of 5 persons are shown on Figure 8 and 9. At five times volume reduction, nutrients concentrated factor of 3.9, 4.8 and 4.9 and a recovery percentages of 78.6, 97.8 and 99.6 % could be achieved respectively for NH_3, K and PO_4.
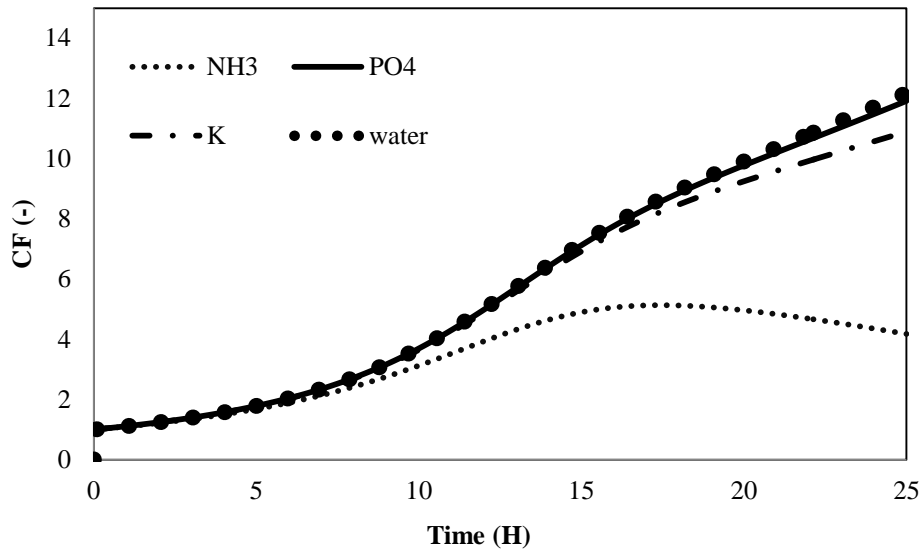
Figure 8 Time course of NH_3, K, PO_4 concentration and the volume concentration level calculated with the proposed design parameters

	NH3	K	PO4
▨ Draw	21.4	2.2	0.4
■ Feed	78.6	97.8	99.6
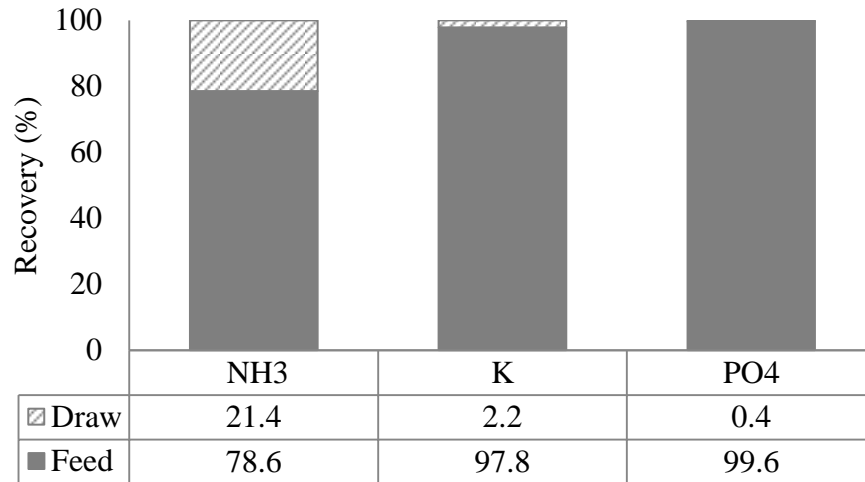
Figure 9 Recovery of NH_3, K, PO_4 at 5 times urine volume reduction calculated with the proposed design parameters

4.4 CONCLUSION

A numerical model was used to evaluate the required volume of draw solution to concentrate hydrolyzed urine into 1/5 of its initial volume and recover the nutrients (NH_3, K, and PO_4). In this chapter the following points were assessed: 1) the relationship among the initial draw solution concentration, volume, and the membrane area, 2) the effect of the draw solution initial osmotic pressure variation on ammonia concentration factor and recovery percentage, 3) the effect of the membrane area variation on ammonia concentration factor and recovery percentage. The results show that: 1) the required membrane area decreases with the increase of the initial draw solution concentration however this effect becomes negligible when the initial draw solution volume set exceeds urine initial volume. 2) NH_3 concentration factor increases with the importance of the initial draw solution concentration. At 5 times volume reduction levels of urine, 1.1 to 1.4 concentration factor of NH_3 were obtained and 22.7 - 27.5% of NH_3 could be recovered with 300 cm^2 membrane area case. 3) The reduction of the area from 342 to 56 cm^2 enhanced the concentration factor of NH_3 that increased from 1.4 to 3.9. To reduce 5 liter of urine to 1/5 in 12 hours operation we suggested a membrane area of 280 cm^2 and a draw solution volume of 5 L with the osmotic pressure of 32.6 MPa.

4.5 REFERENCES

Hellström, D., Johansson, E., Grennberg, K., 1999. Storage of human urine: acidification as a method to inhibit decomposition of urea. Ecol. Eng. 12, 253–269.

Lind, B.-B., Ban, Z., Bydén, S., 2001. Volume reduction and concentration of nutrients in human urine. Ecol. Eng. 16, 561–566. doi:10.1016/S0925-8574(00)00107-5

Maurer, M., Pronk, W., Larsen, T.A., 2006. Treatment processes for source-separated urine. Water Res. 40, 3151–3166.

Nybrant, T., Jonsson, H., Sonesson, U., Frostell, B., Mingarini, K., Thyselius, L., Dalemo, M., Sundqvist, J-O, (1996) Systems Analysis of Organic Waste. The ORWARE model case study Part One. Swedish Environmnetal Protection Agency, Stockholm, Sweden

Pahore, M, M, Ito, R, Funamizu, N, 2011. Performance evaluation of on-site volume reduction system with synthetic urine using a water transport model. Environ. Technol. 33, 229-235

Phuntsho, S., Shon, H.K., Hong, S., Lee, S., Vigneswaran, S., 2011. A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: evaluating the performance of fertilizer draw solutions. J. Membr. Sci. 375, 172–181.

Zhang.J., She, Q., Chang,V., W., Tang, C.Y.R.D. Webster: Mining Nutrients (N,P,K) from urban source separated urine by forward osmosis dewatering. J. Environ. Sci Technol., 48(6), 3386-3394, 2014.

CHAPTER 5
CONCLUSIONS AND RECOMMANDATIONS

This research was carried out to address the transportation and management challenges related to the direct application of human urine as a liquid fertilizer. The volume reduction was identified as a requirement to make urine fertilizer cost effective therefore; forward osmosis process was proposed as an emerging and promising technology for the concentration process. By using FO process, water contained in urine is expected to move through a semipermeable membrane driven by an osmotic pressure gradient created by a draw solution of high osmotic pressure. This research assessed the phenomena occurring during the concentration process, proposed a numerical model to estimate the amount of water that could be reduced and the amount of nutrient that can be recovered and proposed a design for the implementation of the FO unit. The important conclusions of this study can be enumerated as follow:

5.1 FINDINGS

5.1.1 Evaluation of forward osmosis for synthetic and real hydrolyzed urine concentration

➢ Forward osmosis experiments were carried out with synthetic and real hydrolyzed urine using a cellulose triacetate membrane and sodium chloride draw solution. The volumes of both synthetic and real hydrolyzed urine were reduced to 1/2-1/5 with a 3-4 mol/L NaCl concentration. Forward osmosis presented similar results indicating that synthetic urine could be used in FO experiments were controlled conditions are necessary.

➢ Solute activity was found to influence the osmotic pressure variation during urine concentration. The feed solution osmotic pressure is lowered owing to the high concentration level reached and to the molecules interactions in urine solution. The consideration of the activities for high concentration solutions showed good estimation on the water flux from the osmotic pressure.

➢ The organic matter in real hydrolyzed urine had a negligible effect on the osmotic pressure variation; therefore, inorganic solutes have major effects on water flux calculation.

5.1.2 New model for forward osmosis simulations

➢ The simulated results represent well the evolution of the water flux and the volume change of the feed and draw solutions. The diffusion of synthetic hydrolyzed urine nutrients (NH_3, K, and PO_4) was well estimated. This model with the inclusion of the multicomponent diffusion is a mean to improve the FO operation performances in the applications such as urine concentration were the recovery of nutrients is important.

> The model developed can substantially help to predict the flux variation under different system conditions at high osmotic pressure difference conditions and therefore help to optimize the performances and to propose new designs for FO applications to urine concentration.

5.1.3 Forward osmosis unit for hydrolyzed urine concentration

> The required membrane area decreases with the increase of the initial draw solution concentration and volume however this effect becomes negligible when the draw solution volume exceeds urine initial volume.

> NH_3 concentration factor slightly increase with the importance of the initial draw solution concentration. At 5 times volume reduction levels of urine, 1.1 to 1.4 concentration factor of NH_3 were obtained and 22.7 - 27.5% of NH_3 could be recovered with 300cm^2 membrane area.

> The reduction of the membrane area from 342 to 56 cm^2 enhanced the concentration factor of NH_3 that was increase from 1.4 to 3.9. To reduce 5 liters of urine to 1/5 in 12 hours operation we suggested a membrane area of 280 cm^2 and a draw solution volume of 5 L with an osmotic pressure of 32.6 MPa.

5.2 RECOMMANDATIONS

The model parameters obtained where performed under specific condition of temperature and flow rate and membrane type. However they can be applied to FO studies using the same conditions provided in our research (diffusivity and osmotic pressure are temperature sensitive)

Some part of the research work which was not address in the scoop of our PhD study may be considered for future investigations such as a long term urine concentration. The FO membrane will be subject to fouling and a development of microorganisms that could reduce the performances. Therefore there is a need to study effect of long term operation on the membrane water permeability and rejection performances.

SUPPLEMENTARY MATERIALS CHAPTER 2

Activity calculation

Table S1 shows an example of the typical data input in PHREEQC. The activities of the solutions were estimated by the freezing point depression before estimation of the osmotic pressure difference from the activity. Figures S1.a and S1.b show the comparison of the measured activities with that estimated from the simulation in NaCl solution and SHU. The concentration axes represent the sum of Na and Cl concentrations in Fig. S1.a, and the sum of the hydrolyzed urine component concentrations in Fig. S1.b. The diagonal line shows an ideal case. A good correlation was obtained between the simulated and the measured values in both NaCl solution and SHU, therefore, the calculation by Phreeqc could apply to estimate the osmotic pressure.

Table S1 Example of the typical data input in PHREEQC

```
SOLUTION 0
  temp    25
  pH      9.4 charge
  pe      4
  redox   pe
  units   mol/kgw
  density 1
  Amm     0.816 as AmmH+
  C       0.475
  Ca      0
  Cl      0.106
  K       0.048
  Mg      0.001
  Na      0.142
  P       0.022 as PO4-3
  -water  0.5 # kg



EQUILIBRIUM_PHASE
Hydroxyapatite   0        0
Calcite          0        0
Calciumhydroxide 0        0
DCPD             0        0
MAP              0        0
Sodiumhydrogencarbonate0        0



PHASES
DCPD
    CaHPO4 = Ca+2 + HPO4-2
    log_k      -6.6

Calciumhydroxide
    Ca(OH)2=Ca+2 + 2OH-
    log_k      -5.26

MAP
    MgAmmHPO4 = Mg+2 + AmmH+ + PO4-3
    log_k    -13.15

Sodiumhydrogencarbonate
        NaHCO3=Na+ + HCO3-
        log_k   -0.25
```
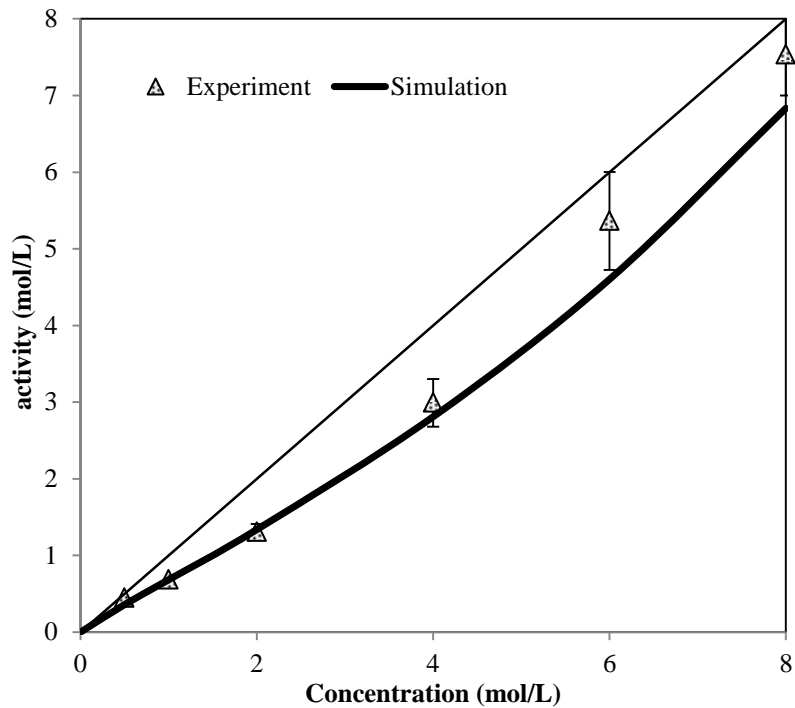
Figure S1.a Experimental and simulated activities in NaCl solution
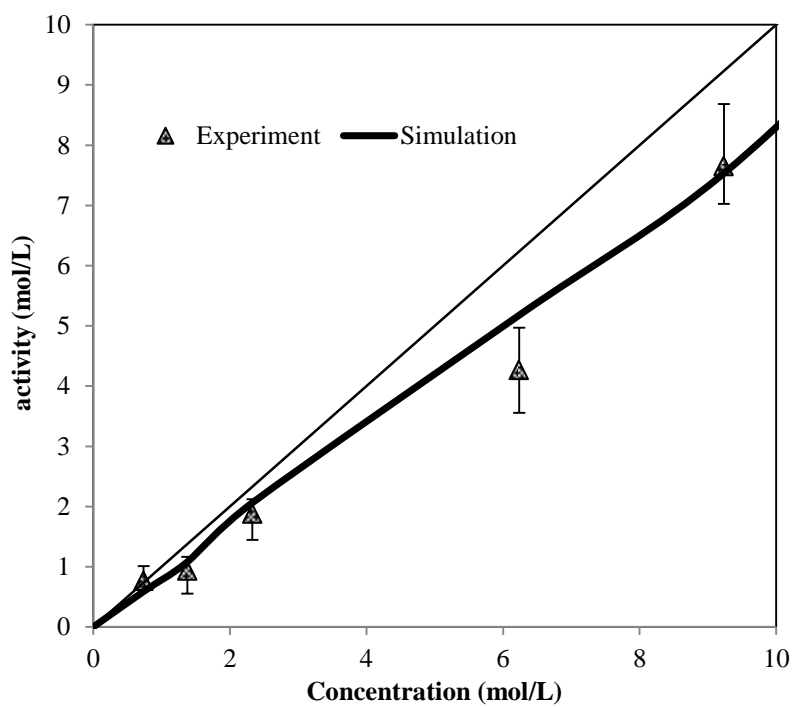
Figure S1.b Experimental and simulated activities in SHU

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SUPPLEMENTARY MATERIALS CHAPTER 3

Diffusion-Advection-equations

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} = D_i\frac{\partial^2 C_i}{\partial x^2} \tag{1}$$

Where, C_i (mol/m^3) is concentration of component i, u (m/s) is velocity of advection flow, D_i (m^2/s) is diffusivity of component i, t (s) is time, x (m) is distance from the surface of the layer of feed solution side. The membrane consists of several layers, which have different diffusivities. Therefore, Eq. (1) can be redefined as;

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} = \frac{\partial}{\partial x}\left(D_i\frac{\partial C_i}{\partial x}\right) \tag{2}$$

initial condition

$$C_i = 0 \text{ (at } t = 0, \text{for any x)} \tag{3}$$

boundary conditions

$$C_{i,0} = C_{\text{FS}} \text{ (feed solution)} \tag{4}$$
$$C_{i,n} = C_{\text{DS}} \text{ (draw solution)} \tag{5}$$

Eq. (2) was discretized by Crank-Nicolson method.

$$\frac{C_{i,x}{}^{t+1} - C_{i,x}{}^{t}}{\Delta t} = \frac{\partial}{\partial x}\left(D_{i,x+1/2}{}^{t+1/2}\frac{C_{i,x+1}{}^{t+1/2} - C_{i,x}{}^{t+1/2}}{\Delta x}\right)$$ $$- u\frac{C_{i,x+1/2}{}^{t+1/2} - C_{i,x-1/2}{}^{t+1/2}}{\Delta x}$$	(6)
$$\frac{C_{i,x}{}^{t+1} - C_{i,x}{}^{t}}{\Delta t} = \frac{1}{\Delta x}\left(D_{i,x+1/2}{}^{t+1/2}\frac{C_{i,x+1}{}^{t+1/2} - C_{i,x}{}^{t+1/2}}{\Delta x}\right.$$ $$\left. - D_{i,x+1/2}{}^{t+1/2}\frac{C_{i,x}{}^{t+1/2} - C_{i,x-1}{}^{t+1/2}}{\Delta x}\right)$$ $$- u\frac{C_{i,x+1}{}^{t+1/2} + C_{i,x}{}^{t+1/2} - \left(C_{i,x}{}^{t+1/2} + C_{i,x-1}{}^{t+1/2}\right)}{2\Delta x}$$	(7)

where, $t + 1$ is next time step of step t, $t + 1/2$ is average of step t and step $t + 1$, $x + 1$ is next position of position x, $x + 1/2$ is average of position x and position $x + 1$ ($D_{i,x+1/2} = D_{i,x+1} + D_{i,x}$).

Simplifying Eq. 7 gives following equation.

$$\frac{C_{i,x}^{t+1} - C_{i,x}^{t}}{\Delta t} = \frac{1}{\Delta x}\left(\frac{D_{i,x+1}^{t+1/2} + D_{i,x}^{t+1/2}}{2}\frac{C_{i,x+1}^{t+1/2} - C_{i,x}^{t+1/2}}{\Delta x}\right.$$
$$\left.- \frac{D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}}{2}\frac{C_{i,x}^{t+1/2} - C_{i,x-1}^{t+1/2}}{\Delta x}\right)$$
$$- u\frac{C_{i,x+1}^{t+1/2} - C_{i,x-1}^{t+1/2}}{2\Delta x} \tag{8}$$

$$\frac{C_{i,x}^{t+1} - C_{i,x}^{t}}{\Delta t} = \frac{1}{2\Delta x^2}\left(\left(D_{i,x+1}^{t+1/2} + D_{i,x}^{t+1/2}\right)C_{i,x+1}^{t+1/2}\right.$$
$$- \left(D_{i,x+1}^{t+1/2} + 2D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)C_{i,x}^{t+1/2}$$
$$\left.+ \left(D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)C_{i,x-1}^{t+1/2}\right) - u\frac{C_{i,x+1}^{t+1/2} - C_{i,x-1}^{t+1/2}}{2\Delta x} \tag{9}$$

By discretizing for time direction,

$$C_{i,x}^{t+1} - C_{i,x}^{t} = \frac{\Delta t}{2\Delta x^2}\left(\left(D_{i,x+1}^{t+1/2} + D_{i,x}^{t+1/2}\right)\frac{C_{i,x+1}^{t+1} + C_{i,x+1}^{t}}{2}\right.$$
$$- \left(D_{i,x+1}^{t+1/2} + 2D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)\frac{C_{i,x}^{t+1} + C_{i,x}^{t}}{2}$$
$$\left.+ \left(D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)\frac{C_{i,x-1}^{t+1} + C_{i,x-1}^{t}}{2}\right)$$
$$- \frac{u\Delta t}{2\Delta x}\left(\frac{C_{i,x+1}^{t+1} + C_{i,x+1}^{t}}{2} - \frac{C_{i,x-1}^{t+1} + C_{i,x-1}^{t}}{2}\right) \tag{10}$$

$$-\frac{\Delta t}{4\Delta x^2}\left(D_{i,x+1}^{t+1/2} + D_{i,x}^{t+1/2}\right)C_{i,x+1}^{t+1} + \left(1\right.$$
$$+ \frac{\Delta t}{4\Delta x^2}\left(D_{i,x+1}^{t+1/2} + 2D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)\bigg)C_{i,x}^{t+1}$$
$$- \frac{\Delta t}{4\Delta x^2}\left(D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)C_{i,x-1}^{t+1} + \frac{u\Delta t}{4\Delta x}\left(C_{i,x+1}^{t+1} + C_{i,x+1}^{t}\right)$$
$$= \frac{\Delta t}{4\Delta x^2}\left(D_{i,x+1}^{t+1/2} + D_{i,x}^{t+1/2}\right)C_{i,x+1}^{t}$$
$$+ \left(1 - \frac{\Delta t}{4\Delta x^2}\left(D_{i,x+1}^{t+1/2} + 2D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)\right)C_{i,x}^{t}$$
$$+ \frac{\Delta t}{4\Delta x^2}\left(D_{i,x}^{t+1/2} + D_{i,x-1}^{t+1/2}\right)C_{i,x-1}^{t} + \frac{u\Delta t}{4\Delta x}\left(C_{i,x-1}^{t+1} + C_{i,x-1}^{t}\right) \tag{11}$$

here, u (=Jw in program) can be calculated by following equation,

$$u = Jw = A \cdot R \cdot T \cdot \sum_{i}^{\text{nelements}} \left(C_{i,\text{nba\_s}}{}^{t+1/2} - C_{i,\text{nba\_b}}{}^{t+1/2} \right)$$ (12)

$$= \frac{A \cdot R \cdot T \cdot}{2} \sum_{i}^{\text{nelements}} \left(C_{i,\text{nba\_s}}{}^{t+1} + C_{i,\text{nba\_s}}{}^{t} - C_{i,\text{nba\_b}}{}^{t+1} - C_{i,\text{nba\_b}}{}^{t} \right)$$

where, A (m/(Pa s)) is permeability of water through the active layer, R (J/mol/K) is gas constant, T (K) is absolute temperature, nba_b (-) is the position of surface of active layer of feed solution side, nba_s (-) is the position of the active layer surface of draw solution side.

To solve these systematic equations, Newton Raphson Method (NRM) was applied.

The vector and first derivation are as follows for the range of ($n\text{first}_i + 1 \leq j \leq n\text{final}_i - 1$);

$$
\begin{aligned}
fvec(j) = & \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + D_{i,j}{}^{t+1/2} \right) C_{i,j+1}{}^{t+1} \\
& - \left(1 + \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + 2D_{i,j}{}^{t+1/2} + D_{i,j-1}{}^{t+1/2} \right) \right) C_{i,j}{}^{t+1} \\
& + \frac{\Delta t}{4\Delta x^2} \left(D_{i,j}{}^{t+1/2} + D_{i,j-1}{}^{t+1/2} \right) C_{i,j-1}{}^{t+1} - \frac{Jw\Delta t}{4\Delta x} \left(C_{i,j+1}{}^{t+1} + C_{i,j+1}{}^{t} \right) \\
& + \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + D_{i,j}{}^{t+1/2} \right) C_{i,j+1}{}^{t} \\
& + \left(1 - \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + 2D_{i,j}{}^{t+1/2} + D_{i,j-1}{}^{t+1/2} \right) \right) C_{i,j}{}^{t} \\
& + \frac{\Delta t}{4\Delta x^2} \left(D_{i,j}{}^{t+1/2} + D_{i,j-1}{}^{t+1/2} \right) C_{i,j-1}{}^{t} + \frac{Jw\Delta t}{4\Delta x} \left(C_{i,j-1}{}^{t+1} + C_{i,j-1}{}^{t} \right)
\end{aligned}
$$ (13)

$$fjac(j, j+1) = \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + D_{i,j}{}^{t+1/2} \right) - \frac{Jw\Delta t}{4\Delta x}$$

$$fjac(j, j) = -\left(1 + \frac{\Delta t}{4\Delta x^2} \left(D_{i,j+1}{}^{t+1/2} + 2D_{i,j}{}^{t+1/2} + D_{i,j-1}{}^{t+1/2} \right) \right)$$ (14)

$$fjac(j, j-1) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,j}{}^{t+1/2}+D_{i,j-1}{}^{t+1/2}\right) + \frac{J_W\Delta t}{4\Delta x}$$

$$fjac(j, \text{nba\_b}_i) = \frac{A\cdot R\cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,j+1}{}^{t+1} + C_{i,j+1}{}^{t} - C_{i,j-1}{}^{t+1} - C_{i,j-1}{}^{t}\right)$$

$$fjac(j, \text{nba\_s}_i) = -\frac{A\cdot R\cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,j+1}{}^{t+1} + C_{i,j+1}{}^{t} - C_{i,j-1}{}^{t+1} - C_{i,j-1}{}^{t}\right)$$

At the boundaries which are next to bulk solution, Eq. (13) is rewritten as;

$$
\begin{aligned}
fvec(\text{nfirst}_i) = {} & \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2}+D_i{}^{t+1/2}\right)C_{i,\text{nfirst}_i+1}{}^{t+1} - \Bigg(1 \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2}+2D_{i,\text{nfirst}_i}{}^{t+1/2}+D_{i,\text{nFS}_i}{}^{t+1/2}\right)\Bigg) C_{i,\text{nfirst}_i}{}^{t+1} \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i}{}^{t+1/2}+D_{i,\text{nFS}_i}{}^{t+1/2}\right)C_{i,\text{nFS}_i}{}^{t+1} \\
& - \frac{J_W\Delta t}{4\Delta x}\left(C_{i,\text{nfirst}_i+1}{}^{t+1} + C_{i,\text{nfirst}_i+1}{}^{t}\right) \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2}+D_{i,\text{nfirst}_i}{}^{t+1/2}\right)C_{i,\text{nfirst}_i+1}{}^{t} \\
& + \left(1 - \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2}+2D_{i,\text{nfirst}_i}{}^{t+1/2}+D_{i,\text{nFS}_i}{}^{t+1/2}\right)\right) C_{i,\text{nfirst}_i}{}^{t} \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i}{}^{t+1/2}+D_{i,\text{nFS}_i}{}^{t+1/2}\right)C_{i,\text{nFS}_i}{}^{t} + \frac{J_W\Delta t}{4\Delta x}\left(C_{i,\text{nFS}_i}{}^{t+1} + C_{i,\text{nFS}_i}{}^{t}\right)
\end{aligned}
$$

$$
\begin{aligned}
fvec(\text{nfinal}_i) = {} & \frac{\Delta t}{4\Delta x^2}\left(D_i{}^{t+1/2}+D_{i,\text{nfinal}_i}{}^{t+1/2}\right)C_{i,\text{nDS}_i}{}^{t+1} - \Bigg(1 \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nDS}_i}{}^{t+1/2}+2D_{i,\text{nfinal}_i}{}^{t+1/2}+D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right)\Bigg) C_{i,\text{nfinal}_i}{}^{t+1} \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfinal}_i}{}^{t+1/2}+D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right)C_{i,\text{nfinal}_i-1}{}^{t+1} \\
& - \frac{J_W\Delta t}{4\Delta x}\left(C_{i,\text{nDS}_i}{}^{t+1} + C_{i,\text{nDS}_i}{}^{t}\right) + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nDS}_i}{}^{t+1/2}+D_{i,\text{nfinal}_i}{}^{t+1/2}\right)C_{i,\text{nDS}_i}{}^{t} \\
& + \left(1 - \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nDS}_i}{}^{t+1/2}+2D_{i,\text{nfinal}_i}{}^{t+1/2}+D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right)\right) C_{i,\text{nfinal}_i}{}^{t} \\
& + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfinal}_i}{}^{t+1/2}+D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right)C_{i,\text{nfinal}_i-1}{}^{t} \\
& + \frac{J_W\Delta t}{4\Delta x}\left(C_{i,\text{nfinal}_i-1}{}^{t+1} + C_{i,\text{nfinal}_i-1}{}^{t}\right)
\end{aligned}
$$

(15)

$$fjac(\text{nfirst}_i, \text{nfirst}_i + 1) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2} + D_{i,\text{nfirst}_i}{}^{t+1/2}\right) - \frac{J_{\text{W}}\Delta t}{4\Delta x}$$

$$fjac(\text{nfirst}_i, \text{nfirst}_i) = -\left(1 + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i+1}{}^{t+1/2} + 2D_{i,\text{nfirst}_i}{}^{t+1/2} + D_{i,\text{nFS}_i}{}^{t+1/2}\right)\right)$$

$$fjac(\text{nfirst}_i, \text{nFS}) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfirst}_i}{}^{t+1/2} + D_{i,\text{ nFS}_i}{}^{t+1/2}\right) + \frac{J_{\text{W}}\Delta t}{4\Delta x}$$

$$fjac(\text{nfirst}_i, \text{nba\_b}_i) = \frac{A \cdot R \cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,\text{nfirst}_i+1}{}^{t+1} + C_{i,\text{nfirst}_i+1}{}^{t} - C_{i,\text{ nFS}_i}{}^{t+1} - C_{i,\text{ nFS}_i}{}^{t}\right)$$

$$fjac(\text{nfirst}_i, \text{nba\_s}_i) = -\frac{A \cdot R \cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,\text{nfirst}_i+1}{}^{t+1} + C_{i,\text{nfirst}_i+1}{}^{t} - C_{i,\text{ nFS}_i}{}^{t+1} - C_{i,\text{ nFS}_i}{}^{t}\right)$$

$$fjac(\text{nfinal}_i, \text{nDS}_i) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nDS}_i}{}^{t+1/2} + D_{i,\text{nfinal}_i}{}^{t+1/2}\right) - \frac{J_{\text{W}}\Delta t}{4\Delta x}$$

$$fjac(\text{nfinal}_i, \text{nfinal}_i) = -\left(1 + \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nDS}_i}{}^{t+1/2} + 2D_{i,\text{nfinal}_i}{}^{t+1/2} + D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right)\right)$$

$$fjac(\text{nfinal}_i, \text{nfinal}_i - 1) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nfinal}_i}{}^{t+1/2} + D_{i,\text{nfinal}_i-1}{}^{t+1/2}\right) + \frac{J_{\text{W}}\Delta t}{4\Delta x}$$

$$fjac(\text{nfinal}_i, \text{nba\_b}_i) = \frac{A \cdot R \cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,\text{nDS}_i}{}^{t+1} + C_{i,\text{nDS}_i}{}^{t} - C_{i,\text{nfinal}_i-1}{}^{t+1} - C_{i,\text{nfinal}_i-1}{}^{t}\right)$$

$$fjac(\text{nfinal}_i, \text{nba\_s}_i) = -\frac{A \cdot R \cdot T}{2}\frac{\Delta t}{4\Delta x}\left(C_{i,\text{nDS}_i}{}^{t+1} + C_{i,\text{nDS}_i}{}^{t} - C_{i,\text{nfinal}_i-1}{}^{t+1} - C_{i,\text{nfinal}_i-1}{}^{t}\right)$$

(16)

where, nDSi and nFSi indicate concentrations in draw and feed solutions, nfirsti and nfinali are respectively boundaries contacting with feed and draw solutions. The advection term marked with red color is ignored for active layer. The concentrations at boundary between active layer and support layer is described as Eq. (17).

$$fvec(\text{nba\_s}_i) = \frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+D_{i,\text{nba\_s}_i}{}^{t+1/2}\right)C_{i,\text{nba\_s}_i+1}{}^{t+1}-\left(1\right.$$

$$+\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+2D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)\right)C_{i,x}{}^{t+1}$$

$$+\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)C_{i,\text{nba\_s}_i-1}{}^{t+1}$$

$$-\frac{J_W\Delta t}{2\Delta x}\left(C_{i,\text{nba\_s}_i+1}{}^{t+1}+C_{i,\text{nba\_s}_i+1}{}^{t}\right)$$

$$+\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+D_{i,\text{nba\_s}_i}{}^{t+1/2}\right)C_{i,\text{nba\_s}_i+1}{}^{t}$$

$$+\left(1-\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+2D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)\right)C_{i,\text{nba\_s}_i}{}^{t}$$

$$+\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)C_{i,\text{nba\_s}_i-1}{}^{t}$$

(17)

$$fjac(\text{nba\_s}_i,\text{nba\_s}_i+1)$$
$$=\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+D_{i,\text{nba\_s}_i}{}^{t+1/2}\right)C_{i,\text{nba\_s}_i+1}{}^{t+1}$$
$$-\frac{J_W\Delta t}{2\Delta x}\left(C_{i,\text{nba\_s}_i+1}{}^{t+1}+C_{i,\text{nba\_s}_i+1}{}^{t}\right)$$

$$fjac(\text{nba\_s}_i,\text{nba\_s}_i)=-\left(1+\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i+1}{}^{t+1/2}+2D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)\right)$$

$$fjac(\text{nba\_s}_i,\text{nba\_s}_i-1)=\frac{\Delta t}{4\Delta x^2}\left(D_{i,\text{nba\_s}_i}{}^{t+1/2}+D_{i,\text{nba\_s}_i-1}{}^{t+1/2}\right)$$

$$fjac(\text{nba\_s}_i,\text{nba\_b}_i)=\frac{A\cdot R\cdot T}{2}\frac{\Delta t}{2\Delta x}\left(C_{i,\text{nba\_s}_i+1}{}^{t+1}+C_{i,\text{nba\_s}_i+1}{}^{t}\right)$$

$$fjac(\text{nba\_s}_i,\text{nba\_s}_i)=-\frac{A\cdot R\cdot T}{2}\frac{\Delta t}{2\Delta x}\left(C_{i,\text{nba\_s}_i+1}{}^{t+1}+C_{i,\text{nba\_s}_i+1}{}^{t}\right)$$

(18)

The concentrations in bulk solutions are calculated by consideration of the flux and volume change. The volumes of feed and draw solution, V_{FS} and V_{DS} (m3), can be estimated as;

$$\frac{\partial V_{FS}}{\partial t} = -J_w S$$

$$\frac{\partial V_{DS}}{\partial t} = J_w S$$

(19)

The discretization can be described as follows;

$$V_{FS}{}^{t+1} - V_{FS}{}^{t} = -J_w S \Delta t$$

$$V_{DS}{}^{t+1} - V_{DS}{}^{t} = J_w S \Delta t$$

(20)

The vector and first derivation for NRM is;

$$fvec(\text{nVF}) = V_{FS}{}^{t+1} - V_{FS}{}^{t} + J_w S \Delta t$$

$$fvec(\text{nVD}) = V_{DS}{}^{t+1} - V_{DS}{}^{t} - J_w S \Delta t$$

$$fjac(\text{nVF}, \text{nVF}) = 1$$

$$fjac(\text{nVD}, \text{nVD}) = 1$$

$$fjac(\text{nVF}, \text{nba\_b}_i) = -\frac{A \cdot R \cdot T}{2} \cdot S \Delta t$$

$$fjac(\text{nVF}, \text{nba\_s}_i) = \frac{A \cdot R \cdot T}{2} \cdot S \Delta t$$

$$fjac(\text{nVD}, \text{nba\_b}_i) = \frac{A \cdot R \cdot T}{2} \cdot S \Delta t$$

$$fjac(\text{nVD}, \text{nba\_s}_i) = -\frac{A \cdot R \cdot T}{2} \cdot S \Delta t$$

(21)

The concentrations can be described as;

$$\frac{\partial C_{i,FS} V_{FS}}{\partial t} = -J_s = -J_w S C_i|_{\text{at FS}} + S D_i \left. \frac{\partial C_i}{\partial x} \right|_{\text{at FS}}$$

$$\frac{\partial C_{i,DS} V_{DS}}{\partial t} = J_s = J_w S C_i|_{\text{at DS}} - S D_i \left. \frac{\partial C_i}{\partial x} \right|_{\text{at DS}}$$

(22)

The discretization is;

$$\frac{C_{i,\text{FS}}{}^{t+1} - C_{i,\text{FS}}{}^{t}}{\Delta t} V_{\text{FS}}{}^{t+1/2} + C_{\text{FS}}{}^{t+1/2} \frac{V_{\text{FS}}{}^{t+1} - V_{\text{FS}}{}^{t}}{\Delta t}$$
$$= -J_{\text{w}} S C_{i,\,\text{FS}}{}^{t+1/2} + S D_i \frac{C_{i,\text{FS+1}}{}^{t+1/2} - C_{i,\text{FS}}{}^{t+1/2}}{\Delta x}$$

$$\frac{C_{\text{DS}}{}^{t+1} - C_{\text{DS}}{}^{t}}{\Delta t} V_{\text{DS}}{}^{t+1/2} + C_{\text{DS}}{}^{t+1/2} \frac{V_{\text{DS}}{}^{t+1} - V_{\text{DS}}{}^{t}}{\Delta t}$$
$$= J_{\text{w}} S C_{i,\,\text{DS}}{}^{t+1/2} - S D_i \frac{C_{i,\text{DS}}{}^{t+1/2} - C_{i,\text{DS}-1}{}^{t+1/2}}{\Delta x}$$

(23)

$$C_{\text{FS}}{}^{t+1} V_{\text{FS}}{}^{t+1} - C_{\text{FS}}{}^{t} V_{\text{FS}}{}^{t}$$
$$= -\frac{S\Delta t}{2} J_{\text{w}}\left(C_{i,\,\text{FS}}{}^{t+1} + C_{i,\,\text{FS}}{}^{t}\right)$$
$$+ D_i \frac{S\Delta t}{2\Delta x}\left(C_{i,\text{FS+1}}{}^{t+1} + C_{i,\text{FS+1}}{}^{t} - C_{i,\text{FS}}{}^{t+1} - C_{i,\text{FS}}{}^{t}\right)$$

$$C_{\text{DS}}{}^{t+1} V_{\text{DS}}{}^{t+1} - C_{\text{DS}}{}^{t} V_{\text{DS}}{}^{t}$$
$$= \frac{S\Delta t}{2} J_{\text{w}}\left(C_{i,\,\text{DS}}{}^{t+1} + C_{i,\,\text{DS}}{}^{t}\right) - D_i \frac{S\Delta t}{2\Delta x}\left(C_{i,\text{DS}}{}^{t+1} + C_{i,\text{DS}}{}^{t} - C_{i,\text{DS-1}}{}^{t+1} - C_{i,\text{DS-1}}{}^{t}\right)$$

(24)

then,

$$fvec(\text{nFS}) = C_{\text{FS}}{}^{t+1}V_{\text{FS}}{}^{t+1} - C_{\text{FS}}{}^{t}V_{\text{FS}}{}^{t} + \frac{S\Delta t}{2}J_{\text{w}}\left(C_{i,\,\text{FS}}{}^{t+1} + C_{i,\,\text{FS}}{}^{t}\right)$$
$$- D_i\frac{S\Delta t}{2\Delta x}\left(C_{i,\text{FS+1}}{}^{t+1} + C_{i,\text{FS+1}}{}^{t} - C_{i,\text{FS}}{}^{t+1} - C_{i,\text{FS}}{}^{t}\right)$$

$$fvec(\text{nDS}) = C_{\text{DS}}{}^{t+1}V_{\text{DS}}{}^{t+1} - C_{\text{DS}}{}^{t}V_{\text{DS}}{}^{t} - \frac{S\Delta t}{2}J_{\text{w}}\left(C_{i,\,\text{DS}}{}^{t+1} + C_{i,\,\text{DS}}{}^{t}\right)$$
$$+ D_i\frac{S\Delta t}{2\Delta x}\left(C_{i,\text{DS}}{}^{t+1} + C_{i,\text{DS}}{}^{t} - C_{i,\text{DS-1}}{}^{t+1} - C_{i,\text{DS-1}}{}^{t}\right)$$

$$fjac(\text{nFS}, \text{nFS}) = V_{\text{FS}}{}^{t+1} + \frac{S\Delta t}{2}J_{\text{w}} + D_i\frac{S\Delta t}{2\Delta x}$$

$$fjac(\text{nFS}, \text{nFS}+1) = -D_i\frac{S\Delta t}{2\Delta x}$$

$$fjac(\text{nFS}, \text{nVF}) = C_{\text{FS}}{}^{t+1}$$

$$fjac(\text{nFS}, \text{nba\_b}_i) = -\frac{A \cdot R \cdot T}{2} \cdot \frac{S\Delta t}{2}\left(C_{i,\,\text{FS}}{}^{t+1} + C_{i,\,\text{FS}}{}^{t}\right)$$ (25)

$$fjac(\text{nFS}, \text{nba\_s}_i) = \frac{A \cdot R \cdot T}{2} \cdot \frac{S\Delta t}{2}\left(C_{i,\,\text{FS}}{}^{t+1} + C_{i,\,\text{FS}}{}^{t}\right)$$

$$fjac(\text{nDS}, \text{nDS}) = V_{\text{DS}}{}^{t+1} - \frac{S\Delta t}{2}J_{\text{w}} + D_i\frac{S\Delta t}{2\Delta x}$$

$$fjac(\text{nDS}, \text{nDS}-1) = -D_i\frac{S\Delta t}{2\Delta x}$$

$$fjac(\text{nDS}, \text{nVD}) = C_{\text{DS}}{}^{t+1}$$

$$fjac(\text{nDS}, \text{nba\_b}_i) = \frac{A \cdot R \cdot T}{2} \cdot \frac{S\Delta t}{2}\left(C_{i,\text{DS}}{}^{t+1} + C_{i,\,\text{DS}}{}^{t}\right)$$

$$fjac(\text{nDS}, \text{nba\_s}_i) = -\frac{A \cdot R \cdot T}{2} \cdot \frac{S\Delta t}{2}\left(C_{i,\,\text{DS}}{}^{t+1} + C_{i,\,\text{DS}}{}^{t}\right)$$

Table S2 Additional parameters used as input for the numerical simulations

Parameter	Unit	Value
P (water permeability)	m/s/Pa	9.19×10^{-10}
R (perfect gas constant)	J/K/mol	8.314
T (absolute temperature)	K	298
S (membrane area)	m^2	0.01
Δt (simulation time step)	s	1
Δx (simulation spatial step)	m	1×10^{-6}