

Effect of membrane mean pore diameter on water and solute flux in forward osmosis processes



Ibrahim A. Alsayer^{1,*}, Ali A. Merdaw², Ibrahim S. Al-Mutaz³

¹Department of Chemical Engineering, Northern Border University, Arar, Saudi Arabia

²ME Scientific Engineering Ltd., Leeds, West Yorkshire, UK

³Chemical Engineering Department, College of Engineering, King Saud University, Riyadh, Saudi Arabia

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ABSTRACT

Several forward osmosis (FO) experiments were carried out using aqueous solutions of sodium chloride (NaCl) in different concentrations, as draw solution (DS), and freshwater, as feed water (FW). The experiments were conducted at a constant temperature of $\sim 20^{\circ}\text{C}$ and using a symmetric cellulosic membrane in two grades different in their values of the molecular weight cut-off (MWCO), which is related to the mean pore diameter. This study investigates the effect of the membrane mean pore diameter on water flux and DS solute diffusional flux across the membrane. The value of water flux indicates the performance of the FO process, while solute flux is an important factor that determines its practicality. A proportionality factor is used to specify the relationship between water flux and solute flux for each membrane type and operational conditions. The results of this study show that water flux and solute flux increase as the solute concentration difference across the membrane increases. It is also found that, in the range of the tested membranes, membranes with larger mean pore diameters have lower water flux and higher solute flux.

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1. Introduction

Forward osmosis (FO) is the engineered term for the natural process of osmosis. It is a membrane separation process where water is transferred naturally from a feed solution or Feed Water (FW), e.g., brackish or wastewater, towards a Draw Solution (DS), e.g., seawater or concentrated brine, across a semi-permeable membrane, driven by a Net Differential Pressure (NDP). The NDP is the osmotic pressure difference generated by the solute concentration difference across the membrane. FO has many active as well as potential applications. It is currently utilized for some industrial purposes such as the concentration of fruit juice and dairy products and in some medical applications such as hemodialysis, where wastes and excess water are removed from the blood. Membrane processes, in general, are attractive to the industry due to their simplicity (no phase change), applications diversity

at the ambient temperature, and relatively low energy needs, which have a major impact on greenhouse gases reduction (Cheng et al., 2018; Korenak et al., 2017; Luttmiah et al., 2014; Sarp and Hilal, 2018).

In applications such as wastewater treatment for freshwater production, integrating FO into wastewater treatment plants is useful to extract freshwater from the FW with little external energy input; hence, pre-concentrating and reducing the volume of feed. Extracting freshwater can be achieved by utilizing a high-salinity solution, such as DS, at the other side of the membrane. The freshwater can then be regenerated from the diluted DS using other processes, such as Reverse Osmosis (RO).

One of the major problems facing FO process practicability is the need for high-productivity membranes. The synthesis of high-performance FO membrane is still in the early stage of its development. An ideal FO membrane should possess high water flux as well as high solute rejection and good chemical stability. The symmetric membranes, which are composed of one homogenous layer, outperform the asymmetric ones, as adding porous supports decreases water permeation excessively (Loeb et al., 1997). Symmetric membranes do not endure internal solute concentration polarization,

* Corresponding Author.

Email Address: i.alsayer@nbu.edu.sa (I. A. Alsayer)

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Corresponding author's ORCID profile:

<https://orcid.org/0000-0001-5169-3028>

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which may occur in the substrate and intermediate layers of asymmetric membranes (McCutcheon and Elimelech, 2007). However, the current available FO membranes are composite (asymmetric) and made of a multi-layered structure (active skin, intermediate, and support layers).

The interest in FO technology over the past two decades has increased resulting in enormous publications in this field (Wang and Liu, 2021). The main trends of research and development are investigations on new membranes, drawing solutions, and optimizing operational conditions. An ideal DS should provide high osmotic pressure, low viscosity, easy recovery, and non-toxicity (Ge et al., 2013).

This study investigates the FO process using two grades of dialysis membranes available in the market has an average pore diameter of about 2.8nm and 3.9nm. This membrane is symmetrically composed of one active layer. This study attempts to

provide a better understanding of the relationship between water flux and solute flux, and the mean pore diameter, at different DS concentrations and similar temperatures. The experimental work of this study utilizes sodium chloride (NaCl) aqueous solutions as DS, while freshwater is FW.

The FO process can be schematically represented as shown in Fig. 1, where water molecules are represented as continuous and dotted arrows, while the DS solute molecules are represented as spheres. Water is transferred from the FW to the DS driven by the Net Differential Pressure (NDP) obtained from the osmotic pressure difference, $\Delta\Pi$, across the membrane. Water may transfer through the membrane pores or by diffusion through the membrane material. In the opposite direction, the DS solute molecules are transferred from the DS to the FW by diffusion driven by the concentration difference across the membrane (Loeb et al., 1997; Pendergast et al., 2016).

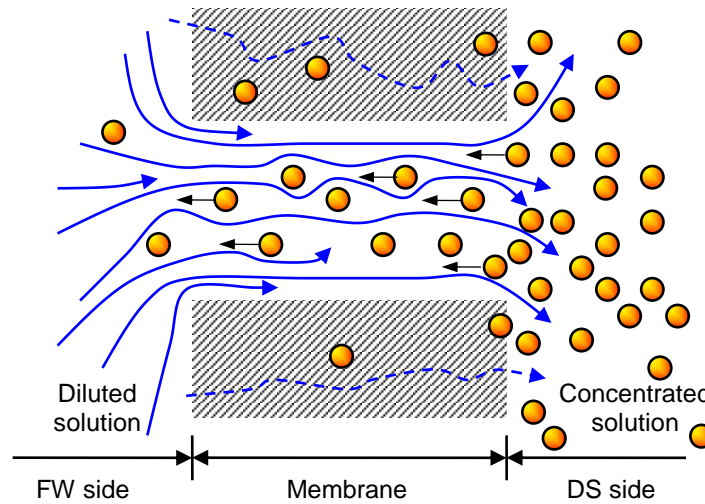


Fig. 1: Schematic representation for the FO process across a pore of a symmetric membrane using an aqueous solution as DS and pure water as FW

Water flux and solute flux in the FO process can be mathematically represented by several phenomenological relationships. Water volumetric flux, J_w , can be defined as follows:

$$J_w = A_w (\Pi_{DS} - \Pi_{FW}) \quad (1)$$

i.e., water flux, with units of, e.g., L/m².h, is driven by the Net Differential Pressure (NDP) across the membrane ($\Pi_{DS} - \Pi_{FW}$), where A_w is a water permeability coefficient with units of, e.g., L/m².h.bar. The DS solute mass flux, J_s , can be represented as:

$$J_s = B_s (c_{DS} - c_{FW}) \quad (2)$$

i.e., the DS solute mass flux, with units of, e.g., g/m².h, is driven by the concentration difference ($c_{DS} - c_{FW}$), in, e.g., g/m³, where B_s is a DS solute permeability coefficient with units of, e.g., m/h.

In FO processes, water flux is proportional to the solute flux:

$$J_s = k_j J_w \quad (3)$$

where k_j is a flux proportionality factor that has units of concentration of, e.g., g/m³, and represents the extent of solute-water mutual transfer across the membrane.

By substituting both Eqs. 1, and 2 into Eq. 3, the following relationship can be obtained:

$$B_s (c_{DS} - c_{FW}) = k_j A_w (\Pi_{DS} - \Pi_{FW}). \quad (4)$$

The osmotic pressure, Π , is the property of the solutions, which results from the dissolution of solutes in an aqueous solution. In physical terms, it is the hydrostatic pressure produced by a solution in a compartment separated by a semi-permeable membrane from another of lower concentration. Several relationships have been developed to predict

the osmotic pressure of the solutions. One of the most commonly used formulas is the van't Hoff equation for ideal solutions (van't Hoff, 1995):

$$\Pi = i_v \frac{c}{M_{wt}} R_g T \quad (5)$$

where i_v is the van't Hoff factor and refers to the number of moles of the dissociated entities when one mole of the solid solute is dissolved (e.g., for glucose $i_v=1$ and for NaCl $i_v=2$), c is the weight concentration of the solute, R_g is the universal gas constant, and T is the thermodynamic temperature.

By substituting Eq. 5 into Eq. 4, the following relationship can be obtained for the case of ideal binary solution on both sides of the membrane:

$$B_S (c_{DS} - c_{FW}) = k_J \frac{i_v R_g T}{M_{wt}} (c_{DS} - c_{FW}). \quad (6)$$

This can be simplified into the following:

$$B_S = k_E A_w \quad (7)$$

where:

$$k_E = k_J \frac{i_v R_g T}{M_{wt}}. \quad (8)$$

The new factor, k_E , is a permeability proportionality factor, a function of temperature, and has units of pressure (e.g., bar). Eq. 7 shows that solute permeability increases proportionally with water permeability, while Eq. 8 shows the effects of the molecular weight of the solute and the temperature on the factor k_E . For example, with low operating temperature and high molecular weight of the DS solute, a lower solute permeability can be obtained.

In spite of the simplicity of the van't Hoff equation, it is limited to ideal solutions. In ionic solutions, due to a phenomenon called ion pairing, a certain number of positive and negative ions will randomly come together and form ion pairs. This reduces the total number of free particles in the solution, and consequently decreases the osmotic pressure from its ideally estimated value by Eq. 5.

However, Eq. 6 can be developed further by incorporating osmotic coefficients that account for the deviation of the solvent from the ideal behavior (McNaught, 1997).

2. Experimental methods

The FO process is investigated in this study using the set-up schematically represented in Fig. 2. It is composed of two plastic (PVC) tanks; the first tank is an osmotic cell that contains the DS, has a volume of 18 L, while the other tank contains the FW and has a volume of 15L. Each tank is equipped with a discharging tap and a water level indicator. The FO cell is composed of 12 membrane tubes arranged in three rows and four columns. The length of each membrane tube is 300mm with a diameter of 16 mm. The membrane tubes are connected horizontally between the DS tank sides. The tubes are positioned to be submerged inside the DS solution, while the FW flows inside them. The total membrane surface area of the membrane is estimated to be 0.181m². The membrane tubes' inputs and outputs are collected outside the DS tank using a configuration of connectors and plastic tubes.

The DS and the FW tanks are equipped with submersible pumps; the DS pump circulates the DS solution inside its tank homogenizing the solute concentration, while the FW pump circulates the FW through the tubular membranes. The flow rate of the DS pump is 10L/min, while the flow rate of the FW pump is 7.44L/min. The average FW flow rate inside each tubular membrane is 0.62L/min, providing a laminar flow pattern with a Reynolds number value of about 922.

The FO membrane used in this study is a dialysis cellulosic membrane, supplied by Medicell International Ltd (UK). Two grades were chosen, DVT03500 and DVT07000, different in their Molecular Weight Cut-Off (MWCO) values, but identical in their thicknesses, materials, and overall dimensions. In order to test each membrane individually, two identical osmotic cells (DS tanks) were made, each using a specific membrane grade.

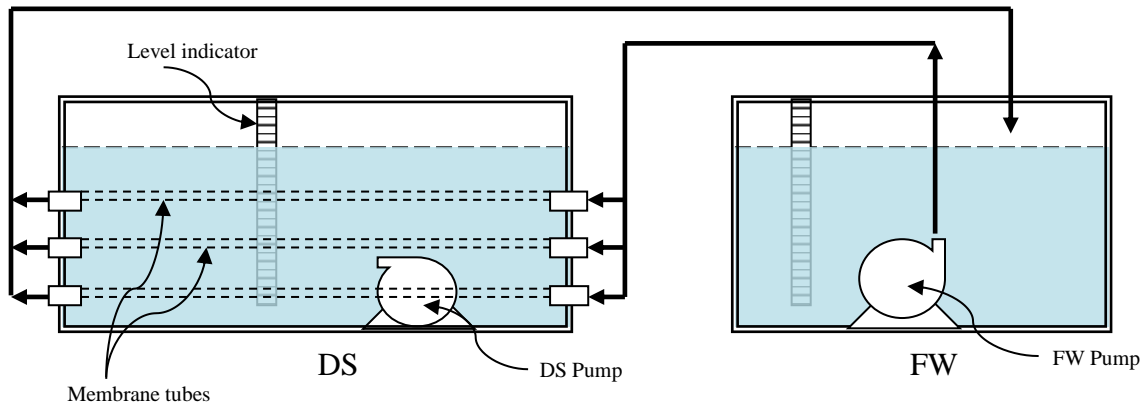


Fig. 2: Schematic representation for the FO bench-scale experimental setup

According to the manufacturer datasheets, this dialysis membrane is made of natural cellulose

(cotton linters). It is fabricated by dissolving cellulose in special inorganic solvents, the polymer is

then reformed by taking away the solvent to form the membrane as a flat sheet. This membrane is highly resistant to organic solvents, elevated temperatures, and extremes of pH. The name code of the membrane refers to its MWCO. A membrane with MWCO of 3500 Daltons has a mean pore diameter of 2.8nm, while a membrane with MWCO of 7000 Daltons has a mean pore diameter of 3.9nm. The mean pore diameter is calculated from the MWCO using the following empirical relationship between the molecular weight and the molecular diameter (Ren et al., 2006):

$$D_p = 0.066 M_{wt}^{0.46} \quad (9)$$

where, D_p is the approximate diameter of the molecule in nano-meters and M_{wt} is the molecular weight in g/mol.

The experimental measurements of the solute concentrations were obtained from readings of the solution's electrical conductivity every 15~30 minutes. An electrical-conductivity meter model MC126 manufactured by Mettler-Toledo (Switzerland) was used. The corresponding values of

the osmotic pressure were calculated using stream analyzer software, OLI software, which predicts the properties of solutions via thermodynamic modeling based on experimental data. The temperature of the solutions was kept around room temperature (18~22°C) during the experiment.

3. Results and discussions

The experiments were carried out in two sets, each with a specific membrane type. All experiments were carried out at a constant temperature of 20°C, and each run lasted for about 7 hours (400~425 minutes). Pure water was used as FW, while aqueous solutions of sodium chloride (NaCl) were used as DS. Table 1 shows the initial FW and DS solute concentration, osmotic pressure, and the Net Differential Pressure (NDP) across the membranes. Due to the initial experimental setting, the initial FW solutions were contaminated by small quantities of NaCl solute diffused from the DS side. The data series of each run was named, as seawater or brine, referring to the DS concentration range used.

Table 1: Initial conditions of FO experiments using the membranes DVT3500 (mean pore diameter of 2.8nm) and DVT7000 (mean pore diameter of 3.9nm)

No.	Membrane type and data series name	DS initial concentration, NaCl g/L	DS initial osmotic pressure, bar	FW initial concentration, NaCl g/L	FW initial osmotic pressure, bar	Initial NDP, bar
1	DVT3500 Seawater	29.988	24.10	0.104	0.08	24.01
2	DVT3500 Brine	42.809	34.40	0.246	0.20	34.20
3	DVT7000 Seawater	33.668	27.05	0.466	0.37	26.68
4	DVT7000 Brine	38.096	30.61	0.270	0.22	30.39

The experimental results of the DS concentration as a function of the experiment time are shown in Fig. 3, while Fig. 4 shows the same for the FW concentration. The DS concentration decreases with time due to the influx of pure water from the FW across the membrane driven by the osmotic

pressure difference, the NDP. In the meantime, solute concentration in the FW increases with time due to the solute diffusion from the DS side driven by the solute concentration difference across the membrane.

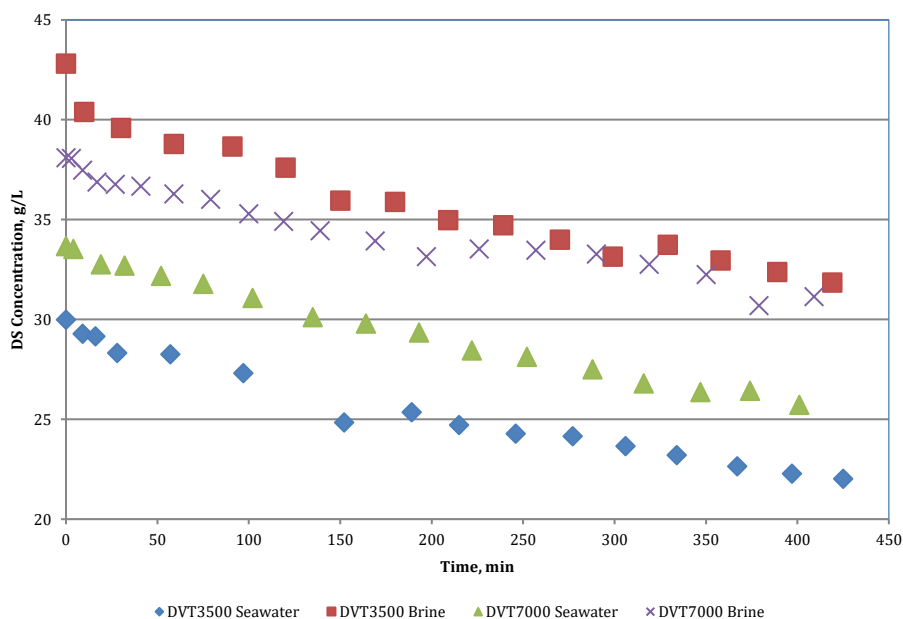


Fig. 3: DS solute (NaCl) concentration as a function of time in several FO experiments carried out at 20°C

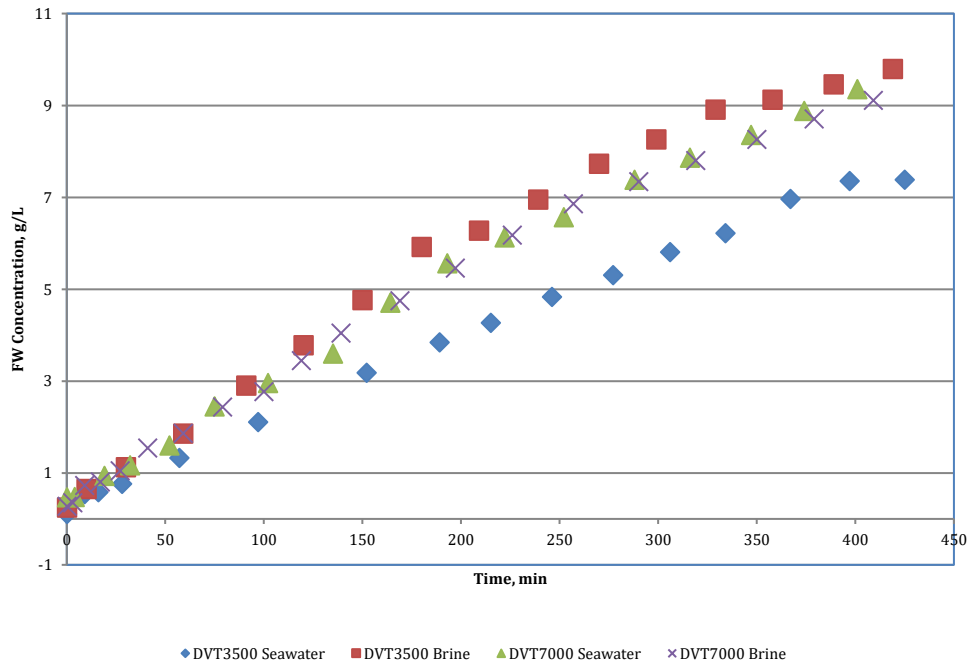


Fig. 4: NaCl concentration in the FW as a function of time in several FO experiments carried out at 20°C

The concentration difference across the membrane ($c_{DS} - c_{FW}$) is converted to osmotic pressure difference ($\Pi_{DS} - \Pi_{FW}$), or Net Differential

Pressure (NDP), and plotted against the experiment time, as shown in Fig. 5. The NDP decreases with time due to DS diluting and FW concentrating.

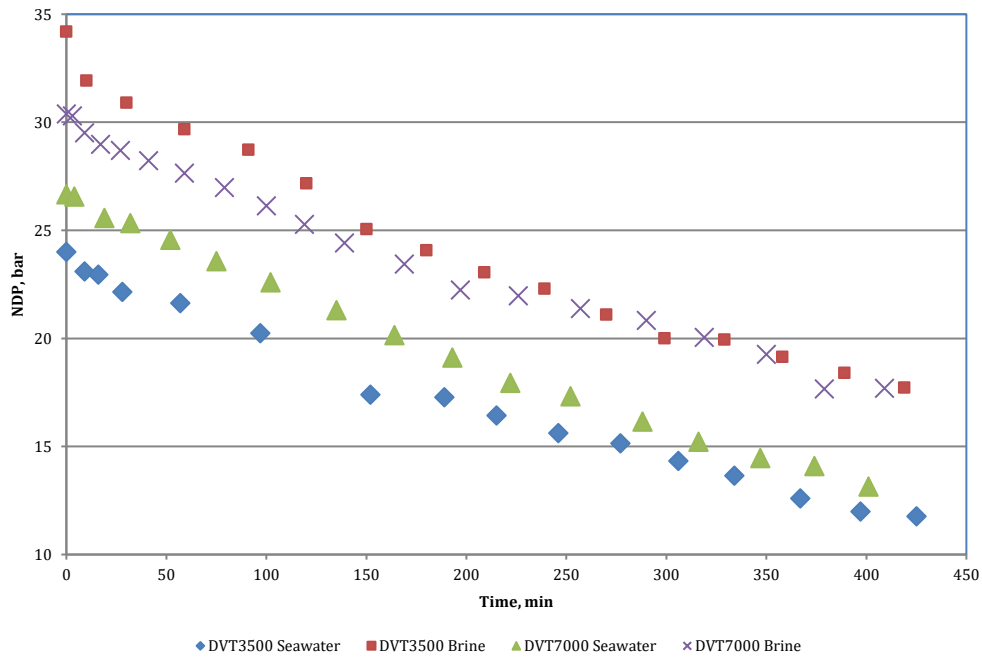


Fig. 5: The NDP as a function of experiment time in several FO experiments carried out at 20°C

The accumulated amounts of the solute transferred into the FW from the DS, as a function of the corresponding amounts of accumulated water transferred from the FW to the DS is plotted in Fig. 6. The results show the proportional relationship between water flux and solute flux, indicated in Eq. 3. It can be pointed that a higher water flux can be

obtained using a higher concentration difference across the membrane; however solute diffusion to the FW side also increases in the meantime. The comparison between the results of the different membranes shows that using a membrane with a smaller mean pore diameter gives higher water flux at a similar experiment time.

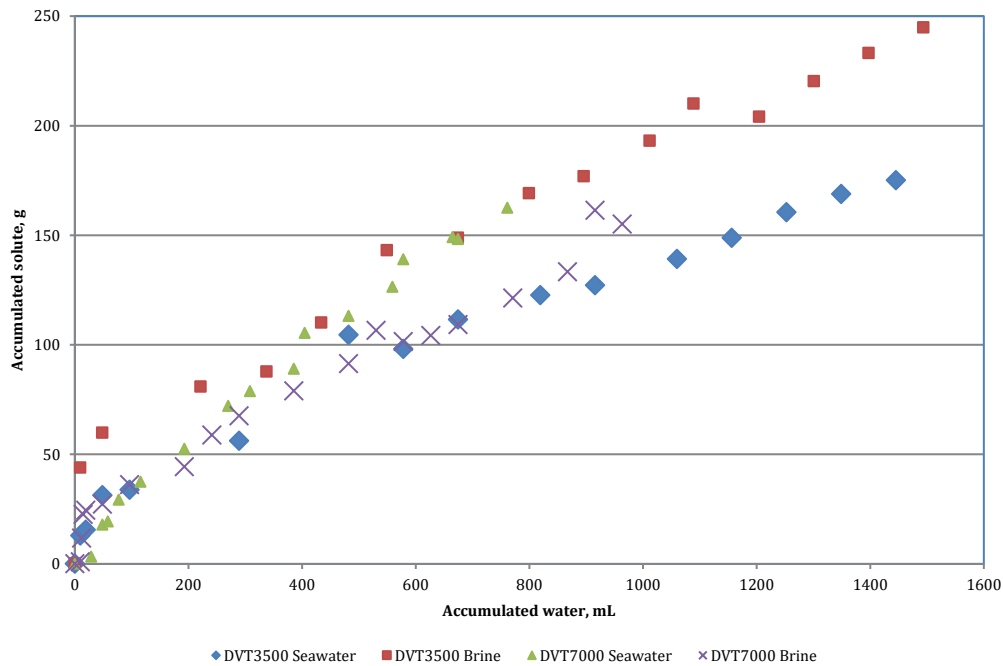


Fig. 6: The accumulated DS solute diffused to the FW as a function of the accumulated water transferred to the DS side in several, ~400 minutes, FO experiments carried out at 20°C

A clearer conclusion can be reached from a comparison of the average experimental results of water flux, J_w , and solute flux, J_s , for both membranes, as listed in Table 2. Water flux, as well as solute flux, using brine as DS, is always higher than that with seawater. This is in agreement with the fact represented in Eqs. 1, and 2 that water flux and solute flux both increase by increasing the osmotic pressure or the solute concentration difference across the membrane. It is also shown that with a membrane having a larger mean pore diameter

(DVT7000), utilizing similar solute concentration differences, water flux decreases, while solute flux increases. A larger mean pore diameter may allow a higher transfer of solute molecules; however, this is limited by the solute diffusivity, which decreases by increasing the solute concentration. The dissociated solute ions, although smaller in size in comparison with the membrane mean pore diameter, are attached to larger-size hydration spheres hindering the mobility of the ions within the solution and inside the membrane material (Merdaw et al, 2011).

Table 2: Experimental results of the average values of water and solute flux in several FO experiments carried out at 20°C and for an experiment time of ~420 minutes

No.	Data series name	Membrane type	Mean pore diameter, nm	Avg. water flux, L/m ² .hr	Avg. solute flux, g/m ² .hr
1	Seawater	DVT3500	2.8	1.085	73.5
2	Brine	DVT3500	2.8	1.191	106.3
3	Seawater	DVT7000	3.9	0.581	110.3
4	Brine	DVT7000	3.9	0.731	116.1

4. Conclusion

Several Forward Osmosis (FO) experiments were carried out using different concentrations of sodium chloride (NaCl) aqueous solutions as Draw Solutions (DS) and freshwater as Feed Water (FW). The experiments were carried out at a constant temperature of 20°C and using two grades of a symmetric cellulosic membrane different in their values of Molecular Weight Cut-Off (MWCO) or mean pore diameter. The results show that water flux, from FW to DS, and solute diffusional flux, in the opposite direction, increase as the solute concentration difference across the membrane increases. It is shown that water flux is proportional to solute flux regardless of the membrane type or the solute concentration range. It is also found, in the range of the tested membranes, that as the mean

pore diameter of the membrane increases, water flux decreases, while solute flux increases.

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Compliance with ethical standards

Conflict of interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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