Effect of Draw Solution On The Treatment of Humic Acid In Forward Osmosis Process

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***Abstract*— This paper presents the effect of draw solution in forward osmosis process for the treatment of synthetic river water. Forward osmosis is a process which depends on the concentration gradient and also osmotic potential to treat water. In conjunction to that, the main factor which affects the entire process of forward osmosis is the draw solution as draw solution acts as the driving force which drives water to pass through semi-permeable membrane by means of concentration gradient. The draw solutions studied in this paper include calcium chloride, calcium nitrate, sodium chloride and fructose. Polyamide coated ultrafiltration membrane was used and different concentrations of draw solutions were used to treat synthetic river water which consists of 15mg/L of humic acid. Time was taken for a fixed volume of water and humic acid concentration at draw solution side was measured using uv-vis spectrometer to calculate the flux and also humic acid rejection respectively. The draw solution with the highest water flux is calcium nitrate with the reading of 2.7 x 10^-4 $m^3/m^2.s$ at 1mol/L, whereas the lowest flux obtained is by fructose with the reading of 2.529 x 10^-05 $m^3/m^2.s$. Whereas for humic acid rejection, it was found to be high at every concentration of draw solultions at approximately 99%. Results from this work may be useful for treating river water by using forward osmosis with the most suitable draw solution.**

Keywords—component; ***Forward osmosis, draw solution, flux, rejection, membrane***

I. INTRODUCTION

In this current era, water treatment is one of the most vital fields which provides human with clean water to be consumed daily. In conjunction to that, many viable methods of water treatment in producing clean consumable water has been developed over the years to drastically decrease the cost and energy needed in addition of reducing any negative impacts it may cause to the environment. Among other researched water treatment methods, the method at which osmosis acts as the fundamental concept fits the current objectives of reducing cost, energy and environmental issues during the production of clean consumable water. Osmosis is a physical phenomenon that has been exploited by human beings since the early days of mankind. Early cultures realized that salt could be used to desiccate foods for long term preservation [1]. Conventionally, osmosis is defined as the net movement of water across a selectively permeable membrane driven by a difference in osmotic pressure across the membrane [1]. Unlike reverse osmosis where hydraulic pressure is required, forward osmosis process simply uses the intrinsic osmotic pressure differential between the two solutions of different osmotic potential (highly concentrated draw solution and saline feed water) separated by a semi-permeable membrane to desalinate water.

Since the forward osmosis process works based on osmotic pressure, one of the most important components which needs to be present to enable the process of forward osmosis to occur efficiently is known as draw solution. Draw solution is the concentrated solution present in the permeable side of the membrane which acts as the source of driving force in forward osmosis process [2]. There are many criterions such as osmotic pressure, water solubility and molecular weight which need to be considered in the selection of draw solution to enable the process of forward osmosis to run at optimum performance [3]. Draw solution types vary from inorganic salts to organic salts.

In Malaysia, river water plays an important role in providing water to citizens and also to the environment. However, despite holding such important position in providing clean consumable water to Malaysia citizens, the majority of the river water present in Malaysia is researched and found to contain low pH value which indicates that the river water in Malaysia is acidic [4] and contain natural organic matter (i.e. humic acid). As a result to that, the river water in Malaysia needs to be treated correctly at low cost and energy before distributing it to the citizens. The current issue faced is the conventional osmosis process used is reverse osmosis in treating river water. According to Liu et al. [5], reverse osmosis has high cost, high energy consumption and has limited recovery which is roughly about 30%-50%. Hence, this research was done as a potential solution to this problem because forward osmosis process can be done at lower cost, energy and also at higher recover rate [6]. Besides, forward osmosis could potentially reduce membrane fouling and toxicity effects of product water as it does not depend on hydraulic pressure [7].

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In spite of that, forward osmosis has its own draw backs. This is discussed by Tang et al. [8], they found that the process of forward osmosis largely depends on the osmotic difference between feed solution and draw solution without the presence of hydraulic pressure which can result in a relatively slow flux of water from feed side to permeate side that can ultimately lead to a slower osmosis process compared to other methods. Besides that, according to Checkli et al.[9], forward osmosis often face low feed solute rejection which can lead to bad quality of water treated. Apart from that, studies done on suitable draw solution for the process of forward osmosis thus far has only be revolving around seawater or brackish water as the feed solution and the research of suitable draw solution used to treat river water has been scarce and lesser still when it comes to river water in Malaysia. Thus, in order to solve these problems this research aimed to determine the water flux of each draw solutions of different osmotic pressure at different concentration where humic acid was used as synthesized river water as feed solution. Moreover, this research also aimed to study the quality of water treated by forward osmosis by measuring the concentration of humic acid in draw solution after the forward osmosis process and also characterize the best performing draw solution.

The scope of this research includes the usage of 3 different categories of draw solutions, namely, organic salts, inorganic salts and fertilizers. Besides that, this research includes the calculation of water flux from feed to permeate for each draw solutions at 5 different concentrations. Following that, the calculation of osmotic pressure based on different concentration and its effect on water flux was discussed. The humic acid (represent natural organic matter normally found in river water) rejection was among the scope of this research where the concentration of humic acid on the permeate side was determined by using uv-vis spectrometer.

II. MATERIALS AND METHODOLOGY

A. Chemicals and Draw Solutions Preparation

The solutes used to form draw solutions are purchased from various sources namely Fisherci (solid calcium chloride 95% purity, solid sodium chloride 95% purity, solid calcium nitrate 95% purity and crystallized fructose 96% purity). Each solute was dissolved in water into 5 same draw solutions with different concentrations of 0.1M, 0.3M, 0.5M, 0.7M and 1.0M . The volume of draw solution at each concentration was 2L. 15mg/L of humic acid was also prepared in 2L as the feed solution of synthetic river water.

B. Membrane Preparation

The membrane used in this study is known as polyamide membrane which was coated over ultrafiltration membrane. The coating solutions were 2% by weight of metaphenlyenediamine (MPD) and 0.15% by weight of trimesoly chloride (TMC) in hexane solution. MPD solution were poured onto the smooth surface of a 3.5 inches in diameter ultrafiltration membrane and left for 30 minutes. Then, the membrane was dry wiped on the rough surface (bottom part) to ensure no reaction occurs with TMC solution at the following step and left to dry for 2 minutes. The membrane was then immersed into TMC solution for 30 seconds and dried for 1 day before immersing into water for 2 hours. The size of the membrane was cut at 3.5 inches in diameter because the contact surface between the membrane with the feed solution and draw solution is 3 inches as shown in Figure 1 [10].

C. Forward Osmosis Experimental

Firstly, the poylamide membrane was placed vertically between the two compartments in the permeation module of Figure 1. Then, 2L of draw solution and feed solution was poured into the respective compartments. The caps and bolts of the module were completely tightened to ensure no leakage. The module was then left untouched for the water from feed solution to be drawn to draw solution. Time was taken for 5 times at every 10mm of water increment shown in the measuring tube of the draw solution side in order to attain average time for the draw solution to draw 10mm of water from the feed solution. After taking time, the draw solution was kept into a vial for uv-vis spectrometer analysis. The steps were repeated for each draw solutions at 5 different concentrations. The room temperature was maintained at 25^{0}C.

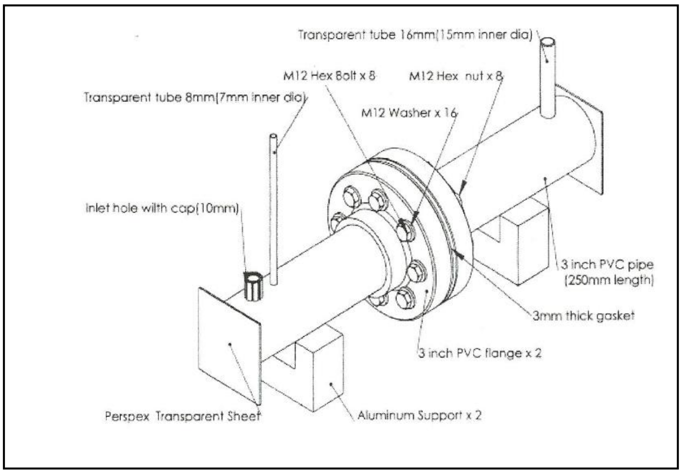

Fig. 1. Permeation module for forward osmosis [10]

D. Flux and Osmotic Pressure Analysis

The fluxes of water (J_w) for each draw solutions at different concentrations were calculated by using the formula below.

$$J_w = \Delta V/(A.\Delta t) \tag{1}$$

Where J_w is the water flux in $m^3/m^2.s$, ΔV is volume of water which permeates through the membrane in m^3, Δt is time taken in seconds and A = effective area of the membrane in m^2. ΔV can be obtained by using the formula below.

$$\Delta V = \pi r^2 L \tag{2}$$

Where r is the radius of the measuring tube at the draw side in m^2 and L is the increment of water level shown in the measuring tube at draw solution side which is for this research, set at 10mm. Whereas, the osmotic pressure of each draw solution can be calculated by using the formula as shown below.

$$\pi = JMRT \tag{3}$$

Where π is the osmotic pressure in atm, J is the Van Hoff's factor, M is the molarity in mol/L, R is the gas constant in L atm/mol K and T is the temperature in Kelvin.

III. Results And Discussion

A. *Effect of Draw Solution Concentration On Water Flux*

The time taken for all the draw solutions at different concentrations recorded were used to calculate the flux of each draw solution at different concentrations by using equation (1). The data obtained is shown in the Table 1.

TABLE I. EFFECT OF DRAW SOLUTIONS CONCENTRATION ON FLUX

Molarity (mol/L)	**Flux X 10^{-5} ($m^3/m^2.s$)**			
	NaCl	***Ca_2NO_3***	***$CaCl_2$***	***Fructose***
0.1	2.67	3.24	2.59	2.53
0.3	4.72	6.53	4.65	4.48
0.5	7.55	8.44	7.06	6.48
0.7	9.32	10.73	8.29	7.81
1.0	16.5	27.12	15.73	13.91

Based on Table 1, it is clearly shown that the increase in concentration causes an increase in water flux from feed side to permeate side for all of the draw solutions. This phenomenon is explained by Ge et al. [11], where higher concentration of draw solution enable water at feed solution to be pulled at higher rate as compared to lower concentration of draw solution as higher concentration of solute in draw solution increases the solvent concentration gradient between the permeate side and the feed side, thus causing an increase in water potential from feed side to permeate side. Besides that, the increment of water flux can also be explained by using osmotic pressure.

The osmotic pressure of each draw solutions were calculated by using equation (2) and its relation to concentration of draw solution is as shown in Figure 2. The trend of graph as shown in Figure 2 illustrates that the increase in molarity will cause an increase in osmotic pressure.

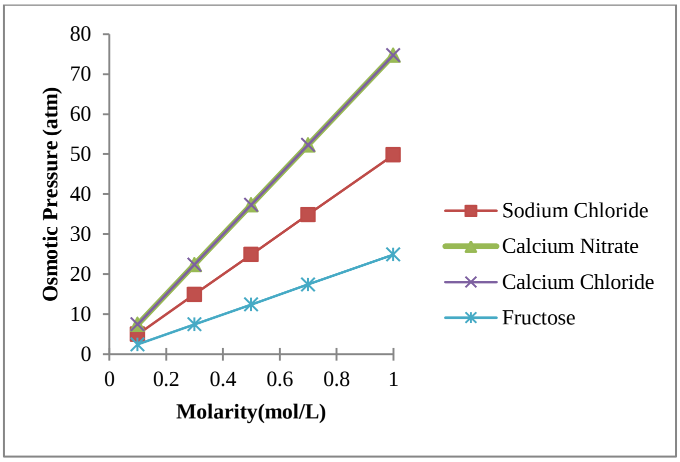

Fig. 2. Osmotic pressure for each draw solutions against molarity

Thus, by relating osmotic pressure to water flux from feed side to permeate side, it can be deduced that the increase in concentration of draw solution causes an increase in osmotic pressure which ultimately increases the water flux of forward osmosis process. This phenomenon is further supported by previous studies done by Xu [12], who proved that higher water fluxes can be achieved by increasing draw solution concentration as increase in concentration will also increase the osmotic pressure thus promoting the process of forward osmosis. According to Phuntsho et al. [13], high osmotic pressure in draw solution increases the osmotic difference between the draw solution and the feed solution which will ultimately form a high osmotic potential that can enhance the drawing of water from feed solution to draw solution.

The data obtained in Table 1 shows disparity in magnitude of flux for all the tested draw solutions compared to the data obtained by Checkli et al. [9] despite showing similar experimental trend. For instance, at 2mol/L of calcium nitrate draw solution, they obtained flux 5.022 x 10^-6 $m^3/m^2.s$ which is much lower compared to the flux of calcium nitrate at 1mol/L figuring 2.7 x 10^-4 $m^3/m^2.s$ in our study. This could be due to the bigger pores of polyamide membrane and usually more porous than cellulose triacetate membrane [14], thus causing the water molecules to be able to pass through polyamide membrane more easily compared to cellulose membrane.

B. *Comparison of Draw Solutions Performance*

In order to select the best performing draw solutions, the experimental data obtained were compared by using the graph shown in Figure 3.

Based on the experimental data tabulated in Figure 3, it is shown that throughout the experiment, calcium nitrate shows the highest flux of water from feed side to permeate side while the lowest flux is shown by fructose as draw solution at every concentration. On the other hand, at each concentration, calcium chloride and sodium chloride shows relatively close flux of water from feed side to permeate side, Fructose recorded the lowest flux as it exhibits lowest osmotic pressure compared to the other draw solution which causes it to have the lowest driving force to draw water from feed side to the permeate side.

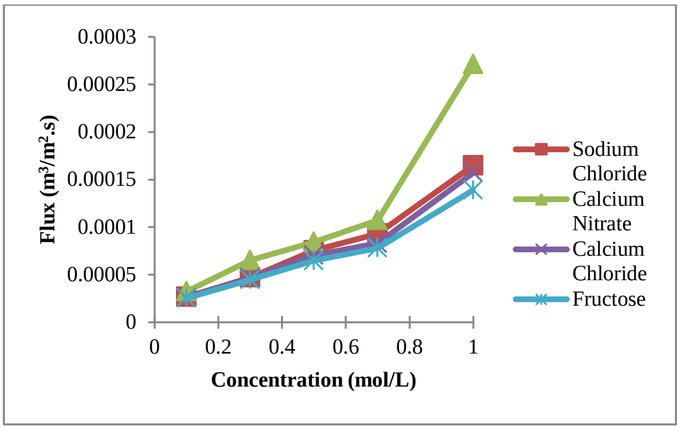

Fig. 3. Water Flux For Each Draw Solution Across Membrame Against Molarity

Whereas, calcium nitrate recorded the highest possible flux of water from feed side to permeate because it exhibits highest osmotic pressure compared to other draw solutions that causes it to have the highest driving force to draw water from feed side to permeate side. These two phenomenons can also be explained by Su et al. [15], where they claim forward osmosis depends very much on osmotic gradient where higher osmotic pressure of draw solution will increase the water potential of water flow from feed side to permeate side and this statement is clearly shown in the difference of flux between calcium nitrate and fructose.

However, the flux of calcium chloride is experimented to be lower than calcium nitrate despite having similar osmotic pressure at 1mol/L. This phenomenon is explained by Chekli et al. [9], where high solubility of draw solution induces higher osmotic pressure and therefore can achieve higher water flux. Besides that, according to Wilson and Steward [16], high solubility is essential in selecting draw solution because high solubility enables the draw solution to dissociate into its respective ions more easily and at a faster rate which will ultimately increase the osmotic pressure of that particular draw solution and lastly induces higher water flux of water from feed side to permeate side in forward osmosis process. The solubility of calcium chloride is of 7.4M which is lower than the solubility of calcium nitrate of 7.9M thus causing calcium chloride to have lower osmotic pressure than calcium nitrate [9]. The calculated osmotic pressure of calcium chloride and calcium nitrate shows the similar result as the formula used is theoretical where solubility of solution is ignored and if considered, will provide a different value of osmotic pressure.

For the case of sodium chloride and calcium chloride, even though calcium chloride has higher osmotic pressure than sodium chloride, it shows lower flux than sodium chloride. Solutes with heavier molecular weight tend to produce less flux in the presence of internal concentration polarization which can reduce the flux of forward osmosis progressively compared to solutes with lighter molecular weight [17]. The presence of internal concentration polarization as mentioned by Gray et al. [3] which occurs within the support layer of the membrane and is characterized by differing solute concentrations at the transverse boundaries of that layer result in a decrement osmotic pressure gradient across the active layer of the membrane and a corresponding reduction in water flux across the membrane. Thus, due to calcium chloride having the molecular which is much higher than molecular weight of sodium chloride, the internal concentration polarization occurs until the extend where flux of calcium chloride to be lower than the flux of sodium chloride. This explanation can also be used on the flux of fructose which is the lowest among all the draw solutions as it has a very high molecular weight which can cause high internal concentration polarization which will reduce the flux of water from feed side to permeate side.

C. Humic Acid Rejection

The rejection of humic acid for each draw solutions were obtained by using equation (4) and the values were tabulated as shown in Fig. 4.

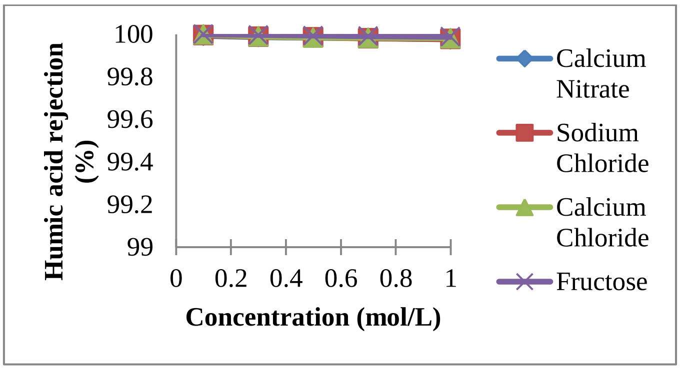

Fig.4 Effect of Draw Solutions Concentration On Humic Acid Rejection

Based on the graph in Figure 7, the trend where increase in molarity causes an increase in humid acid rejection can be deduced. The increase in flux of water from feed side to permeate side caused by draw solution will decrease salt rejection as the driving force of water flux pulls and moves along a small amount of feed solute towards the membrane and forces some to penetrate through the membrane into the draw solution side [18]. The erratic rejection value of sodium chloride which shows the lowest rejection value at 0.7mol/L may be due to the lower scaling factor of sodium ions compared to fructose or calcium ion which allows humic acid to pass through the membrane more easily compared to blockage which might be caused by scaling factors of calcium ions [9]. However, the values of humic acid rejection for each draw solutions are very high which implies that the amount humic acid particles that passed through the polyamide membrane is negligible. This occurs because the pore size of polyamide membrane is not large enough to allow the humic acid solutes to pass through the membrane and instead, causing adsorption of humic acid on the membrane surface to occur due to the structure of the polyamide membrane [19]. Besides that, according to Gu et al. [20], polyamide membrane is usually more hydrophilic with contact angle of approximately 45^o and is negatively charged with zeta potential of approximately 10mV that does attract humic acid solutes.

IV. CONCLUSION

Based on the results and discussion of this research, fertilizer draw solution was found to be the best performing draw solution in the forward osmosis of treating synthetic river water compared to organic or inorganic draw solutions. Besides, it was also found that the high concentration of draw solutions can vastly improve the efficiency of the forward osmosis process by increasing the flux of water from feed side to permeate side. Furthermore, the humic acid rejection value is approximately almost 100% for every draw solution tested even though it decreases with the increase in concentration of draw solutions. This implies that the quality of water treated is high without the presence of humic acid solutes. In conclusion, this research showed that it is best to characterize draw solution at higher concentration and by using fertilizers as it provides high water flux from feed to permeate side without any adverse impacts on the quality of water treated. In order to improve this research, more parameters such as temperature and diffusivity and permeability should be included to characterize the draw solutions for higher efficiency. Besides that, more draw solutions should also be tested in order to obtain the best performing draw solution by means of comparison.

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