Removal of Cl^-, SO_4^{2-} and CO_3^{2-} Salts from Oil Refinery Effluent Using Forward Osmosis

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Abstract— This study explored the effects of feed solution (FS) and draw solution (DS) cross flow rates (CFR) on permeate flux and salt rejection of an oil refinery effluent in forward osmosis (FO). The CFR was varied from 0.125 L/min to 0.156 L/min for both feed and draw solutions. A total of 5 experimental runs were conducted using 1 M $CaCl_2 \cdot 2H_2O$ as the draw solution. Each run lasted for 6 hours. The results showed that cross flow rate had no effects on salt rejection, as there was at least 98% rejection of SO_4^{2-} and CO_3^{2-} and no rejection of Cl^- in all runs. The highest permeate flux obtained, at FS-CFR of 0.156 L/min and DS-CFR of 0.140 L/min was 5.56 L/m²•h, indicating a good correlation between FR and permeate flux. Prospectively, this study sets the stage for further research in the application of FO in oil refinery effluent desalination.

Keywords—Desalination, forward osmosis, permeate flux, salts.

I. Introduction

Salinization of freshwater bodies, ground and surface waters as well as agricultural lands due to different natural and anthropogenic activities continues to endanger aquatic life, availability of potable water and agricultural productivity [1-3].

Oil refinery effluent (ORE) is identified as one of the major sources of saline wastewater. It is reported in refining that 1 barrel of crude oil, about 10 barrels of effluent is generated [4]. This effluent can have salt concentrations as high as 35,000 ppm and removal of these salts is imperative to meet discharge limits as well as make reuse of treated effluent an option [5]. These salts, like the chlorides, carbonates, sulphates, among others, have the tendency of causing abrupt pH changes in water bodies, scales and corrosion in water and wastewater treatment, transport and storage facilities.

Forward osmosis (FO) provides many options and benefits in energy efficient desalination [6]. This osmotically driven membrane process makes use of concentration gradient between two solutions to drive water transport across a semi-permeable membrane until an equilibrium is reached [7]. This is a great advantage over the conventional desalination processes like thermal desalination and reverse osmosis desalination. Thermal desalination makes use of energy to evaporate water from the saline feed and subsequently recover the water through condensation. With RO, high pressures (from 7 bar to 80 bar depending of feed characteristics) are applied to force the movement of water molecules through a membrane against a concentration gradient [8-10]. These processes are energy intensive. Over the years, FO has been applied as a standalone process and in a combined fashion on lab scale, pilot scale and large scale for many separation and niche processes [11-14].

The main challenges associated with the FO process have been the issue of concentration polarization (CP) and reverse solute flux (RSF), both of which are receiving research attention in terms of FO membrane modification and draw solute design to reduce CP and RSF, thereby enhancing water flux and salt rejection [15-18].

This study examines the impacts of draw solution cross flow rate (DS-CFR) and feed solution cross flow rate (FS-CFR) on the removal of Cl^-, SO_4^{2-} and CO_3^{2-} from oil refinery effluent using forward osmosis. A one-factor-a-time (OFAT) approach was used to vary cross flow rates between 0.125 L/min, being the lowest, 0.140 L/min and 0.156 L/min being the highest cross flow rate considered. A draw solution of 1 M $CaCl_2 \cdot 2H_2O$ was used to provide the osmotic gradient. The experiment took place at room temperature (20 ±2 °C) within an average working pH of 5.8. A total of 5 experimental runs were conducted, each lasting for 6 hours.

II. Materials and Methods

A. Equipment and Materials Used

The equipment and materials used included; peristaltic pump (Blue-White Industries, USA), membrane test cell, magnetic stirrer (Favorit, Malaysia), $CaCl_2 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, $NaHCO_3$, all sourced from Sigma Aldrich, South Africa, cellulose triacetate (CTA) membrane (Sterlitech Corp, USA), DR 3900 spectrophotometer (HACH, Germany) and HI98130 pH&EC (Hanna Instruments, Woonsocket RI, USA).

B. Experimental Set-up

The forward osmosis set up was made up of two peristaltic pumps for circulating FS and DS, two 5 L Duran bottles, serving as FS and DS tanks, a membrane test cell (two rectangular shaped PVC blocks) that housed the FO membrane and two magnetic stirrers to ensure continuous homogeneity of the solutions during the experimental period.

C. Membrane Preparation and Properties

The cellulose triacetate (CTA) membrane used in this study had an embedded polymer mesh as support to provide mechanical strength during fluctuating temperatures and pressures. The maximum operating temperature was 60°C

within a working pH range of 3-7. Before usage, the membrane was soaked overnight in deionized water and rinsed thoroughly. After each run, physical membrane cleaning is done after which the membrane is stored in deionized water (DI) water prior to next use.

D. Feed Solution, Draw Solution and Analytical Methods

The feed solution (synthetic ORE) was prepared by adding 4.60 g of calcium sulphate dihydrate, 0.87 g sodium hydrogen carbonate and 4.46 g of calcium sulphate dihydrate to 3 L of dilute real ORE (sourced from the sewer of a local South Africa waste oil refinery's effluent treatment plant). The preparation was done according to the average composition of Cl^-, SO_4^{2-} and CO_3^{2-} in the refinery's effluent, characterized over a period of 4 months using standard methods as used by Tetteh and Rathilal [19].

A draw solution of 1 M $CaCl_2 \cdot 2H_2O$ was used to provide the osmotic gradient for the experiment. Analysis for this study was done for Cl^-, CO_3^{2-} and SO_4^{2-} using a DR 3900 spectrophotometer. Conductivity and pH were determined using HI98130 pH&EC. All analyses were done in triplicates. Table I shows the characteristics (average) of the synthetic ORE.

TABLE I: CHARACTERISTICS OF ORE

Component	Value
Cl^- (mg/L)	423
SO_4^{2-} (mg/L)	200
CO_3^{2-} (mg/L	22
pH	5.86
Conductivity (mS/cm)	5.06

E. Process Description

The experiment was conducted in two modes (A and B). Each mode comprised of two runs. A reference run (REF) was conducted to serve as the basis for the other 4 runs, making a total of 5 runs. Table 3 shows the runs and their respective flow rates. The FR adopted was 0.156 L/min (being 100% of the pump discharge rate), 0.140 L/min (being 90% of the pump discharge rate) and 0.125 L/min (being 80% of the pump discharge rate).

TABLE II: EXPERIMENTAL RUNS

ID	RUNS	FS-CFR (L/min)	DS-CFR (L/min)
A	R1	0.156	0.125
	R2	0.156	0.140
REF	R3	0.156	0.156
B	R4	0.125	0.156
	R5	0.140	0.156

In mode *A,* the FS-CFR was kept constant at 0.156 L/min while the DS-CFR was varied (0.125 – 0.140 L/min). In mode *B*, the DS-CFR was kept constant at 0.156 L/min while the FS-CFR was varied (0.125 – 0.140 L/min). The reference (REF) run (R3) had both FS-CFR and DS-CFR to be the same (100% discharge rate). The FS was circulated at the rejection side of

the membrane while the DS was circulated at the opposite side. Fig 1 shows the process flow diagram (PFD) of the set up.
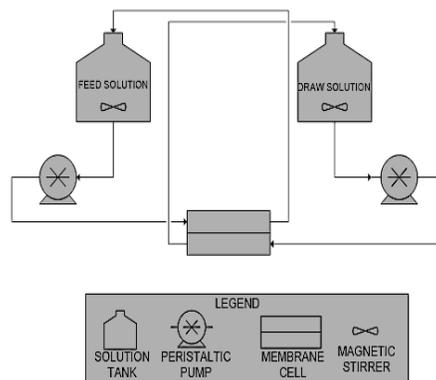

Fig. 1. Process flow diagram of experiment.

The set up was left to run for 6 hours, after which the salt rejection was determined according to equation (1) and permeate flux was determined according to equation (2);

$$\text{Rejection efficiency (\%)} = \frac{C_0 - c}{C_0} \times 100 \quad (1)$$

Where; C_0 and C are initial and final concentrations (mg/L) of salts in the FS and DS samples before and after the experimental run, respectively.

$$\text{Permeate flux (J)} = \frac{V}{A \bullet h} \times 100 \quad (2)$$

Where V is the permeate volume in liters (measured by taking the difference between the initial and final volumes of the DS); A is the effective membrane area in m^2 and h is the time in hours.

III. RESULTS AND DISCUSSION

A. Permeate Flux

Fig 2 presents the impact of both FS and DS flow rates on permeate flux. Run 3, representing the reference run with the same FS-CFR and DS-CFR of 0.156 L/min had the lowest flux of 4.26 L/min compared to all other runs. This may be due to the association of high cross flow rates with creation of turbulence at the bulk solution - membrane surface interface which enhances backwards diffusion of the salt into the bulk of the solution. [20]. In principles, during FO, the DS is diluted by water drawn from the DS. At high CFR, this dilution process becomes slow, consequently influencing permeate flow. Similar

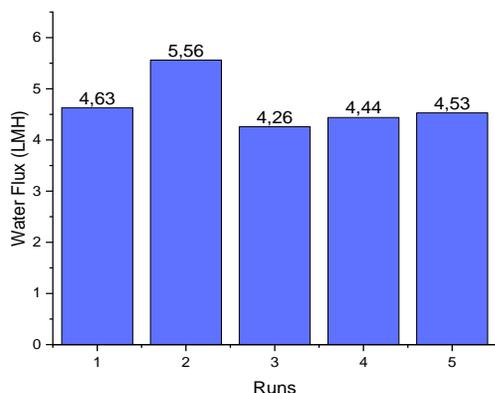observations were made by Aydiner, et al. [21], [22]

Fig 2: Impacts of FS and DS FR on permeate flux

Runs 1 and 2 show the impact of DS-CFR on permeate flux. From R1 to R2, the DS-CFR was increased from 0.125 L/min to 0.140 L/min while the FS-CFR was kept constant at 0.156 L/min. This led to a corresponding increase in the permeate flux from 4.63 $L/m^2 \cdot h$ to 5.56 $L/m^2 \cdot h$, representing 16.7% increase in water flux. Runs 4 and 5 show the impact of FS-CFR on permeate flux. From R4 to R5, FS-CFR was increased from 0.125 L/min to 0.140 L/min while the DS-FR was kept constant at 0.156 L/min. Similar to the effects DS-CFR, there was a corresponding increase in permeate flux from 4.44 L/min to 4.53 L/min, about 2% increase in permeate flux.

Generally, increasing DS CFR to some extent enhances water transport through the membrane. As a principle of FO, dilution of the DS takes place as time goes on. At low DS-CFR, the dilution factor becomes high and the DS soon becomes diluted since the rate of water transport through the membrane will be higher than the flow of the DS. Consequently, the net driving force will be reduced, leading to lower fluxes. Increasing the DS-CFR reduces the rate of this dilution of the DS and this is noted to enhance water flux [23, 24]. This may account for the 16.7 % increase in water flux when the DS-FR was increased from 0.125 L/min to 0.140 L/min (R1 – R2).

The impact of FS-CFR on permeate flux was low. Only 2% increase in permeate flux was recorded when the CFR was increased from 0.125 L/min to 0.140 L/min (R4 – R5). This may be due to the reduction in the net osmotic pressure gradient caused by dilutive internal concentration polarization (DICP). This phenomenon is established when the rejection side of the membrane faces the feed solution and the porous support layer faces the draw solution [25, 26] as used in this study. As water permeates the active layer, the draw solution within the porous layer becomes diluted. With this, the osmotic pressure difference across the membrane becomes lower than the bulk of the two solutions (FS and DS), leading to a reduction in the net osmotic pressure gradient. However, the slight increase in the water flux accompanied by the increase of CFR, may be due to a slight increase in hydraulic pressure at the feed side as observed also by other researchers [20].

B. Impact of FS and DS CFR on Salt Rejection.

The impact of FS and DS CRF on salt rejection is shown in Fig 3. Size exclusion and electrostatic interactions play a significant role in membrane rejection of materials [27, 28]. The mean pore size of the CTA membrane used in this study is estimated to be 0.74 nm, having an isoelectric point at an approximate pH of 4, above which the membrane becomes slightly negatively charged [29, 30].

From the Fig 3, it can be seen clearly that SO_4^{2-} and CO_3^{2-} was almost totally rejected by the membrane – 100% rejection efficiency for SO_4^{2-} and 98% rejection efficiency for CO_3^{2-}. This may be due to the divalent nature of these ions, having hydration radiuses larger than the mean pore size of the membrane. Again, all experiments were conducted within a pH range of 5.4 – 6, which is above the isoelectric point of the membrane; the negative nature of the membrane may have been triggered to cause repulsion of these ions.
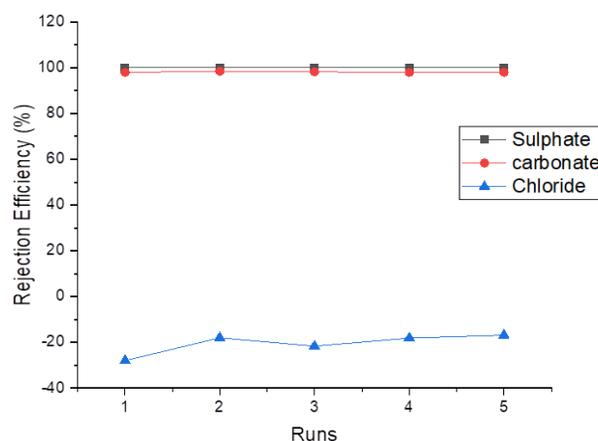

Fig 3: Impacts of FS and DS CFR on salt rejection

The Cl^- were not rejected, rather their concentration increased in the FS. This case of Cl^- is a phenomenon of reverse solute flux. This is the backward movement of solute molecules as a result of a concentration gradient; this is in opposite direction to the water flux [31]. In this study, using 1 M $CaCl_2 \cdot 2H_2O$ makes available more Cl^- in the DS than in the FS which had an initial average Cl^- concentration of 423 mg/L. Again, due to the univalent nature of Cl^-, it easily transports itself through the membrane structure, making the RSF even more pronounced [32]. Much study has been conducted by other researchers [31-33] on the dynamics of RSF.

IV. CONCLUSION AND RECOMMENDATIONS

This study examined the effects of CFR on permeate flux and salt rejection of oil refinery wastewater. Undoubtedly, CFR plays a significant role in enhancing water flux in forward osmosis. Getting an optimum DS and FS CFR will lead to high water fluxes at the same time reduce reverse solute flux. For this study, the best DS and FS CFR were 0.140 L/min and 0.156 L/min respectively. The study has shown that salt rejection is hardly impacted by CFR. In most cases, membrane properties play a greater role in rejection of materials in the membrane process. Much work still abounds for future research in dealing

with reverse solute flux, a phenomenon that is a major drawback for the FO desalination process.

ACKNOWLEDGEMENT

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