

Evaluation of Forward Osmosis for Treatment of Sodium sulphate Rich Brine

T. M. Mogashane, J. P. Maree, N. Nyamutswa, J. Vogel, M. Mujuru and M. M. Mphahlele-Makgwane

Abstract - Acid Mine drainage (AMD), brines and other industrial effluents present an ever-increasing threat to the environment. In forward osmosis (FO), a new promising technology for wastewater treatment, water is driven through a semipermeable membrane from a feed solution to a draw solution due to the osmotic pressure gradient across the membrane. The aim of this study was to evaluate FO for the treatment of Na₂SO₄ rich brine with NaCl or (NH₄)₂SO₄ as the draw solution. Feed (Na₂SO₄) and draw (NaCl or (NH₄)₂SO₄) solutions were circulated through an Aquaporin Inside® HFFO14 module in a counter cross-flow configuration. It was shown that when draw solution was passed through the FO element on a continuous basis while feed was recycled, permeate was passed through the membrane for as long as the osmotic pressure difference was large enough. The feed volume decreased by 73% during this period while the osmotic pressure (OP) difference between draw and feed solutions gradually decreased. Steady state conditions were obtained after 80% of the feed solution had passed through the membrane to the draw solution. Forward Osmosis can be used to concentrate a Na₂SO₄ feed solution as a first step towards water recovery from AMD.

Keywords - Forward osmosis, Draw solution, Osmotic pressure, Mine water

I. BACKGROUND

Acid Mine Drainage (AMD), brines and other industrial effluents present an increasing threat to the environment. Current treatment processes such as High-Pressure Reverse Osmosis (RO), Freeze Crystallization and Distillation have high capital and very high maintenance costs, are beset by scaling of membranes, are technically inadequate and/or produce other pollutants such as brine and sludge [1, 2]. Forward Osmosis has been extensively evaluated for wastewater treatment and seawater desalination in the past few years on pilot and small commercial plants [3, 4].

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T. M. Mogashane, J. P. Maree, M. Mujuru, M. M. Mphahlele-Makgwane are with Department of Water and Sanitation, University of Limpopo, Private Bag X1106, Sovenga, 0727, South Africa.

T. M. Mogashane is with the Department of Chemistry, University of Limpopo, Private Bag X1106, Sovenga, 0727, South Africa.

J. P. Maree ROC Water Technologies, P O Box 70075, Die Wilgers, Pretoria, 0041, South Africa

N. Nyamutswa is with Capricorn District Municipality, Polokwane, South Africa

J. Vogel is with Aquaporin, Nymøllevej 78, DK-2800 Kongens, Lyngby, Denmark

Forward osmosis (FO) is commonly used for separation in processes utilizing the osmotic pressure difference induced by the solute concentration difference between the feed and draw solutions. For an FO membrane to be effective, it must have high water permeability, reduced internal concentration polarization (ICP), high stability, exceptional selectivity, and high mechanical strength. The draw solution (DS) must also be nontoxic and possess the ability to bestow high osmotic pressure, offer energy efficient draw solute recovery, and decreased ICP [4, 6].

The FO process has several economic advantages over RO and in respect of power consumption. FO runs on the concentration difference between the DS and the Feed Solution (FS) since no external force is needed to push the water through the membrane. Energy is needed to maintain the cross-flow of the FS and DS so that the contact with the membrane surface is maintained and provides sufficient shear force to reduce the concentration polarization (CP) [7, 8]. Draw recovery is usually an important feature in respect to energy.

FO uses spontaneous water transportation by osmotic pressure from the feed saline water to the draw solution across a semipermeable membrane. When FO is applied as a pre-treatment for the RO process, it can reduce membrane fouling at the RO stage and minimize energy use [9, 6]. FO then has a high potential to function in a seawater desalination plant using an FO-RO hybrid system. The FO-RO Hybrid Desalination Research Center (FOHC) has evaluated this combination, and constructed an FO-RO hybrid pilot plant of 1000 m³/day capacity which has minimized energy consumption [10, 6].

In the FO process, clean water permeates the semipermeable membrane from the FS which accumulates in the DS, consequently diluting the DS and concentrating the FS. The major disadvantage of this technology is the need for additional step(s) to regenerate (re-concentrate) the DS to keep the required osmotic pressure gradient and also to further treat the concentrated FS [12]. Freeze desalination (FD) can possibly be used to further concentrate the Feed solution after FO. Recovery of high value products such as rare earth metals (REMs) which occur in low concentrations is also enabled by this process. As a result, the revenue from these saleable products can be used to offset the operational and capital costs of the process [13].

The most critical limitations to the commercialization of FO are: (i) the lack of suitable, high-flux membranes, and (ii) finding a suitable draw solution. An ideal FO membrane should

have high water permeability and salt rejection, should be thin without a porous support layer reducing the CP effects, and must also have good mechanical strength [14, 15, 13]. Use of a thin membrane without support layers is problematic because it does not provide adequate mechanical strength to withstand the pressure of the water flow inside the membrane module. Several recent advances have been reported in membrane manufacturing. The thin film composite (TFC) FO membranes have been found to have much higher water flux and salt rejection properties than the current cellulose triacetate (CTA) FO membranes [16, 13]. The innovative claim for this TFC type is the modification of the support layer which is thinner and porous, making it more suitable for the FO process. In particular, the hollow fiber TFC FO membrane is a significant advance since flat sheet membranes make for complexity in the design of spiral-wound modules accommodating two different and independent flows in the module. With the commercialization of TFC-FO membranes, the future prospects of the FO process and its applications will be promising [17, 13].

In the design of FO systems, wide differences are observed in the selection of draw solution considering the potential of osmotic pressure build-up and ease of recovery [18]. Solutes with small molecular weights and high solubilities are expected to generate higher osmotic pressures and thus may result in better water flux [13]. Ammonium bicarbonate is highly soluble in water and generates high osmotic pressure and consequently, in solution, is often a good choice as draw solution. An ammonium bicarbonate draw solution has been used to extract water from saline feedwater across a semipermeable polymeric membrane where the saline feedwater and draw solution have been fed to the FO unit, which flows tangentially to the membrane in a cross-flow mode with concurrent direction [11, 19].

Common chemical fertilizers have been used in preparing draw solutions, and are another economically viable option for desalination of saline water as the diluted fertilizer draw solution, when “exhausted” can be directly applied to soil for agricultural purposes [20]. Of the mostly used fertilizers, $\text{NH}_4\text{H}_2\text{PO}_4$ was found to have the lowest reverse salt flux (RSF), followed by $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ca}(\text{NO}_3)_2$, and $(\text{NH}_4)_2\text{SO}_4$. Due to the presence of divalent anions, the ammonium compounds of sulfate and phosphate as well as $\text{Ca}(\text{NO}_3)_2$ are found to have very low RSF, which is important for any FO process. Preliminary estimates demonstrate that about 1 kg of fertilizer can be used to extract 11–29 L of freshwater from seawater [9, 11].

The detrimental effect of ICP on water flux in the FO process is increased further when solutes with low diffusivities such as magnesium, calcium, sulfate, and certain organic salts are used in the DS. Thus, the RSF can favorably be lower and the water flux unfavorably lower when using inorganic and organic DSs such as magnesium chloride, magnesium sulfate and trisodium citrate, compared to sodium chloride at the same osmotic pressures because of the lower diffusivity of the divalent and organic salts through the membrane’s active and support layers.

An ideal DS produces high water fluxes just as those induced by NaCl and low RSFs like those observed when divalent inorganic and organic salts are used at common DS concentrations [21, 22, 18]. NaCl is an ideal DS for FO because

of high water flux and low RSF as compared to other inorganic and organic DSs as described [18]. NaCl is also cheap and readily available. Thus, NaCl was used in this study in the Draw solution for treatment of Na_2SO_4 rich water and also to enhance FO by lowering reverse salt flux while maintaining high permeate flow.

II. MATERIALS AND METHODS

A. Feedstock

Na_2SO_4 (20 g/L Na_2SO_4) was used as the Feed solution and NaCl (40, 60, 80 g/L) and $(\text{NH}_4)_2\text{SO}_4$ (80 g/L) as the Draw solutions.

B. Equipment

Figure 1 shows the FO system that was used for treatment of a Na_2SO_4 solution. The FO element was provided by Aquaporin A/S, Denmark with characteristics as shown in Table 1. Centrifugal pumps were used to run feed (Na_2SO_4) to the FO element from the one side and draw solution (NaCl or $(\text{NH}_4)_2\text{SO}_4$) from the other side. Storage tanks (300L) were used for the feed and draw solutions.

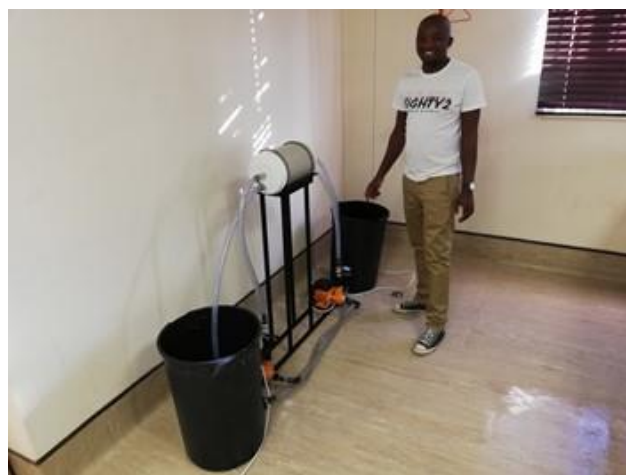


Fig. 1. Forward osmosis laboratory scale plant.: (i) stand, (ii) Forward Osmosis unit, (iii) Feed recycle pump A left (4.8 L/min), (iv) draw recycle pump B right (3.8 L/min) (v) Storage tanks for Feed (300L) and draw solutions (300L)

C. Analytical

Samples were collected at various stages in the FO treatment processes and analysed. Capricorn Laboratory (SANAS accredited) did pH, conductivity analyses. In addition chloride, ammonia and sulphate analyses were carried out by Ion Chromatography (IC). Sodium concentrations were determined using inductively coupled plasma-mass spectrometry (ICP-MS).

D. Procedure

Feed solution (20 g/L Na_2SO_4), stored in Tank A, was recycled through the FO element. The Draw solution was pumped from Tank B through the FO element from the opposite side; either once through (Exp 6) or recycled and returned to Tank B (Runs 7, 8, 9 and 10). Both the feed and draw flow-rates were kept between 3 and 5 L/min. In order to

C. Osmotic pressure difference

Figure 4 shows the OP as a function of concentration in g/L for various compounds [23]. It shows that the monovalent compounds have the highest OP and could therefore be used for Draw solutions. Table 3 shows the effect of NaCl concentration on the up-concentration of a 20 g/L Na₂SO₄ Feed solution. Increasing the NaCl concentration from 40 g/L to 80 g/L resulted in an increased water recovery from 53.4% to 71.4% or an increase in Concentration Factor (CF) from 2.2 to 3.9.

D. Reverse salt flux

1) NaCl as Draw solution

Reverse salt flux (RSF) needs to be kept to a minimum to avoid contamination of the feed solution. The chloride values in **Table 3** (Feed), show the magnitude of reverse flow for when NaCl was used as the Draw solution. It showed that the Cl⁻ concentrations in the Feed, after equilibration had been achieved. It increased from 783 to 5 070 mg/L, as the initial Draw solution concentrations were increased from 40 to 80 g/L. It was concluded that with NaCl as Draw solution much contamination of the Feed will take place. This can be ascribed to the small diameter of Na⁺ and Cl⁻ ions. It is therefore important to select a Draw solution that will allow minimum reverse flow.

2) (NH₄)₂SO₄ as Draw solution

Aqueous (NH₄)₂SO₄ was identified as a possible Draw solution with a low RSF [20]. An experiment was carried out to compare the RSF when (NH₄)₂SO₄ is used as Draw solution with NaCl. A concentration of 80 g/L (NH₄)₂SO₄ was used as it has an OP of 36.0 atm (**Figure 4**) which is significantly higher than the 8.6 atm. of 20 g/L Na₂SO₄.

Table 4 compares the performance of 40 g NaCl /L as with 80 g (NH₄)₂SO₄/L as Draw solutions for the treatment of 20 g Na₂SO₄/L feed solution. The 40 g NaCl/L has an OP of 37.0 atm. compared to the 36.9 atm of (NH₄)₂SO₄. (NH₄)₂SO₄ performed better than NaCl as improved water recovery was achieved with (NH₄)₂SO₄ (60% vs. 53.7%) as well as a higher CF (concentration factor) (2.20 vs. 2.16).

In spite of the better water recovery with (NH₄)₂SO₄ as Draw solution, it was found to be unsuitable as a Draw solution due to its high reverse salt flux. NH₄⁺ migrated through the membrane from the Draw solution to the Feed solution and Na⁺ from the Feed to the Draw solution. This was indicated by the increase in the NH₄⁺ concentration from 100 to 5150 mg/L (as N) in the feed solution. Na⁺ concentration did not increase in a ratio similar to that of SO₄²⁻, as expected. It only increased slightly, from 7155 to 8150 mg/L.

IV. CONCLUSIONS

Single pass mode needs to be used during full-scale operation. During single pass mode of the Draw solution 73% water recovery was achieved compared to 60% in the case of batch mode.

Higher osmotic pressure resulted in higher water recovery i.e. 71.2% water recovery with 80 g/L NaCl compared to only 53.4% in the case of 40 g/L NaCl.

Aqueous NaCl is more suitable than (NH₄)₂SO₄ solution as a Draw solution due to the higher reverse salt flux of NH₄⁺.

Forward Osmosis can be used to concentrate a Na₂SO₄ feed solution with NaCl as the Draw solution.

V. RECOMMENDATION

Applications should be identified where seawater or seawater brine can be used as Draw solution when effluents need to be up-concentrated with the aim of recovering valuable products. Both are rich in NaCl, which was found to be the ideal salt to be used in the Draw solution.

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REFERENCES

- [1] Z. Li, R. V. Linares, S. Sarp and G. Amy, "Direct and Indirect Seawater Desalination by Forward Osmosis," *Membrane-Based Salinity Gradient Processes for Water Treatment and Power Generation*, p. 245–272, 2018. <https://doi.org/10.1016/B978-0-444-63961-5.00009-2>
- [2] N. Zikalala, J. P. Maree, C. Zvinowanda, V. Akinwekomi, T. Mtombeni and L. Mpenyane-Monyatsi, "Treatment of sulphate wastewater by freeze desalination," *Desalination and Water Treatment*, vol. 79, pp. 93-102, June 2017. <https://doi.org/10.5004/dwt.2017.20927>
- [3] S. Zhao, L. Zou, C. Tang and D. Mulcahy, "Recent developments in forward osmosis: opportunities and challenges," *J. Membr. Sci.*, vol. 396, pp. 1-21, 2012. <https://doi.org/10.1016/j.memsci.2011.12.023>
- [4] G. P. S. Ibrahim, A. M. Isloor and E. Yuliwati, "A Review on Current Trends and Future Developments on (Bio-) Membranes," pp. 199-214, 2019. <https://doi.org/10.1016/B978-0-12-813551-8.00008-5>
- [5] Y. Woo, S. Kim, H. Shon and L. Tijing, "Introduction: Membrane Desalination Today, Past, and Future," pp. 1-22., 2019. <https://doi.org/10.1016/B978-0-12-813551-8.00028-0>
- [6] A. Altaee, A. Alanezi and A. Hawari, "Forward osmosis feasibility and potential future application for desalination," *Emerging Technologies for Sustainable Desalination Handbook*, p. 35–54, 2018. <https://doi.org/10.1016/B978-0-12-815818-0.00002-3>
- [7] N. Abdullah, M. Tajuddin and N. Yusof, "Forward Osmosis (FO) for Removal of Heavy Metals," *Nanotechnology in Water and Wastewater Treatment*, p. 177–204, 2019. <https://doi.org/10.1016/B978-0-12-813902-8.00010-1>
- [8] S. Phuntsho, H. Shon, S. Hong, S. Lee and S. Vigneswaran, "A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions," *J Membr Sci*, vol. 375, pp. 172-81, 2011. <https://doi.org/10.1016/j.memsci.2011.03.038>
- [9] L. Chekli, S. Phuntsho, J. Kim, J. Kim, J. Choi, J. Kim, S. Hong, J. Sohn and H. Shon, "A comprehensive review of hybrid forward osmosis systems: performance, applications and future prospects," *Journal of Membrane Science*, vol. 497, pp. 430-449, 2016. <https://doi.org/10.1016/j.memsci.2015.09.041>
- [10] P. Nasr and H. Sewilam, "The potential of groundwater desalination using forward osmosis for irrigation in Egypt," *Clean Techn Environ Policy*, vol. 17(7), p. 1883–95, 2015. <https://doi.org/10.1007/s10098-015-0902-4>
- [11] P. Nasr and H. Sewilam, "Fertilizer drawn forward osmosis for irrigation," *Emerging Technologies for Sustainable Desalination Handbook*, p. 433–460, 2018. <https://doi.org/10.1016/B978-0-12-815818-0.00013-8>
- [12] S. T. Reddy, A. E. Lewis, G. J. Witkamp, H. J. M. Kramer and J. van Spronsen, "Recovery of Na₂SO₄-10H₂O from reverse osmosis retentate

by eutectic freeze crystallization technology,” *Chemical Engineering Research and Design*, vol. 88, pp. 1153-1157, 2010. <https://doi.org/10.1016/j.cherd.2010.01.010>

[13] R. Wang, L. Shi, C. Tang, S. Chou, C. Qiu and A. Fane, “Characterization of novel forward osmosis hollow fiber membranes,” *J Membr Sci*, vol. 355(1-2), p. 158-67, 2010. <https://doi.org/10.1016/j.memsci.2010.03.017>

[14] N. Yip, A. Tiraferri, W. Phillip, J. Schiffman and M. Elimelech, “High performance thin-film composite forward osmosis membrane,” *Environ Sci Technol*, vol. 44, p. 3812-8, 2010. <https://doi.org/10.1021/es1002555>

[15] S. Zhang, G. Han, X. Li, C. Wan and T. Chung, “Pressure retarded osmosis,” *Sustainable Energy from Salinity Gradients*, p. 19-53, 2016. <https://doi.org/10.1016/B978-0-08-100312-1.00002-X>

[16] R. Holloway, R. Maltos, J. Vanneste and T. Cath, “Mixed draw Solutions for Improved forward osmosis performance,” *Journal of Membrane Science*, 2015. <https://doi.org/10.1016/j.memsci.2015.05.016>

[17] P. Pal, “Water Treatment by Membrane-Separation Technology,” *Industrial Water Treatment Process Technology*, p. 173-242, 2017. <https://doi.org/10.1016/B978-0-12-810391-3.00005-9>

[18] H. Ma and B. Hsiao, “Electrospun Nanofibrous Membranes for Desalination,” *Current Trends and Future Developments on (Bio-) Membranes*, p. 81-104, 2019. <https://doi.org/10.1016/B978-0-12-813551-8.00004-8>

[19] T. Cath, A. Childress and M. Elimelech, “Forward osmosis: principles, applications, and recent developments,” *J Membr Sci*, vol. 281, pp. 70-87, 2006. <https://doi.org/10.1016/j.memsci.2006.05.048>

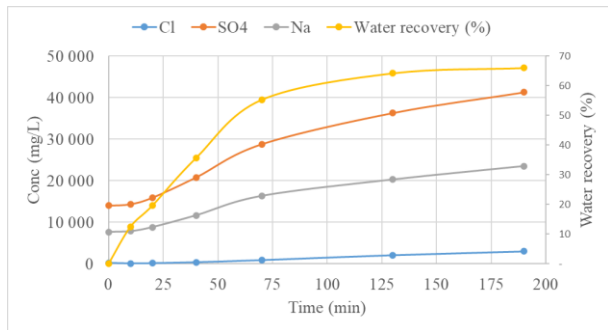
[20] K. Bowden, A. Achilli and A. Childress, “Organic ionic salt draw solutions for osmotic membrane bioreactors,” *Bioresour Technol*, vol. 122, pp. 207-216, 2012. <https://doi.org/10.1016/j.biortech.2012.06.026>

[21] J. Yong, W. Phillip and M. Elimelech, “Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes,” *J Membrane Sci*, vol. 392, pp. 9-17, 2012. <https://doi.org/10.1016/j.memsci.2011.11.020>

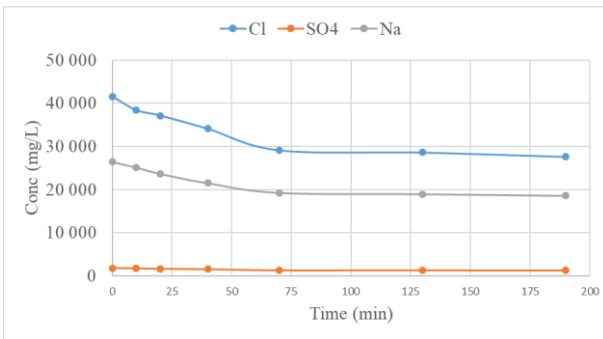
[22] OLI, “<http://www.olisystems.com/>,” 23 11 2015. [Online]. [Accessed 2015].

TABLE II. TEMPORAL BEHAVIOUR OF VARIOUS PARAMETERS DURING CONTINUOUS FLOW DRAW SOLUTION AND RECYCLE OF FEED SOLUTION

Time	Water recovery %	Feed solution			Draw solution			Osmotic Pressure (atm)		
		Na ⁺ (mg/L)	SO ₄ (mg/L)	Cl ⁻ (mg/L)	Na ⁺ (mg/L)	SO ₄ (mg/L)	Cl ⁻ (mg/L)	Feed Na ₂ SO ₄	Draw NaCl	Difference
0.00	0.0	8 188	16 360	28	16 085	1 160	22 385	8.6	31.6	22.9
10.00	16.0	10 450	21 485	43	15 025	1 085	20 830	11.1	29.4	18.3
20.00	23.0	12 265	24 400	65	11 028	770	14 430	12.7	20.6	7.9
35.00	28.0	12 863	25 125	78	8 818	620	11 485	13.1	16.3	3.1
65.00	29.0	12 163	24 003	83	6 478	463	8 218	12.5	11.5	- 1.0
85.00	29.0	12 060	23 695	90	6 158	453	7 968	12.4	11.1	- 1.3
155.00	44.0	15 363	30 215	175	15 935	1 103	22 445	15.7	31.5	15.8
185.00	52.0	16 915	33 548	255	14 230	995	19 893	17.3	27.9	10.6
235.00	59.0	19 090	37 955	398	13 900	963	19 310	19.5	27.2	7.6
275.00	70.0	26 140	50 975	803	18 730	1 315	26 940	26.3	37.7	11.4
315.00	71.0	29 305	54 908	1 085	17 685	1 218	24 820	28.6	35.0	6.3
340.00	73.0	28 085	57 150	1 250	17 223	1 195	23 903	29.0	33.8	4.8

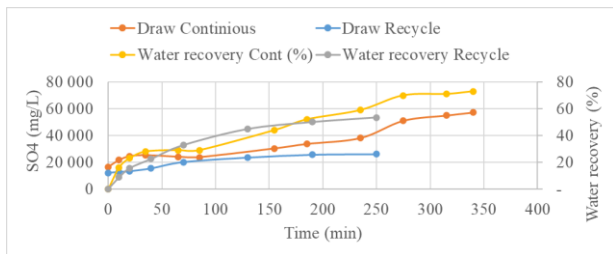


a. Feed solution

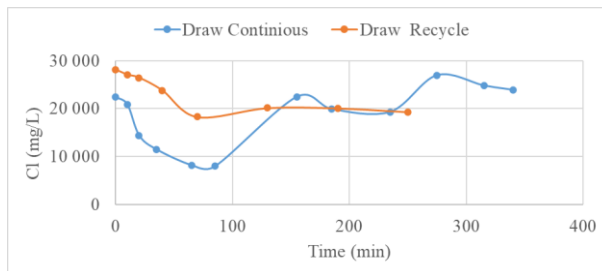


b. Draw solution

Fig. 2. Temporal behaviour of various parameters of Feed (20 g/L Na₂SO₄) and Draw (60 g/L NaCl) solutions (Feed - Recycled; Draw - Recycled)



a. Feed solution



b. Draw solution

