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Performances of PA hollow fiber membrane with the CTA flat sheet membrane for forward osmosis process

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ABSTRACT

Fertilizer drawn forward osmosis desalination has been earlier explored using flat sheet forward osmosis (FSFO) membrane, which highlighted flux and reverse solute flux (RSF) performance. This study evaluated and compared the performances of a newly developed polyamide (PA)-based hollow fiber forward osmosis (HFFO) membrane and cellulose triacetate FSFO membrane. Both membranes were evaluated for pure water permeability, salt rejection rate (1,000 mg/L NaCl) in RO mode. Physical structure and morphology were further examined using scanning electron micrograph (SEM). SEM images revealed that the overall thickness of the HFFO and FSFO membranes was 152 and 91 μm, respectively. Flux and RSF performances of these two membranes were evaluated using nine fertilizer DS as NH_4Cl, KNO_3, KCl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $NaNO_3$, and $CO(NH_2)_2$ in active layer–feed solution membrane orientation. HFFO membrane clearly showed better performance for water flux with five DS ($(NH_4)_2SO_4$, $NH_4H_2PO_4$, KNO_3, $CO(NH_2)_2$, and $NaNO_3$) as they showed up to 66% increase in flux. Beside thick PA active layer of HFFO membrane, higher water flux outcome for forward osmosis (FO) process further highlighted the significance of the nature of support layer structure, the thickness and surface chemistry of the active layer of the membrane in the FO process. On the other hand, most DS showed lower RSF with HFFO membrane with the exception of $Ca(NO_3)_2$. Most of DS having monovalent cation and anions showed significantly lower RSF with HFFO membrane.

Keywords: Fertilizer draw solution; Forward osmosis (FO); Flat sheet FO membrane; Flux; Hollow fiber FO membrane; Reverse salt flux

1. Introduction

Energy intensive thermal- and membrane-based desalination processes are currently being used extensively to meet the growing demands of clean water. The rising energy prices have really made it difficult to economically produce good quality water. Although thermal desalination was initiated many decades ago, but due to comparatively low energy systems, in the last 30 years, membrane-based desalination processes gained popularity and now competing the long

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established distillation-based technologies [1]. Membrane-based technologies now claim major share of the installed desalination capacity in the world [2].

Forward osmosis (FO) is a newly introduced membrane-based desalination technique harnessing the natural available power, that is, osmotic pressure (OP) of draw solution (DS) to induce flux thus avoids any additional external energy source to drive desalination. Due to this particular reason, in a very short period of time, FO technology has been evaluated for a wide range of applications ranging from sea/brackish water desalination [3–5] to power generation [6]. Fertilizer drawn forward osmosis (FDFO) is an innovative FO process [7] using commercially available fertilizers as DS to desalinate water for agricultural use. Additionally, opposite to other FO processes, final diluted DS does not necessarily require separation of the remaining DS and thus product permeated water is used directly for fertigation. It helps FDFO process taking a real advantage from low-cost FO desalination approach.

Beside aforesaid FO inherent advantages, FO membrane and DS characteristics are considered as the major impediments in the commercialization of FO system [8]. Similarly, FDFO process has also seen certain limitations for its practical applications [7]. Apart from the fertilizer, DS-related issues such as excessive DS recovery, high nutrients concentration in permeated water, risk of possible nutrients loss to feed solution (FS), membrane associated issues such as low water flux and high RSF are also noticed. FO flux is directly linked to initial capital cost and operating cost of FO system. High flux FO operation means small FO plant footprint and reduced reverse solute flux (RSF) reflects reduction in DS leakage to FO waste streams.

FO membranes are mainly classified into two main groups (1) flat sheet and (2) hollow fiber. Earlier studies with CTA flat sheet forward osmosis (FSFO) membranes highlighted issues such as low water flux (J_w) and high RSF [9,10], which also affect FDFO process directly. Lower performance ratio of 16.48% indicated serious issues with FSFO membrane [7]. Initially, only the asymmetric (active layer embedded on a porous support layer used to increase the structural strength of the membrane) FSFO membrane was produced and tested for various applications. The asymmetric structure of this membrane causes enhancing concentration polarization (CP) on both sides of the membrane consequently results in reduction in the actual water flux through the membrane. CP drastically reduces the available driving force (OP gradient ($\Delta\pi$)) at the membrane surface and causes sharp decline in flux that results in poor FO operational result performance.

Since FO flux mainly relies on $\Delta\pi$ across the membrane surface contacting DS and FS to drive osmosis, therefore, the accumulated CP affects it seriously [11–14]. External concentration polarization is usually linked with DS and FS concentration whereas internal concentration polarization (ICP) is mainly associated with thick dense membrane and support layer structure [9]. Membrane fouling and CP are considered as the two serious operational problems with FO systems directly affecting their outcome [12–16]. To overcome this issue, efforts were directed to develop an ideal FO membrane having thin film on a highly porous and very fine support layer, having high water permeability, low salt permeability, and enough strength structure layers that gives minimum CP effects, especially ICP.

Hydration Technologies Innovations (HTI) first introduced commercial flat sheet CTA FO membrane [15]. To reduce the intensity of the membrane-related issues critical for quick FO commercialization, many research groups worked on development of new and improved FO membranes. Some of the resulted positive outcomes include novel dual-layer hollow fiber membranes [17], well-constructed cellulose acetate (CA) FO membrane [12], thin-film composite (TFC) FO hollow fiber membrane [18,19], high-performance thin-film membrane [20], thin-film nano-composite using functionalized multi-walled nanotubes [21], double-skinned FO membrane [22], acetylated methyl cellulose membrane [23], and cellulose triacetate/cellulose acetate (CTA/CA)-based membranes [24].

Hollow fiber forward osmosis (HFFO) membrane development work was initiated by various research groups [25,26] to produce better performing FO membrane carrying minimum FO operational issues. In comparison with FSFO membranes, most of the developed HFFO membranes demonstrated proven performance in terms of high water flux and lower RSF [19,27–32].

Up to date, many studies have been done to explore FO use in different practical applications using FSFO membrane, but no serious attempt is yet made for using HFFO [33–39]. Hence, this study may be considered as a late first genuine step to evaluate HFFO membrane for any commercial application as FDFO.

As such, the main objective of this study was to categorically compare HFFO membrane performance with FSFO membrane and notice its effects on FDFO desalination process efficiency. HFFO membrane was evaluated for different fertilizer DS and flux, RSF results were compared with the FSFO membrane outcome to identify specific membrane properties critical for higher FO process performances. Comparison of

FDFO performance for these two different membranes with multiple DS further provided us better understanding about how different DS properties and membrane characteristics manipulate FO output.

2. Materials and methods

2.1. Experimental setup

Bench scale HFFO setup as shown in the Fig. 1 was used for this study. Two peristaltic pumps (Cole-Palmer, USA) were used to supply FS and DS to HFFO membrane module. Cross-sectional flow rates were maintained at 400 mL/min for both FSFO and HFFO membrane units. While changing DS, each FO system was washed thoroughly at the end of each test for 30 min using distilled water at 400–800 mL/min. Temperature of the DS and FS stream was kept constant at 25 ± 1˚C using temperature water bath controlled by heater/chiller.

Water permeation through HFFO membrane was evaluated by measuring weight loss of FS using a weighing scale (CUW 4200H by CAS, Korea) connected to a computer data logging system, which was later used to calculate water flux in these particular FO tests. A conductivity data logger probe was immersed in FS tank to record changes in FS conductivity at certain time intervals. This data helped in measuring RSF during FO operations. An identical bench scale FO setup was used for FSFO membrane evaluation stated elsewhere [7].

2.2. Membranes used

HFFO membrane lumens, supplied by Samsung Cheil Industries, Korea, were used in this study. HFFO lumens were composed of active polyamide (PA) TFC layer inside of porous polyethersulfone hollow fiber substrate. Inside and outside diameters of these hollow fiber lumens were 0.9 and 1.2 mm, respectively, and HFFO module carried average FO membrane area of 3.96×10^{-2} m^2.

Simultaneously, commercially available CTA FO membrane supplied by HTI, USA, was used separately with FSFO lab setup. FO lab experimental cell carried flat sheet membrane of size 26 × 77 mm. Thus, FSFO membrane represented an average membrane area of 2.02×10^{-3} m^2.

All tests for both FSFO and HFFO were carried out in active layer – feed solution (AL-FS) membrane orientation. Smooth active layer of FSFO membrane was placed toward FS side, and rough surface carrying polyester mesh support layer was faced toward DS side. Similarly, for HFFO setup, FS was directed to flow through lumens whereas DS was flowed through FO module shell outside fiber.

2.3. Chemicals and reagents

Nine commonly used fertilizers including NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, $(NH_4)_2HPO_4$ (DAP), $NH_4H_2PO_4$ (MAP), $Ca(NO_3)_2$, $NaNO_3$, and $CO(NH_2)_2$ (Urea) were selected to use as DS to evaluate and compare

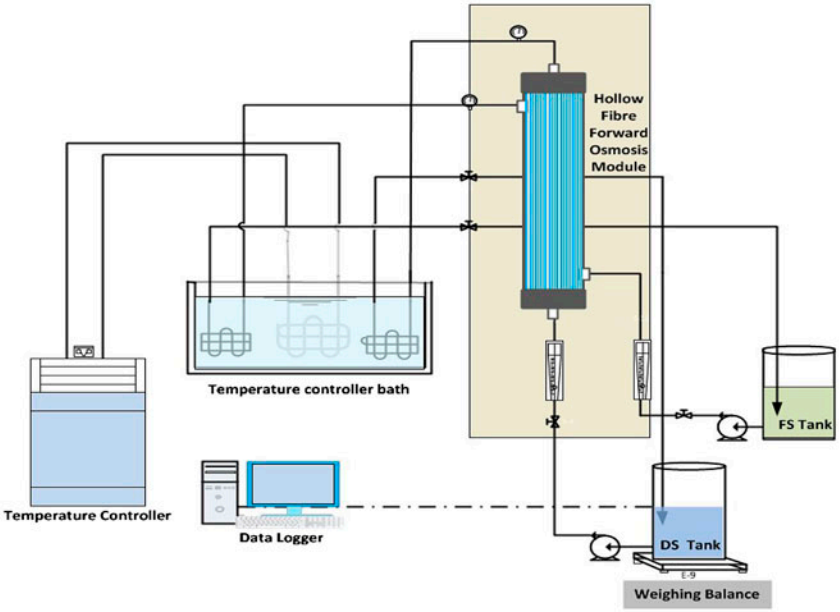

Fig. 1. Schematics of lab scale HFFO setup used in this study.

performance of these two FO membranes for FDFO process. Membrane performance was evaluated against 1 M individual fertilizer DS concentration. DI water was used as FS for the whole study.

2.4. FO operating setup summary

Details of the HFFO and FSFO membrane test setup are summarized in Table 1.

3. Results and discussion

3.1. HFFO and FSFO membranes comparison

HFFO and FSFO membranes were used for FDFO process comparison. Physical properties of both membranes are summarized in Table 2. Membrane thickness was evaluated using micrometer, and its surface characteristics were further assessed using scanning electron micrograph (SEM). HFFO membrane comparatively shows about 66% overall higher membrane thicknesses as HFFO and FSFO membranes show thickness of 152 ± 3 and 91 ± 2 μm, respectively. Thus, the HFFO thickness is about 66% higher than FSFO membrane. Similarly, thickness of polyamide active layer of HFFO membrane is also high as compared to thickness of active CTA layer of FSFO membrane.

Table 1
Summary of the operating conditions for bench scale HFFO and FSFO membrane systems for FDFO process comparative study

Description	Details
DS used	NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $Ca(NO_3)_2$, $NaNO_3$, and $CO(NH_2)_2$
Fertilizer DS concentrations	1 M
Feed water type	Deionized (DI) water
Membrane orientation	AL-FS
Temperature	25 ± 1.0°C
Parameters evaluated	FO flux and RSF
HFFO module type	PA lumens-based hollow fiber module
FSFO membrane type	CTA flat sheet membrane
DS/FS flow rates	400 mL/min for both DS/FS
HFFO membrane active area	39.6×10^{-3} m^2
FSFO membrane active area	2.02×10^{-3} m^2

Table 2
Comparison of FSFO and HFFO membrane characteristics and physical properties

	Flat sheet FO	Hollow fiber FO
Source	HTI, USA	Samsung Cheil Industries, Korea
Active layer (AL) material	Cellulose Triacetate	Polyamide
Support layer (SL) material	Polyester mesh	Polyether sulfone
Thickness (Overall) (μm)	91 ± 2	152 ± 3
Thickness (AL) (μm)	45 ± 2	65 ± 3
Thickness (SL) (μm)	46 ± 2	87 ± 3
Pure water permeability (Lm^{-2} h^{-1} bar^{-1})	1.012	1.80
Salt rejection (%)	90	98
Membrane surface charge	Negatively charge[a]	Neutrally charge [b]
Support layer surface charge	Negatively charge	Neutrally charge
Contact angle of the active layer (°)	61[c]	–
Contact angle of the support layer (°)	87[d]	–

Sources: [a][41]; [b][42]; [c][43]; [d][16].

Pure water permeability (PWP) and the salt rejection rate (1,000 mg/L NaCl) of both membranes were evaluated in RO mode. FSFO membrane was evaluated for higher pressure (5–15 bars) whereas HFFO was evaluated at extremely low pressure (up to 1.5 bars) to avoid fiber damage. The PWP and the salt rejection of the HFFO membrane were 1.80 L m^{-2} h^{-1} bar^{-1} and 98%, respectively, while for FSFO membrane the PWP and rejection were 1.012 L m^{-2} h^{-1} bar^{-1} and 90%, respectively. In comparison with FSFO, HFFO membrane showed PWP value higher by 78% and salt rejection higher by 9%.

Fig. 2 shows SEM images of both PA HFFO membrane and CTA FSFO membrane. Both membranes show a huge difference in making and structure. Fig. 2(a) shows top image of horizontally cut HFFO membrane. A thick PA active layer was seen on top of an outer layer of polyethersulfone. The PA active layer presents excellent intrinsic separation properties with a hydrophilic rejection layer that provides good mechanical strength to FO hollow fibers.

Similarly, in Fig. 2(b), a side view of the CTA FS membrane shows top dense CTA layer embedded on a polyester mesh support layer. Membrane acetate contents (in wt.%) directly affect the PWP and salt permeability as well [40]. Water diffusion coefficient

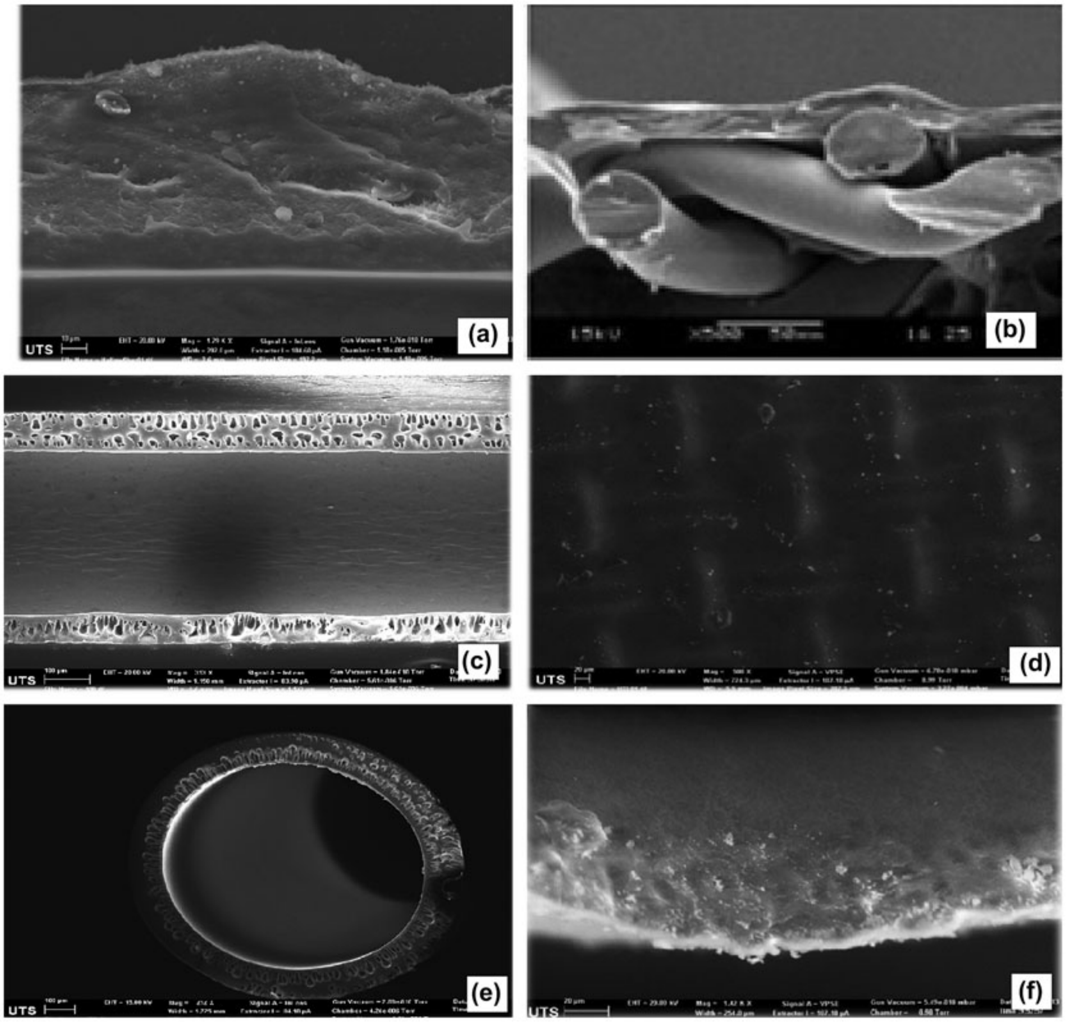

Fig. 2. SEM images for both FO membranes used in our study. (a) cross-section of HF FO membrane showing the inside active PA layer supported by outside PES layer, (b) FSFO membrane, with CTA active dense layer embedded on polyester mesh, (c) HFFO horizontally cut, larger view, (d) FSFO active layer (top view), (e) and (f) HFFO cross-section. *Adapted from [45].

decreases as the acetate content of the membrane is increased. Similarly, salt permeability is also reduced with any increase in membrane acetate contents suggests that a better CTA membrane may be made by controlling its acetate contents in the membrane along with the thickness of the membrane.

3.2. Comparative performances of FO membranes in terms of water flux and RSF

Lab FO units for both flat sheet membrane cell and hollow fiber module were operated on similar operation conditions. The FO flux outcome was evaluated for various fertilizer DS used in FDFO process, and these results were then compared for their effectiveness for FDFO process. These were evaluations in term of AL-FS membrane orientations. Due to severe ICP issues, FO operation in this orientation relatively shows less flux output [44].

3.3. Overall flux evaluation and comparison

Fig. 3 shows the flux performances for HFFO (PA) membrane and compares it with FSFO (CTA) membrane flux results. These two membranes showed a mixed trend when HFFO flux output was compared with FSFO flux results using nine different fertilizers including NH_4Cl, $Ca(NO_3)_2$, $NaNO_3$, KNO_3, MAP, $(NH_4)_2SO_4$, KCl, DAP, and urea as DS at 1 M concentration. Some of the fertilizers DS showed compara-

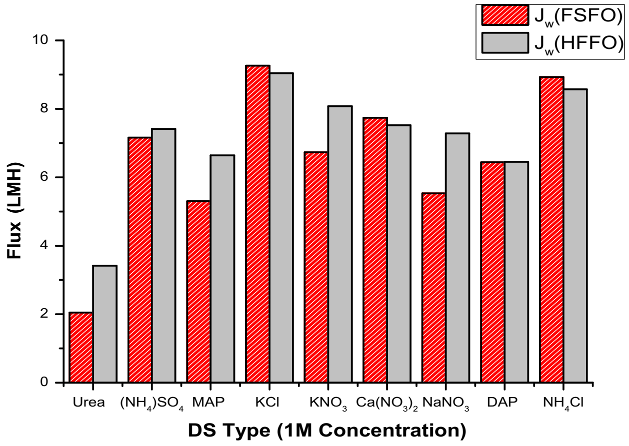

Fig. 3. Comparison of flux outcome for FSFO and HFFO membranes..

tively higher flux outcome with HFFO membrane while others show lower flux. Results show that with these two FO membranes, flux varied from −4 to 68% for different fertilizer DS. Urea showed the highest increase followed by $NaNO_3$, KNO_3, MAP, $(NH_4)_2SO_4$. NH_4Cl, KCl, and $Ca(NO_3)_2$ showed lower flux results with HFFO membrane and DAP nearly gave the same flux. Urea, $NaNO_3$, MAP, KNO_3, and $(NH_4)_2SO_4$ show that with HFFO, flux was increased by 67, 32, 25, and 8%, respectively, whereas NH_4Cl, $Ca(NO_3)_2$ and KCl, respectively showed flux decrease of 4.0, 3.0, and 2.0% for HFFO. Flux for $(NH_4)_2HPO_4$ (DAP) nearly remained the same for both membranes.

Comparing the physical appearance of the active layer of these two membranes (Fig. 2(a) and (d)), it is evident that hollow fiber PA seems to be very porous as compared to a true dense flat sheet CTA membrane. Porous structure of HFFO membrane apparently helped diffuse water molecules comparatively easily and faster through the PA membrane surface, and thus, it comparatively delivered high flux output. From the general theory of permeation and osmosis, it may be concluded that as HFFO substrates seem highly porous with a narrow pore size distribution against a really dense CTA layer of FSFO membrane, the latter might resist speedy penetration of water molecules deep through the membrane active layer at a high rate and thus deliver comparatively low flux.

Further, Fig. 3 results indicate that for these membranes, the flux variation with a particular DS is affected with the anion part of the DS solute. It was observed that most of nitrate-based DS as $NaNO_3$ and KNO_3 gave higher flux with HFFO membrane and chloride-based DS (NH_4Cl and KCl) provided higher flux with FSFO membranes. It is likely that smaller hydrated diameter species have more chances to diffuse through the membrane [46,47]. As the NO_3^- and Cl^- anions carried the smallest hydrated radii size among all anions, they penetrated deep into the support layers of HFFO and FSFO membranes SL to reach close to the their active layers. However, active layers of these membranes responded differently for DS carrying NO_3^- and Cl^- and delivered inconsistent flux outcome. HFFO and FSFO membrane showed varying flux outcome for NO_3^- and Cl^--based DS.

Moreover, the associated cationic part of the DS also significantly affects FO flux for a particular DS. HFFO membrane gave high flux with monovalent cation-based nitrate DS as $NaNO_3$ and KNO_3 whereas FSFO showed high flux with divalent cation-based nitrate DS as $Na(NO_3)_2$. This indicates that the FO flux for a particular membrane is associated with both DS properties and membrane characteristics.

Dense CTA flat sheet membranes gave lower water flux output due to increased CP phenomenon [28]. Interfacially polymerized TFC membranes on hydrophilic porous substrates show reduced ICP effects and exhibit high water flux [48]. Hydrophilicity of porous substrates plays an important role on TFC FO membranes. These fluctuations in FO performance consequences for similar DS and operating conditions are attributed to the active rejection layer and support layer characteristics.

3.4. RSF evaluation and comparison

RSF of eight fertilizers DS was evaluated for both HFFO and FSFO membranes. RSF is an important performance parameter used to evaluate the effectiveness of FO process as it represents the unwanted loss of valuable DS diffused through the FO membrane toward the FS, valuable fertilizer in the FDFO process. Difference of solute concentration in DS and FS on both side of the membrane drives RSF.

Overall, RSF results indicate that in comparison with FSFO membrane, HFFO performed extremely well for RSF outcome for most of the fertilizer DS. Contrary to flux outcome comparison, irregular behavior was observed when HFFO and FSFO membranes RSF results were evaluated and compared for different fertilizer DS (1 M concentrations). Most of the fertilizer DS showed very low RSF with HFFO (Fig. 4). $NH_4H_2PO_4$, KCl, KNO_3, KCl, NH_4Cl, and MAP DS gave lower RSF values whereas $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ comparatively delivered higher RSF values among these fertilizers.

The results in Fig. 4 were evaluated for RSF percentage variation for HFFO and FSFO membranes.

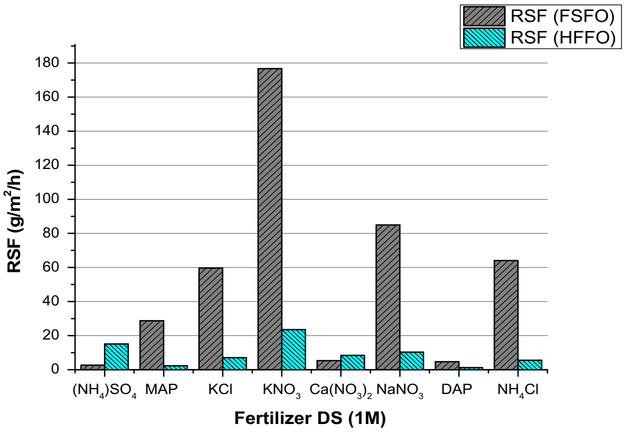

Fig. 4. RSF with HFFO and FSFO membranes for fertilizer DS.

FSFO membrane showed relatively inferior results for RSF. Comparison to HFFO, FSFO membrane showed 1,145, 739, 650, 727, 280, and 1,058% higher RSF for $NH_4H_2PO_4$, KCl, KNO_3, $NaNO_3$, DAP, and NH_4Cl DS, respectively.

Further, NH_4Cl and KCl DS carrying monovalent cations and anion gave similar RSF for FSFO and HFFO membrane whereas the other DS pair as KNO_3 and $NaNO_3$ also carrying monovalent cations and anions showed significant difference in RSF outcome (Fig. 4). $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ carrying a divalent cation and divalent anion showed less RSF with both membranes. Ca^{2+} thus shows less RSF as compared to Na^+ or K^+. HFFO membrane comparatively indicated the high RSF value for divalent cation- and anion-based DS such as $(NH_4)_2SO_4$ and $Ca(NO_3)_2$. Divalent cations and anions (Ca^{2+}, ${SO_4}^{2-}$) or trivalent anions (${PO_4}^{3-}$) have high hydrated radii, hence exhibits low RSF.

FSFO showed better performance in terms of RSF for $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ DS as it, respectively showed 82 and 36% less RSF for these two DS. Low RSF demonstrated by FSFO membrane for divalent ionic compounds could be attributed to ion size exclusion and Donnan electrostatic effect FSFO [17,25]. Comparative data also proved that divalent cations or anions reduce or slow down the relative permeation of respective monovalent cations and anions.

3.5. Flux and RSF behavior with hydrated radii

For water permeation (flux) or a salt diffusion (RSF) through a specific membrane, both size of water molecule and DS species matter are important. DS ionic size, solute structure and membrane pore shape play an important role in delivering any particular flux through the membrane. FO performance-related parameters as flux and RSF have affinity between DS radii, water molecule size, and membrane pore size. Ionic and dipole permeabilities are extremely sensitive to the ionic/dipolar radii [49,50]. Large molecules are retained at the membrane surface by electrostatic interactions whereas small, weakly charged ions can enter the pores. Anions hold their hydration shells relatively more strongly than the cations for a given charge density [51].

Fig. 3 shows that HFFO membrane exhibited better flux outcome for a particular DS carrying the same OP. For many reasons, solute concentration alone is not sufficient to give good estimates of OP [52]. OP is not solely a function of the number of solute particles in solution, but it is also related to the solute size [53]. Osmotic potential of organic solutions is largely a function of the size of their solute particles [54]. Solutes influence osmotic potential by altering the molecular spacing of the free water molecules in solution and therefore different solutes differently influence the osmotic potential [55]. This also authenticates that a close relation between the hydrated radii and membrane pore size.

Results presented in Figs. 3 and 4 are further evaluated with different prevailing theories to further identify the main issues related to the difference in performance of these two membranes.

Both HFFO and FSFO membranes were asymmetric and permeable to both salt and water. Water flux and salt diffusion seem to be closely linked with each other. Results from Fig. 4 indicate the influence of interactions of some strange intermolecular and intramolecular forces, which play an important role for the specific diffusion of different solutes through semi-permeable membranes. Characterizing DS by their valancy, comparison of the results in Fig. 4 shows that DS containing monovalent cations (NH_4^+, K^+) and anions (NO_3^-, Cl^-) exhibited better results with HFFO CA membrane. DS containing either a divalent cation (Ca^{2+}) or divalent anion (SO_4^{2-}) exhibited better performance for RSF with CTA flat sheet FO membrane. Low RSF for divalent cation- and anion-based DS showed that CTA FSFO membrane behaves similar to NF membrane for divalent ions rejection properties. Inconsistent trends for RSF results may only be associated with the membrane active layer properties as their surface charge, membrane pore size, and pore geometry.

Fig. 4 indicates that RSF for monovalent cation-based NO_3^- and Cl^- DS reduced significantly with HFFO membrane. AL of HF membrane does not allow nitrates to diffuse through the PA active layer. In comparison with HFFO, FSFO membrane showed 650 and 727% higher RSF for KNO_3, and $NaNO_3$, respectively. Nitrate-based DS exhibited high flux and lower RSF with HFFO (Figs. 3 and 4). Furthermore, compared to FSFO, HFFO membrane showed 739 and 1,054% lower RSF for chloride-based DS. However, chloride-based DS showed higher flux for FSFO membrane.

The results indicate that in comparison with CTA FSFO, PA HFFO membrane carries smaller pore with unique configurations, which reduce RSF through the membrane. These membrane pores do not allow even the smaller size Cl^- and NO_3^- ions pass through the HF membrane but at the same time high RSF value for divalent DS indicates that the membrane allows DS carrying large size divalent Ca^{2+} and SO_4^{2-} move faster through the membrane. It confirms that only hydrated radii size does not direct flux or RSF for any membrane rather membrane properties are more vital for FO performance. Similarly, the pore size of membrane AL may not suggest any particular flux or RSF outcome. PA membrane showed better control of monovalent cationic or anionic DS whereas CTA membrane shows better control of diffusion for divalent cation- or anion-based DS.

In any FO process, RSF and water flux movement through the FO membrane are in opposite directions [56,57]. Water molecules in a high flux FO process push solute molecules backward and result low RSF. Similar types of opposite forces affect osmosis and diffusion for all flux and RSF outcome. Figs. 3 and 4 show that high FO flux outcome reduces RSF. RSF does not reduce linearly with the flux rise for all evaluated DS which indicates that flux rise itself does affect RSF outcome significantly. Literature still lacks data which may exactly define water and solutes molecules movement patterns through the membrane pores during any membrane filtration process as NF, RO, and FO. Due to these unclear hidden issues, effects of such phenomenon are not yet incorporated to derive equations for FO flux and RSF.

It is impossible to have an ideal membrane of zero thickness [58]. All natural and synthetic membranes come with a finite thickness. Table 2 shows that HFFO membrane comparatively carries thick active layer and support layer. HFFO membrane exhibited same thickness same as of conventional RO membrane [59]. Water molecules face more obstacles to cross-thicker membrane. Higher flux with HFFO membrane indicated that thin active layer of FSFO has dense and non-porous membrane structure. Due to smooth pore geometry and structure, water molecules comparatively have better probability to move quickly through micro porous HFFO membrane structure shown in Fig. 2(a).

Fouling development reduces water flux sharply as fouling make water diffusion passage through the membrane thick [44]. Fouling tends to increase the thickness of the membrane which hamper flow of water molecules, but flux reduction due to fouling and scaling is mainly contributed due to pore blocking [60]. Membrane development work is focused to construct a thinner membrane; however, Fig. 3 results indicate that only the thickness of the specific membrane does not effect FO flux notably rather it highlighted role of other membrane characteristics as pore density, pore size, pore structure, and pore depth, which are not yet evaluated in details. These parameters seem more critical and relevant than membrane thickness for FO flux and RSF outcome. However, influence of AL thickness on FO outcome is not ruled out completely.

CP reduces the net OP available across the AL of FO membrane [3]. In FO process, CP increases as the thickness of the membrane or SL increases [3,16,61–63]. ICP effects can be reduce by using thinner and more porous support layer as it reduces mass transfer resistance [14]. For most of the DS, higher flux outcome (Fig. 3) by HFFO membrane comprises of thick active and support layers (Table 2) reveal that the thickness of the membrane may not be considered as the main parameter linked to CP rather AL and SL membrane material characteristics and DS properties together contribute to CP buildup in diverse ways.

Figs. 3 and 4 result indicate that for different DS, both HFFO and FSFO membranes showed varying behaviors for flux and RSF outcome. It is evident from these results that the differences in flux and RSF outcome are owing to varying membrane properties and DS characteristics as well. Different DS affects flux and RSF performance inconsistently for these membranes as for 1 M KNO_3 DS; water flux increases whereas RSF decreases for HFFO membrane. Similar types of varying results were also noticed with other evaluated DS. DS properties seem directly linked with membrane structure, porosity, pore density, pore size, pore structure, solute affinity with water, AL, and SL membrane surface charge, membrane thickness, water and solute flow patterns within membrane pores for any particular FO performance outcome. Further studies on these fundamental parameters are suggested to understand and predict any resultant FO flux or RSF outcome for a specific membrane.

4. Conclusions

PA HFFO and CTA FSFO membranes were evaluated in this study for FDFO process. Summarizing main findings of our study as:

- HFFO membrane comparatively gave up to 66% higher flux outcome for different fertilizer DS.

- HFFO membrane performed well for RSF as FSFO membrane showed up to 1,184% higher RSF values for fertilizer DS. Most of the DS showed lower RSF values with HFFO except DS having divalent cations or anions.
- FO flux and RSF outcome for FO membranes are mainly associated with hydrated radii of anions associated with other cation of the DS. Most of the Cl^--based DS gave better flux outcome with FSFO whereas NO_3^--based DS exhibited better flux results with HFFO. Divalent cationic or anionic parts of the DS significantly affected RSF and flux results.
- The study confirms close links and associations between DS properties and membrane characteristics for FO performance.

Higher water flux and low RSF outcome for HFFO membrane confirmed that HFFO membrane is a better choice for FDFO process.

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