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Highlights

- Distillery wastewater was dewatered using three forward osmosis (FO) membranes
- 3M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw solutions resulted in a stable flux for all membranes
- COD, melanoidins and antioxidants content was similar for all membranes
- Flux and cleaning ease of HTI-TFC membrane was best but reverse salt flux was high

Graphical abstract

Influence of Forward Osmosis (FO) membrane properties on dewatering of molasses distillery wastewater

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Abstract

This work presents a comparison of three forward osmosis (FO) membranes viz. HTI-TFC, HTI-CTA, and aquaporin-TFC for water recovery from a high strength wastewater of sugarcane molasses distillery. Surface properties of the membranes were assessed using scanning electron microscopy (SEM), zeta potential measurement and attenuated total reflection infrared spectroscopy (ATR-IR). A commercial magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (1 M to 4 M) solution was used as the draw and a 3 M concentration was identified to be optimal in obtaining stable flux. During a 24 h FO operation, the average water flux and water recovery respectively were 2.8 L/m²h and 81% (HTI-TFC), 2.4 L/m²h and 71% (HTI-CTA) and 1.9 L/m²h and 66% (aquaporin-TFC). FO operation over five 24 h cycles along with membrane physical cleaning after every cycle resulted in water recovery of 82-70% for HTI-TFC and HTI-CTA membranes and 65-52% for aquaporin-TFC membrane. The rejection of distillery wastewater components that contribute to the COD, melanoidins and antioxidants content was similar for all the three membranes. Fouling due to deposits on the membrane surface occurred for all membranes but the ease of cleaning was better for HTI-TFC followed by HTI-CTA and aquaporin-TFC membranes. Periodic physical cleaning by water flushing was adequate to remove surface deposits. Overall, HTI-TFC membrane was most suited for concentrating

37 distillery wastewater, but the effect of high reverse salt flux of this membrane needs
38 to be further investigated.

39

40 **Keywords:** Forward Osmosis (FO); Membrane properties; Distillery wastewater;
41 Water recovery; Membrane reuse

42

1. Introduction

In engineered forward osmosis (FO) process, a semi-permeable membrane separates the feed and draw solutions. Water from the lower osmotic pressure feed passes through the membrane to the higher osmotic pressure draw, leading to the concentration of the feed and dilution of the draw solutions. FO has been widely studied for desalination and has been extensively used for the treatment of complex wastewater streams such as landfill leachate [1, 2], oil and gas exploration wastewater [3-5], olive mill wastewater [6] and digested sludge centrate [7].

The sugarcane molasses based alcohol distillery is a key agro-industrial sector in India. There are presently over 350 units, with an average ethanol production between 30-60 kL/day [8]. The industry is highly water intensive with a water consumption of 9-21 L/L alcohol and wastewater generation of 7-15 L/L alcohol. The wastewater generated is classified as highly polluting, with chemical oxygen demand (COD) of 80-160 g/L, total dissolved solids (TDS) of ~50 g/L, dark brown color and the presence of complex organic compounds [9, 10]. The industry is facing stringent regulations from the Central Pollution Control Board (CPCB) that mandates zero liquid discharge (ZLD); in addition, maximum fresh water consumption of 15 L/L alcohol is permitted and the balance demand is to be met by effluent recycling [8]. To comply with these requirements, wastewater treatment by reverse osmosis (RO) and multiple effect evaporation (MEE) are in practice. Although these are established technologies, fouling in RO and scaling in MEE continue to be serious challenges. There is an interest in exploring FO as an alternate treatment for distillery wastewater, due to its low fouling propensity.

The most common commercial FO membranes investigated for various applications include thin film composite (TFC) and cellulose triacetate (CTA) membranes from Hydration Technology Innovations (HTI) and more recently, pre-commercial Aquaporin InsideTM membrane (aquaporin-TFC) from Aquaporin A/S [11]. The target is to achieve high permeability and high rejection along with low reverse solute flux. The HTI-TFC membranes have been reported to have superior water permeability and stability over a wider pH range as compared to the HTI-CTA membranes [12]. With the discovery of aquaporin proteins (also known as water channels) in living cells [13], membranes incorporating aquaporins have been

prepared. These second-generation biomimetic membranes promise low salt/water permeability ratio [14, 15].

The HTI-CTA, HTI-TFC and aquaporin-TFC membranes have been tested extensively for domestic and municipal wastewater treatment [16-18]. For usage in sewage treatment, different CTA flat sheet membranes have been compared [19] and HTI-CTA spiral wound module has been pilot tested for long-term operation with intermittent cleaning [20]. Performance of hybrid FO-membrane bioreactor (FOMBR) with HTI-TFC membrane for treating municipal wastewater has been studied [21]. HTI-TFC and aquaporin-TFC membranes have been compared for removal of trace organics such as atrazine, 2,6-dichlorobenzamide and desethyl-desisopropyl-atrazine [22]. HTI-TFC membranes have also been examined for applications such as phosphorous recovery [23, 24], removal of trace organics including pharmaceuticals [25-27] and sludge thickening and dewatering [28]. However, there are no reports comparing different FO membranes in the treatment of complex industrial wastewaters.

In an earlier study, we concentrated synthetic melanoidins (Maillard reaction product) and sugarcane molasses distillery wastewater using aquaporin-TFC membrane [29]. This work goes further to understand whether membrane properties affect the FO performance, including ease of cleaning, for this application. Specifically, two commercial membranes (HTI-TFC and HTI-CTA) and one test membrane (aquaporin-TFC) were characterized and their performance for dewatering distillery wastewater using magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) draw solution was evaluated.

2. Materials and methodology

2.1 Membranes and their characterization

TFC and CTA membranes were purchased from HTI, USA. Sample FO membranes (aquaporin-TFC) were gifted by Aquaporin A/S, Denmark. As per manufacturer's instructions, the membrane flat sheets were immersed in water for 30 min prior to use.

Both virgin and fouled FO membranes were characterized. Zeta potential was measured with a SurPASS electrokinetic analyser (Austria) using 1 mM KCl solution as the electrolyte and polypropylene as the reference membrane. Membrane samples

of 10 mm X 20 mm were fixed on the sample holders using double sided adhesive tape. The gap height in the cell was maintained at 100 μ m. When the electrolyte was passed using hydraulic pressure through the channel between the sample holders, the generated streaming potential (streaming current) was measured by the electrokinetic analyzer. Membrane surface morphology was analysed by scanning electron microscopy (SEM). Air-dried membrane samples were freeze fractured under liquid nitrogen and coated with Pd in an Ar atmosphere. These coated membranes were then mounted to view under a microscope (Zeiss-EVO/MA10, Germany). Using air-dried membrane samples, surface groups were identified using attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) (IR Affinity 1, FTIR spectrophotometer, Shimadzu). Membrane contact angle was measured using sessile drop technique using the instrument from Tech Inc Ltd. (Chennai, India).

2.2 Feed and draw solutions and their analysis

Molasses distillery wastewater was collected from an open lagoon in a sugar-distillery complex in Northern India (Simbhaoli Sugars Limited, Brajnathpur unit, Uttar Pradesh). The wastewater (pH 4.8, osmotic pressure 40 bar, viscosity 2.09 ± 0.03 cP, COD 120 g/L, melanoidins content 78 g/L, TDS 136 g/L) was used as obtained, without dilution. Osmotic pressure of feed and draw solutions were measured using Gonotec Osmomat 010 freezing point cryoscopic osmometer (Germany) in terms of osmolarity (osmol/kg). The osmolarity of the solution was converted to osmotic pressure using modified Morse equation [30]. Because of the inherently high osmotic pressure of the distillery wastewater, magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was used as the draw solution. Compared to commonly used NaCl draw solution, the osmotic pressure of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution at the same concentration is significantly higher (Figure S1 in supplementary sheet). Industrial grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ flakes purchased from Advance Chemical Sales Corporation, New Delhi, India were dissolved in deionized water to obtain different concentrations of the draw solution. Elemental analysis of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution (supplementary sheet Table S1) was performed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP - OES) (Perkin Elmer Optima 3300 RL Range: 165-782 nm). All other chemicals were of analytical grade and purchased from Sigma Aldrich, Bangalore, India.

Melanoidins content was obtained by measuring color intensity of the wastewater sample at 475 nm in UV-Visible spectrophotometer (Aquamate, India). The

absorbance obtained at 475 nm was converted to melanoidins content (g/L) by using standard plot. For antioxidant activity, decolorization of 2,2'-Azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS⁺) radical at 734 nm was measured for 2 min in the sample. This gives the Trolox equivalent antioxidant capacity (TEAC) in mM [31]. COD was measured using standard method for water and wastewater analysis as per APHA [32].

2.3 FO experimental set-up and membrane performance

The experimental set-up is as shown in our previous work [29]. A locally fabricated FO cell with symmetric flow channels and working area of 0.0043 m² was used. All experiments were performed in duplicate using fresh membranes, with active side facing the feed. Feed and draw solutions, both at a flow rate of 1 L/min, were circulated in counter-current direction. The container of feed solution (either deionized water or distillery wastewater) was placed on an analytical weighing balance (A&D Japan) connected to a computer and the change in weight was automatically captured by WinCT software. The draw solution container was placed on a magnetic stirrer and continuously stirred at 500 rpm to maintain its homogeneity.

The water flux (J_w) and reverse salt flux (J_s) of each FO membrane was studied over 3 h using deionized water (0.5 L) as feed and 1 M MgCl₂.6H₂O (2 L) as draw. The relatively large draw volume was used to maintain constant osmotic pressure for the duration of the FO experiment.

The water flux (J_w), reverse salt flux (J_s), water recovery (F_c) and rejection (r) was determined as follows:

$$J_w = \frac{\Delta V}{A \times \Delta t} \quad (1)$$

$$J_s = \frac{C_t V_t - C_o V_o}{A \times \Delta t} \quad (2)$$

$$F_c = \frac{\Delta V}{V_o} \times 100\% \quad (3)$$

$$r = \left(\frac{C_t V_t}{C_o V_o} \right) \times 100\% \quad (4)$$

Where J_w in L/m²h was calculated by measuring the change in weight of feed at 5 min intervals and converting into volume change i.e. ΔV (L) of feed, A (m²) is the effective membrane area and Δt (min) is the measuring time interval. J_w and F_c was calculated for each 5 min time interval and average value was reported.

Simultaneously, conductivity of deionized water as feed solution was recorded using a 1 mS/cm probe (Acma Technology, India). The conductivity value was converted into total dissolved solids (TDS) using a standard plot of 1-25 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Thus, J_s in $\text{g/m}^2\text{h}$ was calculated by substituting V_0 , V_t as volume of the feed solution in L at time = 0 and time = t in h respectively. C_0 , C_t are the salt / organic components concentrations of feed solution in g/L at time = 0 and time = t in h respectively. J_s and r was calculated based on bulk concentrations and volumes at the beginning and end of the FO run. Reverse salt flux relative to water flux was also calculated as ratio of J_s to J_w in g/L. This equation gives the loss of solute to feed side. Water recovery was calculated with distillery wastewater as feed.

The variation in water flux with varying draw solution concentration was evaluated by stepping up the draw concentration from 1 M (conductivity 76.1 mS/cm) to 4 M (conductivity 133 mS/cm) as per the procedure described by Zou and co-workers [33]. Experiments were first conducted with deionized water as the feed. The FO run lasted 60 min for each draw solution concentration, wherein the first 30 min was allowed for stabilization followed by flux measurement over the next 30 min. To avoid salt accumulation, the porous support side of the membrane was flushed with deionized water before proceeding to higher draw solution concentration. The flushing was done until the rinse water conductivity reached 0.055 mS/cm (same as fresh deionized water). Using the same membrane, the procedure (with draw solution concentration from 1 M to 4 M) was repeated with distillery wastewater as feed to measure the decline in water flux due to foulants present in the real wastewater.

Using fresh membrane of each type, long duration (24 h) FO was done with distillery wastewater feed and 3 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw. Water recovery and rejection of melanoidins, COD and antioxidant activity was analyzed at the conclusion of the experiment. Additionally, corresponding water flux for each type of membrane was measured. After 24 h FO with distillery wastewater, the membrane surface was rinsed with 20 mL deionized water to remove the deposited foulants. The suspension was analyzed for surface charge and particle size using Zetasizer (Nano-ZS, Malvern instruments, UK).

The hydraulic resistance of the fouling layer was calculated using the conventional resistance-in-series model adapted for FO [34]:

$$R_m = \frac{\Delta \Pi}{\mu J_w^o} \text{ and } R_t = \frac{\Delta \Pi}{\mu J_w'} \quad (4)$$

$$R_t = R_m + R_f \quad (5)$$

Where J_w^o and J_w' in L/m^2h are the water flux with feed of deionized water and distillery wastewater respectively, $\Delta \Pi$ in Pa is the osmotic pressure difference between the bulk draw and feed solutions, μ in Pa s is the viscosity of the permeate, R_m (m^{-1}) and R_f (m^{-1}) are the resistances due to membrane and fouling respectively and R_t (m^{-1}) is the total hydraulic resistance.

2.4 Long-duration FO with intermittent membrane cleaning

Cleaning of each of the three FO membranes was evaluated over 120 h operation divided into 5 cycles (C1-C5) of 24 h each. Between each cycle, 30 min physical cleaning on both sides of the membrane was done by circulating deionized water at the maximum possible flow rate of 1.8 L/min. Experiments were done in duplicate with fresh membrane for each 120 h run.

3. Results and discussions

3.1 Membrane performance with deionized water

The water flux and reverse salt flux with deionized water as feed and 1 M $MgCl_2 \cdot 6H_2O$ as draw is shown in Figure 1. The highest water flux obtained with the HTI-TFC membrane ($8.4 \pm 0.59 L/m^2h$) is nearly 1.5 times the water flux of the HTI-CTA ($4.81 \pm 0.06 L/m^2h$) and aquaporin-TFC ($5.81 \pm 0.03 L/m^2h$) membranes. The TFC membranes are relatively more hydrophilic with lower contact angle (33.2° for HTI-TFC and 42.6° for aquaporin-TFC) than CTA membrane (contact angle of 46.9°). Also, the thickness of the non-woven support in HTI-CTA membrane reportedly enhances internal concentration polarization (ICP) and reduces the flux [35]. However, the presence of aquaporins in the aquaporin-TFC membranes did not enhance the water flux as expected; this was attributed to prominent concentration polarization by the divalent draw solution [36]. The ratio of reverse salt flux to water flux (J_s/J_w) of the aquaporin-TFC membrane ($0.06 \pm 0.03 g/L$) was lower than of HTI-CTA ($0.2 \pm 0.01 g/L$) and HTI-TFC ($0.3 \pm 0.01 g/L$) membranes. This could be due to the selective nature of aquaporin proteins, which allow only water molecules to pass through [14]. A detailed water flux pattern and reverse salt flux of the three membranes is given in Figure S2 of the supplementary sheet.

Figure 1. Water flux and reverse salt flux of FO membranes with deionized water as feed.

3.2 Membrane performance with distillery wastewater

FO water flux was measured for the three membranes by increasing the draw solution concentration from 1 M to 4 M with deionized water feed followed by distillery wastewater feed. The flux profile at each step-up concentration of the draw solution is given in supplementary sheet (Figure S3, S4 and S5). For all the membranes, even at the lowest $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ concentration of 1 M, there was significant deviation in the flux between deionized water and distillery wastewater. This drop in flux from the deionized water baseline is attributed to high salinity (conductivity of 42.3 mS/cm) and viscosity (2.09 ± 0.03 cP) of the wastewater. At lower draw concentrations (up to 0.75 M), no permeate movement from feed to draw was observed.

Figure 2 summarizes the drop in water flux of distillery wastewater feed with the corresponding baseline flux of deionized water for all the three membranes. The drop in flux initially increases with increasing draw concentration but becomes constant thereafter (40-41% at 2 M and 3 M with HTI-TFC, 48-49% at 3 M and 4 M with HTI-CTA and 40% at 3 M and 4 M with aquaporin-TFC). Beyond a point, increasing the

draw solution concentration (to increase the driving force) does not enhance the flux due to internal and external concentration polarization [37]. This is seen with the HTI-TFC membrane at 4 M draw concentration. The critical draw solution concentration (a threshold concentration above which fouling in FO occurs) [33] for distillery wastewater is between 2 M-4 M as the corresponding average flux decline in all three membranes remained in the same range (35-51%). We also saw in our previous work with aquaporin-TFC membrane [29] that compared to 2 M and 4 M draw solutions, 3 M draw solution displayed stable flux throughout with higher water recovery and higher rejection of COD, melanoidins and antioxidant activity. Based on these results, 3 M draw concentration was chosen for further experiments with all the membranes.

Figure 2. Percentage reduction in water flux of FO membranes at different draw solution concentrations (1 M to 4 M); red bar shows water flux with distillery wastewater as feed, blue bar shows water flux with deionized water as feed.

Figure 3a shows the water flux and water recovery over 24 h for all the three membranes. In the first 8 h, the average water flux was 4.66 L/m²h, 3.2 L/m²h and 3.36 L/m²h for HTI-TFC, HTI-CTA and aquaporin-TFC respectively. After 16 h, average water flux reduced to 3.73 L/m²h, 2.7 L/m²h and 2.74 L/m²h respectively. With HTI-TFC, because the flux was relatively higher than with the other two membranes, the feed volume reduced to the point that no feed circulation was possible after 22 h operation and the experiment was terminated. At the conclusion of the experiments (Figure S6 in supplementary sheet), the average water flux was 2.8 L/m²h (HTI-TFC), 2.4 L/m²h (HTI-CTA) and 1.94 L/m²h (aquaporin-TFC). The

average water recovery was 81% (HTI-TFC), 71% (HTI-CTA) and 66% (aquaporin-TFC) but the average rejection of COD (82-88%), melanoidins (96-98%) and antioxidant activity (77-82%) was similar for all the three membranes (Figure 3b). Loosely bound deposits were visible on the surface of all the three membranes as discussed further in Section 3.3. The deposits modify the membrane surface characteristics and offer additional hydraulic resistance (as seen in deposits during submerged nanofiltration of molasses fermentation wastewater [38]), causing flux decline as well as restricting the movement of solutes to the draw side. Table 1 summarizes the bulk concentration of the distillery wastewater components that contribute to the COD, melanoidins and antioxidants content in the feed over 24 h FO, along with the final feed volumes for all the membranes.

Figure 3. HTI-TFC, HTI-CTA and aquaporin-TFC membranes (a) water flux and water recovery profile (b) rejection of COD, melanoidins and antioxidant activity in distillery wastewater feed with 3 M draw concentration after 24 h FO.

Table 1. Distillery wastewater characteristics before and after FO with different membranes (24 h operation with 3 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw).

FO membrane type	Initial Parameters*			Final Parameters		
	COD (g/L)	Melanoidins (g/L)	Antioxidant activity (mM)	COD (g/L)	Melanoidins (g/L)	Antioxidant activity (mM)
HTI-TFC	106±14	80±4	69±3	300±15	267±8	213±2
HTI-CTA				227±16	189±8	155±2
aquaporin-TFC				155±15	141±6	102±7

*The feed for FO experiments was taken from the same lot of distillery wastewater and the average is shown. In all experiments, starting feed volume was 0.5 L that reduced to 0.15 L (HTI-TFC), 0.20 L (HTI-CTA) and 0.28 L (aquaporin-TFC) after 24 h. The final volumes include the system hold-up of approx. 50 mL. All analysis was done in triplicate.

The effect of physical cleaning of the fouled membranes with water flushing at higher flow rate was studied. The experiment was performed over 120 h over 5 cycles (C1-C5) of 24 h each with cleaning between cycles. As shown in Figure 4a, all the fresh membranes (C1) showed a steady drop in flux to 1 $\text{L/m}^2\text{h}$ even though the starting flux for HTI-TFC (6 $\text{L/m}^2\text{h}$) was higher than for HTI-CTA and aquaporin-TFC (4.8 $\text{L/m}^2\text{h}$) membranes. Between the first cleaning (C2) and fourth cleaning (C5), the average water flux was 4.2 $\text{L/m}^2\text{h}$ (HTI-TFC), 4 $\text{L/m}^2\text{h}$ (HTI-CTA) and 2.8 $\text{L/m}^2\text{h}$ (aquaporin-TFC). Water recovery for HTI-TFC and HTI-CTA membranes

remained in the range of 70-82% but aquaporin-TFC showed a drop from 65% (C1, C2) to 52% (C3-C5). The average total resistance R_t for all the three membranes after 120 h is shown in Figure 4b. HTI-CTA and aquaporin-TFC membranes have an inherent higher membrane resistance (R_m) of $1.3 \times 10^{16} \text{ m}^{-1}$ compared to HTI-TFC ($0.7 \times 10^{16} \text{ m}^{-1}$). Resistance due to fouling (R_f) was as follows: aquaporin-TFC ($0.81 \times 10^{16} \text{ m}^{-1}$) > HTI-TFC ($0.65 \times 10^{16} \text{ m}^{-1}$) > HTI-CTA ($0.23 \times 10^{16} \text{ m}^{-1}$). The cleaning strategy of water rinsing at higher flow rates between cycles is effective in restoring the water flux for HTI-TFC and HTI-CTA membranes. The flux drop for all membranes is due to fouling because of surface deposits (as discussed in Section 3.3) as well as the increased osmotic pressure of concentrated feed (approximately 70 bar). In this work, both HTI-TFC and HTI-CTA membranes showed surface deposits that were easily removed by water rinsing. Dilutive ICP is also expected to play a role in flux decline because of higher reverse salt flux [39] especially for the HTI-TFC ($0.3 \pm 0.01 \text{ g/L}$) and HTI-CTA ($0.2 \pm 0.01 \text{ g/L}$) membranes.

Figure 4. HTI-TFC, HTI-CTA and aquaporin-TFC membranes (a) Performance with intermittent physical cleaning (b) Resistance to filtration (with 3 M draw concentration after 120 h).

3.3 Membrane interaction with foulants

Distillery wastewater is characterized by the presence of humic acid, biopolymers such as proteins and carbohydrates along with moieties of Maillard reaction product melanoidins and polyphenols in varied sizes. These molecules have a tendency to form a gel-like layer on the membrane surface [40] which was also observed visually in this study. The deposits on the membrane surface were loosely bound and easily dislodged by soaking the membrane in water. Because of the higher initial flux and corresponding higher water recovery, the deposition was more prominent in HTI-TFC membrane than in the other two membranes. The suspension deposited on the HTI-TFC membrane after 24 h FO experiment was collected and analyzed. The average particle size of the deposits was seen to be 1457 ± 215 nm (Figure S7 in supplementary sheet) and they possess a negative zeta potential of -2.49 mV at pH 4.4.

The surface characteristics of the membrane materials were studied to further understand the interaction of the distillery wastewater components with the membrane material. Surface potential measurement indicated the isoelectric points of the three virgin membranes to be pH 4.2 (HTI-TFC), pH 3.4 (HTI-CTA) and pH 2.9 (aquaporin-TFC) showing increasing acidity of the material. The zeta potential at pH 7 for HTI-TFC lies at -25 mV, for HTI-CTA at -40 mV and for aquaporin-TFC

membrane at -77 mV (Figure 5a). When compared to the corresponding virgin membrane, the fouled membrane shows decreasing negative potential with increasing pH. Fouling with distillery wastewater (pH 4.6) causes the isoelectric point of all the three membranes to shift towards acidic pH viz. pH 3.5 from pH 4.2 (HTI-TFC), pH 3.0 from pH 3.4 (HTI-CTA) and pH 2.7 from pH 2.9 (aquaporin-TFC). The corresponding zeta potential at pH 7 increased from -28 mV to -32 mV for HTI-TFC, from -40 mV to -53 mV for HTI-CTA and from -78 mV to -80 mV for aquaporin-TFC membrane. The net negative charge on the membrane surface (that is maximum in aquaporin-TFC membrane) results in electrostatic repulsion of the anions present in the wastewater. However, as discussed in Section 3.2, solute rejection in this work is similar for all the three membranes, possibly because interaction between foulants and the membrane surface is not a dominant factor affecting solute rejection and corresponding fouling behavior [37].

The ATR-FTIR spectrum of the three membranes (Figure 5b) shows the presence of different functional groups on the active layer. The characteristic peak of polyamide is observed in HTI-TFC virgin membrane at 1610 cm^{-1} due to aromatic ring, which gets masked in the corresponding fouled membrane. A new peak is observed at 2324 cm^{-1} due to the nitrile ($\text{C}\equiv\text{N}$) group of aromatic compounds present in distillery wastewater. In the fouled HTI-CTA membrane, the aromatic peak at 1610 cm^{-1} gets masked and a new peak noticed around 1499 cm^{-1} due to the stretching of the $\text{C}=\text{C}$ group of aromatic compounds. In aquaporin-TFC membranes, no distinct change in the spectra was noticed which corroborates with the marginal change in zeta potential after FO. Figures 5c-h shows SEM micrographs of the three membranes before and after FO of distillery wastewater. The presence of foulants on the membrane surface is clearly visible for all the membranes. The pitted surface on the aquaporin-TFC membrane indicates the presence of aquaporin; at many places the pores are overlaid by the foulants resulting in a smooth surface.

Figure 5. FO membranes HTI-TFC, HTI-CTA and aquaporin-TFC in virgin and fouled state (a) zeta potential (b) FTIR-ATR; SEM images of virgin membranes (c) HTI-TFC (d) HTI-CTA (e) aquaporin-TFC membrane; SEM images of fouled membranes after 120 h operation (f) HTI-TFC (g) HTI-CTA (h) aquaporin-TFC.

3.4 Membrane selection for distillery wastewater

The three FO membranes tested in this study possess different characteristics. The HTI-TFC membrane with the 3 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw appears to be most suited for treating distillery wastewater overall (Table 2), with higher isoelectric point, less negative zeta potential and low contact angle. The HTI-TFC membrane provides high water flux and recovery and high rejection of organics; additionally the foulants deposited on the membrane surface are easy to dislodge. The drawback is the high reverse salt flux that causes ICP and contributes to flux decline. In this context, aquaporin-TFC membrane may still be a suitable choice due to its low reverse salt flux even though the water flux is lower and the fouled membrane is not easily cleaned with water rinsing alone. A clear trend is observed in this work; however, literature reports [37, 41] suggest there is minimal correlation between membrane properties and foulants properties, and the performance is also influenced by the nature and concentration of the draw solution used. This aspect needs to be investigated further for this application.

In this application, freshwater could be obtained from the diluted draw solution using reverse osmosis (RO) and nanofiltration (NF) [42]. Compared to state-of-the art

technologies such as MEE and RO being used for distillery wastewater treatment, FO offers several advantages. Multi stage membrane filtration costs less than evaporation as observed in concentrating corn-based stillage [40]. FO results in higher water recovery and retention of organic solutes than RO [43]. Membrane fouling coupled with investment and operational cost for high pressure pump in RO of industrial wastewater reduces the process efficacy and increases the treatment cost [44]. FO followed by RO is reported to be economical and efficient to reduce both operational and capital expenditure of seawater desalination [44]. Thus distillery wastewater concentration by FO followed by freshwater recovery from the diluted $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw solution by NF/RO merits further investigation.

Table 2. Comparison of tested FO membranes for distillery wastewater concentration with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw solution (rated 1-3 among the three membranes tested, with the best for a parameter rated 1).

Parameters	HTI-TFC	HTI-CTA	aquaporin-TFC
Deionized water flux	1	3	2
Reverse salt flux	3	2	1
Water recovery from distillery wastewater	1	2	3
Rejection of COD, melanoidins, antioxidant activity from distillery wastewater	1	1	1
Ease of cleaning by water rinsing after distillery wastewater FO	1	1	3

4. Conclusions

- Among the three FO membranes tested for distillery wastewater feed using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as draw, the water flux of HTI-TFC is superior compared to HTI-CTA and aquaporin-TFC membranes. However, the high reverse salt flux of HTI-TFC membrane could be a limitation in long-term operation and needs to be investigated further. Here the low reverse salt flux in the aquaporin-TFC membrane may provide an alternative despite the somewhat lower water flux compared to the HTI-TFC membrane.

- Irrespective of the draw concentration used, water flux with distillery wastewater deviates substantially from the baseline flux with deionized water. So operation at higher draw solution concentration where flux is stable is recommended.
- Though fouling due to deposits on the membrane surface occurs during FO of distillery wastewater, the ease of cleaning depends on the total resistance offered by the membrane during FO process. The resistance offered by the membrane is directly proportional to the recovery of initial flux. Periodic physical cleaning by water flushing is adequate to remove the surface deposits.

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642 **Supplementary sheet**

643 The osmolarity (osmol/kg) of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions (0.5 M, 1 M, 2 M, 3
644 M, 4 M) was determined using Gonotec Osmomat 010 freezing point cryoscopic
645 osmometer (Germany).

646

647 **Figure S1.**Osmotic pressure at different concentrations of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

648

649 **Table S1.** Elemental analysis of industrial grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ used for preparing
 650 draw solution

Constituent	Concentration (mg/L)
Magnesium	73410
Calcium	406
Potassium	3636
Boron	92
Iron	1.57
Sodium	3023
Phosphorus	2.17
Lead	0.27
Chlorides	297567
Phosphate	<0.04
Nitrate	32
Sulphate	3450
Zinc	BDL
Copper	BDL

651 BDL: Below detection limit

652

Figure S2. Time profile of three FO membranes with deionized water feed and 1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ draw solution (a) water flux (b) reverse salt flux.

Figure S3. Water flux of HTI-TFC membrane for varying draw solution concentration with deionized water and distillery wastewater feeds.

Figure S4. Water flux of HTI-CTA membrane for varying draw solution concentration with deionized water and distillery wastewater feeds.

Figure S5. Water flux of aquaporin-TFC membrane for varying draw solution concentration with deionized water and distillery wastewater feeds.

Figure S6. Average water flux and water recovery after 24 h FO with distillery wastewater feed and 3 M draw solution.

Figure S7. Particle size distribution of deposits on HTI-TFC membrane surface after distillery wastewater FO.