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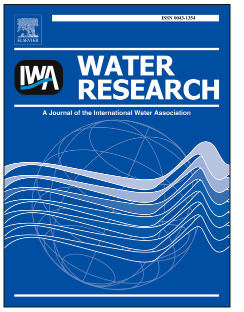

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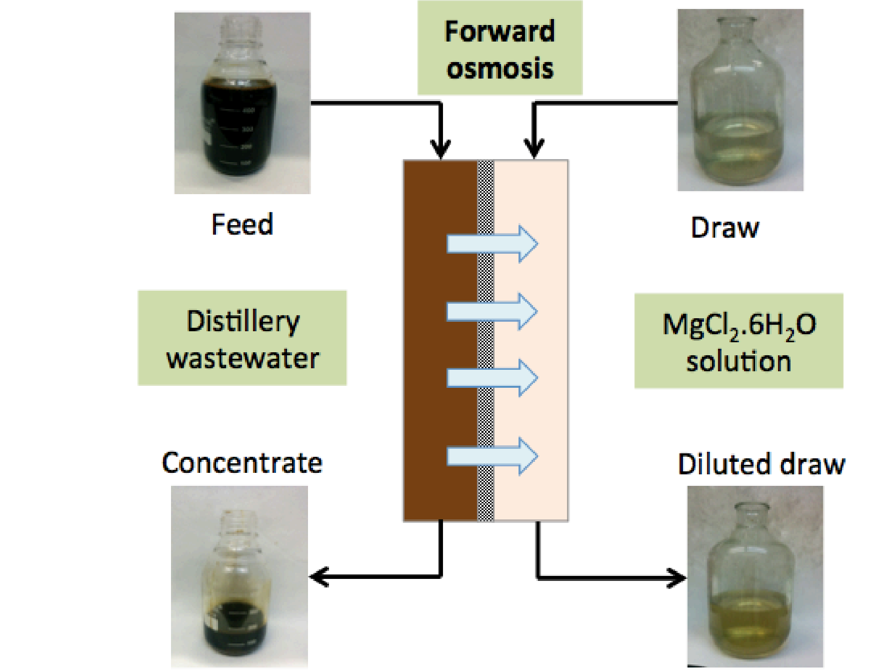
Graphical Abstract



Average water flux (24h) (L/m²h)	Rejection (%)			Water recovery (%)
	COD	Melanoidins	Antioxidant activity	
2.66	85.4	97.3	95	65

3M draw solution concentration; 1L/min flow rate

Concentrating molasses distillery wastewater using biomimetic forward osmosis (FO) membranes

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ABSTRACT

Treatment of sugarcane molasses distillery wastewater is challenging due to the presence of complex phenolic compounds (melanoidins and polyphenols) having antioxidant properties. Due to zero liquid discharge regulations, Indian distilleries continue to explore effective treatment options. This work examines the concentration of distillery wastewater by forward osmosis (FO) using aquaporin biomimetic membranes and magnesium chloride hexahydrate ($MgCl_2.6H_2O$) as draw solution. The operational parameters viz. feed solution and draw solution flow rate and draw solution concentration were optimized using 10% v/v melanoidins model feed

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solution. This was followed by trials with distillery wastewater. Under the conditions of this work, feed and draw flow rates of 1 L/min and draw solution concentration of 2M $MgCl_2.6H_2O$ for melanoidins model solution and 3M $MgCl_2.6H_2O$ for distillery wastewater were optimal for maximum rejection. Rejection of 90% melanoidins, 96% antioxidant activity and 84% COD was obtained with melanoidins model feed, with a corresponding water flux of 6.3 L/m^{2}h. With as-received distillery wastewater, the rejection was similar (85-90%) to the melanoidins solution, but the water flux was lower (2.8 L/m^{2}h). Water recovery from distillery wastewater over 24h study period was higher with FO (70%) than reported for RO (35-45%). Repeated use of the FO membrane over five consecutive 24h cycles with fresh feed and draw solutions and periodic cleaning showed consistent average water flux and rejection of the feed constituents.

Keywords: Forward Osmosis (FO); Biomimetic aquaporin membranes; Molasses distillery wastewater; Melanoidins; Antioxidant activity.

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1. Introduction

Sugarcane molasses based alcohol distilleries in India are one of the most water intensive and polluting industrial sectors with a fresh water consumption of about 9-21 L/L alcohol and wastewater generation of 7-15 L/L alcohol (GoI, 2014). The wastewater has a very high organic load, low pH, high total dissolved solids, unpleasant odor and dark brown color. A major cause of color is melanoidins, a product of Maillard reaction between reducing sugars and amino acids, which constitutes 2% (w/v) of the wastewater (Arimi et al., 2014; Yadav and Chandra, 2012). Melanoidins are characterized by complex structure, possess antioxidant properties and are not readily biodegradable. The presence of these compounds deters biological treatment and color removal in distillery wastewater poses a major challenge. On the other hand, its antioxidant properties can be exploited in applications like food preservation and personal care products. Considering the stringent regulations imposed by the Central Pollution Control Board (CPCB) on fresh water consumption (maximum of 15 L/L of alcohol production) and zero liquid discharge (ZLD) from distilleries, alternatives to existing treatment options like anaerobic digestion, incineration and reverse osmosis continue to be of interest. As fresh water is required for various non-process applications like steam generation, cooling tower make-up water, washing of fermenters, distillation units, floors etc., appropriately treated wastewater offers potential for reuse. Furthermore, antioxidant components in distillery wastewater could be an additional value added resource that could be recovered.

Forward osmosis (FO) is a membrane based separation process operating on osmotic pressure difference between the low osmotic pressure feed solution and the high osmotic pressure draw solution separated by a semi-permeable membrane. In combination with other membrane separation processes like reverse osmosis, membrane distillation and microfiltration, FO has been used for treatment of various complex wastewaters to either enrich the feed in trace components by reducing the feed volume or to reclaim the wastewater for direct potable reuse. Examples of such applications include (i) selective removal of pharmaceutical micropollutants (carbamazepine, diclofenac, ibuprofen and naproxen) from synthetic feed (Madsen et al., 2015; D'Haese et al., 2013; Jin et al., 2012; Xie et al., 2012; Hancock et al., 2011; Linares et al., 2011); (ii) dewatering drilling wastewater from oil and gas exploration (Hickenbottom et al., 2013); (iii) treatment of domestic wastewater in osmotic membrane reactor (OMBR) (Zhang et al., 2014; Alturki et al., 2012; Zhang et al., 2012a; 2012b; Cornelissen et al., 2010; Achilli et al., 2009); (iv) treatment of municipal wastewater (Hey et al., 2017; Hey et al., 2016a; 2016b); (v) nutrient recovery from domestic wastewater (Devia et al., 2015); (vi) upgrading rain water to replace fresh water for cooling water make-up in steam plant (Wang et al., 2014).

In most of the above-listed applications, cellulose triacetate (CTA) and thin film composite (TFC) commercial FO membranes were used. CTA membrane was compared with newly developed biomimetic aquaporin membrane for rejection of three trace organics. Partial rejection was reported with CTA membrane whereas over 97% rejection was obtained with aquaporin membrane (Madsen et al., 2015). CTA and TFC membranes were also tested along with aquaporin membranes for municipal wastewater treatment (Hey et al., 2016a; 2016b). Biomimetic FO membranes have been largely studied for desalination (Grzelakowski et al., 2015, Tang et al., 2013) where high water flux (~ 20 L/m^2h) and high salt rejection (~ 97%) have been obtained at 5 bar (Zhao et al., 2012).

This work investigates the applicability of FO for dewatering sugarcane molasses distillery wastewater while concentrating the color imparting constituents. Initial experiments to optimize the FO operational conditions (flow rate of draw solution and feed solution, draw solution concentration and operation time) were done using melanoidins model solution. This was followed by trials with distillery wastewater. Biomimetic aquaporin based FO membranes were used and the FO performance (water flux, reverse salt flux, rejection) over time was evaluated.

2. Materials and method

2.1 Materials

Thin film composite (TFC) FO membranes with aquaporin proteins embedded into the polyamide layer were gifted by Aquaporin A/S, Denmark. These Aquaporin Inside^{TM} membranes (Table S1 in supplementary data sheet) were characterized by high water and low reverse salt flux and are stable between pH 2-11 (Perry et al., 2015). Industrial grade magnesium chloride hexahydrate ($MgCl_2.6H_2O$) purchased from Advance Chemical Sales Corporation, New Delhi was used for preparing the draw solutions. All the other chemicals were of analytical grade and used as obtained. Deionized water of conductivity 0.005 μS/cm was used for baseline experiments to evaluate water flux and reverse salt flux. Synthetic melanoidins was prepared in the laboratory using equimolar glucose and glycine solutions autoclaved at 120°C for 15 minutes (Dahiya et al., 2001). The pH of the solution was adjusted to 7. Synthetic melanoidins (10% v/v) prepared in deionized water was used as model feed solution to optimize the operational parameters. Molasses distillery wastewater was collected from sugar-distillery complex in Northern India (Simbhaoli Sugars Limited, Brajnathpur unit, Uttar Pradesh). The wastewater was stored at 4°C and was used without dilution.

2.2 Experimental procedure

Figure 1 shows the schematic representation of the experimental set-up. The FO test cell was locally fabricated with symmetric flow channels and active membrane area of 0.0043 m^2. Membranes were soaked in deionized water for about 30 minutes before placing in the FO cell between two stainless steel meshes. The membrane active side faced the feed solution. Kemflo booster pumps (Electrotech Industries, India) with maximum flow rate of 1.8 L/min were used to circulate feed solution and draw solution on either side of the membrane. Flow rate was controlled by adjusting the valve settings and was measured using in-line flow meter on feed side and draw side. The feed solution container was placed on an analytical balance (A&D, Japan) connected to a computer to record the weight change every 5 minutes. Conductivity of the feed solution for deionized water was measured continuously using conductivity meter (Acmas Technology, India) with a 1 mS/cm probe. Draw solution stored in a large tank was placed on a magnetic stirrer (IKA, India) and constantly stirred at 500 rpm. All the experiments were done in duplicate using fresh membranes.

Figure 1. Schematic representation of FO experimental set-up.

The water flux (J_w) in L/m^2h and reverse salt flux (J_s) in g/m^2h for deionized water feed was calculated by Eq. (1) and (2) respectively,

$$J_w = \frac{\Delta V}{A \text{ X } \Delta t} \tag{1}$$

$$J_s = \frac{(V_t\, C_t - V_0\, C_0)}{A \text{ X } \Delta t} \tag{2}$$

where, ΔV is the volume change of feed solution, A is the effective membrane area, Δt is the measuring time interval (5 min), V_0, V_t are volume of the feed solution at time = 0 and time = t respectively, C_0, C_t are the salt concentrations of draw solution at time t = 0 and time = t respectively. The salt concentration was determined from the standard curve between total dissolved solids (TDS) (mg/L) and conductivity (μS/cm). The TDS of $MgCl_2.6H_2O$ for preparing the standard curve was determined by gravimetric method and conductivity was measured by conductivity meter.

Water flux and reverse salt flux of virgin membranes were measured initially with deionized water feed and 1M and 3M $MgCl_2.6H_2O$ draw solutions. The effect of operational parameters on water flux and rejection was studied using 10% melanoidins model feed solution. Depending upon the experiment duration, feed volume varied from 0.25 L to 1 L and the corresponding draw solution from 1 L to 4 L. 0.25 L melanoidins model feed was taken against 1 L of 2M $MgCl_2.6H_2O$ and 3h experiments were conducted to optimize draw solution concentration (1M, 2M and 3M at fixed flow rate of 1 L/min) and flow rate (0.8 L/min, 1 L/min and 1.5 L/min at fixed draw solution concentration of 2M). The flow rates of feed solution and draw solution were maintained same throughout the experiment to create similar turbulence on both sides of the membrane. Effect of time (4h to 24h) was also studied under optimized flow rate and draw solution concentration. Subsequently, melanoidins model feed was replaced by distillery wastewater and experiments were carried out at fixed flow rate (1 L/min). Since the osmotic pressure of distillery wastewater was higher than that of 10% melanoidins solution, the draw solution concentration was increased up to 4M.

Stability of the FO membranes for distillery wastewater concentration was studied at fixed flow rate and draw solution concentration over five 24h cycles (C1-C5). Fresh wastewater and draw solution was used for each cycle. Before each new cycle, feed and draw solution in the module and pipeline was replaced by deionized water to wash out any residual feed solution or draw solution from the previous cycle. For physical cleaning, the membrane was cleaned by circulating 0.5 L deionized water on both sides of the membrane at 1.8 L/min for 30 minutes before the next FO cycle. Chemical cleaning was done by circulating 0.5 L of 0.5N NaOH solution for 30 minutes at 1.8 L/min on both sides of the membrane, followed by flushing with deionized water.

2.3 Analytical methods

Feed solution, before and after FO, was analyzed for melanoidins, COD and antioxidant activity. COD was measured using standard method of water and wastewater analysis by APHA. Melanoidins content was determined by absorbance at 475nm in a UV-Vis spectrophotometer (Aquamate, India) (Dahiya et al., 2001). Trolox equivalent antioxidant capacity (TEAC), determined by the capacity to decolorize $ABTS^{+}$ radical solution in 2 minutes (Rufián-Henares and Morales, 2007), was used as a measure of antioxidant activity. Rejection (r) of melanoidins, COD and antioxidants was determined using Eq. 3 and water recovery (f_c) was calculated by Eq. 4,

$$r = \frac{X_t V_t}{X_0 V_0} \times 100\% \quad (3)$$

$$f_c = \frac{\Delta V}{V_0} \times 100\% \quad (4)$$

where X_t and X_0 are the melanoidins concentration (g/L), COD concentration (g/L), or antioxidant activity (mM) as per analysis, V_0 and V_t are volume of the feed solution at filtration time t = 0 and t = t respectively.

The osmomolarity (Osmol/kg) of the solutions was determined using Gonotec Osmomat 010 freezing point cryoscopic osmometer (Germany) and the value was converted to osmotic pressure using modified Morse equation (Wilson and Stewart, 2013). The morphology of the membranes was studied by scanning electron microscopy (SEM) using a Zeiss-EVO/MA10 instrument (Zeiss, Germany). The membrane samples were air dried and freeze fractured under liquid nitrogen. The samples were coated with Pd in an Ar atmosphere before examination. Membrane zeta potential was measured using 1mM KCl solution with polypropylene membrane as reference (SurPASS electrokinetic analyser, Anton-Paar, Graz, Austria).

3. Results and discussions

3.1 Membrane and feed solution characteristics

The water flux (Figure S1 in supplementary data sheet) of the membrane with 1M draw solution was 6 L/m^{2}h and the corresponding reverse salt flux relative to the water flux (J_s/J_w) was 0.06 g/L. At a higher draw solution concentration of 3M, both the water flux and reverse salt flux increased to 8 L/m^{2}h and 0.6 g/L respectively. The membrane morphology and zeta potential are shown in Figure 2(a) and (b) respectively. The SEM image of active layer shows the presence of embedded aquaporin proteins on a polyamide layer. The protein vesicles appear evenly distributed on the surface. The pitted surface is likely due to the loss of aquaporin protein vesicles during freeze fracturing of the membranes for SEM analysis. The isoelectric point of the virgin membrane lies approximately at 2.9 pH. At neutral pH of 7, the decreasing negative potential becomes constant between -80mV and -90mV. This is consistent with the membrane surface having both acidic and basic functional groups.

Figure 2. Virgin biomimetic membrane: (a) SEM image of the top surface, and (b) zeta potential measurement.

The average characteristics of the two feed solutions used in this study are presented in Table 1. As-is synthetic melanoidins prepared by heating glucose and glycine does not have any free water molecules; it also has high osmotic pressure (around 55 bar). Thus, the melanoidins preparation was diluted to 10% so that the absorbance at 475nm of model feed solution was similar to that of real distillery wastewater. The pH of the model feed solution (pH 7.3) and distillery wastewater (pH 4.3) was different but pH adjustment of distillery wastewater leads to precipitation of melanoidins molecules. The antioxidant activity, conductivity and COD were higher for distillery wastewater as in addition to melanoidins, it contains other constituents like polyphenols and salts.

Table 1. Characteristics of FO feed solutions

3.2 Concentration of melanoidins model feed solution

Figure 3 shows the effect of varying flow rate and draw solution concentration on water flux, rejection of COD, melanoidins and antioxidant activity. The flux profiles with time are presented as supplementary data (Figure S2a and Figure S2b).

At a fixed draw solution concentration of 2M, the average water flux for all the three flow rates remained in the range of 6-7 L/m^2h (Figure 3a). The rejection obtained was 61-85% (COD), 80-90% (melanoidins) and 78-98% (antioxidant activity). COD rejection decreases visibly at higher flow rate. As per the analytical methods used, COD measured the concentration of all organics, melanoidins measured the colored compounds and the antioxidant activity measured the compounds with radical scavenging capacity. Melanoidins consist of a range of small to large polymeric molecules (Wang et al., 2011; Le et al., 1998; Yaylayan and Kaminsky, 1998). The synthetic melanoidins prepared in this work are therefore composed of polymers with broad range of molecular weight between 5-40 kDa (Cämmerer et al., 2002) along with some unreacted sugars and amino acids. Further, melanoidins contain a pure melanoidins core (typically large in size) with bound melanoidins polymers of smaller size; the latter have higher color and higher antioxidant activity than the counterpart pure melanoidins core (Rufian-Henares and Morales, 2007).

The increase in flow rate from 0.8 L/min to 1.5 L/min of feed solution and draw solution creates turbulence on the membrane active side and support side respectively. This turbulence decreases the concentrative internal concentration polarization on the feed solution side, while the increase in the flow rate on the draw solution side aggravates the dilutive external concentration polarization; this eventually increases the mass transfer (Hawari et al., 2016). As the synthetic melanoidins feed solution contains low molecular weight compounds (unreacted sugars, amino acids, small colored compounds etc.) that contributes to the COD, movement of these small molecules to the draw solution side across the membrane on increasing the flow rate to 1.5 L/min lowers the COD rejection. The higher molecular weight melanoidins (including the bound melanoidins polymers) are largely retained by the membrane thus showing high rejection of antioxidant activity and melanoidins content. The fact that some small colored compounds pass through the membrane is confirmed by increase in the absorbance of the post-FO draw solution. Of the three flow rates, 1 L/min was the best in terms of higher rejection; the water flux was also most stable throughout the 3h study period.

Figure 3. Water flux, rejection of COD, melanoidins and antioxidant activity at (a) varying flow rate **(**2M draw solution, 3h operation time), and (b) varying draw solution concentration (1 L/min flow rate, 3h operation time).

At a fixed flow rate of 1 L/min, draw solution concentration was varied between 1M and 3M (Figure 3b). Increasing the draw solution concentration enhances the water flux as higher solute concentration corresponds to higher osmotic pressure, raising the osmotic gradient across the membrane. The maximum average water flux was 7.6 L/m^{2}h with 3M draw solution. At 2M and 3M draw solution concentration, rejection of melanoidins (86-90%) and antioxidant activity (96-98%) was similar but COD rejection decreased from 84% (2M) to 57% (3M). This may be attributed to increased concentration polarization across the membrane at higher water flux (7.6

L/m^{2}h at 3M compared to 6.3 L/m^{2}h at 2M), confirming that there is a limit to increasing draw solution concentration to improve FO performance (Klaysom et al., 2013). Increase in the concentration gradient across the membrane at higher draw solution concentration of 2M and 3M has no influence on the antioxidant activity and melanoidins rejection. This indicates that the radical scavenging components in the feed solution (melanoidins core with bound compounds) get concentrated and the FO membrane restricts the passage of high molecular weight melanoidins compounds. The decrease in COD rejection is once again attributed to the migration of the unreacted low molecular weight sugars, amino acids etc. present in the feed solution.

Based on these results, flow rate of 1 L/min and draw solution concentration of 2M was chosen. Figure 4a shows the FO performance over a 24h period. The water flux declined marginally from 5.92 L/m^2 h (4h) to 5.15 L/m^2 h (24h). The water flux variation with time is presented in Figure S3 of the supplementary data. Rejection of COD, melanoidins and antioxidant activity increased initially but a drop was observed at 16h before the values for all the parameters stabilized between 85-98% at 24h. It was anticipated that increasing duration of FO would steadily increase the rejection. The observed fall at 16h could be due to deposition of melanoidins on the active side of the membrane surface, which would have reduced its content in the feed solution that was analyzed for calculating the rejection. The deposits were subsequently re-suspended in the feed due to the scouring action of the feed flow so an increase in rejection is seen after 24h of operation. The membrane surface after 24h FO shows a thin, non-uniform layer of melanoidins deposition. This deposition was only on the surface and the material was readily re-suspended when the used membrane was stored in water. The SEM image of the used membrane top surface at a high magnification of 10000X (Figure 4c) shows no visible foulants.

Figure 4. (a) Water flux as a function of time and average rejection of COD, melanoidins and antioxidant activity over 24h, and (b) photo of membrane active side after 24h operation (c) SEM image of the top surface of used membrane (24h operation).

3.3 Concentration of distillery wastewater

As osmotic pressure of distillery wastewater (40 bar) is substantially higher than 10% melanoidins (5 bar), higher draw solution concentration would be required for effective dewatering. Figure 5a shows the water flux and rejection results at varying draw solution concentrations for 4h duration. Since distillery wastewater has low pH (4.7) it was adjusted to pH 7 to replicate the melanoidins model feed. There were fluctuations in the water flux over time and the average value was marginally lower (2.5 L/m^2h) compared to that of as-received wastewater (2.8 L/m^2h) (Figure S4 of supplementary data sheet). Due to pH adjustment, feed COD dropped to 73 g/L, from 120 g/L for as-received wastewater. The reason for this change could be precipitation of melanoidins at higher pH. Also, increase in conductivity (45 mS/cm) and intensity of color (absorbance measured at 475 nm) were observed. Further experiments were therefore continued with as-received wastewater without pH adjustment. Increasing the draw solution concentration from 2M to 4M enhanced the water flux while the rejection of COD (82-90%), melanoidins (87-92%) and antioxidant activity (84-92%) remained similar.

Water flux and water recovery from distillery wastewater over a 24h period is shown in Figure 5b and the corresponding rejection results are summarized in Table

2. The initial water flux for draw solution concentrations of 3M and 4M was around 4 L/m^{2}h, but it reduced to 2.66 L/m^{2}h (3M) and 2.54 L/m^{2}h (4M) over 24h study period. The water recovery after 24h was marginally higher at 3M (65%) than at 4M (58%). The experiment with 3M draw solution gave better water flux and recovery compared to the experiment at 4M. This could be due to the higher fouling with the 4M draw solution compared to the 3M draw solution, because the 4M draw solution gave higher flux in the beginning (at least 4h, as proved in Fig 5a) and then decreased with time. The critical water flux (Zou et al., 2013) for distillery wastewater as feed is well below 4 L/m^{2}h (Figure S5 in supplementary sheet) and the "critical draw solution concentration" (the threshold draw solution concentration above which severe fouling occurs) is also below 3M. The long-term study indicates the fouling susceptibility of the membrane.

Table 2 shows that the melanoidins and antioxidant activity rejection remained constant but COD rejection at 3M reduced marginally from 90% (4h) to 85.2% (24h). The slight decrease in COD rejection was due to migration of small color causing compounds across the membrane with increasing concentration polarization. This was supported by the observation that the draw solution became lightly colored, with increase in absorbance at 475nm, at the end of the 24h run.

A mass balance was done for the 24h FO with distillery wastewater using 3M draw solution. The mass balance shows that from the initial COD (64.2 g), melanoidins (40.2 g) and antioxidant activity (36.5 g) present in the feed, the concentrate retained 54.7 g COD, 39.09 g melanoidins and 34.4 g antioxidant activity. The balance was in the permeate or deposited on the membrane. The calculated mass of melanoidins in the permeate was 1.075 g while the experimentally determined value was 0.5 g indicating around 0.575 g is deposited on the membrane (Figure 5c).

Figure 5. Distillery wastewater dewatering (a) over 4h by varying draw solution concentration (2M-4M): water flux and rejection of COD, melanoidins and antioxidant activity (b) over 24h at 3M and 4M draw solution concentration: water flux and water recovery, and (c) mass balance of melanoidins over 24h FO with 3M draw solution.

Table 2. Characteristics of distillery wastewater concentrate after 24h operation.

The FO performance with the synthetic melanoidins (Figure 3b) and real distillery wastewater (Figure 5a) with increasing draw solution concentration is different. As summarized in Table 1, there is considerable difference in the properties of the two feed solutions both in terms of physical properties (viscosity and osmotic pressure) as well as composition (e.g. the COD of the real wastewater is nearly 6 times higher than that of the synthetic melanoidins feed solution). Due to the high COD in the real wastewater, the external concentration polarization and fouling is higher and could be a cause for improved rejection. Membrane fouling is observed and regular physical/chemical cleaning is required to restore the water flux (as shown below in Figure 6a).

Stability of the FO membrane for concentration of as-received distillery wastewater was studied using 3M draw solution and flow rate of 1 L/min over five consecutive 24h cycles (C1-C5). As shown in Figure 6a, there was a steady drop in the water flux from 4 L/m^2h to 2 L/m^2h after 12h filtration and further decrease to 1 L/m^2h after 24h. This decreasing trend was found to be similar in all the five cycles. Physical cleaning (after C1, C2 and C4) and chemical cleaning (after C3) restored the water flux to approximately its initial value (4 L/m^{2}h). C1 (fresh membrane) and C4 (chemically cleaned membrane) showed higher water recovery of 70% while C2, C3, and C5 (physically cleaned membrane) showed water recovery of 52%. Fouling in osmotically driven membrane process is usually external and reversible (She et al., 2016); the reversibility is also due to the fouling layer being loose and sparse (Lee et al., 2010). The external fouling can be easily removed by physical cleaning. However, in distillery wastewater, the functional groups in melanoidins (R-OH and R-COOH) are likely to interact with the membrane surface, causing irreversible fouling. Thus intermittent chemical cleaning of the membrane improves the membrane reusability.

Figure 6b shows that the average water flux over the 5 cycles is similar (2.5±0.3 L/m^{2}h). This indicates that periodic membrane cleaning removes the solids deposited on the membrane surface and improves the longevity of the membrane. The rejection of melanoidins (90±4%), antioxidant activity (95±3%), and COD (85±5%) was high and did not show much variation among the five cycles.

Figure 6. Biomimetic FO membrane performance for distillery wastewater rejection over 5 cycles (C1-C5), each of 24h duration with physical/chemical cleaning (a) water flux and water recovery, and (b) average water flux and corresponding rejection of COD, melanoidins and antioxidant activity.

3.3 Suitability of FO for distillery wastewater treatment

To comply with ZLD norms, Indian distilleries are adopting several measures. Due to the high organic load, anaerobic treatment (biomethanation) with biogas generation is the most common primary treatment. In some distilleries, the biomethanated wastewater is further concentrated by reverse osmosis (RO) or evaporation. Both the biomethanated wastewater and the concentrate (from RO or evaporation) are being used for biocomposting with sugarcane press mud, a sugar industry waste. In a typical operation, the ratio of wastewater to press mud is maintained at 2.5:1 or 3.5:1 (GoI, 2014). Yet another treatment is evaporation followed by incineration of the concentrate. Options like RO, evaporation and incineration are characterized by high capital cost and are highly energy intensive. Biocomposting requires land, is limited by availability of sugarcane press-mud, and is difficult to carry out in the rainy season; further, the compost requires time to stabilize.

In comparison to wastewater concentration by RO or evaporation, FO could be a relatively energy efficient option. The major advantage with FO is high water recovery and relatively low energy requirement. Water recovery from distillery wastewater over 24h study period was higher with FO (70%) than reported for RO (35-45%) (Nataraj et al., 2006). In another study, nanofiltration (NF) at 5 bar transmembrane pressure could only produce a water permeability of 2.66 L/m^2h bar with serious reversible and irreversible fouling (Liu et al., 2013). Organic fouling in FO is mostly reversible and amenable to physical cleaning; it can be easily controlled by optimizing the feed flow rate (Lee et al., 2010). Fouling can be further minimized by selecting a proper draw solution with less back diffusion.

The limitation with FO is appropriate management of the diluted draw solution. In some cases, the diluted draw can be utilized e.g. where fertilizers like urea are used as the draw solution, the diluted draw can be directly applied on land. Elsewhere, the diluted draw solution needs to be concentrated by RO for reuse in the FO process. Considering the high osmotic pressure of distillery wastewater (40 bar), the choice of inorganic salts, that are conventional draw solutes, is also somewhat limited. Another challenge in draw solution reuse is its contamination by the feed. The rejection of melanoidins/color components in distillery wastewater by the FO membrane in this work was not 100%, as observed by the change in color of the draw solution. Repeated concentration of the contaminated $MgCl_2.6H_2O$ draw solution by RO will progressively build-up the concentration of the color compounds thereby affecting the properties of the draw solution. Periodic purging of the concentrated contaminated draw solution along with make-up with fresh concentrated draw solution would be necessary to maintain the effectiveness of the draw solution. Further investigations are required to confirm if the combined FO-RO process for distillery wastewater treatment could be a better option than RO alone in terms of acceptable OPEX (operational expenditure) and CAPEX (capital expenditure).

4. Conclusions

- Melanoidins, the key color and antioxidant component in distillery wastewater, can be concentrated by FO. As rejection is not 100%, the small molecules migrating to the draw side can pose a challenge in draw solution reuse.
- Rejection of COD, melanoidins and antioxidant activity remains high over long-term FO of distillery wastewater. However, both reversible and irreversible membrane fouling occurs.
- Higher water recovery can be obtained from FO of distillery wastewater as compared to RO. Further investigations on membrane fouling and draw solution recovery are required to establish the superiority of FO over RO for the concentration of this wastewater.

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flux and water recovery, and (b) average water flux and corresponding rejection of COD, melanoidins and antioxidant activity.

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Supplementary Data Sheet

Figure S1: Water flux profile with deionized water as feed solution and $MgCl_2.6H_2O$ (1M and 3M) as draw solution.

Figure S2a: Water flux profile at different flow rates (0.8 L/min, 1 L/min and 1.5 L/min) with 2M draw solution of $MgCl_2.6H_2O$ and 10% (v/v) melanoidins feed solution.

Figure S2b: Water flux profile with different concentrations (1M, 2M, 3M) of $MgCl_2.6H_2O$ as draw solution and 10% (v/v) melanoidins feed solution, at flow rate of 1L/min.

Figure S3: Water flux profile with 10% (v/v) melanoidins feed solution and 2M $MgCl_2.6H_2O$ draw solution.

Figure S4: Water flux profile of distillery wastewater feed with different concentration (2M, 3M, 4M) of $MgCl_2.6H_2O$ draw solution.

Figure S5: Comparison of water flux for distillery wastewater and DI water feed solutions using 3M $MgCl_2.6H_2O$ as draw solution.

Table S1: Biomimetic membrane specifications (as reported by the manufacturer).

Table 1. Characteristics of FO feed solutions*

Parameters	**10% melanoidins**	**Distillery wastewater**
pH	7.3±0.1	4.3±0.2
Conductivity (mS/cm)	7.47±0.54	38.87±1.01
Chemical Oxygen Demand (COD) (g/L)	21.78±2.09	120.78±17.80
Trolox equivalent antioxidant capacity (TEAC) (mM)	16.85±3.31	54.74±2.26
Melanoidins (g/L)	69.75±4.27	80±4.26
Polyphenols (g/L)	-	9.46±0.79
Osmotic pressure (bar)	5	40
Viscosity (cP)	1.56±0.07	2.07±0.03

** Average of three replicates*

Table 2. Distillery wastewater concentrate characteristics after 24h operation

Draw solution concentration (M)	Average water flux over 24h (L/m^{2}h)	Rejection (%)			Water recovery (%)
		COD	Melanoidins	Antioxidant activity	
3	2.66	85.2	97.3	94.2	65
4	2.54	76	97.1	90	58

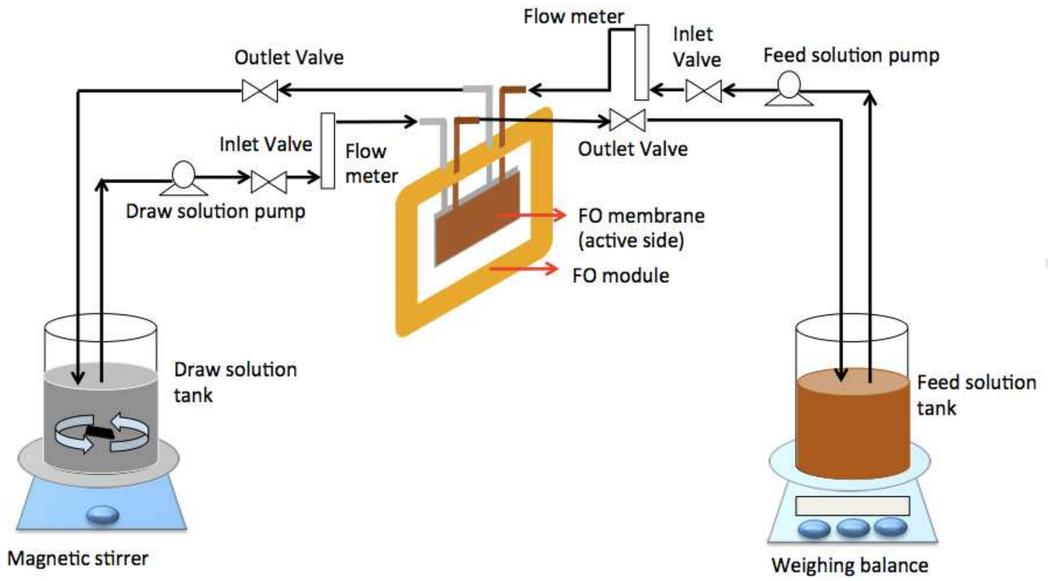
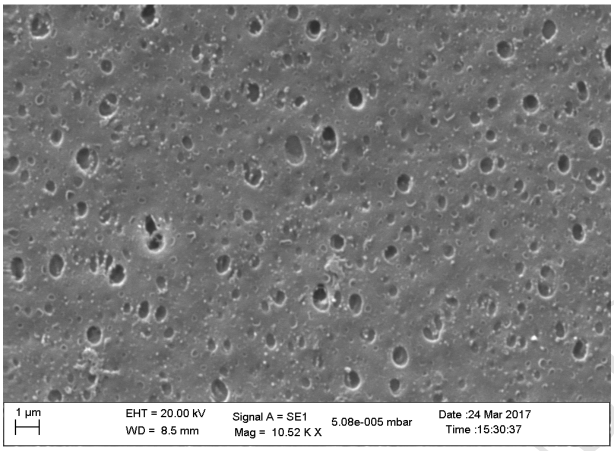


Figure 1. Schematic representation of FO experimental set-up.

(a)



(b)

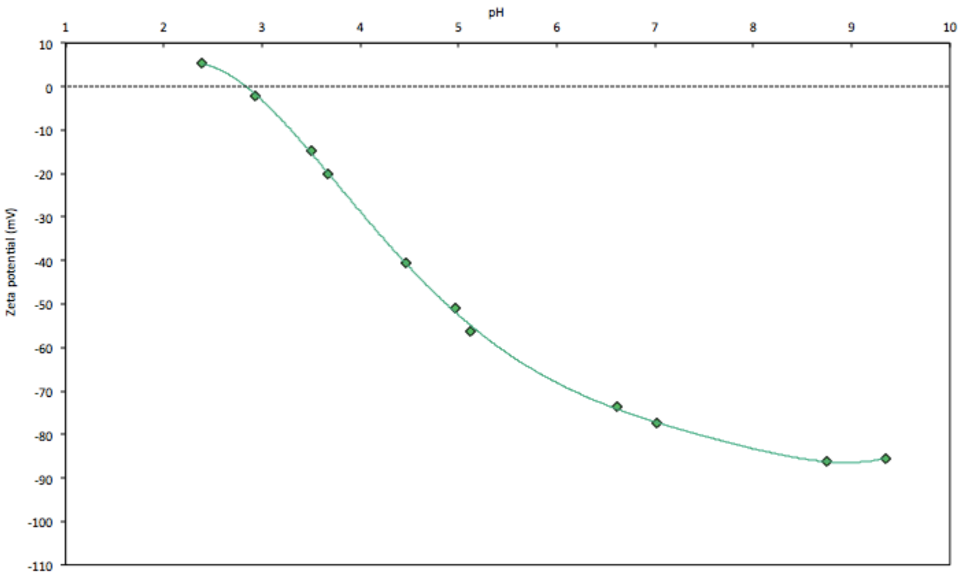


Figure 2. Virgin biomimetic membrane: (a) SEM image of the top surface, and (b) zeta potential measurement.

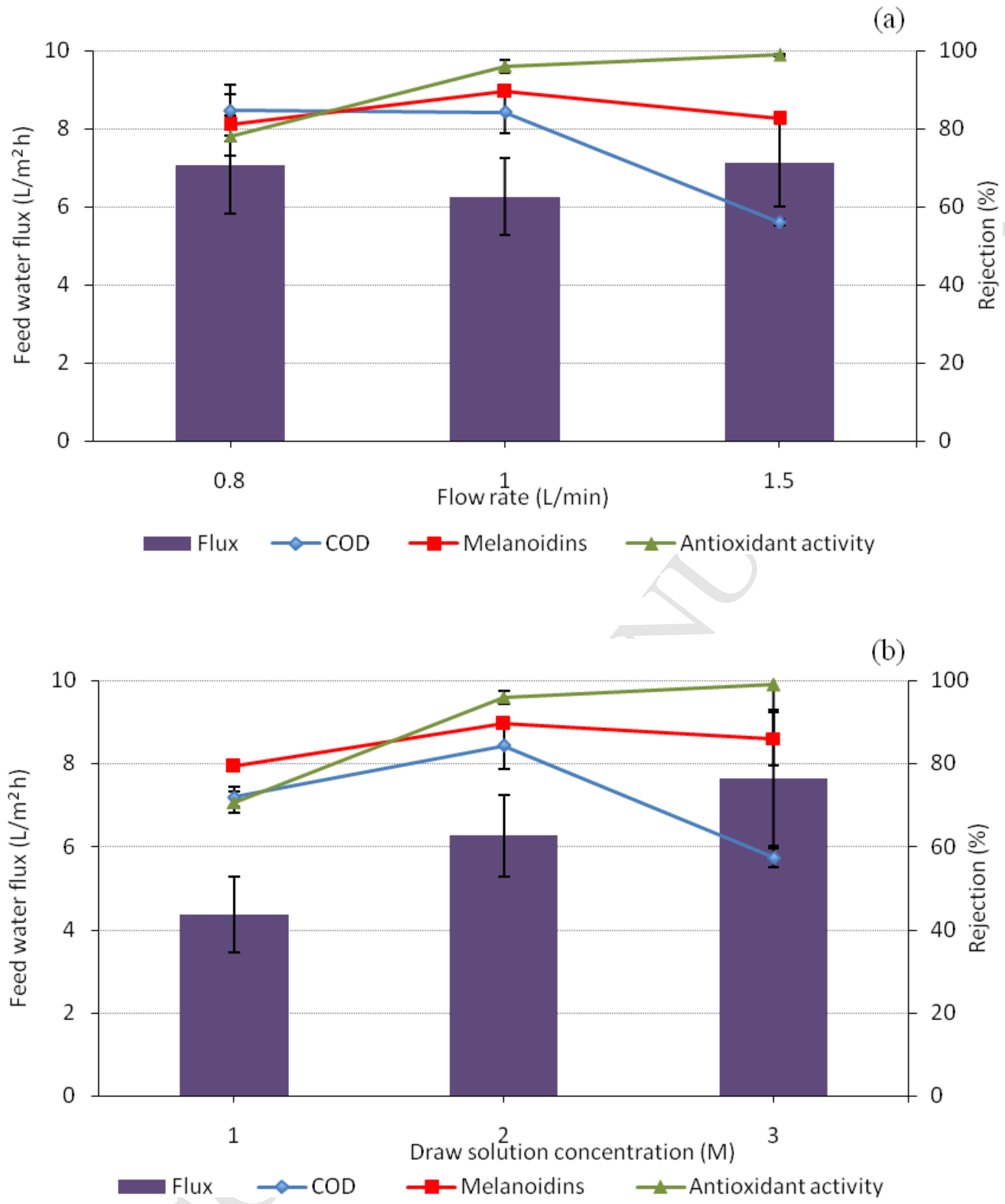


Figure 3. Water flux, rejection of COD, melanoidins and antioxidant activity at (a) varying flow rate **(**2M draw solution, 3h operation time); (b) varying draw solution concentration (1 L/min flow rate, 3h operation time).

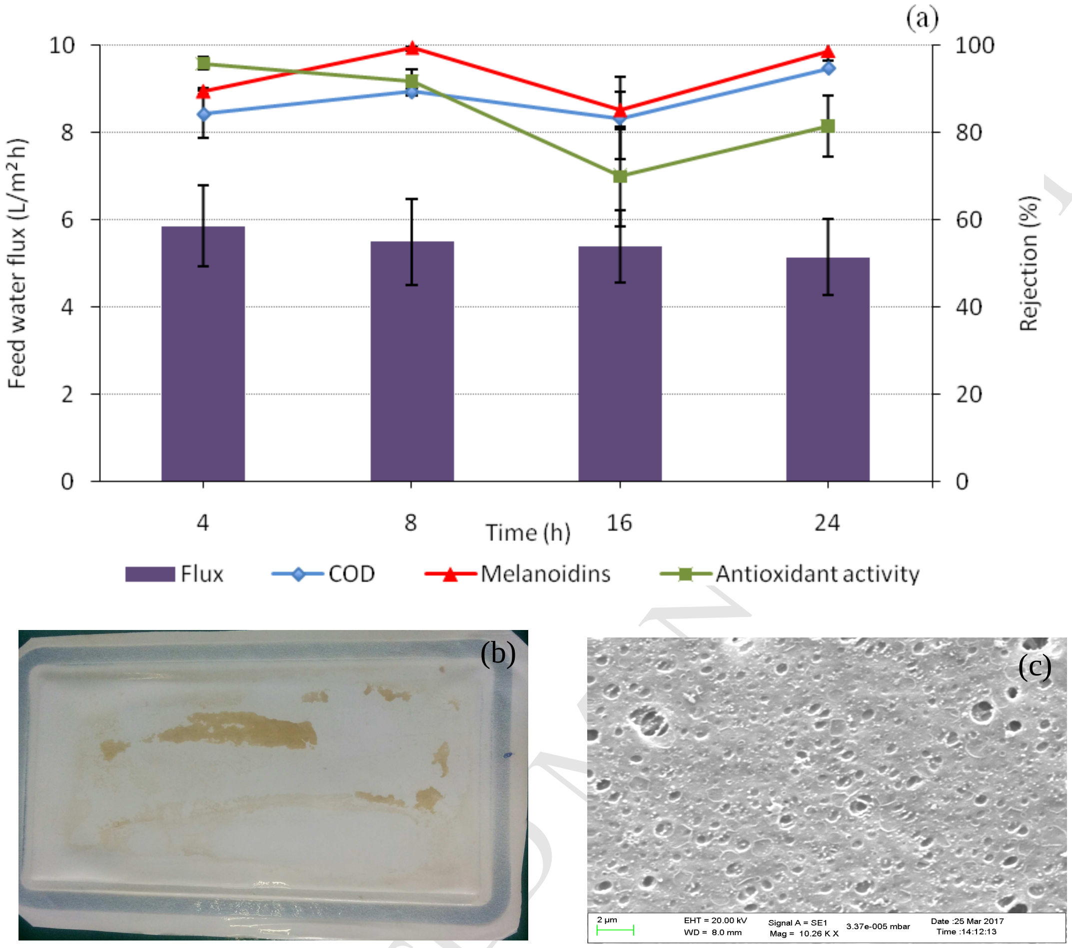
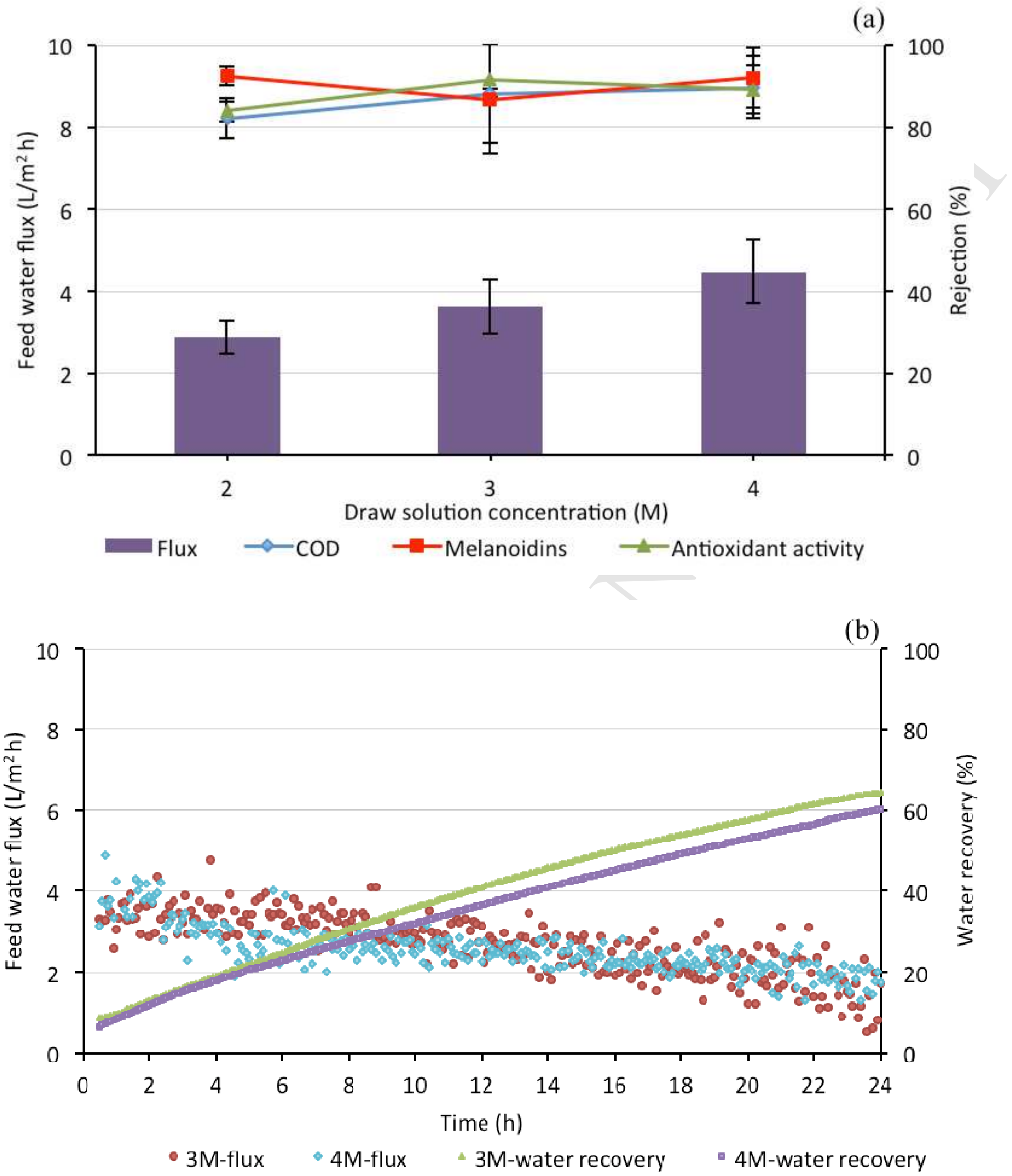


Figure 4. (a)Water flux as a function of time and average rejection of COD, melanoidins and antioxidant activity over 24h, (b) photo of membrane active side after 24h operation, and (c) SEM image of the top surface of used membrane(24h operation).



(a)
10
8
6
4
2
0
100
80
60
40
20
0
Feed water flux (L/m² h)
Rejection (%)
2
3
4
Draw solution concentration (M)
Flux
COD
Melanoidins
Antioxidant activity
(b)
Feed water flux (L/m² h)
Water recovery (%)
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (h)
3M-flux
4M-flux
3M-water recovery
4M-water recovery

(c)

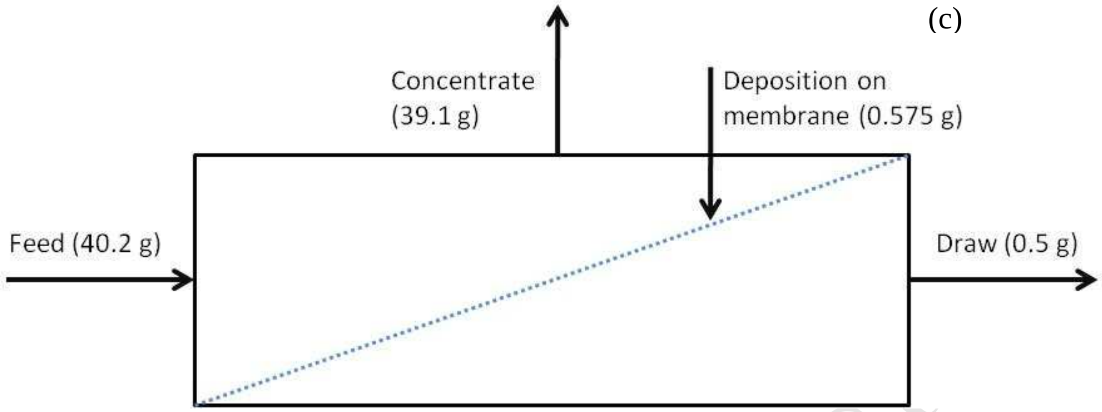
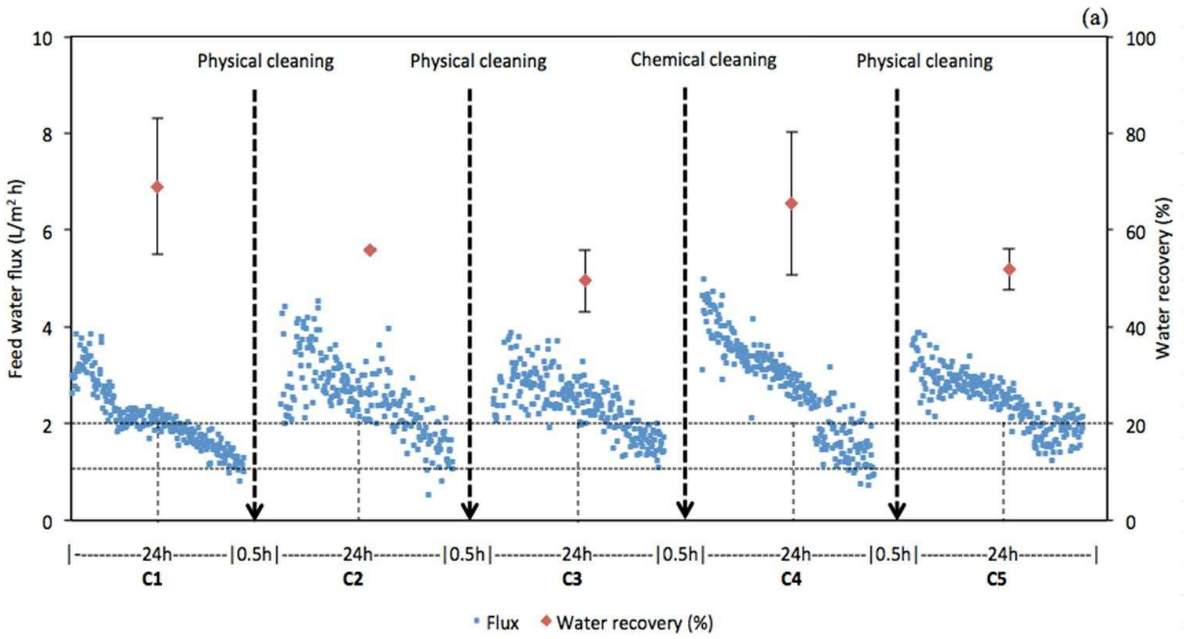


Figure 5. Distillery wastewater dewatering (a) over 4h by varying draw solution concentration (2M-4M): water flux and rejection of COD, melanoidins and antioxidant activity (b) over 24h at 3M and 4M draw solution concentration: water flux and water recovery, and (c) mass balance of melanoidins over 24h FO with 3M draw solution.



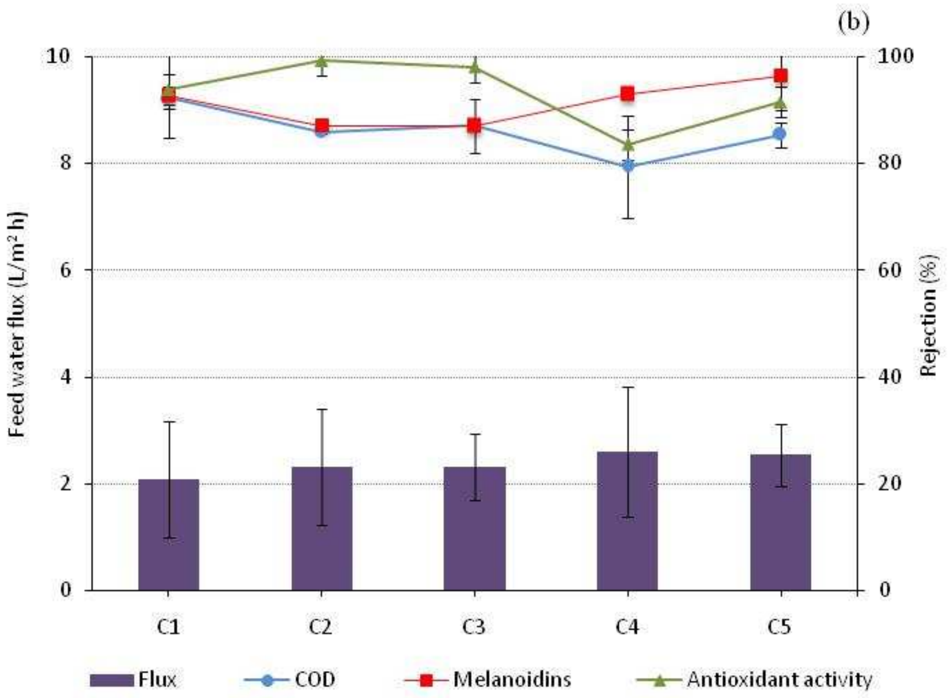


Figure 6. Biomimetic FO membrane performance for distillery wastewater recovery over 5 cycles (C1-C5), each of 24h duration with physical/chemical cleaning (a) water flux and water recovery, and (b) average water flux and corresponding rejection of COD, melanoidins and antioxidant activity.

Highlights

- Distillery wastewater and melanoidins solution were concentrated by forward osmosis
- Aquaporin biomimetic membranes and $MgCl_2.6H_2O$ draw solution were used
- Rejection of organics, melanoidins and antioxidant activity was over 85%
- Water recovery of 70% was obtained with distillery wastewater feed
- Membrane performance was retained with periodic cleaning