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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 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 24 h study period was higher with FO (70%) than reported for RO (35–45%). Repeated use of the FO membrane over five consecutive 24 h cycles with fresh feed and draw solutions and periodic cleaning showed consistent average water flux and rejection of the feed constituents.

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

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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., 2012a, 2014; Alturki et al., 2013, 2012b; Cornelissen et al., 2010; Achilli et al., 2009); (iv) treatment of municipal wastewater (Hey et al., 2016a, 2017, 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™ 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 min (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

Fig. 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 min 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 min. 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.

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 Eqs. (1) and (2) respectively,

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

$$J_s = \frac{(V_t C_t - V_0 C_0}{A \times \Delta t} \tag{2}$$

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 3 h 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 (4 h–24 h) 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 24 h 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