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# Identification of the type of foulants and investigation of the membrane cleaning methods for PRO processes in osmotic power application

Elham Abbasi-Garravand<sup>a</sup>, Catherine N. Mulligan<sup>a,\*</sup>, Claude B. Laflamme<sup>b</sup>, Guillaume Clairet<sup>c</sup>

<sup>a</sup> Department of Building, Civil and Environmental Engineering, Concordia University, 1455 de Maisonneuve Blvd. W., Montreal, Québec H3G1M8, Canada

<sup>b</sup> Institut de recherche d'Hydro-Québec, Shawinigan, Québec, Canada

<sup>c</sup> H2O Innovation Inc., Québec City, Québec, Canada

#### HIGHLIGHTS

- · Effect of fouling on a commercial membrane in PRO mode was investigated.
- Models were able to predict membrane fouling in PRO processes.
- · Complete blocking (CBM) was the main fouling mechanism for all different feed waters.
- Fouling rate was minimized by ultrafiltration compared to sand filtration.

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#### ABSTRACT

Pressure retarded osmosis (PRO) is a membrane based technology used for generation of osmotic power as a sustainable energy. The main challenge of PRO technology is the membrane fouling which reduces the permeate flux and osmotic power generation which consequently increases the cost. In this research, different quality feed waters were used to identify the main foulants on the surface of a commercial semi permeable membrane in the PRO process. In addition, two cleaning methods were investigated to determine the desirable cleaning methods. According to the results, the main inorganic foulants using synthetic salt water were iron, aluminum, calcium, sodium, and silica and when sea water was used as the draw solution, the same foulants, in addition to magnesium and potassium were detected. The organic foulants were humic substances, polysaccharides and proteins for both synthetic salt and sea water draw solutions. According to the results, the water flux recoveries were 98.4%, 98%, 97.5%, 97.3%, and 97.2% after each sequential chemical cleaning, respectively. Therefore, the most successful cleaning method was with acidic and basic cleaners. This research indicates that chemical cleaning can decrease the membrane fouling in PRO processes and consequently improve the osmotic power generation.

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#### 1. Introduction

Pressure retarded osmosis (PRO) has attracted significant attention in recent years [1–10]. PRO is used to generate osmotic power based on the salinity gradients [11–15]. This technology is a membrane based process that its driving force is the osmotic pressure. Water moves from a feed solution with a lower osmotic pressure toward a draw solution with a higher osmotic pressure via a hydraulic pressure [16]. In comparison with forward osmosis (FO) process, a back pressure is applied on the high salinity draw solution side to produce power by releasing the pressure from the solution through a turbine [17,18].

\* Corresponding author. *E-mail address:* mulligan@civil.concordia.ca (C.N. Mulligan).

http://dx.doi.org/10.1016/j.desal.2017.01.038 0011-9164/© 2017 Elsevier B.V. All rights reserved. Like other technologies, the PRO process has some disadvantages such as internal and external concentration polarization, salt reflux and high operating pressure [19].

The semi permeable membrane at the heart of the PRO process plays an important role in controlling the osmotic power generation [20]. The main obstacle of using PRO technology is the membrane fouling that is a time-dependent and irreversible phenomenon and imposes a high cost to the system in terms of energy consumption [21–24].

Some of the possible ways for preventing the membrane fouling are pretreatment, optimization of operating conditions, and improvement of the anti-fouling properties of a membrane. However, using an appropriate cleaning method is an unavoidable part of the membrane processes. Periodic cleaning of the membrane removes the foulant materials and restores the productivity of the membrane [25,26].

In order to reduce and control the membrane fouling in PRO mode, it is necessary to determine the type of foulants. According to the type of

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foulants, an appropriate cleaning procedure can be used. Therefore, the membrane can be cleaned more efficiently and effectively and as a result, the performance of the PRO processes improves [27]. Physical cleaning which comprises surface flushing and membrane backwashing has been used widely to control the membrane fouling in osmotically driven membranes [27,28]. Chemical cleaning is also an efficient method to remove foulants from the membrane surface. Some important parameters that should be considered in chemical cleaning are cleaning agent type, cleaning agent concentration, temperature, pH, flow rate, and cleaning time. It is also necessary to choose a suitable cleaning agent that is compatible with the membrane because some cleaning agents damage the membrane surface and reduce its performance irreversibly [29,30]. Many researchers have studied the fouling phenomena and cleaning methods in FO membranes [25,31-34]. However, very few publications have addressed the foulant identification and membrane cleaning methods in PRO processes [28].

The objectives of this research were to understand the physicochemical characterization of foulants in the PRO process and also to determine the appropriate cleaning method to decrease and control the fouling in PRO processes. In the few available publications on PRO membrane fouling, artificial foulants were mainly used in order to study the fouling phenomena [16,17,20]. In this research, however, different feed waters including untreated river water were used in order to identify the foulants on a commercial semi permeable membrane using realistic conditions in the PRO process. The tests were performed using synthetic salt water and sea water as the draw solutions. Also, two physical and chemical cleaning methods were used to study the effect of cleaning on control and decrease fouling in the PRO mode.

#### 2. Materials and methods

#### 2.1. Chemicals

The prepared synthetic salt water was a combination of demineralized water, sodium chloride and calcium chloride. Calcium chloride was added in order to observe the effect of calcium ion on PRO membrane fouling. The used Na/Ca ratio was selected based on its ratio in sea water [35,36] which was 26. As the typical salinity of Saint Lawrence River at its estuary is 30 g/L [37], the used salt concentration was 30 g/L. Sodium chloride (NaCl-10 kg-S271-10) was used to prepare salt water in this study. This reagent salt was provided by Fisher Scientific Co. Calcium chloride dihydrate (CaCl<sub>2</sub>-3 kg-C79-3) was purchased from Fisher Scientific Co. as an additive to salt water. In order to do the cleaning tests, Lavasol VII (potassium hydroxide) and AM11(an organic acid/trade secret) were used as a basic cleaner from Professional Water Technologies Inc. and as an acidic cleaner from Applied Membrane Inc., respectively. All experiments were done at LTE (Laboratoire des technologies de l'énergie) in the Hydro-Québec Research Institute located at Shawinigan, Québec, Canada.

#### 2.2. Sea water and river water sampling

In all experiments, the sea water was taken from the Saint Lawrence River at the Station Aquicole located in Rimouski, Québec in the estuary of Saint Lawrence and was sent to the Hydro-Québec lab at Shawinigan, Québec. Fresh water was taken from the Saint-Maurice River at the entrance of pressure channels in the hydroelectric Shawinigan-2 power plant. The river water was transported to Hydro-Québec LTE lab (Laboratoire des technologies de l'énergie) by a 2 m<sup>3</sup> polypropylene tank which was mounted on a trailer (Magnum Water Trailer – MWT500).

#### 2.3. Water quality

In order to investigate the sea water and fresh waters (river water, filtered and permeate waters from the multimedia sand filter,

ultrafiltration and microfiltration) characteristics, the parameters such as color, iron, total organic carbon (TOC), silica, suspended solids, alkalinity, hardness, pH, salinity, conductivity, turbidity, dissolved solids, sodium, calcium, magnesium, potassium and silt density index (SDI) were measured. The parameters such as SDI, turbidity, hardness, monovalent and divalent cations, silica and total organic carbon (TOC) are important in membrane fouling. As the river water was brought to the lab in volumes of 2 m<sup>3</sup> every 2 weeks and the fouling tests were done continuously, it was not possible to use the same feed water for all experiments. The amount of iron, silica, sodium, potassium, calcium, and magnesium were measured by optima 4300 DV ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) from Perkin Elmer Inc. For TOC analysis, TOC-L (Laboratory Total Organic Carbon Analyzer) from Shimadzu Corporation was used. The amount of color and suspended solids were measured by a DR 6000™ UV VIS Spectrophotometer from the Hach Company. Alkalinity and hardness were measured by titration of sulfuric acid (0.02 N) and titration of Titraver EDTA (0.02 N) respectively. Salinity, pH, conductivity, and dissolved solids were measured by an HO440d Benchtop Dual Input Multi-Parameter Meter from the Hach Company. Turbidity was measured by a Ratio Turbidimeter/XR 115/230 V from the Hach Company. SDI was measured by using a Simple SDI: auto manufactured by SDI Solutions, a division of Procam Controls Inc.

The results in Tables 1 and 2 demonstrate the average physiochemical characteristics of different used feed waters and sea water. The high level of potassium in Table 1 might be related to the amount of potassium in the natural minerals that exist in the water. The removal efficiencies of sodium and potassium were very low using microfiltration and ultrafiltration which is expected due to the high MWCO (Table 2).

SDI was specified by using the standard method D4189 of American Society for Testing and Measuring (ASTM). Due to the different shapes, sizes and nature of the particulates, the quality of particulates may not be measured absolutely [38]. In this method the rate of clogging (SDI<sub>15</sub>(500 mL)) was calculated by passing a fixed volume of the water (500 mL) through a 0.45 µm membrane filter during a specific time (15 min) at a constant pressure of 30 Psi (207 kPa) [39]. The direct method (method 10129) for the low range test (0.3 to 20 mg/L C) and the USEPA ManVer Buret titration method (method 8226) for the range of 0 to 25,000 mg/L as CaCO<sub>3</sub> were used for TOC and hardness respectively [36]. For color, and the iron platinum-cobalt standard method (method 8025), the USEPA FerroVer method (method 8008: 0.02 to 3 mg/L), and the 1-(2-Pyridylazo)-2- Naphthol PAN method (method 8149) were used, respectively. The used methods for silica, and suspended solids were as follows respectively: the silicomolybdate method (method 8185: 1.0 to 100 mg/L), and the photometric method (method 8006: 5.0 to 750 mg/L).

Table 1	
Physio-chemical characteristics of	sea water.

Parameters	Sea water
Apparent color (mg/L PtCo)	7.00
Total iron (mg/L Fe)	0.00
TOC (mg/LC)	1.85
Silica (mg/LSiO <sub>2</sub> )	0.7
Suspended solids (mg/L)	0.00
Total alkalinity	78.00
Hardness (mg/L as CaCO <sub>3</sub> )	4500.00
pH	7.75
Salinity (%)	30
Conductivity (µS/cm)	37,000.0
Turbidity (NTU)	0.503
Dissolved solids (mg/L)	22.6
Sodium (mg/L)	8750.00
Calcium (mg/L)	324.00
Magnesium (mg/L)	1100.00
Potassium (mg/L)	404.00

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