Journal of Membrane Science 541 (2017) 291–299

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Contaminant rejection in the presence of humic acid by membrane distillation for surface water treatment

Le Han[a], Tong Xiao[a], Yong Zen Tan[a], Anthony G. Fane[b], Jia Wei Chew[a,b,*]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore
[b] Singapore Membrane Technology Centre, Nanyang Environmental and Water Research Institute, Nanyang Technological University, Singapore 637141, Singapore

ARTICLE INFO

Keywords:
Direct contact membrane distillation
Contaminant
Surface water
Membrane fouling, humic acid

ABSTRACT

Membrane distillation (MD) is a promising means for high-purity separations like those needed for potable water. The benefits of MD have not been realized for the treatment of surface or ground water, whereby the presence of both humic acid and calcium are detrimental to other membrane-based processes. Accordingly, this study investigated the efficacy of MD in rejecting various contaminants, namely, ibuprofen, boron and arsenic, in the presence of typical feeds comprising humic acid, calcium chloride and sodium chloride. Feeds investigated ranged from DI water to synthetic feeds mimicking surface water to NEWater brine (i.e., reverse osmosis concentrate from a local wastewater treatment plant in Singapore). Results consistently indicate constant permeate fluxes and low conductivities throughout the experiments with varying concentrations of humic acid and calcium, along with varying pH values, which implies negligible membrane fouling and wetting. Also, complete rejections of boron and arsenic were achieved, while rejection of ibuprofen was approximately 90%. The detection of the non-volatile ibuprofen and humic acid in the permeate suggests some hydrophobic interactions with the membrane. Finally, a cost analysis was carried out to evaluate MD against the conventional nanofiltration (NF) process. Although MD is currently at a higher cost than NF, (i) the availability of improved membranes tailored for MD and low-cost heat would decrease costs to at least those of NF, and (ii) the performance of MD is superior in terms of sustained flux over prolonged periods, capable to treat feeds with higher concentrations of foulants, and better permeate quality.

1. Introduction

A wide range of emerging contaminants, e.g., trace organic compounds (TrOcs) like pharmaceutical and personal care products (PPCPs), inorganic matter like boron and heavy metals etc., can be found in natural and engineered aquatic environments. For example, various TrOcs like ibuprofen and bisphenol A in groundwater have triggered the establishment of standards for monitoring their concentrations in ground water [1]. It should be noted that the boron concentrations in seawater can range around 5 mg/L and up to 100 mg/L has been found in ground water, while the uppermost limit for boron in drinking water can be an order-of-magnitude lower than that of ground water at 2.4 mg/L according to the WHO guidelines and an even lower tolerance limit is set for some plants to boron of 0.3 mg/L [2–4]. In addition, arsenic found in surface and ground water often exceeds the limit in drinking water of 10 μg/L [5,6]. This indicates that the removal of such trace contaminants is necessary, because these contaminants threaten not only human health, but also aquatic organisms and agricultural plants [1,7–9].

Since conventional water treatment processes have not been designed to and cannot effectively remove these emerging contaminants, membrane technology has gained much interest in resolving this issue. However, not all membrane-based separation processes can achieve this. Rejections of aromatic compounds by polyamide nanofiltration (NF) membranes was reported to be 25–50% [10], rejections of boron by a reverse osmosis (RO) or electrodialysis (ED) process was found to be 30–50% [9,11], while rejection of arsenic (namely, As (III)) by NF was 8–85% [12–14]. Moreover, forward osmosis (FO), suggested as an alternative process with better rejection than the above processes, has solute-membrane interactions that are similar to those of NF and RO, thereby the underlying phenomena like solute permeability, reverse solute diffusion and internal concentration polarization are expectedly similar [4,15,16]. Therefore, membrane processes like reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED) and forward osmosis (FO) tend to fail to satisfactorily retain these contaminants due to the various phenomena of solute sorption-diffusion through the membrane, membrane fouling, or other complex interactions between the membrane and the water matrix. To this end, membrane distillation (MD)

---

* Corresponding author at: School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore.
E-mail address: jchew@ntu.edu.sg (J.W. Chew).

http://dx.doi.org/10.1016/j.memsci.2017.07.013
Received 8 May 2017; Received in revised form 4 July 2017; Accepted 7 July 2017

Nomenclature

A	membrane surface area (m^2)
c_F , c_P	solute concentration of feed and permeate, respectively (mg/L)
J	permeate flux ($kg/m^2/h$)
m_{ads}	amount of solute on the unit membrane surface (mg/m^2)
R	solute rejection (%)
t	time (h)
V	solution volume (L)
m_P	mass of overflowed permeate (kg)

could be a promising alternative.

Membrane distillation (MD) is a thermally-driven technology with a theoretical 100% retention of non-volatile components. Due to the vapor pressure difference across the hydrophobic membrane, the most volatile component (typically water) vaporizes at the pore openings at the feed-membrane interface, transfers through the vapor-filled (non-wetted) pores and then condenses at the permeate-membrane interface, thereby achieving efficient separation of components of different volatilities. With regards to contaminants the rejection of TrOCs, boron and other inorganic ions have been reported as over 90–99% [17]. However, the unexpected penetration of some non-volatile solutes like humic acid and trace organic compounds through the MD membrane has been reported [18–20], leading to an increasing attention to the permeate quality achievable. Other advantages of MD include no requirement for an external hydraulic pressure, applicability for feeds of various salinities, potential utilization of waste heat, and, more significantly, less extensive fouling [17,21,22]. Furthermore, the integration of MD with a membrane bioreactor (MBR) is gaining traction in waste water treatment [23,24].

In spite of the presence of various other components in practical feeds, lab-based experiments have tended to primarily focus on the targeted contaminant like boron [25], arsenic [26,27] and trace organic compounds [18], thus neglecting the influence of the inorganic salts and natural organic matter (NOM) inevitably present. In particular, membrane fouling by NOM in MD is a critical issue that still calls for considerable research effort [19,22]. In some cases negligible permeate flux decline due to humic acid was observed regardless of the ionic concentration of sodium chloride (NaCl) and calcium chloride ($CaCl_2$) [28,29]. In other cases significant flux decline (up to 40%) was observed due to the fouling by humic acid induced by the calcium ions (referred to as Ca^{2+}-carboxyl complexation), which was found to be dependent on pH [30]. These contradictory observations of the effect of humic acid fouling on MD permeate flux further imply that the study of contaminant rejection should be concurrent with that of membrane fouling and/or pore wetting by NOM. Although extensive reports of the impact of fouling on contaminant rejection are available for NF, FO and ED, that for MD remains unknown. Rejection has been reported to improve due to enhanced steric hindrance in NF and FO [31,32] or further solute-foulant complexation in ED [11], while deteriorated rejections have been attributed to restricted back diffusion in NF [33]. Therefore, an analogous study on the concurrent filtration of NOM and contaminants on MD performance is warranted, particularly in view of the different driving force and transport mechanism for MD. Additionally, the cost-effectiveness of MD in treating surface or ground water needs to be evaluated, since past cost analyses have focused on brackish water or brine [34].

In this study, the performance of direct contact membrane distillation (DCMD) in rejecting ibuprofen, boron and arsenic (which are representative of emerging organic and inorganic contaminants) in surface or waste water was assessed. The feeds ranged from DI water to synthetic mixes mimicking surface water to NEWater brine, a reverse osmosis concentrate from a local municipal wastewater treatment facility. Specifically, NEWater is reclaimed water used mainly in the industries, and produced via a water reclamation plant, microfiltration, reverse osmosis and finally ultraviolet disinfection [35]. The latter two feeds contained inorganic salts (namely, NaCl, $CaCl_2$) and natural organic matter (NOM; namely, humic acid). Firstly, the impact of salt and humic acid concentrations, as well as pH, on membrane fouling and pore wetting was studied. Secondly, the rejection of contaminants in both the absence and presence of other components (namely, NOM and inorganic salts) was evaluated. Finally, a cost analysis was carried out to compare MD with NF for the same production capacity, and further appraise means to lower the costs of MD to improve its practical feasibility.

2. Materials and methods

2.1. Chemicals and membranes

De-ionized (DI) water (Merck-Millipore), sodium chloride (NaCl, Merck-Millipore), calcium chloride ($CaCl_2$, Merck-Millipore), humic acid sodium salt (HA, $C_9H_8Na_2O_4$, Sigma-Aldrich) were used to simulate surface water. 1 g/L NaCl (~ 20 mM NaCl) was added to the feeds to allow for the monitoring of the permeate quality via a conductivity meter (Mettler-Toledo). Humic acid is ubiquitous in natural water and wastewater effluent [36,37], and is represented in this study by humic acid sodium salt, which is a typical model organic foulant widely used [11,38,39]. For the synthetic surface water in this study, the composition was set at 1 g/L NaCl (20 mM NaCl), 8 mM $CaCl_2$ and 100 mg/L HA (100 mM HA), unless otherwise stated. In addition, NEWater brine, which is a reverse osmosis concentrate from a local wastewater treatment plant (Singapore) was also investigated as a more realistic feed, with compositions characterized in Table 1.

Ibuprofen (IBU, $C_{13}H_{18}O_2$, Sigma-Aldrich), boron (boric acid, $B(OH)_3$, Sigma-Aldrich) and arsenic (sodium arsenite, $NaAsO_2$ with As (III), Merck-Millipore) were the model contaminants studied, as detailed in Table 2. In particular, the arsenite species used here is representative of arsenic of varying oxidation states [5], including arsenate that is likely more prevalent in toxic environments. Solution pH not only influences HA fouling [30], but also the form that IBU (pKa = 4.6) and boron (pKa = 9.2) exist in. Past studies have also reported on the effect of pH on varying rejection rates for boron [3,9] and arsenic [12]. In this study, the feed solution pH was adjusted by the addition of 0.1 M of sodium hydroxide (NaOH) or nitric acid (HNO_3) to 2.6 ± 0.2, 7.2 ± 0.2 and 11.0 ± 0.2. It should be noted that changing the pH of the DI water feed alone did not affect the flux, which indicates that the membrane was unaffected by pH. The initial concentrations in the feed of IBU, boron and arsenic were 5 mg/L, 5 mg/L and 0.5 mg/L, respectively. While the concentration of IBU used was higher than reported [1], since IBU can also represent various organic micro-pollutant, that for boron and arsenic used were in the range detected in seawater and brackish groundwater [2,38]. Table 2 indicates that the vapor pressure of IBU and boron are very low, compared to that for water at 25 °C

Table 1
Composition of NEWater brine (pH =7.5 ± 0.1).

Species concentration (mg/L, unless stated otherwise)			
Na^+	298.1 ± 4.1	Cl^-	295.7 ± 4.0
Ca^{2+}	114.6 ± 5.3	SO_4^{2-}	260.5 ± 0.6
K^+	70.2 ± 0.2	NO_3^-	64.4 ± 1.7
Mg^{2+}	14.2 ± 0.1	HCO_3^-	40.7 ± 1.5
Si	18.6 ± 0.2	PO_4^{3-}	37.2 ± 0.2
Conductivity (mS/cm)	2.45 ± 0.01	TOC	34.7 ± 2.1
Biopolymer	3.0 ± 0.8	Humic substance	11.8 ± 1.2
Building Blocks	11.8 ± 1.2	LMW neutrals	7.9 ± 0.6

The organic composition was determined by LC-OCD (DOC-Labor Model 8).