WATER RESEARCH 49 (2014) 265–274

Available online at www.sciencedirect.com

ScienceDirect

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

Relating rejection of trace organic contaminants to membrane properties in forward osmosis: Measurements, modelling and implications

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A R T I C L E I N F O

Article history:
Received 19 August 2013
Received in revised form
17 November 2013
Accepted 19 November 2013
Available online 1 December 2013

Keywords:
Forward osmosis
Solute rejection
Membrane surface charge
Trace organic contaminants (TrOCs)
Permeate flux
Pore hindrance transport model
Pore size

A B S T R A C T

This study elucidates the relationship between membrane properties and the rejection of trace organic contaminants (TrOCs) in forward osmosis (FO). An asymmetric cellulose triacetate (CTA) and a thin-film composite (TFC) polyamide FO membrane were used for this investigation. The effective average pore radius (r_p), selective barrier thickness over porosity parameter (l/ε), surface charge, support layer structural parameter (S), pure water permeability coefficient (A) and salt (NaCl) permeability coefficient (B) of the two membranes were systematically characterised. Results show that measured rejection of TrOCs as a function of permeate water flux can be well described by the pore hindrance transport model. This observation represents the first successful application of this model, which was developed for pressure-driven nanofiltration, to an osmotically-driven membrane process. The rejection of charged TrOCs by the CTA and TFC membranes was high and was governed by both electrostatic repulsion and steric hindrance. The TFC membrane exhibited higher rejection of neutral TrOCs with low molecular weight than the CTA membrane, although the estimated pore size of the TFC membrane (0.42 nm) was slightly larger than that of the CTA membrane (0.37 nm). This higher rejection of neutral TrOCs by the TFC membrane is likely attributed to its active layer properties, namely a more effective active layer structure, as indicated by a larger l/ε parameter, and pore hydration induced by the negative surface charge.

1. Introduction

More than four billion people live in areas where drinking water security and ecosystem biodiversity are being threatened by freshwater shortages. This problem is being exacerbated by urbanization, population growth and climate change (Grant et al., 2012). As a result, significant research efforts have been made to facilitate the extraction of clean water from unconventional resources, such as seawater and wastewater effluent, to augment drinking water supplies. Membrane filtration processes, such as reverse osmosis (RO)

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http://dx.doi.org/10.1016/j.watres.2013.11.031

and nanofiltration (NF), have contributed to a remarkable increase in the utilisation of unconventional water resources (Elimelech and Phillip, 2011; Shannon et al., 2008). However, numerous trace organic contaminants (TrOCs) are being frequently detected in wastewater and sewage-impacted water bodies (Basile et al., 2011; Carballa et al., 2004; Schwarzenbach et al., 2006; Snyder et al., 2003). As a result, in addition to existing membrane processes such as NF and RO, novel treatment technologies, which can potentially provide a more efficient and cost-effective barrier against TrOCs, have also been explored.

Forward osmosis (FO) is one such novel membrane process that has the potential to advance water and wastewater treatment (Cath et al., 2006; Zhao et al., 2012). In FO, a semi-permeable membrane is placed between a feed solution and a concentrated draw solution with high osmotic pressure. The extraction of water is driven by the osmotic pressure difference and, at the same time, salt and contaminants in the feed solution are being rejected by the FO membrane. To produce freshwater, FO is usually combined with pressure-driven membrane processes, such as NF and RO (Hoover et al., 2011; Shaffer et al., 2012; Yangali-Quintanilla et al., 2011), or thermal processes, such as conventional column distillation (McCutcheon et al., 2005; McGinnis and Elimelech, 2007) and membrane distillation (Cath et al., 2005; Martinetti et al., 2009). In these hybrid treatment systems, TrOCs in the feed are first subjected to rejection by the FO membrane and then by the subsequent process that is used to both concentrate the draw solution and produce freshwater, thereby providing a dual barrier for TrOCs. Hence, it is of paramount importance to better elucidate the removal of TrOCs in the FO process.

High removal efficiency of TrOCs by the FO process has been demonstrated in several previous studies. Cartinella et al. (2006) found a near complete rejection of three hormones in FO. Cath et al. (2010) reported the rejection of six TrOCs, ranging from 72% (salicylic acid) to more than 99% (diclofenac). A comprehensive study on the removal of 23 TrOCs revealed that the rejection of charged TrOCs was consistently above 80%, whereas the rejection of neutral TrOCs varied from 40 to 90% (Hancock et al., 2011b). A similar observation was also reported by Valladares Linares et al. (2011) when examining the removal of 13 TrOCs. Alturki et al. (2013) elucidated the mechanisms governing the rejection of 40 TrOCs compounds by FO, indicating that the rejection of charged TrOCs is governed by both electrostatic interaction and size exclusion, while rejection of neutral compounds is dominated by size exclusion.

It is noteworthy that to date most studies investigating the removal of TrOCs by the FO process employed an asymmetric cellulose triacetate (CTA) membrane. Given the recent progress in the development of new membrane materials for FO applications, polyamide thin-film composite (TFC) membranes have been recently introduced. These TFC membranes have been reported to have higher water permeability and solute rejection compared to their CTA counterparts (Wang et al., 2010; Wei et al., 2011; Yip et al., 2010). Because there are considerable differences between asymmetric CTA and polyamide TFC membranes, it is worthwhile to systematically examine their rejection performance and provide insights into the relationship between membrane properties and TrOCs rejection.

In this study, we examine and compare the rejection of 12 TrOCs by an asymmetric CTA and a polyamide TFC membrane as a function of permeate water flux. Key properties of the CTA and TFC membranes were characterised to facilitate the understanding of their TrOC rejection behaviour. The membrane pore hindrance transport model was used to predict the rejection of the TrOCs as a function of permeate water flux and model predictions were compared with the experimentally measured data. Rejection of TrOCs by the CTA and TFC membranes was related to the membrane properties and mechanisms responsible for the rejection of TrOCs were proposed and elucidated.

2. Materials and methods

2.1. *Trace organic contaminants*

Twelve TrOCs, frequently detected in secondary treated effluent and sewage-impacted water bodies at trace levels, were used for this investigation. The TrOCs were selected to cover a diverse range of properties including charge, hydrophobicity and molecular weight (Table 1). A combined stock solution containing 1 g/L of each TrOC was prepared in methanol. The stock solution was kept at −18 °C in the dark and was used within one month.

2.2. *Forward osmosis and reverse osmosis systems*

A bench-scale FO system consisting of a cross-flow membrane cell with a total effective membrane area of 123.5 cm^2 was employed. The membrane cell had two identical and symmetrical flow chambers with length, width and channel height of 130, 95, and 2 mm, respectively. The circulation flow rates of the feed and draw solutions were kept constant at 1 L/min (corresponding to a cross-flow velocity of 9 cm/s). The draw solution reservoir was placed on a digital balance (Mettler Toledo Inc., Hightstown, NJ) and weight changes were recorded by a computer to calculate the permeate water flux. A conductivity controller (Cole–Parmer, Vernon Hills, IL) was used to maintain a constant draw solution concentration when inorganic salt was used as the draw solute. Further details of this conductivity control system are available elsewhere (Xie et al., 2012a).

A bench-scale RO system with a rectangular stainless-steel cross-flow cell was used to characterise the membrane pore radius and membrane transport parameters. The RO membrane cell had an effective membrane area of 40 cm^2, with channel length, width and depth of 100, 40 and 2 mm, respectively. The unit was equipped with a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed solution was kept constant using a chiller/heater (Neslab RTE 7). Permeate flow was measured by a digital flow meter (FlowCal 5000, Tovatech, South Orange, NJ).

2.3. *Characterization of forward osmosis membranes*

An asymmetric CTA and a polyamide TFC membrane were acquired from Hydration Technology Innovations (Albany,