Water Research 131 (2018) 45–51

Contents lists available at ScienceDirect

Water Research

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

High rejection reverse osmosis membrane for removal of *N*-nitrosamines and their precursors

Takahiro Fujioka [a, *], Kenneth P. Ishida [b], Takuji Shintani [c], Hitoshi Kodamatani [d]

[a] *Water and Environmental Engineering, Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan*
[b] *Research & Development Department, Orange County Water District, 18700 Ward Street, Fountain Valley, CA 92708, USA*
[c] *Division of Advanced Membrane Science and Technology, Graduate School of Science, Technology and Innovation, Kobe University, 1-1 Rokkodai-cho, Kobe 657-8501, Japan*
[d] *Division of Earth and Environmental Science, Graduate School of Science and Engineering, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan*

ARTICLE INFO

Article history:
Received 5 August 2017
Received in revised form
11 December 2017
Accepted 12 December 2017
Available online 12 December 2017

Keywords:
N-nitrosodimethylamine
N-nitrosamine precursor
Heat treatment
Reverse osmosis
Potable water reuse

ABSTRACT

Direct potable reuse is becoming a feasible option to cope with water shortages. It requires more stringent water quality assurance than indirect potable reuse. Thus, the development of a high-rejection reverse osmosis (RO) membrane for the removal of one of the most challenging chemicals in potable reuse – *N*-nitrosodimethylamine (NDMA) – ensures further system confidence in reclaimed water quality. This study aimed to achieve over 90% removal of NDMA by modifying three commercial and one prototype RO membrane using heat treatment. Application of heat treatment to a prototype membrane resulted in a record high removal of 92% (1.1-log) of NDMA. Heat treatment reduced conductivity rejection and permeability, while secondary amines, selected as *N*-nitrosamine precursors, were still well rejected (>98%) regardless of RO membrane type. This study also demonstrated the highly stable separation performance of the heat-treated prototype membrane under conditions of varying feed temperature and permeate flux. Fouling propensity of the prototype membrane was lower than a commercial RO membrane. This study identified a need to develop highly selective RO membranes with high permeability to ensure the feasibility of using these membranes at full scale.

1. Introduction

Potable reuse (PR) has been increasingly considered as a viable and powerful option to cope with water scarcity in many parts of the world (Burgess et al., 2015). Most PR schemes employed over the past decade are based on indirect potable reuse (IPR), which is implemented through the augmentation of drinking water sources (e.g. dams and aquifers) with highly treated wastewater. To make PR more economically feasible, the water industry has devoted significant attention on direct potable reuse (DPR) (Arnold et al., 2012). In DPR, recycled water with a short retention time is transported directly to the entrance of drinking water treatment plants, so that capital and operating costs associated with infrastructure and water quality monitoring can be reduced considerably. One of the critical considerations when shifting from IPR to DPR is the quality assurance of recycled water (Drewes and Khan, 2015; Leverenz et al., 2011). In fact, a feasibility study of DPR initiated by the California State Legislature (USA) has recommended greater focus on the identification and removal of low molecular weight trace organic compounds (TOrCs) (CSWRCB, 2016).

Among low molecular weight TOrCs, *N*-nitrosodimethylamine (NDMA; $C_2H_6N_2O$) – a probable carcinogenic chemical (USEPA, 1993) – is one of the more challenging compounds in PR. For example, an adsorption process using granular activated carbon only removed NDMA up to 50% (Fleming et al., 1996; Schmidt and Brauch, 2008). To date, NDMA is essentially removed by a combination of direct photolysis by UV irradiation and an advanced oxidation process (AOP) that is based on hydrogen peroxide dosage (Leverenz et al., 2011). California has established a notification level (NL) of 10 ng/L for NDMA and a public health goal (PHG) of 3 ng/L. No reliable removal credits for NDMA have been granted for the application of a reverse osmosis (RO) process.

NDMA, an *N*-nitrosamine, is a hydrophilic compound with a molecular weight of 74 g/mol and is uncharged at pH 6–8. Because

* Corresponding author.
E-mail address: tfujioka@nagasaki-u.ac.jp (T. Fujioka).

https://doi.org/10.1016/j.watres.2017.12.025
0043-1354/

of its small molecular size and uncharged property, NDMA readily permeates through an RO membrane. Brackish water RO membranes are typically able to achieve 40–70% rejection of NDMA at lab-scale levels (Bellona et al., 2011; Fujioka et al., 2012b; Hofs et al., 2013; Miyashita et al., 2009; Steinle-Darling et al., 2007) and at 5–80% at pilot- to full-scale levels (Bellona et al., 2008; Farré et al., 2011a; Fujioka et al., 2013b; Plumlee et al., 2008; Poussade et al., 2009). Any improvement to the selectivity of RO membranes and assignment of removal credits for NDMA can improve the safety of recycled water and possibly reduce the load on any UV or UV/AOP.

Formation of NDMA downstream of the RO process has also gained increased concern in DPR. NDMA can form through a reaction between residual chloramine and NDMA precursors in RO permeate (McCurry et al., 2017; Sgroi et al., 2015; Soltermann et al., 2013). These NDMA precursors include dimethylamine (DMA) and tertiary amines (Mitch et al., 2003; Schreiber and Mitch, 2005; Shah and Mitch, 2011). Although these precursors are well removed by RO membranes (e.g. >99%) (Krauss et al., 2010; Miyashita et al., 2009), significant NDMA precursors still remain in RO permeate (Farré et al., 2011b) that are not degraded by UV/AOP (or are reaction products). Thus, the development of a highly selective RO membrane for enhanced removal of NDMA and NDMA precursors could help to improve on the safety of recycled water in DPR. In addition, improvement of the selectivity of RO membranes is expected to become more important in PR to mitigate future water quality issues associated with non-regulated or unidentified emerging TOrCs (Debroux et al., 2012; Werber et al., 2016a).

To improve the rejection of RO membranes, a simple membrane modification technique based on an immersion of RO membranes in high-temperature ultrapure water has been proposed (Fujioka et al., 2015). Heat treatment can enhance the rejection of uncharged and low molecular weight compounds (e.g. boric acid); however, water permeability also decreases. Heat treatment during the interfacial polymerisation process has the effect of tightening the membrane structure and improving its salt rejection (Shintani et al., 2009). To the best of our knowledge, there are still no RO membranes with a reported ability to remove NDMA >90% (1.0-log).

This study aimed to achieve over 1.0-log removal of NDMA by modifying three commercial and one prototype RO membrane using heat treatment. In addition to NDMA, this study included five additional *N*-nitrosamines and five secondary amines to demonstrate the separation performance and stability of heat-treated RO membranes for a range of feed temperatures and permeate flux. Fouling propensity of heat-treated RO membranes was also examined using treated wastewater. Lastly, the feasibility and implication of using high rejection RO membranes for full-scale DPR schemes are discussed.

2. Materials and methods

2.1. Chemicals

Certified 100 mg/L solutions of six analytical grade *N*-nitrosamines (Table S1) – NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine (NDEA), *N*-nitrosopiperidine (NPIP) and *N*-nitrosomorpholine (NMOR) – were purchased from Ultra Scientific (Kingstown, RI, USA). Five analytical grade secondary amines – DMA hydrochloride, pyrrolidine (PYR), diethylamine (DEA), piperidine (PIP) and morpholine (MOR) – selected as *N*-nitrosamine precursors were purchased from Tokyo Chemical Industry (Tokyo, Japan). Physicochemical properties of these *N*-nitrosamines and secondary amines are summarised in Table 1. The *N*-nitrosamines and secondary amines, all of which have a Log *D* value of <2.0, are classified as hydrophilic compounds (Van der Bruggen et al., 2006). pK_a values of *N*-nitrosamines are well below 8; thus, they are uncharged at pH 8. In contrast, the secondary amines (except MOR) are all protonated at pH 8 with pK_a values well beyond 8. MOR is protonated by ~75% at pH 8. Among the selected *N*-nitrosamines, NDMA has the lowest minimum projection area, i.e., the area of the compound projected with the minimum plane of its circular disk (Fig. S2). Stock solutions containing four or six *N*-nitrosamines in methanol were prepared at 1 μg/mL of each compound. Stock solutions of each secondary amine were prepared at 100 mM in ultrapure water. All stock solutions were stored at 4 °C in the dark. Analytical grade NaCl, $CaCl_2$ and $NaHCO_3$ were purchased from Wako Pure Chemical Industries (Tokyo, Japan). Activated sludge effluent from a municipal wastewater treatment plant in Japan was treated by ultrafiltration (UF) and used for fouling experiments. Total organic carbon, pH and conductivity of the UF-treated wastewater was 6.5 mg/L, 6.5 and 1112 μS/cm, respectively.

2.2. Membranes and membrane treatment system

Three commercial brackish water RO membranes – ESPA2, ESPAB and HYDRApro®501 – and one prototype membrane were supplied as flat sheet samples by Hydranautics/Nitto (Osaka, Japan). All of the RO membranes are thin-film composite polyamide. ESPA2 is commonly used in water recycling applications (Fujioka et al., 2012a). ESPAB is employed in the second stage of seawater desalination to achieve a high rejection of boron. HYDRApro®501 (HYDRA) is an RO membrane that is designed for industrial process applications. The prototype membrane (Prototype) is a proprietary RO membrane.

A bench-scale RO treatment system was comprised of a stainless steel membrane cell (Iwai Pharma Tech, Tokyo, Japan), high-

Table 1
Physicochemical properties of the selected *N*-nitrosamines and secondary amines.

Compound	Molecular formula	Molecular weight [Da]	Log *D* at pH 8[a]	pK_a[a]	Minimum projection area[a] [Å]
N-Nitrosamines					
NDMA	$C_2H_6N_2O$	74.1	0.04	3.5	19.5
NMEA	$C_2H_8N_2O$	88.1	0.40	3.4	21.9
NPYR	$C_4H_8N_2O$	100.1	0.44	3.3	25.0
NDEA	$C_4H_{10}N_2O$	102.1	0.75	3.3	25.4
NPIP	$C_5H_{10}N_2O$	114.1	0.89	3.3	27.2
NMOR	$C_4H_8N_2O_2$	116.1	−0.18	3.1	25.2
Secondary amines					
DMA	C_2H_7N	45.1	−2.64	10.5	15.8
PYR	C_4H_9N	71.1	−2.80	11.4	22.5
DEA	$C_4H_{11}N$	73.1	−1.98	10.6	20.3
PIP	$C_5H_{11}N$	85.2	−1.69	10.4	25.6
MOR	C_4H_9NO	87.1	−1.03	8.5	21.5

[a] Chemicalize (http://www.chemicalize.org).