Water Research 93 (2016) 179–186

Contents lists available at ScienceDirect

Water Research

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

Rejection of pharmaceutically-based *N*-nitrosodimethylamine precursors using nanofiltration

Gwen C. Woods [a, *, 1], A.H.M. Anwar Sadmani [a, c], Susan A. Andrews [a], David M. Bagley [b], Robert C. Andrews [a]

[a] Department of Civil Engineering, University of Toronto, 35 St. George Street, Toronto, ON M5S 1A4, Canada
[b] Department of Chemical Engineering, University of Wyoming, Dept. 3295, 1000 E. University Avenue, Laramie, WY 82071, United States
[c] Department of Civil, Environmental & Construction Engineering, University of Central Florida, 12760 Pegasus Drive, Orlando, FL 32816, United States

ARTICLE INFO

Article history:
Received 18 November 2015
Received in revised form
3 February 2016
Accepted 3 February 2016
Available online 21 February 2016

Keywords:
NDMA
Ranitidine
Doxylamine
Nizatidine
Loose membrane
Formation potential

ABSTRACT

N-Nitrosodimethylamine (NDMA) is a disinfection by-product (DBP) with many known precursors such as amine-containing pharmaceuticals that can enter the environment via treated wastewater. Reverse osmosis and tight nanofiltration membranes (MW cutoff < 200 Da) are treatment technologies that demonstrate high removal of many compounds, but at relatively high energy costs. Looser membranes (>200 Da) may provide sufficient removal of a wide range of contaminants with lower energy costs. This study examined the rejection of pharmaceuticals that are known NDMA precursors (~300 Da) using nanofiltration (MW cutoff ~350 Da). MQ water was compared to two raw water sources, and results illustrated that NDMA precursors (as estimated by formation potential testing) were effectively rejected in all water matrices (>84%). Mixtures of pharmaceuticals vs. single-spiked compounds were found to have no impact on rejection from the membranes used. The use of MQ water vs. surface waters illustrated that natural organic matter, colloids, and inorganic ions present did not significantly impact the rejection of the amine-containing pharmaceuticals. This study illustrates that NDMA formation potential testing can be effectively used for assessing NDMA precursor rejection from more complex samples with multiple and/or unknown NDMA precursors present, such as wastewater matrices.

1. Introduction

N-nitrosodimethylamine (NDMA) is a potential human carcinogen (EPA, 2008; Hebert et al., 2010) with much higher health risks when compared to those associated with traditional halogenated disinfection byproducts (DBPs) (Mitch et al., 2003a). The formation of NDMA in drinking water treatment processes is typically associated with chloramine disinfection (Mitch et al., 2003b; Sacher et al., 2008). The dominant NDMA formation mechanism involves a slow reaction between chloramines and amine-based precursors (Schreiber and Mitch, 2006). While investigating potential NDMA precursors, previous studies have focused on the model precursor dimethylamine (DMA) (Gerecke and Sedlak, 2003) and other secondary amines (Schreiber and Mitch, 2006), tertiary and quaternary amines containing a DMA moiety (Kemper et al., 2010; Lee et al., 2007), natural organic matter (NOM) (Chen and Valentine, 2008; Mitch et al., 2009), as well as quaternary amine-based coagulants (Park et al., 2009), and anion exchange resins (Kemper et al., 2009) that are used in water treatment processes. Recent studies have demonstrated that pharmaceuticals and personal care products (PPCPs) with substituted amine groups may serve as significant precursors to NDMA formation upon chloramine disinfection (Le Roux et al., 2011; Shen and Andrews, 2011, 2013).

One approach to minimize the formation of NDMA during water treatment is to physically remove precursors prior to chloramination. Previous studies have investigated various precursor treatment options that might result in reduced NDMA formation potential (NDMA-FP). NDMA-FP was slightly reduced (<10%) during conventional treatment using coagulation (Krasner et al., 2008); however, the application of amine-based coagulation polymers caused an increase (>43%) in NDMA-FP (Mitch et al., 2009). Adsorption of NDMA precursors onto granular and powdered activated carbon (GAC and PAC, respectively) as well as

* Corresponding author.
E-mail address: Gwen.Woods-Chabane@HDRinc.com (G.C. Woods).
[1] Present address: HDR Engineering, 431 W Baseline Road, Claremont, CA 91711, United States.

http://dx.doi.org/10.1016/j.watres.2016.02.002
0043-1354/

biological activated carbon (BAC) has been demonstrated as an effective strategy for the reduction of NDMA-FP values (up to 80%) (Farré et al., 2011; Hanigan et al., 2012); however, the efficiency of activated carbon is greatly affected by adsorbate physicochemical properties and water composition (Huerta-Fontela et al., 2011; Verliefde et al., 2007). When considering pre-oxidation of NDMA precursors over typical dosages applied for disinfection, ozone and chlorine have been reported to be more effective oxidants when compared to chlorine dioxide, UV, and $KMnO_4$ (Chen and Valentine, 2008; Krasner et al., 2013; Shah and Mitch, 2012). Pre-oxidation processes, however, may result in the formation of toxic transformation products (Radjenovic et al., 2009; Rivera-Utrilla et al., 2013) and other DBPs associated with each pre-oxidant (Shah et al., 2012). Limited research has probed NDMA precursor removals using membranes and has demonstrated an average of 50%–>98% removal of precursors by microfiltration (MF) and reverse osmosis (RO) membranes, respectively (Miyashita et al., 2009; Sedlak and Kavanaugh, 2005). Nevertheless, there is a lack of studies regarding the impact of membrane treatment on NDMA formation during drinking water production, specifically, when considering the importance of PPCP-based NDMA precursors. This study investigated the rejection of pharmaceutically-based NDMA precursors by nanofiltration and subsequent reduction of NDMA-FP that results from chloramine disinfection when treating surface waters. This approach is useful to verify the ability of a given membrane to reject NDMA–specific precursors without using the laborious analytical techniques required to measure many pharmaceutical precursors, and is also applicable for complex sample matrices with unknown precursors present (e.g., wastewater).

2. Material and methods

2.1. Selected nanofiltration membrane

A polyamide nanofiltration (NF) membrane (NE70, NE 4040-70, Saehan-CSM Membranes, Woongjin Chemical America, Inc., CA, USA) was used to investigate the removal of NDMA precursors. Due to the large molecular weight cut-off (MWCO = 350 Da) of the membrane, filtration could be conducted at a lower pressure and potential operating costs when compared to using tight NF or RO membranes.

2.2. Selected pharmaceuticals

Three pharmaceuticals containing DMA groups, previously demonstrated as significant NDMA precursors (Shen and Andrews, 2011), were selected for this study (Table 1). The MWs (≤332 g/mol) of the compounds were less than the MWCO of the selected membrane (350 Da). Past research (Sadmani et al., 2014a,b,c) has suggested that high rejections (up to 96%) of pharmaceuticals with MWs smaller than the membrane MWCO were achievable due to enhanced size and/or charge effects resulting from the compounds' complexations with natural water components.

2.3. Characterization of source water matrices

Two lake waters (Lake Ontario and Lake Simcoe) that serve as drinking water sources for millions of Southern Ontario (Canada) residents, were selected for the current study and sampled in August–September, 2015. Lake Ontario and Lake Simcoe waters were collected from the Ajax Water Supply Plant (Ajax, Ontario) and Barrie South Surface Water Treatment Plant (Barrie, Ontario), respectively. These waters represent a range of water matrix characteristics (Table 2), with further FEEM and LC-OCD characterization provided in Table S1. A laboratory-prepared water (Milli Q®) was used as well to serve as a control. Total organic carbon (TOC) and dissolved organic carbon (DOC) (0.45 μm filtered) were analyzed using an Aurora 1030 TOC analyzer (O–I Corporation, College Station, TX, USA) following Standard Method 5310 D (APHA, 2005). UVA at 254 nm was measured using a diode array spectrophotometer (Hewlett Packard 8452A, Mississauga, ON, Canada). Fluorescence excitation-emission matrix (FEEM) spectra were obtained using an Agilent Cary Eclipse spectrofluorometer with excitation (230–380 nm) and emission (250–600 nm) wavelength ranges and increments (10 nm) set, with Raman corrections applied based on the methods discussed in Peiris et al. (2009, 2010). Liquid chromatography-organic carbon detection (LC-OCD) analyses of feedwater samples were performed using a DOC-Labor System (Karlsruhe, Germany) following the protocol developed by Huber et al. (2011). The inductively coupled plasma (ICP) method described in Standard Method 3120 B (APHA, 2005) was applied on an ICP-atomic absorption optical spectrometer (Optima 7300 DV Perkin–Elmer, Shelton, CT) to analyze cations in the water matrices.

2.4. Experimental protocol and nanofiltration set-up

2.4.1. Precursor removal

The selected pharmaceuticals were spiked, at a concentration of 25 nM, into MQ or surface waters that were adjusted to pH 8. Nanofiltration experiments were conducted using a bench-scale, flat-sheet membrane filtration apparatus consisting of three stainless steel cross-flow membrane cells (Sepa CF II, Steriltech Corp., Kent, WA, USA), a constant flow diaphragm pump, a piston pump, pressure gages, flow meters, a chiller/heater, stainless steel storage and equalization tanks, and stainless steel tubings (Fig. 1). The membrane surface was 155 cm^2 for each of the 3 membrane cells. Filtration was carried out at a system recovery of ~50% (recovery = permeate flow/influent flow), which is within the range practiced in full-scale systems (30–90%) (DiGiano et al., 2000). Pressure was held constant at 60 psi for all experiments, and the pure water permeability of the NE 70 membrane was measured as 11.3 ± 0.3 Lm^{-2} h^{-1} bar^{-1}. The membrane operating conditions were not varied so that the impact of water matrices could be investigated under the same operating conditions.

Experiments were conducted with triplicate permeate samples (i.e., the 3 parallel membrane cells), and with feed and equalization tank samples collected in duplicate. Overall, thirteen rejection experiments were conducted: nine experiments with the three pharmaceuticals spiked individually into each of the three waters (MQ, Lake Ontario, and Lake Simcoe waters), and four experiments with mixtures of the compounds spiked into feedwaters. Percent recovery was determined based upon Eq. (1) below. In order to account for potential water matrix effects on NDMA formation from chloramination, system blank trials were also conducted. These included running Lake Ontario and Lake Simcoe waters through the membrane independently, then spiking pharmaceuticals into feed and permeate samples, and conducting NDMA formation potential (NDMA-FP) tests to evaluate the effect of feed and permeate matrices on NDMA formation. The molar conversion of known concentrations of each compound in both lake waters was compared to molar conversion in MQ. The matrix effects were normalized to NDMA formation in MQ according to Eq. (2) below. The resulting adjustment factors were subsequently multiplied by data obtained from lake water experiments.