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N-Nitrosodimethylamine (NDMA) Precursors Leach from Nanofiltration Membranes

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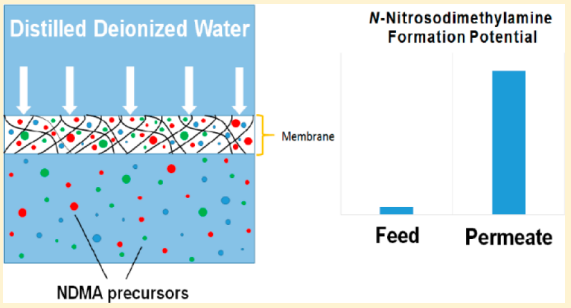
Supporting Information

ABSTRACT: Membrane filtration processes have been widely used as effective means of providing safe and reliable water for both potable and nonpotable purposes. In our laboratory, we have observed that *N*-nitrosodimethylamine (NDMA) precursors leach from virgin membranes. Therefore, in this study, we aimed to examine (i) the potential leaching of NDMA precursors from different types of nanofiltration membranes and (ii) membrane cleaning techniques using different types of background solutions to prevent the leaching. The results showed that for three different types of nanofiltration membranes, leaching of high levels of NDMA precursors (~180−450 ng/L) was observed. Leaching continued even after membranes had been washed with ~3900 L of distilled deionized water/m^2. Among various cleaning techniques, washing the membrane with a 1 mg/L Cl_2 solution was found to be the most effective for reducing the extent of NDMA precursor leaching.



INTRODUCTION

N-Nitrosodimethylamine (NDMA) forms during drinking water and wastewater treatment, mainly as a result of reactions between chloramines and organic nitrogen-containing precursors.[1,2] NDMA has been the dominant specific *N*-nitrosamine detected in U.S. distribution systems where monochloramine is used as the postdisinfectant.[3] A lifetime cancer risk of 10^{-6} was estimated by the U.S. Environmental Protection Agency (USEPA) for exposure to drinking water containing 0.7 ng/L NDMA.[4] Because of health concerns, the California Department of Health Services set an NDMA action level of 10 ng/L.[5] Though there has not been a federal regulation for nitrosamines in drinking water in the United States, the USEPA currently considers nitrosamines as one of the potential groups of contaminants for future regulatory action.[6]

NDMA precursor sources can be classified into two main categories: natural and anthropogenic. Algae, natural organic matter (NOM) and its fractions,[7−11] dissolved organic nitrogen in natural waters, and soluble microbial products have been considered as natural sources of NDMA precursors. Amine-containing polymers,[12−14] anion exchange resins,[15] pharmaceuticals and personal care products, fungicides, pesticides, and herbicides,[16,17] effluent-impacted waters,[19−21] and constituents released from different materials (rubber seals, gaskets, etc.)[22,23] have been identified as anthropogenic sources of NDMA precursors.

Nanofiltration (NF) membranes are widely used in water treatment because of their ability to remove various contaminants, including harmful trace organics, viruses, and dissolved organic matter. NF membranes are generally made from polyamide composites, cellulose acetate blends, and polypiperazine amide; however, the exact chemistry is wide-ranging, and several additives and surface-coating substances are employed.[24] Any noncovalently bound chemicals can potentially be released to the product water during membrane filtration. Whether some of the chemicals released from NF membranes (or any membranes, for that matter) are precursors to NDMA formation has not been addressed previously. Some studies have been conducted on the removal of NDMA precursors by membranes,[18,25] but these did not mention NDMA precursor leaching either because they conducted the experiments to examine the removal of model NDMA precursors or the NDMA formation potential tests were conducted after a long period of membrane module operation.

This paper adds knowledge to the literature in two ways: (i) evaluation of potential leaching of *N*-nitrosodimethylamine (NDMA) precursors from different types of NF membranes and (ii) investigation of cleaning techniques to minimize leaching.

MATERIALS AND METHODS

Five commercially available NF membranes (ESNA 1 LF2, NF 270, TS40, TS80, and SB90) made of different materials (polyamide, polypiperazine amide, and cellulose acetate) were obtained (Table 1). All filtration experiments were conducted under a constant operating pressure of 34.5 bar (500 psi) using a cross-flow filtration cell described elsewhere.[26] The effective area of the membrane cell was 140 cm^2. During filtration experiments, 500 mL samples were collected from the permeate side of the membranes in different intervals and NDMA

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Table 1. Characteristics of NF Membranes

Designation	Manufacturer	Polymer type	Molecular weight cutoff (Da)	NaCl Rejection (%)	pH range (25 °C)	Typical flux (L m^{-2} h^{-1}/psi)
ESNA 1-LF2	Hydranautics	polyamide	200	80	2−10	21/75
NF270	Dow Filmtech	polyamide	200−400	99.2	2−11	72−98/130
TS40	Trisep	polypiperazine amide	200	40−60	2−11	34/110
TS80	Trisep	polyamide	150	80−90	2−11	34/110
SB90	Trisep	cellulose acetate	150	85	−	51/225

formation potential (NDMA FP) tests were conducted. A detailed explanation of the method was provided elsewhere.[15,28] In brief, during the FP tests, collected permeate samples were reacted with an excess chloramine solution (100 mg/L as Cl_2) at pH 7.8 in the presence of a phosphate buffer and stored in the dark for 5 days to provide complete reaction of NDMA precursors with chloramine to yield NDMA. In this study, it should be noted that the NDMA FP tests were conducted under an excess chloramine dose (100 mg/L as Cl_2) rather than practical doses (2−3 mg/L) to determine the highest concentration of NDMA that could form. Before each filtration experiment, NDMA FP tests were conducted for distilled and deionized (DDI) water to determine initial, background levels. NDMA was analyzed during the formation potential experiments following USEPA Method 521.[27] After 5 days of reaction time, residual chloramine concentrations were measured and samples were quenched accordingly with sodium thiosulfate. Prior to extraction, *N*-nitrosodimethylamine-d_6 (NDMA-d_6) was added to the quenched samples as a surrogate. NDMA was extracted from water samples by solid-phase extraction. The extracts were spiked with *N*-nitrosodi-*n*-propylamine-d_{14} (NDPA-d_{14}) as an internal standard and analyzed using a Varian GC 3800-MS/MS 4000 instrument equipped with an RTX-5MS (Restek 30 m, 0.25 mm, 0.25 mm) column in chemical ionization mode. The minimal reporting level of the method was determined to be 3 ng/L (Table S1 of the Supporting Information). In this study, NDMA FP tests were conducted for each sample with two measurements. The bars in data plots represent mean values, and the error bars show the data range.

Membrane Cleaning Procedures. Membranes were cleaned using three procedures: (1) distilled and deionized (DDI) water alone, (2) sequential application of base (NaOH at pH 10.5) and acid (HCl at pH 2.5), and (3) 1 mg/L free chlorine (as NaOCl). During the study, the pH values of the DDI water and chlorine cleaning solution were 6.8 and 8.1, respectively. At the end of each cleaning procedure, membranes were thoroughly rinsed with DDI water until no residual cleaning chemical remained in the permeate water. Residuals of acid−base and chlorine cleaning were monitored in the permeate by measuring pH and chlorine levels, respectively. Chlorine was determined following Standard Method 4500-Cl F.[29]

RESULTS AND DISCUSSION

Figure 1 displays the NDMA formation potential leaching from NF membranes as a function of DDI water volume passed through the membranes. Regardless of the membrane type, leaching of NDMA precursors (>150 ng/L NDMA FP) from membranes was observed. NDMA precursor leaching potentials of membranes were also investigated for various brands in a subsequent set of experiments (Figure 2). The results suggest that the leaching phenomenon was not specific to one single manufacturer. Also, variability was observed in the leaching

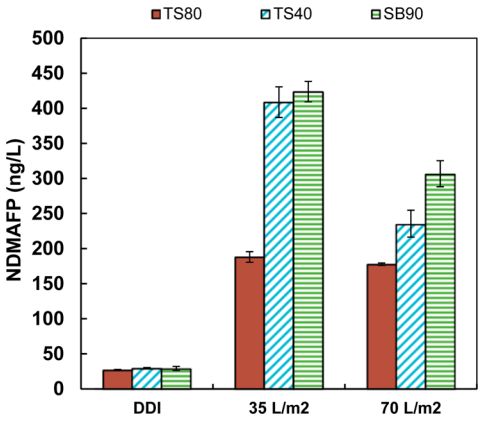

Figure 1. Leaching potentials of NF membranes for different materials.

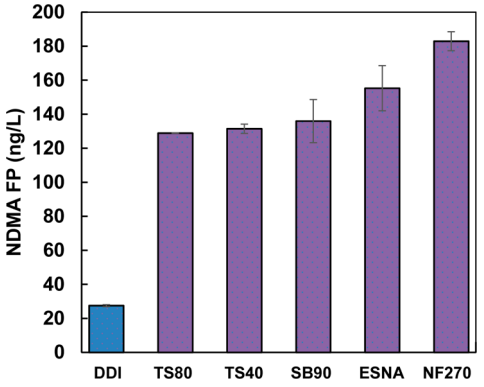

Figure 2. Leaching potentials of NF membranes for different manufacturers.

from different coupons of the same membrane. While the specific source of precursors is unknown, a possible explanation is that precursor leaching is caused by incomplete reactions of polymers or additives in the manufacturing process. Precursors could come from the active layer or the support layers of the membrane. The release of NDMA precursors from membranes was also monitored during wetting of membranes overnight in a glass jar filled with DDI water; however, the NDMA formation potential of the DDI water did not increase. Pressure and flux were required to release the precursors, suggesting that they were tightly entrapped within the polymeric structure.

To further investigate the leaching potential and cleaning of the TS80 and TS40 membranes, a large volume of water was processed (Figure S1 of the Supporting Information). The initial permeate NDMA FP dropped rapidly after passing 350 L m^{-2} h^{-1} of DDI water. Leaching continued through duration of the experiment (up to 3900 L m^{-2} h^{-1}), but the FP levels were approaching those of DDI water. In Figure S1 of the Supporting Information, the total time spent for filtration was around 26 h and the flux observed during filtration was around 155 L m^{-2} h^{-1}. This suggests that under full-scale operation

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fluxes (approximately 15−25 L m^{-2} h^{-1}), reduction in precursor levels to below the observed values at 3900 L m^{-2} h^{-1} (Figure S1 of the Supporting Information) may take more than 26 h. However, predicting the actual occurrence at full scale is beyond the scope of this paper; further site-specific measurements would be needed.

In practice, acidic and basic solutions are used to remove foulants from membranes.[30] In this study, the effectiveness of acids and bases for the removal of NDMA precursors from membranes was tested for the TS80 polyamide membrane. Initially, the pH of the DDI water solution was adjusted to 10.5, and then the solution was passed through the membrane. Results showed that passing the basic solution reduced the amount of NDMA FP leaching from the membrane to ∼70 ng/L, which was still above the DDI water FP level. Afterward, the feed solution was replaced with a pH 2.5 solution and passed through the polyamide membrane. Here there was an initial increase in the NDMA FP of the permeate, which then decreased to the levels of the basic cleaning (Figure S2 of the Supporting Information). In summary, neither basic nor acidic conditions reduced FP leaching below that of DI water flushing. It will be interesting to determine whether this result holds for other membrane materials.

It is known that chlorination reduces the formation of NDMA by deactivating its precursors.[28,31] Therefore, the effectiveness of chlorine on deactivation of NDMA precursors was investigated using 1 mg/L chlorine containing a DDI water feed solution that was passed through all three (TS80, TS40, and SB90) membranes. As a result of this cleaning, the NDMA precursor leaching potential of TS80, TS40, and SB90 membranes significantly decreased, and NDMA FP levels in the permeate solutions approached the NDMA FP level of DDI water (Figure 3). After the membrane had been cleaned with a

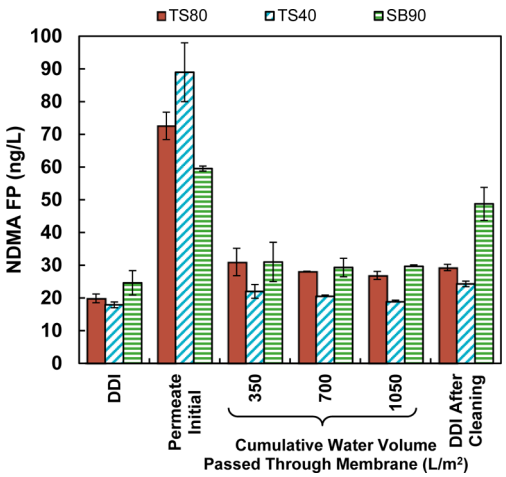

Figure 3. Cl_2 and DDI water cleaning of TS80, TS40, and SB90 membranes.

1 mg/L chlorine solution, the system was flushed with DDI water to remove residual chlorine, and then a DDI water feed solution with no chlorine was passed through the membranes to evaluate whether the leaching of the precursor ceased. Results showed that while the permeate NDMA FP values of TS80 and TS40 membranes were close to DDI water levels, the SB90 membrane had an increase in NDMA FP. One plausible explanation may be the chlorine concentration was insufficient to completely deactivate or remove NDMA precursors from the SB90 membrane because of the nature and quantity of precursors in the SB90 material. The effect of chlorine cleaning on the polyamide membrane surface chemistry was also examined with ATR-FTIR and ζ potential measurements. These techniques revealed that chlorine cleaning did not make a measurable impact on the surface characteristics of the studied membrane (Figures S3 and S4 of the Supporting Information). Furthermore, a comparison of the absolute flux and salt rejection for chlorine exposed and DDI water was made. Membrane flux and salt rejection also were not significantly altered by the 1 mg/L chlorine cleaning (Figures S5 and S6 of the Supporting Information). These findings are limited to the membrane studied here and to the chlorine dose (1 mg/L) and contact time (permeation for 1.8 h) used. Other membranes may be less chlorine tolerant, and larger doses may be problematic. However, some currently available membranes produced for water and wastewater treatment have a maximal continuous chlorine tolerance of 1−10 ppm to allow for cleaning (and prevention) of biofouling.[32] If NDMA precursors leach from those membranes, they could likely be eliminated by chlorination with little or no risk of membrane damage.

This study showed that NDMA precursors leach from five different NF membranes (three materials) that were obtained from three different membrane manufacturers; thus, it is important to pay attention to the leaching of such precursors in both laboratory NDMA studies and practical applications. Previous researchers also investigated the leaching potentials of different water treatment chemicals such as resins and polymers. The results indicated that application of these chemicals during water treatment enhanced NDMA precursor concentrations in the treated water effluent from low levels (∼20 ng/L) to very high levels (∼600 ng/L).[15,33] Therefore, the detected levels of NDMA leached from resins and polymers were comparable to levels observed in this study (∼50−550 ng/L). While long-term use of the membranes will likely wash out all of the available precursors, NDMA formed during the startup period of a membrane unit process could be significant if chloramine is used as a disinfectant. It should be noted that the observed high NDMA FPs in this study, at large chloramine doses (100 mg/L as Cl_2), may or may not be a concern for the water treatment facilities because of the small chloramine doses applied in practice (usually 2−3 mg/L). The actual NDMA concentrations in real plants would be lower than the concentrations observed in these experiments. Washing membranes with a small dose of chlorine (e.g., 1 mg/L) is suggested here as one possible method for minimizing the leaching of NDMA precursors from TS80 and TS40 NF membranes. This idea is supported in a "proof-of-concept" manner and would need to be further evaluated in practice. Alternatively, chlorination of downstream (prior to the addition of ammonia for chloramination) may also be a viable option for reducing the level of formation of NDMA in the product water, as long as it does not result in high levels of regulated DBPs (i.e., THMs and HAAs). Lastly, leaching of NDMA FP from membranes should be considered during laboratory testing and research related to NDMA.

■ ASSOCIATED CONTENT

Supporting Information

Large volume DDI water (TS80−TS40) and base−acid cleaning data (TS80), ATR-FTIR spectrum, and ζ potential measurements for the TS80 membrane; absolute fluxes and salt rejection results for chlorine-treated and untreated TS80

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membrane; a comparison of chlorine and DDI water wash; and detection and minimal reporting limits of NDMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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