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N-nitrosamine rejection by reverse osmosis: Effects of membrane exposure to chemical cleaning reagents

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HIGHLIGHTS

- Caustic cleaning exerted notable changes to permeability & N-nitrosamine rejection.
- No changes in the bonding structure of the polyamide active layer were observed.
- Caustic followed by acidic cleaning could alleviate the impact of caustic cleaning.

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ABSTRACT

The impact of chemical cleaning on the removal of N-nitrosamines by low pressure reverse osmosis (RO) membranes was investigated. The results show that caustic chemical cleaning resulted in an increase in membrane permeability but caused a notable decrease in the rejection of N-nitrosamines. The impact of caustic chemical cleaning was particularly obvious for N-nitrosodimethylamine (NDMA) and N-nitrosomethylethylamine (NMEA), which have the lowest molecular weight amongst the N-nitrosamines investigated in this study. A correlation between the increase in permeability and the decrease in the rejection of either NDMA or NMEA could be observed. The rejection of conductivity also decreased as the membrane permeability increased, indicating that conductivity rejection can be an indicative parameter of predicting changes in NDMA and NMEA rejection during RO plant operation. The impact of caustic cleaning was not permanent and could be significantly reduced by a subsequent acidic cleaning step.

1. Introduction

Potable water reuse has been recognised as an effective and reliable measure to augment the supply of drinking water in many parts of the world where fresh water resources are under severe stress [1]. In this practice, reservoirs or underground aquifers are replenished with high quality reclaimed water. The reclamation of water for potable purposes is accomplished by an array of several advanced treatment processes such as reverse osmosis (RO), activated carbon adsorption, and advanced oxidation [1,2]. The deployment of these advanced treatment processes is to ensure effective removal of pathogenic agents and trace organic chemicals of concern. Notable examples of these trace organic chemicals are N-nitrosodimethylamine (NDMA) and several other N-nitrosamines. Other N-nitrosamines that have previously been reported in treated wastewater include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), and N-nitrosodiphenylamine (NDPhA) [3–7]. Some of these N-nitrosamines have also been identified as potential human carcinogens and their concentrations in reclaimed water intended for potable reuse have been regulated in Australia and several other countries at 10 ng/L or less [8].

RO is a key treatment process in water reclamation applications for the removal of organic matter, inorganic salts and trace organic chemicals [9–11]. Due to its high performance on solute separation, RO process in water reclamation plants is also accounted for some degrees of N-nitrosamine removal from the reclaimed water which is used for the augmentation of drinking water source. Nevertheless, the removal of NDMA by the RO process appears to be highly variable. For example, NDMA rejections by the same type of RO membranes reported

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from pilot- and full-scale studies range from negligible to 86% [12]. On the other hand, NDMA rejections by RO membranes obtained from laboratory-scale experiments varied from 50 to 70% [13–15]. In recent studies, Fujioka et al. [13,16] reported that changes in pH, ionic strength and temperature of the feed as well as membrane fouling can significantly affect NDMA rejection by RO membranes. These results can account for some but not all of the discrepancy in the rejection values of NDMA by RO membranes reported in the literature.

In addition to feed solution characteristics and operating conditions, the separation performance of RO membranes may also be affected by the alteration of membrane surface characteristics particularly caused by chemical cleaning. Because membrane fouling is an inherent phenomenon in almost all pressure driven membrane processes, chemical cleaning is inevitable. Typical cleaning chemicals include sodium hydroxide (NaOH) citric acid (CA), hydrochloric acid (HCl) and ethylenediaminetetraacetic acid (EDTA) [17,18]. Although chemical cleaning can restore the performance of RO membranes exposed to wastewater foulants [19,20], it may also modify polyamide membrane structures, resulting in an increase in permeability or decrease in salt rejection [17]. Simon et al. [21] investigated the effects of chemical cleaning by exposing a NF270 nanofiltration membrane to several cleaning reagents (i.e., NaOH, CA, sodium dodecyl sulphate (SDS) and EDTA) and reported that these chemical cleaning agents (with the exception of CA) increased membrane permeability by up to 30%. Simon et al. [21] reported that the rejection of neutral solutes was more significantly affected by chemical cleaning than that of charged compounds. When the NF270 membrane was exposed to NaOH solution (pH 12), its permeability increased by 30% and the rejection of carbamazepine (molecular weight 253.3 g/mol) decreased from 80 to 50%. Thus, periodical chemical cleaning can potentially lead to a decrease in the rejection of N-nitrosamines including NDMA in full-scale RO installations. Nevertheless, to date, the impact of chemical cleaning on the rejection of N-nitrosamines by RO membranes has not been fully understood.

The aim of this study was to provide a comprehensive understanding of the effects of chemical cleaning on the rejection of N-nitrosamines by RO membranes. The cleaning agents used in this investigation include three general cleaning chemical solutions (NaOH, HCl, CA) and three proprietary cleaning solutions. The impact of chemical cleaning was elucidated by examining the membrane pure water permeability, surface charge through zeta potential measurements, and separation performances of salts and select organic solutes.

2. Materials and methods

2.1. RO membranes

Two low pressure RO membranes – namely TFC-HR (Koch Membrane Systems, San Diego, CA, USA) and ESPA2 (Hydranautics, Oceanside, CA, USA) – were used in this study. They are classified as thin-film composite membranes that consist of an ultrathin polyamide active layer on top of a porous polysulfone support layer. These membranes are commonly deployed in several full-scale RO plants for potable water reuse applications in the USA and Australia [22,23].

2.2. Chemicals

Eight N-nitrosamines (Supplementary material Fig. S1) were purchased from Sigma-Aldrich (St. Louis, MO, USA) as analytical grade standards. Their molecular weight ranges from 74 to 158 g/mol. Further description of their physicochemical properties can be found elsewhere [13]. An N-nitrosamine stock solution containing 10 mg/L of each N-nitrosamine was prepared in pure methanol. A surrogate stock solution of 100 μg/L of each deuterated N-nitrosamines (N-nitrosodimethylamine-D6, N-nitrosomethylethylamine-D3, N-nitrosopyrrolidine-D8, N-nitrosodiethylamine-D10, N-nitrosopiperidine-D10, N-nitrosomorpholine-D8, N-nitrosodipropylamine-D14 and N-nitrosodi-n-butylamine-D9) was also prepared in pure methanol. The deuterated N-nitrosamines supplied by CDN isotopes (Pointe-Claire, Quebec, Canada). These stock solutions were kept at −18 °C in the dark and were used within 1 month of preparation.

Six chemical cleaning agents were used in this investigation (Table 1). Analytical grade NaOH, HCl and CA from Ajax Finechem (Taren Point, NSW, Australia) were used as cleaning reagents based on recommendations from the membrane manufacturers (Supplementary material Table S2). The cleaning solution was prepared by dissolving the reagent in Milli-Q water. Three proprietary formulations designed for membrane cleaning in full-scale RO plants were also used. They are referred to as MC3, MC11 and PC98. Floclean® MC3 is an acidic based while Floclean® MC11 and PermaClean® PC98 are caustic based chemical cleaning formulations. MC3 and MC11 were supplied in powder form and the cleaning solution was prepared at 25 g/L as recommended by the manufacturer. PC98 was supplied in liquid form and was prepared at 4% (w/w) as recommended by the manufacturer.

2.3. Membrane filtration system

A laboratory scale cross-flow RO filtration system was used for this investigation (Supplementary material Fig. S3). The membrane cell was made of stainless steel and could hold a 4 cm × 10 cm flat sheet membrane sample. The channel height of the cell was 2 mm. The feed solution was fed from a stainless steel reservoir to the membrane cell by a high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA). The permeate flow rate and cross flow velocity were regulated by adjusting a bypass valve and back-pressure valve (Swagelok, Solon, OH, USA). The permeate flow was continuously monitored with a digital flow meter (FlowCal, GJC Instruments Ltd., Cheshire, UK) and the retentate flow was monitored with a rotameter. Feed solution temperature was controlled in the feed reservoir using stainless steel heat exchanging pipes connected to a chillier/heater unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA).

2.4. Simulated chemical cleaning protocols

Chemical cleaning was simulated by immersing a membrane sample in a glass container containing a cleaning chemical solution. The flat sheet membrane samples were first rinsed with Milli-Q water to remove any preservative materials from the membrane surface. In addition to these cleaning chemical solutions, Milli-Q water was also used for cleaning to obtain control membrane samples, and these control samples are designated as virgin membrane in this study. The containers were submerged in a temperature-controlled water bath (SWB1, Stuart®, Staffordshire, UK) and the temperature was maintained at 30 ± 0.5 °C according to the membrane manufacturer's recommendation (Supplementary material Table S2). The simulated cleaning was carried out for 25 h. This cleaning simulation over 25 h

Table 1
Properties of the selected cleaning solutions.

Chemical	pH	Chemical formula/ingredients	Abbreviation
Sodium hydroxide	12.0	NaOH	NaOH
Chloridric acid	2.1	HCl	HCl
Citric acid	2.1	$C_6H_8O_7$	CA
Floclean® MC3	3.3	Organic acids and chelating agents containing tripolyphosphate (SDP)	MC3
Floclean® MC11	11	Detergent builders, pH buffer, chelating agents containing EDTA, SDP and sodium trisodium phosphate	MC11
PermaClean® PC98	10.7	Amphoteric surfactant and chelating agents containing EDTA	PC98