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Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications

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Abstract

Commercial polyamide nanofiltration (NF), reverse osmosis (RO), and ultra-low pressure RO (ULPRO) membranes (NF-90, NF-200, TFC-HR, and XLE) as well as a cellulose triacetate RO membrane (CTA) were employed to investigate the effect of fouling on transport of organic micropollutants. Due to foulant precipitation and cake-layer formation, membrane surface characteristics changed considerably in terms of contact angle (an index of hydrophobicity), zeta-potential, functionality, and surface morphology, which potentially affected transport of contaminants as compared to unfouled (virgin) membranes. The transport of ionic organic micropollutants was hindered as a result of improved Donnan exclusion (electrostatic repulsion) likely due to a more negative surface charge as quantified by zeta-potential measurements. Membrane fouling also resulted in an increased adsorption capacity and reduced mass transport through partitioning and diffusion of solutes across the membrane. These effects led to an increase in rejection of hydrophobic non-ionic solutes (e.g., disinfection byproducts and chlorinated solvents) by fouled membranes. However, the increasing surface charge has the potential to result in a larger molecular weight cut-off of a fouled membrane due to membrane swelling, which can lead to lower rejection for hydrophilic non-ionic solutes, especially where nanofiltration membranes with a larger molecular weight cut-off are employed. Membrane fouling facilitated the transport of hydrophobic and hydrophilic organic contaminants through CTA membranes resulting in elevated concentrations of target solutes in the permeate. Findings of the study indicate that membrane fouling significantly affects the rejection of organic solute by CTA, NF, and ULPRO membranes while it is less important for thin film composite RO membranes.

Keywords: Membrane fouling; Emerging organic contaminants; Reverse osmosis; Nanofiltration

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1. Introduction

Integrated membrane systems (IMS), such as microfiltration (MF) followed by nanofiltration (NF) or reverse osmosis (RO), are considered the industry standard for augmentation of drinking water supplies with sources of impaired quality. The removal efficiencies of IMS for organic micropollutants are drawing more attention due to the potential adverse ecological and human health effects associated with the presence of certain emerging contaminants. The rejection of trace organic compounds by NF/RO membranes represents a complex interaction of steric hindrance, Donnan exclusion, solution effects on the membrane, and solute/membrane properties [1]. Although previous studies have contributed greatly to the current knowledge base regarding the separation of emerging organic pollutants, little is known about the rejection of commercially available membranes under fouled conditions representative of full-scale operation.

Membrane fouling is considered a major obstacle for efficient membrane operation due to declining permeate flux, increased operational cost, and shortened membrane life [2–5]. Water constituents such as particles, colloids, salts, natural organic matter (NOM), and soluble microbial products derived from biological wastewater treatment can adsorb and deposit onto membrane surfaces resulting in membrane fouling. Previous studies have demonstrated that membrane fouling and the characteristics of foulants are determined by feedwater composition, the concentration of the constituents (such as colloids, hydrophilic carbon, and hydrophobic organic matter), water chemistry (pH,

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ionic strength, and divalent cation concentration), membrane properties (surface morphology, hydrophobicity, and charge), temperature, and hydrodynamic conditions (initial permeate flux and cross-flow velocity) [3,6–9].

Due to foulant precipitation and cake-layer formation, membrane surface characteristics can change significantly. Roudman and DiGiano found a significant increase in hydrophobicity for nanofiltration membranes after adsorption of NOM [10]. Cho et al. reported that NOM fouling caused both a reduction in negative surface charge and a decrease of the hydrophobicity of hydrophobic membranes and an increase of the hydrophobicity of hydrophilic membranes [11]. The surface charge of a NF membrane and an UF membrane became very similar after adsorption of NOM [12]. The roughness of RO membranes increased by five to six times in a whey concentration process as a result of additive and protein adsorption [13]. Findings of these studies imply that membrane fouling has the potential to affect rejection mechanisms of organic solutes as a result of modified electrostatic, steric, and hydrophobic/hydrophobic solute–membrane interactions.

Up to date, most research studies attempting to relate physical–chemical properties of solutes and membranes to solute rejection were conducted with virgin membranes without taking into account the change of membrane properties as a result of membrane fouling during long-term operation [14–19]. Given the limited studies on the role of physical–chemical interactions between fouled membranes and organic micropollutants, the objectives of the study were two-fold—to characterize change of membrane surface properties due to adhesion of foulants; and to investigate the interactions between foulants–membranes and contaminants–foulants–membranes.

2. Methods and materials

2.1. Indicator compounds

The indicator compounds for this study were chosen to represent the physical–chemical properties of emerging organic contaminants, such as molecular weight, molecular size, hydrophobicity (in terms of the octanol–water partitioning coefficient, i.e., $\log K_{\mathrm{ow}}$) and acid dissociation constant ($\mathrm{p}K_{\mathrm{a}}$). Table 1 summarizes the properties of the selected solutes. The disinfection by-products (DBPs) bromoform and chloroform and the organic solvent trichloroethylene were selected as hydrophobic non-ionic indicators with $\log K_{\mathrm{ow}}$ values above 2. The aromatic acids 2-naphthalenesulfonic acid (NSA) and 2,4-dihydroxybenzoic acid (DHB) were deprotonated in the experimental pH range of 3–9, and representative of negatively charged compounds. The anti-epileptic drug primidone is not dissociable and with a $\log K_{\mathrm{ow}}$ value of 0.91 represented hydrophilic non-ionic solutes. The molecular weights of the indicator compounds were in the range of 119–253 g/mol, representative of compounds partially removed by common RO and NF membranes with molecular weight cut-off (MWCO) from 100 to 300 Da. The molecular widths of the compounds varied from 2.70 to 6.23 Å, while the nanopores of the commercial RO and NF membranes employed were determined to vary between 2.2 and 12 Å [20].

2.2. Reagents and analytical methods

All chemicals used were of reagent grade or higher, purchased from Sigma–Aldrich (Louis, MO), Chem Service (Chester, PA), and Fisher Scientific Inc. (Fairlawn, NJ). Type I water was Milli-Q grade obtained from an ultrapure laboratory water purification system (Barnstead, Dubuque, IA).

Concentrations of 2-naphthalenesulfonic acid and 2,4-dihydroxybenzoic acid were quantified using a 1046A Hewlett-Packard fluorescence detector (Hewlett-Packard, Wilmington, DE) at excitation/emission wavelengths of 320/370 and 314/390 nm, respectively. Primidone was extracted and separated from water samples by solid phase extraction using one gram of RP-C-18 material (Bakerbond Polar Plus, Mallinckrodt-Baker, Phillipsburg, NJ). Primidone was detected by a Hewlett-Packard Series 1100 HPLC (Wilmington, DE) equipped with a reverse phase column (Supelco Discovery C-18, particle size 5 μm, pore size 180 Å, 25 cm × 4.6 mm), and an ultraviolet (UV) detector (at 220.2 nm). Bromoform, chloroform, and trichloroethylene were quantified according to EPA method 551.1 for trihalomethanes (THMs) using a HP 6890 series gas chromotograph with a micro electron capture detector (Wilmington, DE).

Conductivity was measured using an electrical conductivity meter (Cole-Parmer, Vernon Hills, IL). pH was determined using an Accumet AP63 portable pH meter (Fisher Scientific, Pittsburgh, PA). Ultraviolet absorbance (UVA) at the wavelength of 254 nm was analyzed using a Nicolet 8740 UV/vis spectrophotometer (Nicolet Instruments of Discovery, Madison, WI) with a 1-cm quartz cell for feed and a 4-cm quartz cell for permeate samples. Dissolved total organic carbon (TOC) was quantified using a Sievers 800 TOC analyzer with autosampler (Ionics Instruments, Boulder, CO).

2.3. Target membranes and characterization

The selected membranes are commercially available membranes representing different properties, including two NF membranes (manufacturer reported NF-90 with MWCO of 200 Da and NF-200 with MWCO of 300 Da), one ultra-low pressure RO (ULPRO) membrane (XLE) manufactured by DOW/Filmtec (Edna, MN), and two RO membranes (TFC-HR and CTA) from Koch Membrane Systems (San Diego, CA). The physical–chemical properties of the virgin membranes are summarized in Table 2.

Prior to membrane characterization and filtration tests, virgin membrane specimens were thoroughly rinsed in Type I water and stored at 4 °C. Water was replaced periodically. Fouled membrane specimens were rinsed gently with Type I water using a rinsing bottle. Membrane specimens were dried at room temperature for 24 h prior to surface analysis.

Membrane hydrophobicity was characterized by sessile drop contact angle measurement by placing a droplet of Type I water (5 μL) onto membrane surface. The measurement was performed using a NRL Goniometer-Model 100-00 (Ramé-hart Inc., Surface Science Instrument, Landing, NJ). To minimize the interference from roughness and morphology of membrane