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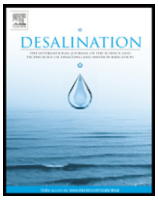

Characterization and removal of natural organic matter by an integrated membrane system

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ABSTRACT

Natural organic matter (NOM) fractionation of French River water (Nova Scotia, Canada) was performed at an integrated membrane system employing ultrafiltration (UF) and nanofiltration (NF) for water treatment. An attempt was made to evaluate this surface water and the effect of UF treatment on disinfection by-product (DBP) precursor removal. Each NOM fraction was assessed in terms of trihalomethane and haloacetic acid formation potential. The NOM fractionation was performed by separation into six fractions: hydrophobic acid (HOA), base (HOB) and neutral (HON) and hydrophilic acid (HIA), base (HIB) and neutral (HIN). The raw water was found to be mostly comprised of HIN (approximately 50%) and HOA (approximately 35%). Upon treatment with UF, 66% of the DOC was removed. The key finding of this work was that the HOA fraction was the main contributor to DBP formation potential. Removal of 93% of the HOA components through UF treatment resulted in a reduction of trihalomethane and haloacetic acid formation potential of 54 and 30%, respectively, despite the fact that HOA comprised 35% of the NOM in the raw water. The results also showed that the UF component of the system contributes to the overall DBP precursor removal at this full-scale plant.

1. Introduction

Natural organic matter (NOM) present in drinking water sources is problematic as it produces disinfection by-products (DBPs) during chlorination which can potentially cause long-term adverse health effects [1]. The adverse effects related to the formation of chlorinated organic compounds have driven water utilities to consider advanced NOM removal treatment processes. In recent years, there have been a number of research projects conducted to evaluate integrated membrane systems such as ultrafiltration (UF) followed by nanofiltration (NF) in terms of treatment efficacy [2]. UF membrane pretreatment is efficient in reducing turbidity, particles and suspended solids [3] and is effective for the reduction of NF membrane fouling resulting from the accumulation of particles and suspended solids. However, UF membranes have been shown to not provide complete removal of NOM [4,5]. The residual organic matter present in the water can be removed by NF treatment processes [6–8]. Owen et al. [9] proposed that NF with a molecular weight cut-off of 400 to 800 Da is effective in removing NOM and thereby controlling the formation of DBPs.

Natural organic matter present in water is considered as a major foulant for NF membranes [10,11]. In order to understand the role of specific NOM components responsible for NF fouling, it is necessary to thoroughly characterize NOM in feed water. Humic substances, a component of NOM, have been found to control the rate and extent of NF fouling in some studies [12,13]. Nilson and DiGiano [6] observed that hydrophobic NOM fractions were responsible for the majority of permeate flux decline and were highly rejected by NF membranes compared with hydrophilic NOM. Other studies have revealed that the non-humic fraction of NOM (e.g., hydrophilic and neutrals) are responsible for determining the rate and extent of flux decline [14,15]. Fan et al. [16] described the order of fouling potential of different NOM fractions as: hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophobic charged. This finding was well supported by a study carried out by Lee et al. [17], who found that polysaccharides and proteins (hydrophilic neutrals) with lower molecular weight significantly foul low pressure membranes. Similar results were observed by Cho et al. [18] and Speth et al. [19] in NF membranes and Zhao et al. [20] for reverse osmosis membranes. Furthermore, many bench-scale studies with synthetic feed waters have demonstrated the high degree of fouling associated with proteins and polysaccharides [17,21–24]. In summary, there has been a wealth of research on NOM fouling of both low and high pressure membranes. In contrast, the objective of this research was to characterize NOM and assess DBP formation potential in raw and UF treated water at a full-scale plant. Although other studies have characterized NOM and its association with DBP formation, this study specifically assessed the ability of UF membranes to remove DBP precursors and identified the key components involved in removal. To accomplish this, raw water and UF permeate samples were fractionated, following a procedure developed by Leenheer [25] and modified by Marhaba et al. [26], into six different NOM fractions. Disinfection by-product formation was then assessed before and after UF treatment. Although NF water quality parameters are presented as well as some anecdotal

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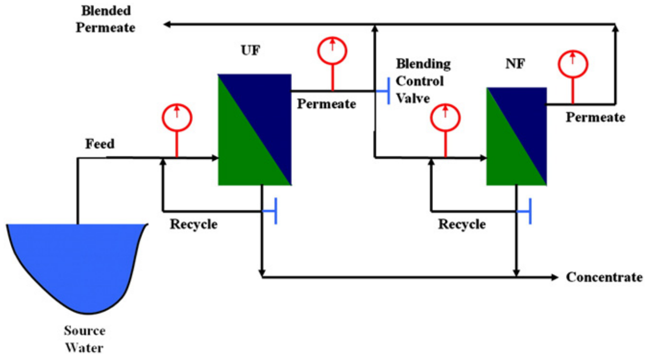

Fig. 1. Process overview of Tatamagouche drinking water treatment plant.

data regarding NF fouling, the focus of this work is on the ability of the UF system to remove different components of DOC from the raw water.

2. Materials and methods

2.1. Tatamagouche drinking water treatment plant

The Tatamagouche drinking water treatment plant is located on the north shore of Nova Scotia, Canada. The plant consists of an integrated membrane design: UF followed by NF membranes (Fig. 1). The French River water is pumped from an infiltration gallery under the riverbed to coarse screens for removal of coarse debris. It is then passed into two UF membrane skids operated in parallel. The raw water enters three membrane tanks each containing six UF modules (ZeeWeed 1000, GE Water and Process Technologies, Canada), which have a nominal and absolute pore size of 0.02 and 0.01 μm, respectively. The UF permeate is then sent to the break tank from which it enters the NF units. The NF systems are protected with two 5 μm cartridge filters, for protection from debris, after which there are two NF membrane skids that operate in parallel. Each skid contains a total of six pressure vessels and each pressure vessel contains four spiral wound NF membrane modules (PRO-100NF, GE Osmonics, USA). The average salt rejection of the NF membrane is 98%. The NF permeate is disinfected with chlorine and pumped into the distribution reservoir. The NF concentrate and UF backwash residual waste streams are discharged back to the river.

2.2. Water quality characteristics

The French River raw water and UF permeate collected from the full scale plant were used for bench-scale NOM fractionation as well as trihalomethane (THM) and haloacetic acid (HAA) formation potential experiments. It is important to note that there is a high degree of seasonal variation in the source water quality, however the results presented in this paper are representative of the water quality from this source outside of discrete events such as heavy rain falls. The French River, which flows through the surrounding agricultural and natural land-use areas, is vulnerable to degradation due to source run-off materials (e.g. soil, silt, organic matter) from agricultural fields. The major raw water quality characteristics include low alkalinity (<5 mg $CaCO_3$/L) and periodic elevation of color and turbidity levels from natural occurring organic matter. These characteristics are similar to other surface water sources in Nova Scotia and Atlantic Canada [27]. Dissolved organic carbon samples were analyzed using a Shimadzu TOC-Vcph Total Organic Carbon Analyzer. The samples were placed in 50 mL head-space free vials and acidified below a pH of 2 with phosphoric acid for preparation. Samples were first filtered through a 0.45 μm filter paper (Cole-Parmer® Nylon Membranes) before acidifying and placing them in vials.

Table 1
Raw and treated water characteristics.

	pH	UV_{254} (cm^{-1})	Alkalinity (mg/L as $CaCO_3$)	DOC (mg/L)	SUVA[a] (L/mg-m^{-1})
Raw	6.7	0.096	27.3	5.3	1.8
UF permeate	6.6	0.064	36.0	1.9	3.2
NF permeate	6.7	0.001	12.7	0.32	0.31

[a] Specific UV absorbance.

2.3. NOM fractionation

The dissolved organic matter from the raw water and UF permeate was separated into six organic fractions: hydrophobic acid (HOA), base (HOB) and neutral (HON) and hydrophilic acid (HIA), base (HIB) and neutral (HIN). Resins were cleaned and packed into 2.5×120 cm Kontes Chromaflex chromatography columns following resin preparation procedures developed by Leenheer [25]. The hydrophobic fractions were absorbed onto DAX-8 resins (SUPELCO, Bellefonte, PA) by varying the influent pH to 7, 10 and 2 to extract the HON, HOB and HOA fractions respectively. The hydrophilic base fraction was absorbed onto AG-MP 50 (BIO-RAD, Hercules, CA) resins at a pH of 2 and extracted following the modifications proposed by Marhaba et al. [26]. The hydrophilic acid fraction was subsequently absorbed onto WA 10 resins (SUPELCO) at a pH of 2 and the hydrophilic neutral fraction was that which remained after the sample had passed through each of the five columns.

2.4. Molecular weight by HPSEC

High performance size exclusion chromatography (HPSEC) (Perklin Elmer, Series 200) with a UV/VIS detector was used to determine the molecular weight distribution of NOM present in water samples. The samples were brought to a pH between 3 and 7, passed through a 0.45 μm membrane filter and analyzed using a TSK G3000SW column (7.5 mm×300 mm). The column contained silica-based, hydrophilic bonded phase packing materials that minimize interaction with compounds present in the sample. Sodium acetate with a flow rate of 0.7 mL/min was used as a mobile phase (eluent). The sample injection volume was 20 μL and analysis time was 30 min for each sample. The column was calibrated with sodium polystyrene sulphonate (PSS) standards with different molecular weights (14,900, 7540, 5180, 1530 Da) and all PSS standards and samples were detected at a wavelength of 254 nm. Although predictions of molecular weight of organics outside the calibration range by extrapolation of the calibration curve from the HPSEC software may not be completely accurate, values have been reported in previous studies [28,29].

2.5. Disinfection by-product formation potential

Six isolated organic fractions of raw and UF permeate waters were chlorinated according to the uniform formation condition protocol [30] proposed by Summers et al. [31] to determine THM and HAA formation potentials. The detailed DBP formation potential method is described elsewhere [32]. In brief, a stock solution of 1500 mg/L sodium

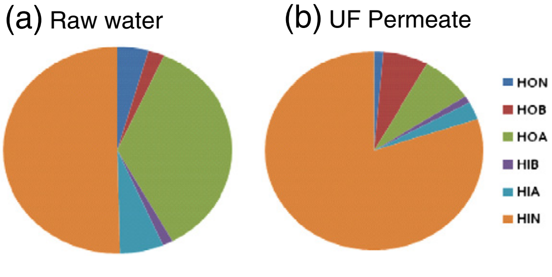
(a) Raw water (b) UF Permeate

Fig. 2. Composition of the organic matter in (a) raw and (b) UF permeate waters. Fractionation of NF permeate was not conducted due to the low DOC concentration.