Nanofiltration (NF) membrane process with pre-ozoneation for brine treatment

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1. Introduction

Water scarcity has become a critical issue around the world and this issue will be further aggravated as population grows [1]. In attempts to alleviate water stress, alternative sources of water such as seawater and wastewater are actively being evaluated for beneficial uses [2]. In particular, potable water reuse from municipal wastewater can be a viable option for easing water stress for regions facing limited and/or dwindling fresh water resources such as Tucson, Arizona [3, 4]. Municipal wastewater is a sustainable water source and can tremendously reduce cost of water treatment, pumping, transport, and storage as compared to water importation and desalination [5].

Among water treatment technologies, membrane driven processes have proven to be the most effective against removing chemical and biological contaminants, thus providing high quality water suitable for potable use [6]. Specifically, reverse osmosis (RO) and nanofiltration (NF) membranes can effectively remove recalcitrant trace organic compounds such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) with several different mechanisms including size exclusion, electrostatic repulsion, and hydrophobic adsorption [7, 8]. However, the major challenge with membrane driven processes is the production of a highly concentrated waste stream known as brine or concentrate [9]. Brine has high concentrations of inorganic and organic constituents since the substances rejected by the membrane concentrate in the brine stream while the purified water penetrates through membrane.

There are several options for brine management. Marine discharge, that is the discharge of brine into marine water bodies including bays, estuaries, and/or oceans, is one of the dominant practices of brine management [10]. However, this practice may contaminate receiving water bodies and is not generally viable for in-land communities such as Arizona. While brine disposal into sewers can also be an option, the addition of inorganic and organic contaminants into sewage lowers biochemical oxygen demand and increase total dissolved solids, hence potentially aggravating activated sludge processes. Zero liquid discharge (ZLD) is a combination of processes inducing very high recovery rate (nearly 99 %) using techniques such as thermal distillation/evaporation. However, currently available ZLD technologies raise operating costs significantly and often prohibitively.

One promising opportunity for brine management is additional stages of membrane treatment; however, pre-treatment is essential to reduce the potential for irreversible membrane fouling. Since membrane brines contain high concentrations of organic constituents, these constituents can bind to membrane surfaces and rapidly result in fouling potential. Indeed, the presence of natural organic matter (NOM) is ubiquitous and it is a major contributor in membrane fouling. Therefore understanding the role NOM characteristics play in guiding selection of pre-treatment technologies for higher water recovery is critical. Important physicochemical properties of NOM in membrane fouling include hydrophobicity, size, and electrostatic interactions [11]. Hydrophobic interaction between NOM and membrane surfaces leads to attachment of organic foulants on the surface of membranes. Molecular size influences not only the dispersion of NOM towards and away from
membrane surface, but also tendency of pore blocking of a membrane. Electrostatic attraction and repulsion also play crucial roles in organic fouling potential.

Ozone is strong oxidant that is widely used for removal of organic contaminants. Ozone oxidation offers promise as a pre-treatment technology for membrane process due to the transformation of NOM intrinsic to water [12]. The electrophilic nature of ozone prompts transformation of hydrophobic NOM into smaller molecules, which helps NOM diffuse away from membrane surface. Furthermore, ozonation increases negative charge of NOM, thus leading to electrostatic repulsion from negatively-charged membranes.

The primary objective of this study is to investigate an application of NF membrane process with pre-ozonation in order to minimize the amount of brine generated and to reduce organic contaminant concentrations within the brine. To this end, the effects of pre-ozonation on fouling reduction in NF membrane process were investigated. In attempts to investigate possible alteration of fouling mechanism, molecular size change of NOM measured by size-exclusion chromatography (SEC) and aromaticity change represented by specific UV absorbance (SUVA) were investigated.

2. Methods
2.1. Brine generation

A spiral wound membrane system with two pressure vessels operated in parallel with two Dow Filmtec NF270-4040 membrane elements was employed to generate brine. Desired recovery rate (85 %) was achieved by recirculating the concentrate stream back into the feed tank while the permeate stream was discarded. As feed water, Colorado river water was used. 1.5 mg/L of antiscalant (Nalco Permatreat PC 191) was spiked into the feed water.

2.2. Ozonation of brine

The generated brine was ozonated at the two ozone doses (1.8 mg/L and 7.5 mg/L) using a pilot-scale ozone flow-through generator (Modular 8HC, Xylem Wedeco, Germany).

2.3. Fouling propensity test

The fouling propensity test was conducted using a laboratory flat sheet membrane system consisting of membrane cell, feed tank, temperature controller, pump, and data acquisition system. A constant temperature of feed water (25°C) was employed during the fouling test. Dow Filmtec NF90 membrane was compacted using DI water at the same pressure as one applied for the test water (brine) for 24 hours, then was used for fouling propensity test.

2.4. Analysis

Dissolved organic carbon (DOC) was measured using Shimadzu TOC-L CSH Total Organic Carbon Analyzer (Shimadzu Corp., Japan). Metals were analyzed by an Agilent 7700x Series ICP-
MS in helium collision gas mode. 20 µL of an aqueous solution containing equal concentrations (5 mg/L each) of scandium, germanium, indium, and bismuth was then added to each tube as an internal standard.

Size exclusion chromatography (SEC) was implemented to obtain apparent molecular weight (AMW) of dissolved organic matters (DOMs) using an Agilent 1290 high performance liquid chromatography (HPLC) (Palo Alto, CA) hyphenated with diode array detector (DAD) at wavelength of 254 nm. A silica-based column (Waters Protein-Pa 125; particle size 10 µm, diameter 7.8 mm, and length 300 mm) was used as a SEC column. 2.4 mM sodium phosphate, 1.6 mM disodium hydrogen phosphate, and 96.0 mM sodium chloride solution was used as an eluent [13]. Polystyrene sulfonates with molecular weights (MWs) ranging from 1100 Da to 32900 Da were used as MW standards (Polymer Standards Service, Mainz, Germany). Specific UV absorbance (SUVA) was calculated by UV absorbance at 254 nm divided by TOC value. The UV absorbance value was measured using Horiba Aqualog fluorometer.

3. Key findings

Fig. 1 illustrates that increasing ozone dose substantially reduces fouling propensity. In order to quantify the extent of fouling reduction by ozonation, the modified fouling index (MFI) was calculated [14, 15]. The MFI can be obtained from the slope of the linear region in the plot of \( \frac{t}{V} \) versus \( V \) as expressed:

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\frac{t}{V} = \frac{\eta R_m}{\Delta P A} + \frac{\eta I}{2\Delta P A^2} V \text{,} \tag{1}
\]

where \( \eta \) is the dynamic viscosity, \( R_m \) is the intrinsic membrane resistance, \( \Delta P \) is the applied transmembrane pressure, \( I \) is a measure of the membrane fouling potential of the feed water, and \( A \) is the membrane area. MFI is proportional to the fouling potential and inversely proportional to the transmembrane applied pressure, so MFI can be a good indicator to compare fouling potential among different feed waters. Fig. 2 shows MFI values at different ozone doses. At 7.5 mg/L of ozone dose, MFI values were reduced by 79%, which is equivalent to 79.1% reduction of fouling potential of feed water.
In cross-flow membrane processes, two phenomena can be considered for the explanation of organic membrane fouling: mass transfer of NOM and attractive force between NOM and membrane surface and/or cake layer. First, smaller NOM can more easily disperse away from the membrane surface. Ozone is a strong oxidant and can break macromolecules into smaller fractions, thereby possible to enhance mass transfer of NOM. As shown in Fig. 3, however, SEC result reveals little size shift of NOM after the ozonation. Hence, there was no enhanced mass transfer expected due to the ozonation. Ozone to DOC ratio is often considered as an operating parameter in ozone oxidation processes and its values applied in this study were 0.1 mg/mg and 0.4 mg/mg corresponding to 1.8 mg/L and 7.5 mg/L ozone doses, respectively. These low ozone doses would cause minor change of functional groups of NOM rather than breaking NOM down into smaller fractions [16], which can be a reason of the little size change of NOM.

On the other hand, reduction in the interactive force between NOM and membrane likely reduced the membrane fouling potential. Particularly, the aromatic interaction was expected to be reduced since the aromaticity of NOM represented by SUVA was significantly reduced after the ozonation. Ozone is a strong oxidant and possesses high reactivity with aromatic moieties which are susceptible to being electrophilic. The reduced electrophilic nature by ozonation possibly reduced electrostatic interactions between aromatic moieties of NOM and membrane surface.
In conclusion, the ozonation of surface water brine significantly reduced the fouling propensity. Therefore, the application of ozone to brine treatments will contribute to maximizing water recovery rate of NF membrane, eventually enabling more options of brine treatment in in-land areas such as Arizona.

4. References