Understanding aging impact on membrane structure and seasonal variation of natural organic matter in water from a membrane drinking water treatment plant

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ABSTRACT

An autopsy of hollow fiber (HF) PVDF membrane samples at different ages from a full-scale drinking water treatment was performed to investigate the membrane aging impact on membrane structures and properties. Scanning electron microscopic images indicated the fouling occurred on membrane surface; diameter of membrane lumen and pore size decreased with an increase in membrane aging. Membrane aging decreased membrane porosity and breaking strength. Clean water test showed the membrane permeability decreased within aging. Contact angle values decreased with an increase in membrane age, and hypochlorite cleaning resulted in a more hydrophilic membrane surface. Chemical cleaning could partially restore membrane permeability and porosity but negatively impact the breaking strength. Organic foulants dominated in membrane fouling.

Natural organic matter (NOM) in all surface and groundwater can be problematic during the drinking water treatment and vary spatially and temporally. It can be quantitatively expressed as the concentration of dissolved organic carbon (DOC). By characterizing bulk NOM in feed samples between 30/11/2016 and 29/03/2017, the peak NOM content in raw water occurred on December 7, 2016, and reduced afterward in March 2017 over the sampling period. By separating the NOM using XAD resins into hydrophobic, hydrophilic, transphilic fractions, NOM type of most raw water, membrane permeates, and concentrates is dominated by the hydrophilic fraction (HPI). The DOC concentrations in water samples in Nov and Dec 2016 were generally higher than that from March 2017. NOM removal in this treatment plant seemed to be inefficient.

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ABBREVIATIONS AND NOTATION

AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
BSA	Bovine serum albumin
DBP	Disinfection by-product
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
ED	Electrodialysis
EDS	Energy dispersive X-ray spectroscopy
FA	Fulvic acids
GAC	Granular activated carbon
MF	Microfiltration
MWOC	Molecular weight cut off
NF	Nanofiltration
HA	Humic acids
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HF	Hollow fibers
HPI	Hydrophilic
HPLC	High-performance liquid chromatography
HPO	Hydrophobic
HPSEC	High-performance size exclusion chromatography
M	mol/L

PEG	Polyethylene glycol
POC	Particulate organic matter
POM	Particulate organic matter
PSD	Pore size distribution
PVDF	Polyvinylidene fluoride
RO	Reverse Osmosis
SEC	Size exclusion chromatography
SEM	Scanning Electron Microscopy
SUVA	Specific absorption of ultraviolet
TGA	Thermogravimetric analysis
THMs	Trihalomethanes
TMPs	Transmembrane pressures
TOC	Total organic carbon
TPH	Transphilic
UVA	Absorption of ultraviolet
VOC	Volatile organic carbon
XPS	X-ray photoelectron spectroscopy

TABLE OF CONTENTS

Chapter 1. Introduction

1.1 Background

Despite the world spread utilization of ultrafiltration membranes, inevitable membrane fouling and membrane aging threaten the drinking water production industry. Membrane fouling is somehow well-understood recently. Researchers investigated the fouling mechanisms and behavior in relation to membrane surface and types. Using multiple cleaning procedures to control fouling are still recommended in the first place in lab studies and field operations especially to maintain long-term membrane performance. The produced water quality and economic cost must reach a balance in the real applications. During the operation time, the membrane structure is going to change, due to changes in operating and environmental conditions and chemical cleaning. Researchers simply defined it as membrane aging (Regula et al. 2014; Robinson et al. 2016). Apart from the operational factors to the membrane aging, seasonal changes in temperature and water quality in cold regions, like the City of Thunder Bay, cannot be ignored for its geographic location. Membrane samples within longer service time tend to experience a distinct variation in feed water temperature. Plus, the fluctuation in the feed water characteristics has some impacts on the drinking water production.

Natural organic matter (NOM) is a mixture of organic compounds occurs universally in waters (Goslan 2003). It could cause problems such as increasing coagulant demands and forming disinfection by-products although itself is harmless (Piper 2010).

Therefore, the objectives of this study were to: 1.) characterize the impact of membrane aging on membrane structure by collecting membrane samples from a full-scale membrane drinking water treatment plant; 2.) fractionate and characterize NOM of raw water, membrane permeate and concentrates in relation to seasonal changes.

1.2 Thesis plan

This thesis is composed of five chapters. The research background and study objectives are presented in this chapter. In the following Chapter 2, a comprehensive literature review will be presented. Chapter 3 to 4 will present assessments of membrane aging problems and NOM characterization. Finally, Chapter 5 will summarize the results and provide suggestions for further work.

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Chapter 2. Literature Review

2.1 State-of-art in the membrane aging for drinking water treatment

2.1.1 Introduction

Membrane performance deterioration has been a ubiquitous topic since it plays a crucial role in the potable water treatment. Membrane systems stand out for universal treatment capabilities, competitive costs, consistent produced water quality and small footprint (Farahbakhsh and Smith 2006). Four widely used membrane filtration applications are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Fig. 2.1 shows the membrane filtration applications in the water treatment industry based on different water sources.

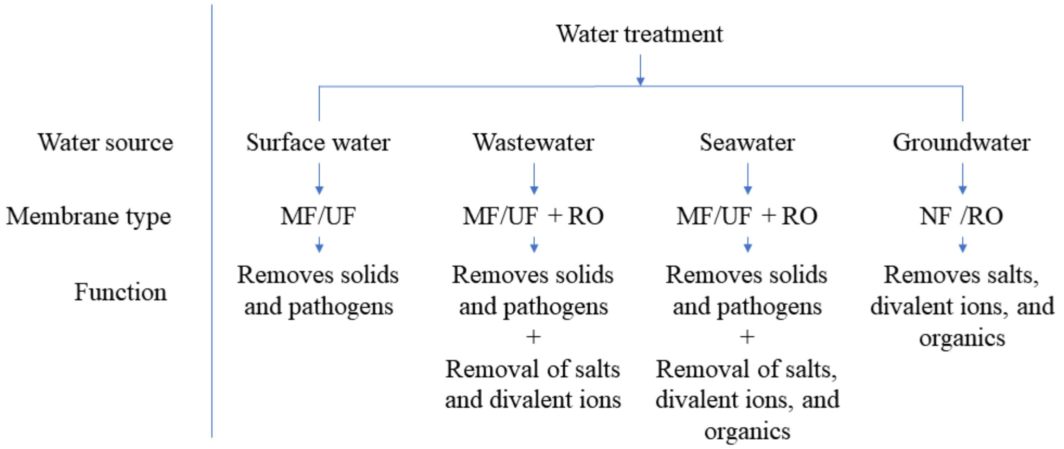

Fig. 2.1 Typical membrane filtration applications in the water treatment industry (adapted from Tng et al. 2015).

A membrane is a barrier to the flow of suspended, colloidal, or dissolved species in any solvent (Duranceau et al. 2011). UF instead of MF removes viruses. Their pore sizes range from 0.1 to 10.00 µm (MF) and 0.001 to 0.1 µm (UF). Both MF and UF require a relatively low applied pressure at 0.7-1.7 atm (MF) and 1.7-10.2 atm (UF) (Chen et al. 2011), respectively. Hence, they are known as low-pressure membranes. NF membrane is ideal for divalent cations, constitutes within molecular weight above 1000, and disinfection by-product (DBP) precursors removal which improves the efficiency of disinfection processes (Chen et al. 2011). RO membrane is a pressure-driven membrane process for dissolved substances removal such as inorganic salts and charged organics (Duranceau et al. 2011). Its exceptional ability to concentrate dilute solutions for salts and chemicals recovery could result in the higher potential of fouling (Chen et al. 2011). Among them, UF and MF are the most cost-effective processes for removing large particles, and it is reported that about 50% of the plants have used UF in surface water treatments (Chen et al. 2011). Its satisfied virus retention and high selectivity have made it the most commonly used technology in worldwide for drinking water production.

Membrane materials can influence the membrane characteristics, for example, membrane selectivity, permeability, mechanical stability, chemical resistance, and thermal stability (Rautenbach and Albrecht 1989). The membrane can be made of organic (polymeric) or inorganic (ceramic or metallic) materials based on the composition (Chen et al. 2011). 80-90% of the membranes installed are polymeric membranes because their prices are far below those of mineral membranes (Regula et al. 2014). Polyvinylidene fluoride (PVDF) hollow fiber membranes have been attracted the most attention, due to its high mechanical strength, flexibility, thermal stability, chemical resistance and good processability among the industrial-scale membrane process applications (Khaye et al. 2002; Wang et al. 2010; Kang and Cao 2014). But they are highly hydrophobic, which tends to experience more severe fouling in the water treatment than hydrophilic materials as many foulants in raw water are hydrophobic (Hilal et al.

2005; Pezeshk and Narbaitz 2012; Robinson et al. 2016). Hydrophilic materials are added to those membranes to enhance the filtration performance (Hilal et al. 2005; Mu et al. 2010; Pezeshk et al. 2011). Still, within the “service time’, retained contaminants from feed solution can adsorb at and/or in the membrane despite the above modifications. Membrane aging is long-term changes in membrane structure during water production. More specifically, it is the deterioration of the surface layer and sublayers of composite membranes due to irreversible deposition of foulants or by frequent exposure to chemical cleaning agents (Antony et al. 2010; Benavente and Vázquez 2004). Applying routine cleanings including physical or hydraulic cleaning and chemical cleaning to maintain long-term performance has become the standard operating protocol. Chemical cleaning agents such as sodium hypochlorite (most commonly used in cleaning) could exacerbate membrane aging (Gaudichet-Maurin and Thominette 2006). Membrane aging could trigger the membrane failure to reach the end of its lifespan resulting in an undesirable economic loss (Prulho et al. 2013). From the manufacturers’ and water treatment plants’ point of view, the paramount operating objective is to avoid any failure causing compromised water quality and reduced capacity or productivity of membrane modules. Therefore, assessing PVDF membrane aging is worth to be discussed.

2.1.2 Membrane characterization

Because membrane aging also presents as changes in its characteristics over long-term use, combined multiple techniques are applied intensively in membrane characterization (Robinson et al. 2016). Fig. 2.2 shows the assessment tools based on five membrane characteristics.

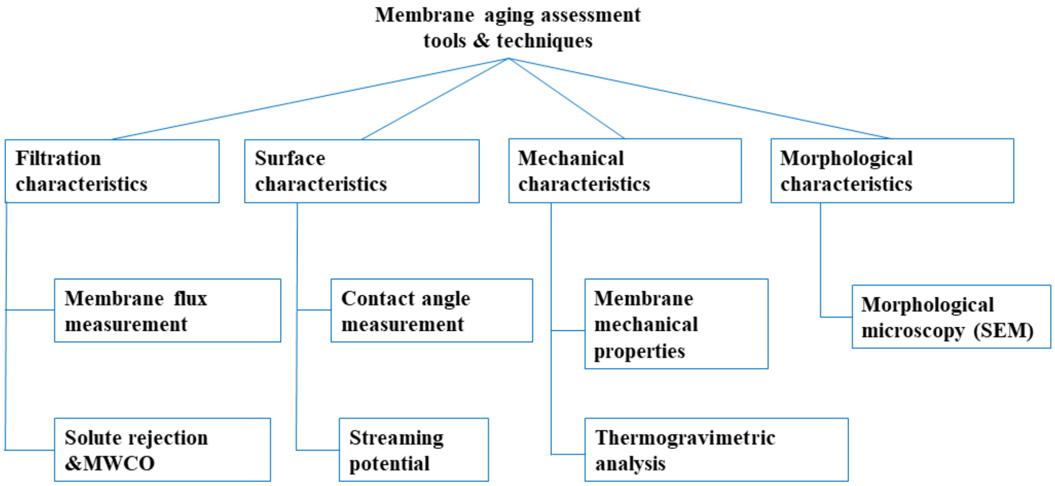

Fig 2.2 Membrane aging assessment tools and techniques (adapted from Tng et al. 2015).

2.1.2.1 Filtration characteristics

In general, lab-scale, bench-scale and full-scale aging studies using pure water during the filtration test. Membrane permeability and resistance are direct measurements of the membrane flux. Pure water permeability test is usually performed at the very beginning of a virgin or fouled membrane and then after a cleaning cycle. If the flux restored greater than the initial flux, the membrane considered having undergone degradation (Yadav and Morison 2010). Resistance is a membrane's impedance to fluid flow which indicates the intrinsic membrane resistance under the clean water test (Robinson et al. 2016). The value of the intrinsic resistance can be determined either by parameters of filtration test or the physical features of a membrane (Eq. (2.1); Eq. (2.2)) (Crittenden et al. 2005):

$$R_t = \frac{\Delta P}{\mu J} \qquad \text{Eq. (2.1)}$$

$$R_t = \frac{8\tau L A}{n r^4 \pi} \qquad \text{Eq. (2.2)}$$

Where ΔP is operating transmembrane pressure; μ is the fluid viscosity; J is the permeate flux; τ is the tortuosity correction factor; L is the membrane pore length; A is the membrane area; n is the number of pores and r is the pore radius.

Lab-scale studies reported that membrane pore size increased positively with the membrane age because the chain scission was removed during cleaning, which “opens” the pore structure leading to higher permeability (Jung et al. 2004; Arkhangelsky et al. 2007; Do et al. 2012a; Pellegrin et al. 2013). Yet some research showed the opposite. They observed a decreasing permeability trend with membrane aging and attributed the results to the disintegration of the membrane surface or degradation in membrane surface chemistry resulting in pore collapse (Arkhangelsky et al. 2008; Do et al. 2012b; Liang et al. 2013; da Costa et al. 2015). It is more interesting to figure out that the operational data in full-scale membrane systems gave another story. They witnessed the increase in membrane resistance within membrane aging (He et al. 2014). They suggested irreversible fouling were severe. Raw water characteristics and cleaning agent exposure also had advert impact (Causserand et al. 2008; Wang et al. 2010; Hajibabania et al. 2012).

Solute rejection is designed to probe membrane rejection capacities which associate with the pore size (Abdullah and Bérubé 2013). In many studies, this often performed on membranes before and after chemical cleaning to see if cleaning agents’ impact on membrane physical characteristics. A range of molecular weight markers or molecules with known molecular weights (i.e., PEG, dextrans) as in the feed solution, the fractional rejection of them is to determine pore size or molecular weight cut-off for the membranes based on membrane selectivity (Jung et al. 2004; Arkhangelsky et al. 2007). Increased pore size would see a decrease in rejection. Arkhangelsky (et al. 2007) using known MWCO eight polyethylene glycol molecules and three polyethylene oxide polymers performed rejection tests on the pristine and chlorine-treated membrane at a constant pressure. They found a significant increase in polymer retention after chemical cleaning, and after a specific molecular weight, polymer rejection reached 100% for the chlorine-treated membrane. This tendency was consistent with Qin et al. (2005) and Wienk et al. (1995). Thus, they agreed that a considerable narrowing of membrane pores and tight pore size distribution occurred after the hypochlorite treatment.

2.1.2.2 Surface characteristics

Membrane hydrophilicity and surface charge reveal membrane fouling. Surface properties are thought to alter after multiple cleaning cycles of frequent exposure to harsh chemicals (Tng et al. 2015). Contact angle measurements via sessile drop technique are widely used to quantify membrane hydrophobicity (Cho et al. 1998). The angle obtained determines the nature of a membrane surface. A high contact angle means higher membrane hydrophobicity, while a lower angle indicates a more hydrophilic surface. In the study of Abdullah and Bérubé (2013), to investigate the sodium hypochlorite exposure on changes in the physical/chemical characteristics of blended PVDF hollow-fiber membranes, they were using a virgin commercial membrane with hydrophilic additives. Results showed a considerably increased contact angle after chemical cleaning. These results are attributed to the removal of hydrophilic additives by sodium hypochlorite, which is agreed with Zhao et al. (2008); Mu et al. (2010) and Puspitasari et al. (2010). In another typical study from Levitsky et al. (2011), they focused on understanding sodium hypochlorite changes in membrane hydrophilicity. They artificially fouled clean PVDF membranes with bovine serum albumin (protein) solution followed by scheduled sodium hypochlorite (NaClO) cleaning at different concentrations to compare the contact angles of virgin and cleaned membrane. Results were more complex. At low NaOCl concentrations, PVDF membranes became more hydrophilic, and surface charge increased due to the gradual elimination of the surface preservation residues (Flosch et al. 1992; Momtaz et al. 2005; Arkhangelsky et al. 2008). In the later stage, with the higher concentration, the complete removal of the residues resulted in increased contact angle values (Neumann and Good 1972). However, Richard and Doneva (2000), Hajibabania et al. (2012) discussed the limitation of sessile drop for measuring contact angle. They pointed out the membrane roughness and pore size could affect the contact angle test. Larger pore size and rougher surface can be responsible for the changes in contact angle values (Richard and Doneva 2000).

Streaming potential measurement can be used to quantify surface charge. Shao and Zydney described the general procedure in 2004. The method summarized as a fluid passing over the membrane at different pressures, the voltage difference or streaming potential measured as a function of the pressure driving force; zeta potential has a linear relationship with steaming potential (Tella et al. 2014). The membrane’s surface charge increases with chlorine exposure (Kwon and Leckie 2006; Arkhangelsky et al. 2007; Tella et al. 2014).

2.1.2.3 Chemical and structural characteristics

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) is widely used to assess the membrane’s chemical and structural properties. This surface technique could easily and rapidly identify the presence of specific functional groups, and shifts in transmission peaks would indicate the alteration in the membrane chemical structure (Tng et al. 2015). Like in the study of Abdullah and Bérubé (2013) mentioned before, by the reduction in the size of the dominant peak, they proved the additives in PVDF membranes are degraded to sodium hypochlorite exposure. In another study of Puspitasari et al. (2010), they found the carbonyl-peak disappeared during the cycled hypochlorite cleaning and aging with NaOCl, respectively. The carbonyl group (C=O) has been found to increase membrane hydrophilicity when added to PVDF membranes (Kang et al. 2003; Marchese et al. 2003). Similar results were reported by Wang et al. (2010); Hajibabania et al. (2012) and He et al. (2014). Moreover, Wang et al. (2010) also mentioned if the sodium hypochlorite cleaning cannot completely remove the foulants, the residues would weaken the infrared absorption of the membrane. Overall, it is a qualitative measurement of change when comparing the results from the virgin and aged membranes or post-NaOCl cleaning. This would provide whether the membrane was missing certain functional groups.

X-ray photoelectron spectroscopy (XPS) can be quantitatively measured the elemental composition and chemical binding of the membrane surface (Tng et al. 2015). This technique can detect C, F, O, N, S atoms that are common in PVDF membrane materials (Robinson et al. 2016). Because alteration of functional groups causes changes in the elemental character of surface layers, this technique is always associated with ATR-FTIR; they are complementary to one another (Puspitasari et al. 2010; Teella et al. 2014).

2.1.2.4 Mechanical characteristics

Mechanical properties of the membrane such as ultimate elongation, tensile strength, yield strength and elasticity can evaluate the aging in membrane physical characteristics (Robinson et al. 2016). Additionally, the estimation of membrane lifetime could be done by examining the mechanical properties of the membrane after its contact with chemicals (Arkhangelsky et al. 2007).

The ultimate elongation is the tensile strain at break. Membranes exposed to NaOCl showed a significant decrease in ultimate elongation (Hajibabania et al. 2012; Rabuni et al. 2015). The ultimate tensile strength is the stress (force per unit cross-sectional area) that the material can handle before fractured. Arkhangelsky et al. (2007), Wang et al. (2010) and Hajibabania et al. (2012) reported a sharp decrease after exposing to NaOCl in tensile strength. These two decreasing trends were attributed to the rearrangement of the molecular structures in the polymeric chains during membrane aging (Hajibabania et al. 2012). Yield strength is the stress at which the material begins to deform permanently. Abdullah and Bérubé (2013), in their assessment of effects of sodium hypochlorite exposure on the characteristics of PVDF based membranes, observed a reduction in the yield strength after exposure. Combined with Scanning Electron Microscopy (SEM) images, they suggested the increase in porosity leading to a reduction in membrane cross-sectional area, thereby affecting the yield strength. Young's modulus, also called the elastic modulus, has a linear relationship with the collapse pressure of thin-walled hollow fiber membranes, which are required to withstand high transmembrane pressure (TMP) without collapsing (Arkhangelsky et al. 2007). It is believed to decrease with membrane aging which demonstrates a decreased membrane rigidity because of the chain breaking of polymer materials treated with NaClO (Arkhangelsky et al. 2007).

PVFD membrane aging experienced a decrease in its mechanical properties. It is related to the chain scission or cross-linking by a dehydrofluorination reaction (Hashim et al. 2011). The breaking of polymeric functional groups by contact with cleaning chemicals inducing a gradual deformation of the membrane structure and declination in mechanical strength will lead to the potential membrane embrittlement (Lovinger 1982).

Thermogravimetric analysis (TGA) is to weight the material while being gradually heated (Lobo and Bonilla 2003). Each polymeric material has a different degradation temperature; at that temperature, it breaks down into shorter-chain components that are volatile; this would indicate the alteration to the mechanical properties (Yadav et al. 2009; Robinson et al. 2016). However, general conclusions cannot be made since both an increase and a decrease in temperature were observed for aging (Regula et al. 2014). Not only the relationship between polymer molecular weight and degradation temperature is not direct, but additives of membranes interference the changes in a polymer that influence the degradation temperature (Lobo and Bonilla 2003).

2.1.2.5 Morphological characteristics

Microscopic visualization techniques like atomic force microscopy (AFM), scanning electron microscopy (SEM) can provide accurate, high-resolution images of many membrane characteristics (Tng et al. 2015). By comparing micrographs of virgin and aged membrane, changes in morphological characteristics are detected. More often, these techniques used to support other characterization results.

AFM determines surface morphology and roughness by scanning the surface with a probe. It used to support the contact angle trends. Surface roughness increased after chemical cleaning and post-cleaning fouling, which resulted from a gradual elimination of the preservation residues in the study of Levitsky et al. (2011).

SEM provides more information such as membrane pore size and thickness. Abdullah and Bérubé (2013) observed an increase in pore size due to aging which was consistent with the decreased resistance result. More importantly, SEM equipped with energy dispersive X-ray spectroscopy (EDS) can characterize the chemical composition of the foulant on or in the membrane (Tng et al. 2015). That can indicate an organic fouling or inorganic fouling occurred to the membrane, which would further show the chemical cleaning efficiency by comparing the images before and after cleaning. It should be noted that related software estimates the pore size instead of directly measuring actual pore sizes.

2.1.3 Conclusions

Membrane aging is complicated and linked with filtration performance (i.e., flux, permeability, resistance), chemical membrane characteristics (i.e., surface charge, hydrophobicity, polymer molecular weight), physical membrane characteristics (i.e., pore size, porosity) and mechanical properties (i.e., tensile strength, yield stress). Multiple techniques have to be employed, and changes in those characteristics are often supported by each other in a study. This literature review narrowed the topic to the PVDF-based membrane aging caused by NaClO exposure as it is the most widely used membrane in drinking water industry. Most lab-scale studies we reviewed artificially aged membranes by soaking in particular concentrations of NaClO. Moreover, studies associated aging phenomena with fouling and chemical cleaning also artificially interfered to accelerate the procedures. Results obtained from these studies could be possibly beyond reality - membrane systems operating under full-scale factory conditions. A lack of data from full-scale membrane filtration plants calls for studies of membrane samples from full-scale membrane plants at different ages. The effect of membrane aging on naturally fouled and protocol-based cleaned membranes from full-scale plants and membrane aging caused by other chemical cleaning agents (acids, enzymes, hydroxide and chelating agents) exposure need further studies.

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2.2 State-of-art in the fractionation of natural organic matter

2.2.1 Aquatic Natural Organic Matter

Natural organic matter (NOM) is defined as an extremely intricate mixture of organic compounds that is ubiquitous in aquatic systems. NOM can be classified into pedogenic NOM that leached from soils or peat bogs and aquagenic NOM that diffused from sediments or released by plankton and bacteria (aquagenic NOM) (Aiken et al. 1985). Furthermore, Croué et al. (2000) described NOM generated by biological processes in a water body (autochthonous) and the surrounding watershed (allochthonous). Due to its complexity, researchers reached a consensus that concentrations of NOM and its sub-groups are reported as the concentration of total organic carbon (TOC) or dissolved organic carbon (DOC) measured in milligrams per liter (mg/L) (Suffet and MacCarthy 1989; Croué et al. 2000).

NOM plays a significant role in the aquatic system. It causes aesthetic concerns such as colour, taste, odour; leads to the binding and transport of organic and inorganic contaminants; mediates photochemical processes; serves as carbon and energy source for biota which can influence levels of dissolved oxygen, nitrogen, phosphorus, sulfur, trace metals, and acidity (Leenheer and Croué 2003). During drinking water treatment, it can react with chlorine disinfectants to produce disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) which are notorious for probable human carcinogens (Krasner et al. 1989; Singer 1999). Coagulation with alum or ferric and flocculation, granular activated carbon (GAC) adsorption, membrane filtration or biological degradation are conditionally operated in water treatment plants to treat NOM, which also contributes to the problems like coagulant demand and membrane fouling potential (Jarvis et al. 2005; Lee et al. 2004; Zularisam et al.

2006). Understanding the type and concentration of NOM is beneficial to the water production industry.

NOM should be regarded as a dynamic combinatorial system because of the degradation and synthesis (Melton et al. 2007). Most NOM is strongly associated with themselves through hydrogen-bonding, non-polar interactions and polyvalent cation interactions (Leenheer 2009); Elsewhere, findings pointed out that some NOMs consist of supramolecular aggregates with a relatively low molar mass (Simpson et al. 2002; Sutton and Sposito 2005). Leenheer and Croué (2003) conclude that NOM is a complex mixture of aromatic and aliphatic hydrocarbon structures attached amide, carboxyl, hydroxyl, ketone and other minor functional groups. The composition of NOM in natural waters can vary regionally and seasonally due to the origination of organic compound. Thus, it is unrealistic to identify the structure of bulk NOM.

2.2.2 Bulk characterization of NOM

Practically, NOM is commonly represented by the value of TOC, DOC, UV adsorption spectra (UV_{254}). Colour could also indicate NOM only when the water is brownish yellow (Uyguner et al. 2007). Those ready-to-test techniques require very easy pretreatment, or none yet provide limited information only on the amount of NOM.

2.2.2.1 Total organic carbon (TOC) / Dissolved organic carbon (DOC)

TOC and DOC are quantitative parameters for the NOM. TOC contains all the C atoms which are covalently bound in organic molecules including particulate matter as carbon black and negligible volatile organic carbon (VOC) (Eq. (2.3)) (Wilderer 2011):

$$\mathrm{TOC} = \mathrm{DOC} + \mathrm{POC} + \mathrm{VOC} \qquad \text{Eq.(2.3)}$$

TOC and DOC can be separated by a 0.45 µm pore size membrane filter because DOC is smaller than 0.45 µm in diameter. POC (particulate organic matter) usually is retained on the filter and represents less than 10% fraction of the TOC (Thurman 1985). VOC is very low in concentration and normally lost. Also, DOC is biologically stable which is a steady-state TOC concentration in various aqueous phases; so that in most cases DOC is used synonymously with TOC (Wilderer 2011).

2.2.2.2 Ultraviolet (UV) absorption spectroscopy

The absorption of ultraviolet (UVA) lights by surface waters is contributed to the aromatic chromophores that comprised NOM (Leenheer and Croué 2003). The UV adsorbance of NOM dissolved in water increases exponentially as the wavelength decreases (Hur et al. 2006; Leenheer 2009). A wavelength range from 220 to 280 nm considers being favorable for NOM measurement while a wavelength above 230 nm believes insignificantly adsorbed by inorganic compounds presented in fresh waters (Weishaar et al. 2003; Matilainen et al. 2011). It has been found an approximately linear correlation between NOM concentration (reported as DOC) and the UV adsorbances of waters at 254 nm thereby UVA_{254} acting as a surrogate parameter for NOM (Korshin et al. 1997; Goslan 2003; Leenheer and Croué 2003; Piper 2010). A comparison of DOC and UVA_{254} data collocated from 119 water sources in 15 references in Fig. 2.3 supports above statements (Krasner et al. 1996; Siddiqui et al. 2000; Volk et al. 2000; Lee et al. 2004; Uyak and Toroz 2007; Fabris et al. 2008; Kim et al. 2011; Spencer et al. 2012; Diemert et al. 2013; Kent et al. 2014; Hong et al. 2015; Chon and Cho 2016; Kimura et al. 2017; Linge et al. 2017; Zhai et al. 2017):

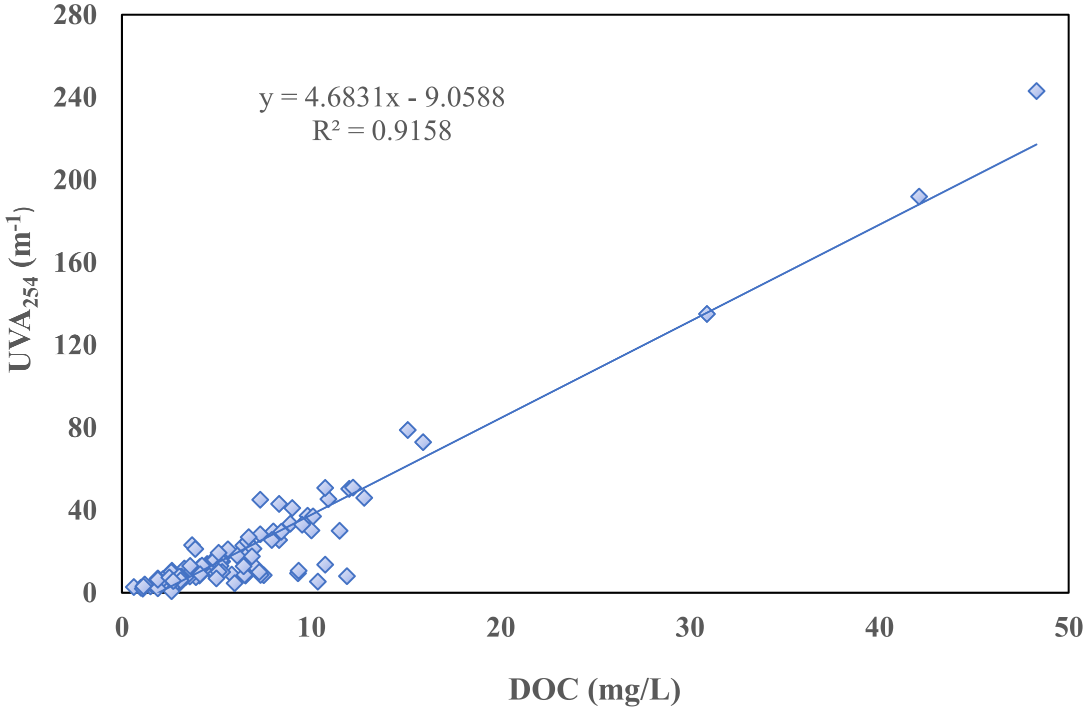

Fig. 2.3 Relationship between DOC and UVA_{254} according to 119 waters

Another useful surrogate for NOM is specific UVA_{254} ($SUVA_{254}$) defined as the UV adsorbance of a water sample measured in inverse meters (m^{-1}) divided by the DOC concentration measured in milligrams per liter (mg/L) (Weishaar et al. 2003). $SUVA_{254}$ is an "average" absorptivity for all molecules of DOC in waters and particularly stands for DOC aromaticity (Traina et al. 1990). Aromaticity can affect the reactivity of NOM with oxidants like chlorine (Reckhow et al. 1990; Li et al. 2000) to form DBPs; the interaction with coagulants (Randtke 1999), inorganic species as mercury (McKnight et al. 1992; Hoch et al. 2000; Waples 2001). The higher SUVA obtain for water, the more aromatic content present in NOM (Goslan 2003).

By measuring two bulk parameters, it could gain some insight on the nature of NOM in waters. However, the linear relationship between DOC and UV_{254} or $SUVA_{254}$ largely depends on NOM types. For example, Piper (2010) found out waters with lower hydrophobic content has a very weak relationship between DOC and UVA_{254} (R^2 =0.59). A full understanding of the specific reactivity or behavior of water requires separation of the NOM.

2.2.3 Variability of Bulk NOM

NOM varies temporally and spatially because of molecular weight, solubility, hydrophobicity, charge density and functional group composition (Sharp et al. 2006). The concentration of DOC ranges from 0.5 to 50 mg/L in streams and rivers and is linked to climate and watershed characteristics (Mulholland 2003). Worrall and Burt (2004) reported that changes in land use, for example, disturbance of peat or vegetation damage, increase the decomposition and production of loosely bound NOM. Hurst et al. (2004) reported that changes in climate and waterbody, such as a rainfall event or snowmelt runoff, lead to high levels of pedogenic NOM because the surface layer of soils is flushed into surrounding aquatic environment (Bishop et al. 2003).

2.2.4 Fractionation of NOM

Because NOM contains countless chemical compositions, evaluation of its character based on the individual compounds is far beyond reality (Leenheer and Croué 2003). Instead, researchers have managed to characterize NOM by grouping NOM molecules into a set of fractions based on polarity (hydrophobic/hydrophilic), acid/neutral/base properties, compound classes (fluvic acid, aromatic amines, sugars, etc.), and even more specific compounds like citric acid (Leenheer and Croué 2003).

Leenheer and Huffman (1976) demonstrated that the potential success of identifying NOM based on polarity, acid/neutral/base, compound classes, specific compounds are 100%, 100%, 50% - 100%, 1-10% respectively. The NOM classification scheme is presented in Fig. 2.4.

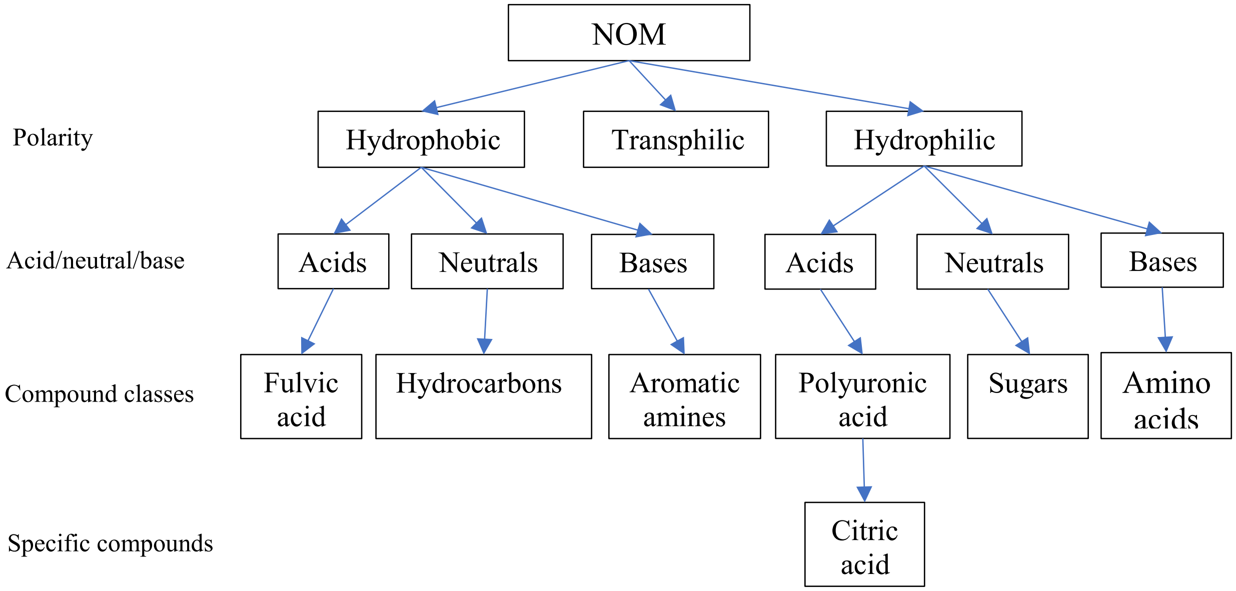

Fig. 2.4 Detailed components of NOM (Adapted from Leenheer and Croué 2003).

Practically, before characterization, particulate organic matter (POM) is separated from the aqueous solution using a 0.45 μm pore size filter. The left, named NOM as well as dissolved organic matter (DOM) in many literature reviews, will then be classified via different methods into groups mentioned above on the condition of the objectives of the study and the available equipment and expected costs. It is essential to assume that NOM fractions isolated by the same procedures will have similar compositions and properties yet the concentration of them may differ (Croué et al. 2000).

Major methodologies for NOM separation/isolation are adsorption and size fractionation. Adsorption contains resin and mineral adsorption. Mineral adsorption has poor chances of success and limited research thus it will not be discussed in the following sections. Size fractionation includes membrane separation and size exclusion chromatography. None of the methods is ideal due to the interactions between NOM and dissolved materials or changes in the chemical structure caused by extreme pH during the isolation process (Aiken 1988; Goslan 2003).

2.2.4.1 Fractionation by resin adsorption

Adsorption techniques vary by the types of adsorbents but share similar theories: controlling the pH of the solute to alter the hydrophobicity of NOM compounds that adsorb and concentrate onto the media they preferred to (Piper 2010).

XAD resins and ion exchange resins are normally used in the fractionation. NOM react with XAD resins and ion exchange resins by weak bonds (dipole and Van der Waal forces) and stronger ionic bonds, respectively. A comparison of XAD and ion exchange resins is listed in Table 2.1.

Table 2.1 Comparison of properties and fractions created by typical XAD and ion exchange resins

Resin types	Resin Name	Resin Properties	Fractions Sorbed	References
Macroporous	XAD-8	Acrylic ester;	Hydrophobic	Leenheer and

Amberlite XAD resins		slight polarity		Huffman (1976)
	Supelite DAX-8	Acrylic ester; moderate polarity	Very hydrophobic acids	Bolto et al. (1999) Chow et al. (2004)
	XAD-7HP	nonionic aliphatic acrylic polymer; weak polarity	Hydrophobic	Chang et al. (2001) Goslan et al. (2002)
	XAD-4	styrene divinylbenzene; aromatic polymer; non-polarity	Hydrophilic acids/ Slightly hydrophilic acids/transphilic	Aiken et al. (1992) Martin-Mousset et al. (1997)/ Bolto et al. (1999)/ Croué et al. (2003)
Ion exchange resins	Bio-Rad AG-MP-50	Cation exchange resin; strong acid; sulfonated; macroporous	Hydrophilic bases	Leenheer (1981)
	Duolite A-7	Anion exchange resin; weak base; phenol-formaldehyde	Hydrophilic acids	Leenheer (1981)
	Amberlite IRA-958	Strong anion exchange resin; polystyrene;	Hydrophilic charged fraction	Bolto et al. (1999) Chow et al. (2004)

All XAD adsorption resins rely on hydrophobic or hydrophilic interactions between the resin and solute (Peuravuori and Pihlaja 1998b). Because water is a polar solvent, causing non-polar organics, termed hydrophobic (HPO), partially separated from the aqueous phase. When Van der Waal forces become the dominant attraction force in acidic condition, it enables HPO molecules of NOM to adsorb onto resins. On the other hand, dipole forces exist in alkaline conditions promoting NOM to the aqueous phase (Piper 2010).

Ion exchange resins not only adsorb NOM by ionic bonding but also accompany inorganic salts that relatively decrease NOM desorption from resin and the reusability of resins because inorganic salts could not easily be removed. XAD resins tend to avoid adsorbing such smaller MW inorganic salts. Thus, XAD resins are most commonly used in NOM characterization.

Aiken et al. (1979) evaluated five Amberlite XAD resins for isolation of fulvic acid from aqueous solution and stated that XAD-8 has the highest recovery of organic solutes from water. Throughout years, XAD-8 has been well accepted to adsorb hydrophobic organic matter (humic substances) until Chang et al. (2001) and Goslan et al. (2002) replaced it by XAD-7HP because the manufactory discontinued XAD-8 and recommended XAD-7HP instead. Malcolm (1985) mentioned that hydrophobic components represent up to 65% of DOC in water and hydrophilic acids components that did not sorb on XAD-8 resin represents up to 30% of DOC. Leenheer (1981) successfully used Duolite A-7 after XAD-8 to isolate hydrophilic acids but with inadequate quantification. Soon afterward, Leenheer and Noyes (1984) developed a method of XAD-8 and XAD-4 in tandem for isolation of hydrophilic acids from the water. In the year of 1992, Malcolm and MacCarthy first quantitatively evaluated the XAD-8 and XAD-4 resin in series to isolate dissolved organic solutes. Meanwhile, Aiken et al. (1992) also used XAD-8 and XAD-4 to separate organic solutes into hydrophobic and hydrophilic components and defined these two fractions as follows (Table 2.2):

Table 2.2 Operational definitions of fractions obtained by XAD-8/XAD-4 resins (after Aiken et al. 1992)

Fractions	**Definition**	**Composition**
Hydrophobic acids	adsorbs on XAD-8 at pH 2 eluted at pH 13;	aliphatic carboxylic acids of 5-9 carbons, one- and two- ring aromatic carboxylic acids, one- and two- ring phenols and aquatic humic substances
Hydrophilic acids	in the XAD-8 effluent at pH 2 but adsorbs on XAD-4, is eluted at pH 13；	polyfunctional organic acids and aliphatic acids of five or fewer carbons

Since then the application of XAD-8/XAD-4 in tandem has been studied extensively. This has been introduced to broad yet not absolute fraction names and definitions. Still, there are many other names have been given throughout in literature depending on the aim of the research and the preference of the author. Table 2.3 presents a summary of common fractions and definitions through varying methods. Note: DAX-8 and XAD-7HP have been substituted for XAD-8 as its discontinuation by the manufactory.

Table 2.3 A summary of typical fractions and definitions

Resins	Fractions	Definition	References
XAD-8/XAD-4	1. Hydrophobic acid 2. Hydrophilic acid	1. Adsorbed on XAD-8 at pH 2; desorbed at pH 13; 2. XAD-8 effluent adsorbed on XAD-4 at pH 2 and desorbed at pH 13	Aiken et al. (1992)
XAD-8/XAD-4	1. Hydrophobic acid (Fulvic acids & humic acids) 2. Hydrophobic neutral 3. XAD-4 acids	1. Adsorbed on XAD-8 at pH 2; desorbed at pH 13; acidified to pH 1 where humic acids precipitates and fulvic acids remains soluble 2. Acidified XAD-8 to pH 2 then Soxhlet extracted with acetonitrile and water; evaporated and freeze-dried 3. XAD-8 effluent adsorbed onto XAD-4 at pH 2; desorbed at pH 13	Malcolm and MacCarthy (1992)
XAD-8/XAD-4	1. Hydrophobic acids 2. Transphilic acid 3. Hydrophilic 4. Ultra-hydrophilic acid	1. Same as in Aiken et al. (1992) 2. Same as XAD-4 acids 3. Adsorbed onto XAD-4 for the second time 4. Non-adsorbed onto either XAD resins	Croué et al. (2000)
XAD-7/XAD-4	1. Hydrophobic organics 2. Hydrophilic acids	1. $\text{DOC}_{\text{(Hydrophobic organics)}} = \text{DOC}_{\text{(Raw water)}} - \text{DOC}_{\text{(XAD-7 effluent)}}$ 2. $\text{DOC}_{\text{(Hydrophilic acids)}} = \text{DOC}_{\text{(XAD-7 effluent)}} - \text{DOC}_{\text{(XAD -4 effluent)}}$	Chang et al. (2001)
XAD-8/XAD-4	1. Hydrophobic NOM 2. Transphilic NOM 3. Hydrophilic NOM	1. Adsorbed on XAD-8 at pH 2 and eluted with Acetonitrile/Water (75%/25%)	Croué (2004)

		2. XAD-8 effluent adsorbed onto XAD-4 at pH 2 and eluted with Acetonitrile/Water (75%/25%) 3. Do not adsorb onto XAD-8 and XAD-4	
DAX-8/XAD-4/ IRA-958	1. Very hydrophobic acid (VHA) 2. Slightly hydrophobic acid (SHA) 3. Hydrophilic charged (CHA) 4. Hydrophilic neutral (NEU)	1. $\text{DOC}_{\text{(VHA)}} = \text{DOC}_{\text{(Raw water)}} - \text{DOC}_{\text{(DAX-8 effluent)}}$ 2. $\text{DOC}_{\text{(SHA)}} = \text{DOC}_{\text{(DAX-8 effluent)}} - \text{DOC}_{\text{(XAD -4 effluent)}}$ 3. $\text{DOC}_{\text{(CHA)}} = \text{DOC}_{\text{(XAD -4 effluent)}} - \text{DOC}_{\text{(IRA-958 effluent)}}$ 4. $\text{DOC}_{\text{(NEU)}} = \text{DOC}_{\text{(IRA-958 effluent)}}$	Chow et al. (2004)
XAD-7HP/XAD-4/AG-MP- 50	1. Hydrophobic acid (Fulvic acid & Humic acid) 2. Hydrophilic acids 3. Non-acid hydrophilic	1. Same as in Malcolm and MacCarthy (1992) 2. Same as in Malcolm and MacCarthy (1992) 3. The effluent from both columns Note: Fulvic acid, Humic acid, and hydrophilic acids were hydrogens saturated by AG-MP-50	Goslan et al. (2002)

Generally, before passing through resins, solutions are commonly acidified to pH 2 to maximize hydrophobicity without causing precipitation of the humic material (Piper 2010). After fractionation with XAD-8/DAX-8/XAD-7HP, the hydrophobic fraction can be further classified into humic acids (HA) and fulvic acids (FA) for HA precipitating at pH 2 (Thurman and Malcolm, 1981). This method to produce FA, HA, and non-humic substances then has been acknowledged as the standard by the US Geological Survey and the International Humic Substances Society (IHSS). On the contrary, the isolation of so-called hydrophilic substances is quite challenging. Croué et al. (2000) first nominated "transphilic" (TPH) for the fractions which adsorbed onto XAD-4 to differentiate it from more hydrophilic NOM which exists in the XAD-4 effluent and well accepted afterward. Once the decks for the definition of fractions have been cleared, XAD resins developed fast with combined methods to study more particular problem such as NOM reactivity with chlorine. Examples of characterization of NOM by XAD resins are outlined in Table 2.4.

Table 2.4 Applications of NOM characterization by XAD resins

NOM Source	Applications	Fractions	Findings	References
Lake; river; contaminated groundwater	To isolate and characterize a large portion of hydrophilic acids by XAD-8/XAD-4; to discuss factors controlling sorption	1. Hydrophobic acids 2. Hydrophilic acids	1. DOC isolated on XAD-8 (23-58%); on XAD-4 (7-25%) 2. Hydrophilic acids had lower MW with greater heteroatom and carboxyl content, and weak aromatic	Aiken et al. (1992)
Control (Side A) and artificially acidified (Side B) lake water	To present the XAD-8/XAD-4 procedure and DOC removal; to discuss factors that affect character of NOM	1. Hydrophobic acids (Fulvic acids & humic acids) 2. Hydrophobic neutral 3. XAD-4 acids	1. DOC isolated on XAD-8 (65%); on XAD-4 (20%) 2. Two sides of the lake were similar in general organic chemical composition although total DOC concentration of each side varied	Malcolm and MacCarthy (1992)
Reservoirs and rivers	To characterize and compare the DOC of various river and reservoir waters	1. Hydrophobic 2. Hydrophilic acids 3. Non-adsorbed Hydrophilic	1. Reservoirs were more abundant in DOC than rivers 2. Hydrophobic fractions dominated in reservoir compared to river whereas non-adsorbed hydrophilic fractions dominated in river 3. Reservoir waters were more	Martion-Mousset et al. (1997)

			reactive with chlorine and ozone than river waters	
Peat catchment	To identify seasonal patterns in the molecular characteristics of NOM constituents isolated from the same source	1. Humic acid 2. Fulvic acid 3. Hydrophilic acid	1. Characteristics of fulvic and hydrophilic fractions exhibited seasonal changes in later summer/ early autumn whereas humic acid exhibited changes during the summer	Scott et al. (2001)
Raw water from reservoir and filtered water in three individual months	To investigate the seasonal changes in the character of NOM and the effect on their fate through the water treatment works	1. Hydrophobic acid (Fulvic acid & Humic acid) 2. Hydrophilic acids 3. Non-acid hydrophilic	1. Hydrophobic NOM increased in autumn compared to winter and summer, and trihalomethane increased in the both hydrophobic and hydrophilic fractions 2. In autumn a significant untreated fulvic acid went through the treatment works and contributed to the trihalomethane formation 3. Hydrophilic non-acid was hardly	Goslan et al. (2002)

			removed and markedly increased in winter	
Moorland peat catchment	To understand the temporal and spatial variations in NOM and the impact on coagulation	1. Humic acid 2. Fulvic acid 3. Hydrophilic acid 4. Hydrophilic non-adsorbed	1. Hydrophobic NOM dominated in the water 2. Hydrophobic NOM had a higher charge density than hydrophilic NOM. 3. Hydrophilic non-adsorbed NOM was hard to remove by coagulation	Sharp et al. (2006)
Raw water collected monthly	To determine the concentrations and fractional distributions of NOM in raw water	1. Hydrophobic fraction 2. Hydrophilic fraction	1. The bulk water source was hydrophobic. 2. High potential for the formation of DBPs due to the high DOC concentration	Bazrafshan et al. (2012)

XAD fractionations have been increasingly applied to assess spatial and temporal variations in NOM types, as well as predict the potential for DBPs formation to shed lights on water treatment process. Disadvantages and operational difficulties such as extreme pH condition, irreversible adsorption, contamination from resin bleeding or overloading, potential chemical changes for the original NOM, well-trained technicians required and time-consuming could hinder the success of the study (Matilainen et al. 2011). Cautious material preparation will be comprehensively discussed in a later chapter.

2.2.4.2 Fractionation by membrane separation

When referring to membrane separation, it usually means ultrafiltration and reverse osmosis (RO). NOM separated by membranes due to molecular sizes within molecular weight cut off (MWCO) from 500 to 30,000 Daltons (Da) (Goslan et al. 2004; Wei et al. 2008). RO tends to concentrate a broad range of organic matter along with inorganic constituents rather than simply separating NOM (Maurice et al. 2002). It is always combined with electrodialysis (ED) for desalting while ultrafiltration theoretically retains only the high molecular weight (MW) fraction (typically >1 kDa) of the organic solutes; small molecules and inorganic salts pass through the membrane (Minor et al. 2014). However, when NOM source came from seawater, ultrafiltration still needs diafiltration with deionized water to remove inorganic salts. Selective examples of membrane separation methods for NOM characterization are outlined in Table 2.5.

Table 2.5 Selective applications of NOM characterization by membrane separation

NOM Source	Applications	Membrane type	Findings	References
Brown-yellow surface water	To separate humus according to molecular size by ultrafiltration membranes	Diaflo ultrafiltration Membranes (kDa)	1. 10% of the organic carbon; 1% of the coloured matter had MW < 1kDa 2. 50 and 90% of organic carbon and colour are found in the fraction had MW >20 kDa	Gjessing (1970)
Coastal seawater	To determine the molecular weight or size distribution of DOM in coastal seawater by ultrafiltration	Diaflo ultrafiltration Membranes (100,10,0.5 kDa)	1. MW< 500 accounted for 24-42% of the total DOC 2. MW> 100 kDa accounted for 8-23% of the total DOC. 3. Distribution of MW changes with the state of decomposition of organic matter	Ogura (1974)
River	To compare ultrafiltration and C_{18} solid-phase extraction (SPE) disks as DOM isolation methods for estuarine samples	Stirred cells Cellulose membrane (1kDa)	1. Desalting procedure in UF did not contribute to the sample DOC 2. For estuarine and coastal DOM which appeared to be more carbohydrate- and protein-rich, ultrafiltration resulted in a higher recovery	Simjouw et al. (2005)

Three surface waters in the peat bog area	To separate NOM according to outer structures by ultrafiltration and to further elucidate the selective enrichment of inner structures in the fractions by NMR	Dead-end Polyethersulfone membrane with pore size cut-off of 0.1μm Cross-flow regenerated cellulose membrane with MWCO of 10kg/mol	1. The large molecular size fractions was rich in polysaccharide material 2. Aromatic structures were most abundant in the intermediate size fraction 3. Fouling layers of the ultrafiltration membrane were enriched in long-chain aliphatic (lipids)	Lankes et al. (2008)
Three seasonal water samples from a reservoir	To study the seasonal changes in the characteristics of the DOM from a reservoir	YMdisc ultrafiltration membranes (30,10,3,1kDa)	1. The physical (MW) fractions exhibited large seasonal changes in UV_{254} and THMFP 2. 10–30 kDa and less than 1 kDa fractions were major components in most seasons	Wei et al. （2008）

Water samples from a treatment plant	To investigate the relationships between MW and DBPs precursors from selective stages of drinking water treatment process	RO (500,100,30,10,3,1,0.5 kDa)	1. MW <0.80 kDa had greatest polarity and aromaticity also accounted for major trihalomethane precursor 2. Advanced drinking water treatment should focus on the removal of low MW (RO fractions) in the source water	Zhao et al. (2009)
Natural freshwater and artificially salted water from lake and river	To better understand how salinity may affect the isolation of aquatic dissolved organic matter via C_{18} SPE and stirred-cell ultrafiltration	Millipore regenerated cellulose membranes (1kDa)	Presence of dissolved salt ions reduced the effectiveness of ultrafiltration in isolating high MW from solution	Kruger et al. (2011)
A boreal watershed	To study mechanisms of DOM migration within the typical small watersheds of the subarctic zone and its possible transformation reactions in the estuarine zone	Cascade filtration through decreasing pore size (100, 20, 10, 5, 0.8, 0.4, 0.22, 0.1, 0.046 μm, 100 kDa, 10 kDa and 1 kDa)	Expected the variability in chemical nature and MW of DOM delivered by small coastal watersheds to the Arctic Ocean during the summer baseflow period.	Ilina et al. (2014)

Overall, membrane separation allows a large volume of water samples being fractionated at a certain time but has higher membrane fouling potential. Unlike resin adsorption, well-defined experimental protocols of membrane separation have not been developed yet. Wei et al. (2008) compared that the properties of chemical fractions (isolated by resin adsorption) tended to be more stable than those of physical fractions (separated by UF) throughout the sampling period. To date, using one or a combination of XAD resins is still recognized as the classic extraction approach with numerous successful examples.

2.2.4.3 Fractionation by size exclusion chromatography (SEC)

Chromatography is a methodology for measuring the molecular size of aquatic substances. The theory of SEC fractionation is the bigger the molecules, the shorter the retention time (Matilainen et al. 2011). When the sample travel across the column, smaller compounds permeate the matrix pores greater than the larger components to be retained longer; larger materials then will elute first and smallest last (Hongve et al. 1996).

High-performance liquid chromatography (HPLC) also called high-performance size exclusion chromatography (HPSEC) coupled with different detectors has become very useful for NOM characterization as its higher resolution chromatograms and shorter analysis times (Becher et al. 1985). This technique can be briefly described that an eluent (mobile phase) is pumped through the column which is packed with the stationary phase at high pressure and the column effluent passes through a detector or multiple detectors like UV-Vis, Fourier transform infrared (FTIR), excitation emission fluorescence and on-line DOC analysers (Goslan 2003; Matilainen et al. 2011). For the eluent, a phosphate buffer solution added sodium chloride or sodium acetate to adjust ionic strength is common; for the columns, silica-based and polymer-based supports are popular (Swietlik et al. 2004; Matilainen et al. 2006; Sarathy and Mohseni 2007; Fabris et al. 2008; Liu et al. 2008, 2010; Soh et al. 2008; Zhang et al. 2008; Korshin et al. 2009; Zhao et al. 2009). Limitations of HPLC/HPSEC system lie in the fact that it is better to compare MW of NOM from waters in the same analysis methods rather than obtain the values of MW (Goslan 2003) and lack of proper standards.

2.2.5 Conclusions

The presence of NOM in drinking water production is undesirable. Understanding and predicting the reactivity of bulk NOM and its fractions in stages of water treatment is essential. Much of the literature showed great interests in NOM variability and DBPs formation, but fewer discussed the seasonal changes in bulk and fractions of NOM in relation to a drinking water ultrafiltration. Resin adsorption method would be chosen in the study. Although this method is relatively mature and systematic, the loss of NOM during the separation due to alteration or synergistic effect should be accepted.

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Chapter 3. Aging impact on ultrafiltration membranes from a full-scale drinking water treatment plant: An autopsy study

3.1 Introduction

Membranes play a significant role in potable water treatment because of universal treatment capabilities and competitive costs. Pore sizes of ultrafiltration (UF) membranes range from 0.01 to 0.05 mm (nominally 0.01 mm) so that they can retain larger organic macromolecules (Koyuncu et al. 2015). Plus, their pore sizes are smaller than the size of the smallest viruses. UF is dominant when water treatment plants are seeking a reliable physical disinfection barrier at a reasonable cost.

Membrane module types and materials vary considerably. For example, hollow fiber (HF) membranes have merits of higher packing density and readily permit backwashing. Material made of polyvinylidene fluoride (PVDF), a semi-crystalline polymer, is known for stability when it is attacked by corrosive chemicals and organic compounds including acids, alkaline, strong oxidants and halogens (Wang et al. 1999). PVDF HF ultrafiltration membranes are often operated in a tangential flow mode to maximize flux rates and membrane life.

Membrane life and performance have attracted the most attention in the industry field. Membrane aging became an important issue recently for its impact on membrane properties. In a full-scale plant, fouling, chemical cleaning, seasonal change in raw water temperature, and operating conditions (sucking and backwashing mechanical forces) are associated with membrane aging (Zsirai et al. 2012; Akhondi et al. 2014; Norafifah et al. 2015). In lab-scale studies, factors that cause membrane aging were isolated and investigated. He et al. (2014)

reported that membrane aging deteriorated the tensile strength of the membrane media, and degraded the intensity of surface resident functional groups, which led to the tendency of accumulation of foulants. Bogati et al. (2015) in our research group studied the effect of chemical cleaning on membrane properties, and they successfully set up an optimized cleaning procedure to achieve a higher permeability recovery which was applied throughout the study.

However, limited studies targeted at the relationship between membrane aging and membrane structure (membrane diameter, pore sizes) from full-scale plant membrane samples. In this study, full-scale membrane samples classified in three age groups by their “service time”, their structures and properties, including membrane morphology, permeability, membrane resistance, dextran rejection, porosity, and break strength, were determined. This study is to throw light upon how membrane aging influences the hollow fiber UF membrane. Note that the characterization of the virgin membrane was performed but the membrane manufacturer and the research group have reached an agreement to not present the results for the trade secret.

3.2 Experimental Section

3.2.1 Membrane bundles preparation

Polyvinylidene fluoride (PVDF) hollow fiber membranes were obtained from a drinking water membrane filtration plant in Canada in three age groups (0.8 years, 1.5 years, 1.8 years) throughout the study. Table 3.1 shows a summary of the membrane characters and plant operational parameters provided by the water treatment plant and the manufacturer.

Table 3.1 A summary of membrane and plant operational conditions

Membrane material	Polyvinylidene fluoride (PVDF); hollow fiber (HF)
Manufacturer's normal pore size	0.020 μm
Operating conditions	Membrane flux at 15-35 L/m^2 h (LMH); 240-360 min permeation (93% recovery) and 300 sec backwashing per operational cycle
Membrane cleaning strategies	Maintenance cleans: 100 mg/L hypochlorite solution daily; Recovery cleans: 500 mg/L hypochlorite solution monthly and 2000 mg/L citric acid solution every two months.

Each performed outside-in flow path lab-scale HF membrane bundle consisted of nine fibers with an effective length of 23 cm sealing end to end with the epoxy glue. After the glue had dried out, a 2-cm length plastic tube was glued again onto the bundle to secure and connect it to the peristaltic pump tubing. A comprehensively effective membrane area was around 62.1 cm^2 per bundle. Six prepared membrane bundles, two bundles for each age group, were immersed in deionized water with 1% sodium metabisulphite ($Na_2S_2O_5$) (Sigma-Aldrich; Product No.: 243973; analytical standard) for preventing biofilms.

3.2.2 Membrane characterization

A schematic diagram of the lab-scale dead-end filtration setup is shown in Fig. 3.1, which would use for membrane permeability test and dextran rejection determination.

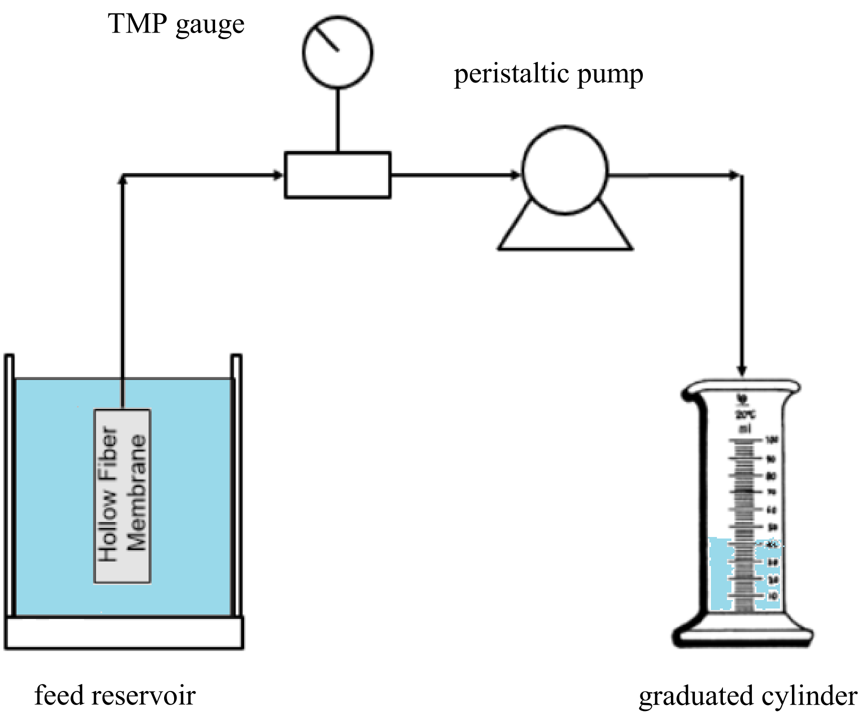


Fig. 3.1 A schematic diagram of the experimental setup

3.2.2.1 Morphology observation

Surface and structure of membranes were visually characterized using a scanning electron microscope (SEM) (SU-70, Hitachi, Japan). Initially, the testing membrane was immersed in liquid nitrogen for 10 min (Tan et al. 2001). The frozen fiber then became flexed at ambient temperature, immediately and carefully taken out and cut into 1 cm length parts and smaller pieces by a sharp blade. To maintain the structure, quick and accurate cutting was significant. Two 1 cm length parts were stuck to two metal stands and coated with carbon by a sputter coater (Model 12560, Fulham, USA) for outer and inner surface observation. Similarly, smaller pieces gathered on two metal stands and coated with gold for cross-section observation. The diameter of lumen and thickness of membrane were measured by the software of ImageJ (Version 1.51d, National Institutes of Health, USA).

3.2.2.2 Pore size distribution

The membrane pore size distribution was determined by analyzing 24 SEM photomicrographs of membrane outer surface. The equivalent diameter of a circle on the surface SEM image represented the pore size in every condition. Four SEM pictures were randomly captured for any given membrane bundles before and after cleaning, respectively. There were 95 and 105 membrane pores for 0.8 years membrane before and after cleaning; 85 and 95 pores for 1.5 years; 55 pores only for 1.8 years after cleaning. ImageJ (Version 1.51d, National Institutes of Health, USA) was employed to define the membrane pore size in SEM photomicrographs.

3.2.2.3 Permeability

Pure water flux characterized the membrane permeability: allowing deionized water to pass through the prepared membrane bundle under varying transmembrane pressure at operating temperature (21±1°C) as shown in Fig. 3.1. The value of pure water flux was measured under steady state condition using the following equation (Chakrabarty et al. 2008):

$$J_{\mathrm{w}} = \frac{\mathrm{V}}{\mathrm{A\Delta T}} \qquad \text{Eq. (3.1)}$$

Where J_w is pure water flux ($\mathrm{Lm^{-2}\,h^{-1}}$), V is the volume of water permeated and collected in the graduated cylinder (L), A is the effective membrane area per bundle ($\mathrm{m^2}$) and ΔT is the setup permeation time.

The permeability (P) is calculated from Eq. (3.2) as follow (Qin et al. 2015):

$$P = \frac{J_w}{\Delta P} \qquad \text{Eq. (3.2)}$$

Where P is permeability ($\mathrm{Lm^{-2}\,h^{-1}bar^{-1}}$), ΔP is the transmembrane pressure (bar).

The membrane permeability reported in the study was corrected to 20°C based on Eq. (3.3) (He et al. 2014):

$$\text{Permeability at } 20°C = \text{Permeability at } T\ °C \times (1.025)^{(20-T)} \qquad \text{Eq. (3.3)}$$

3.2.2.4 Dextran rejection determination

Dextran aqueous solution $(C_6H_{10}O_5)_n$ with specific molecular weight (MW) of 670 kDa (Product no.: 31425, Sigma-Aldrich) was prepared and used to determine membrane rejection. This dextran was commercially available and suitable because it gives a rejection of around 80% (Cui et al. 2017). The dextran solution with a concentration of 60 mg/L was prepared, and the rejection test was similar to the permeability test. The membrane was equilibrated under permeate cycle using the peristaltic pump at the lowest flow rate as shown in Fig. 3.1 (constant flux filtration) under the room temperature (21±1°C). All experiments were conducted six times, and average values were given. After equilibration, permeate and feed samples were collected for carbohydrate measurements (Gaudy 1962): 2 ml of each sample mixed with 5 ml of Anthrone reagent placed in the boiling water bath for 15 mins. After cooling down to the room temperature, took spectrophotometric (DR 2800, HACH, USA) readings at 625nm. The rejection rate (R) was determined according to the equation (Wang et al. 2010):

$$R = \frac{C_f - C_p}{C_f} \times 100\% \qquad \text{Eq. (3.4)}$$

where C_f and C_p represent the feed concentration and the permeate concentration, respectively.

3.2.2.5 Chemical cleaning

Based on the previous studies on optimization of chemical cleaning in our research group, three age groups of membrane bundles were first soaked in 200 ppm of sodium hypochlorite (NaClO)

(Product No.: 239305, Sigma-Aldrich) solution for 2 hours. Then soaked in 2000 ppm of citric acid (Product No.: 251275, Sigma-Aldrich) solution for 2 hours. Last, thoroughly cleaned and rinsed membrane bundles in deionized water to remove the chemical residue (He et al. 2014; Bogati et al. 2015).

3.2.2.6 Porosity

The membrane porosity ε (%) was the volume of the pores divided by the total volume of the porous membrane (Han et al. 2011). A gravimetric method defined as the weight of liquid immersed in the membrane pores often represented the value of the membrane porosity. The membrane sample was immersed in the deionized water which was used as the wetting liquid for 24 h. The water of the outer membrane surface was removed gently and quickly by a filter paper. After that, wet membrane's weight was measured. The dry membrane's weight was measured after drying overnight in the oven at the temperature of 105 °C. Measurements of each sample was taken four times, and average values were reported. The value of membrane porosity was obtained by the equations as follow (Chen et al. 2004; Zhang et al. 2006; Chakrabarty et al. 2008; Chen et al. 2015):

$$\varepsilon = \frac{V_{water}}{V_{membrane}} = \frac{\frac{w_1 - w_2 - w_3}{\rho}}{\left(\frac{\pi}{4}\right)(D^2 - d^2)l} \times 100\% \qquad \text{Eq. (3.5)}$$

$$w_3 = \frac{\pi d^2 l \rho}{4} \qquad \text{Eq. (3.6)}$$

Where, W_1: the weight of wet membrane (g), W_2: the weight of dry membrane (g), W_3: the weight of water in membrane hollow section (g), D: the outer diameter (mm), d: the inner diameter (mm), l: the length of the membrane sample (mm), ρ: the density of deionized water (1.0 g/cm^3).

3.2.2.7 Hydrophilicity

The water contact angle was measured to evaluate the membrane hydrophilicity, using an optical contact angle meter (Theta Lite 100, Biolin Scientific, USA). A drop of deionized water was placed onto the outer surface of a hollow fiber membrane. Waited 10 seconds until the droplet became stable (Chen et al. 2015). A video image system was used to capture the sessile drop images, measuring the contact angle values within the time and an associated software called OneAttension (Version 2.5, Biolin Scientific, USA) was used to analyze the contact angle results. The contact angle of each membrane sample was measured ten times on various positions of its outer surface and then was averaged.

3.2.2.8 Breaking strength

The breaking strength (MPa) of the membrane was calculated as the tensile strength (N) at the break point divided by the cross-section area of the testing membrane (m^2) (Cui et al. 2017). The tensile strength of the hollow fiber membrane was measured by a dual-range force sensor (A.U. Physics Enterprise, MI, USA) at room temperature. Membrane samples were cut into 10 cm long segments and knotted around the hook of the sensor (He et al. 2014). The Data-collection Software (Logger Pro 3, Vernier Software & Technology, USA) recorded every tensile strength at corresponding breaking point while manually slowly pulling the sample. Each sample was measured ten times to evaluate the repeatability.

3.2.3 Statistical analysis

The single factor analysis of variance (ANOVA, at $\alpha = 0.05$) in Microsoft Excel 2016 was applied to all the results to compare the difference among the experimental methods.

3.3 Results

3.3.1 Membrane morphology

The SEM micrographs of the cross-section, the inner surface and the outer surface of the membranes were taken at various magnifications to study the membrane morphology.

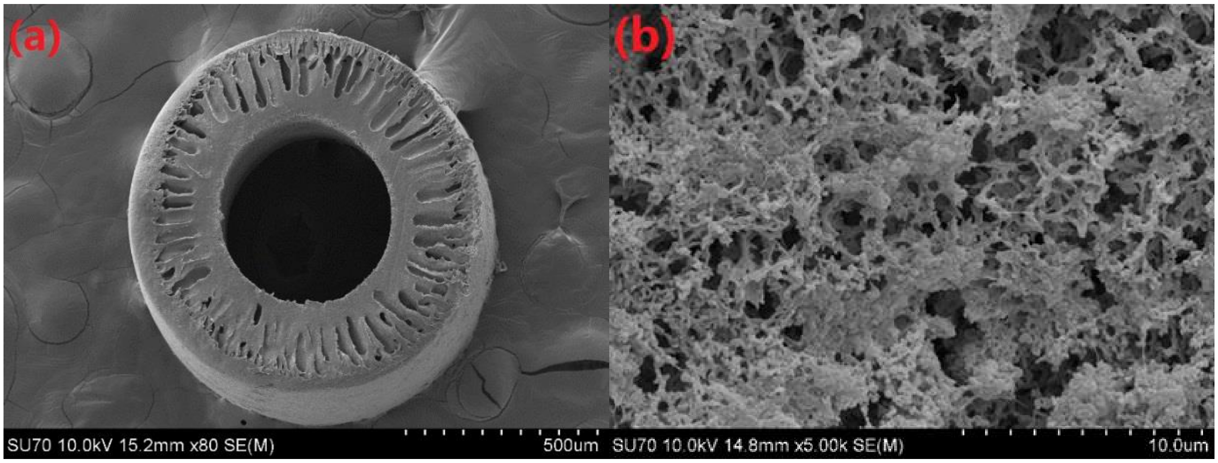


Fig. 3.2. (a) Cross-section morphology of HF membranes

(b) Inner surface morphology of HF membranes

A representative cross-section and inner surface morphology of hollow fiber membranes were shown in Fig. 3.2. Finger-like structures extend from the outer surface to the inner surface, while sponge-like structures gather near the inner surface as shown in Fig. 3.2 (a). There is no visible difference between membranes in three age groups from the view of the cross-section. All membranes display the porous and loose structure on the inner surface.

Table 3.2 summarizes the dimensions of the membrane cross-section in the experimental conditions. The results indicated that the lumen diameter of hollow fiber membrane decreased with the increase in membrane age. The membrane wall thickness ranged between 228.28 μm and 233.39 μm (ANOVA, P>0.05) which did not show a significant difference. After chemical cleaning, results showed that lumen diameter and thickness did not appear any obvious changes compared to the corresponding membranes before chemical cleaning.

Table 3.2. Dimensions of membrane cross-section (Unit: μm)

	0.8 years		1.5 years		1.8 years	
	BC[*]	AC[§]	BC	AC	BC	AC
Lumen diameter	487.23 [♯] (11.36)	491.02 [♯] (10.49)	483.73 [♯] (9.15)	483.71 [♯] (9.08)	480.73 [♯] (9.89)	474.42 [♯] (10.97)
Membrane thickness	228.28 [♯] (5.37)	232.73 [♯] (4.07)	233.79 [♯] (6.82)	233.66 [♯] (4.92)	233.39 [♯] (5.4)	230.63 [♯] (6.74)

[*]: before two-step cleaning; [§]: after two-step cleaning;

[♯]: numbers in brackets are standard deviations

Fig. 3.3 shows the pores on the outer surface morphologies of different HF membranes before and after two-step chemical cleaning. For 0.8 years and 1.5 years membrane, fewer pores were seen due to membrane fouling. For 1.8 years membrane, there were no visible pores which suggested that cumulative foulants blocked the pores, and foulants also covered the membrane outer surface to some extent. The outer surface morphologies of the membrane in three ages showed clearly that more pores emerged on the surface after chemical cleaning.

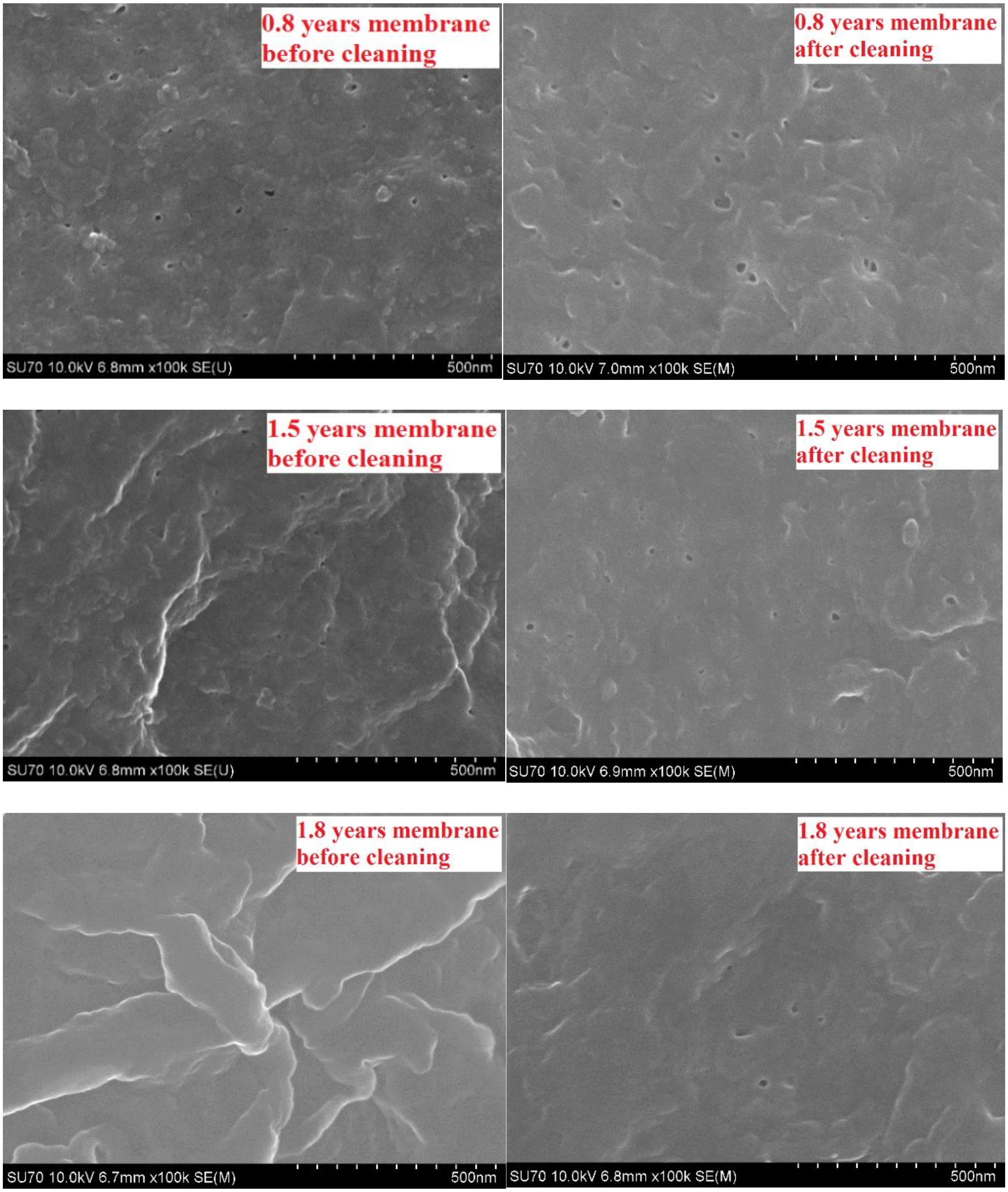
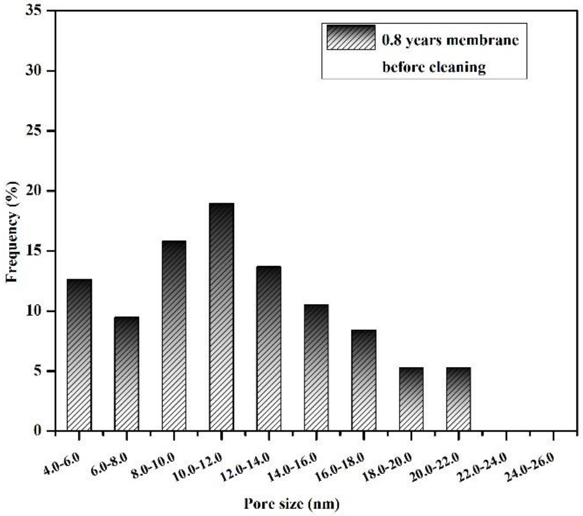
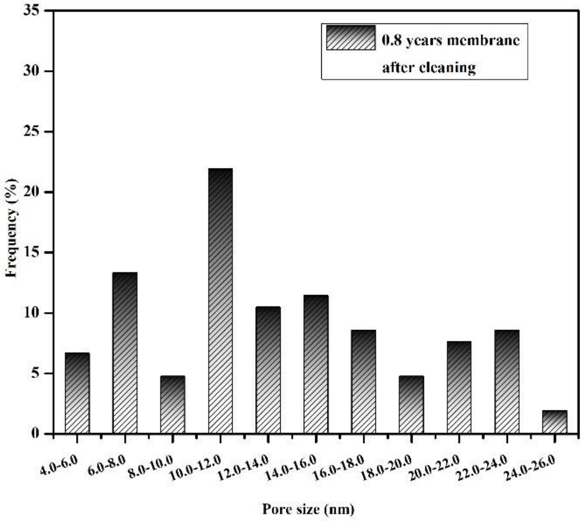


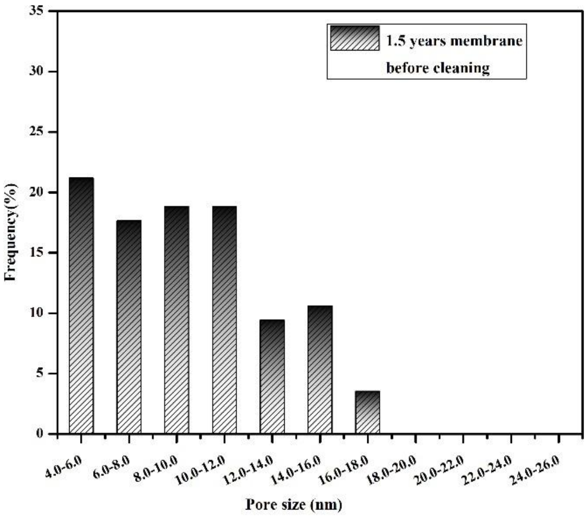
Fig. 3.3 Outer surface morphologies of hollow fiber membranes

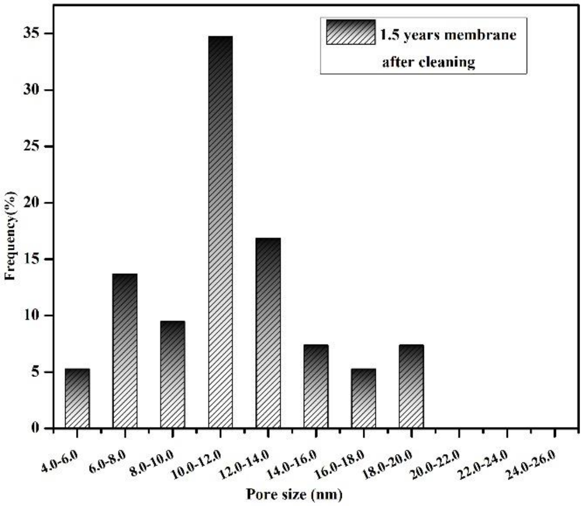
3.3.2 Pore size distribution

The pore size distribution (PSD) of all tested membranes was estimated from the SEM photomicrographs and reported as bar graphs in Fig. 3.4 (a). In both experimental conditions, the pore size distribution of 0.8 years is wider than that of 1.5 years while no analysis of 1.8 years membrane (before cleaning) conducted because no clear pores can be seen on the outer surface. This trend suggested that pore size shorten with the increase in membrane age or filtration time and even recommended chemical cleaning could partially remove foulants. After cleaning, the range for pore size distribution of 0.8 years and 1.5 years extended compared to those before cleaning. (4-22 nm vs. 4-26 nm; 4-18 nm vs. 4-20 nm). The pore size distribution of 1.8 years after cleaning had the narrowest range of 6 nm to 16 nm. In conclusion, during the operational filtration time, membrane fouling became severe, and some foulants were not sensitive to the cleaning agents such as NaClO and citric acid.


0.8 years membrane before cleaning
Frequency (%)
Pore size (nm)
0
5
10
15
20
25
30
35
4.0-6.0
6.0-8.0
8.0-10.0
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


0.8 years membrane after cleaning
Frequency (%)
Pore size (nm)
0
5
10
15
20
25
30
35
4.0-6.0
6.0-8.0
8.0-10.0
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


1.5 years membrane before cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
4.0-6.0
6.0-8.0
8.0-10.0
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


1.5 years membrane after cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
4.0-6.0
6.0-8.0
8.0-10.0
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0

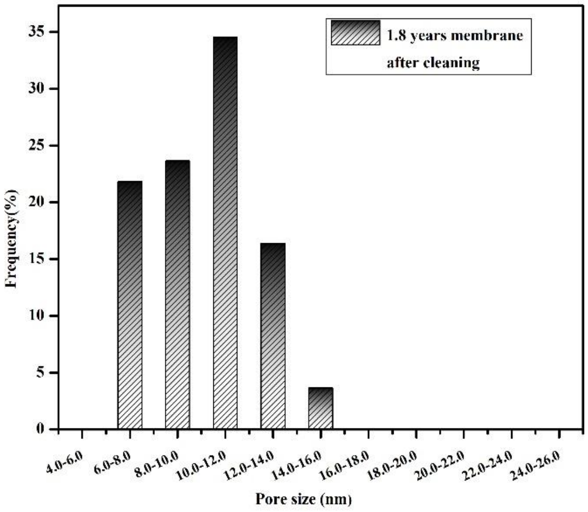
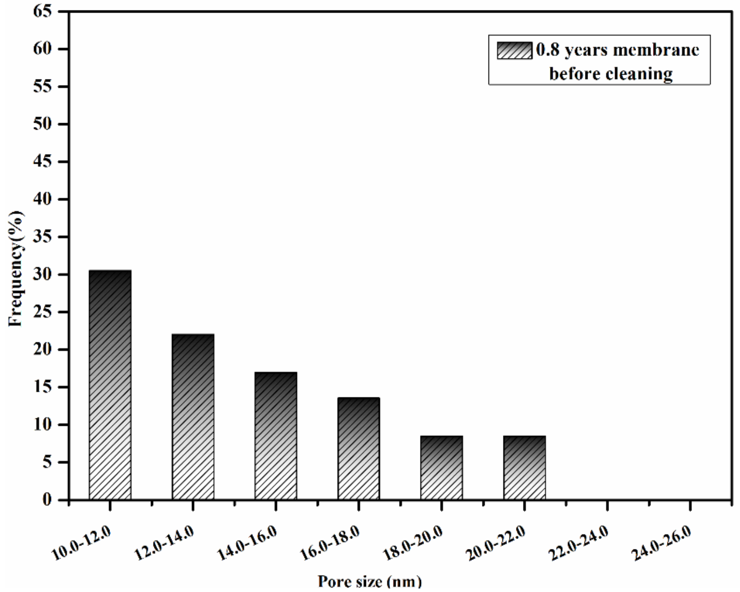
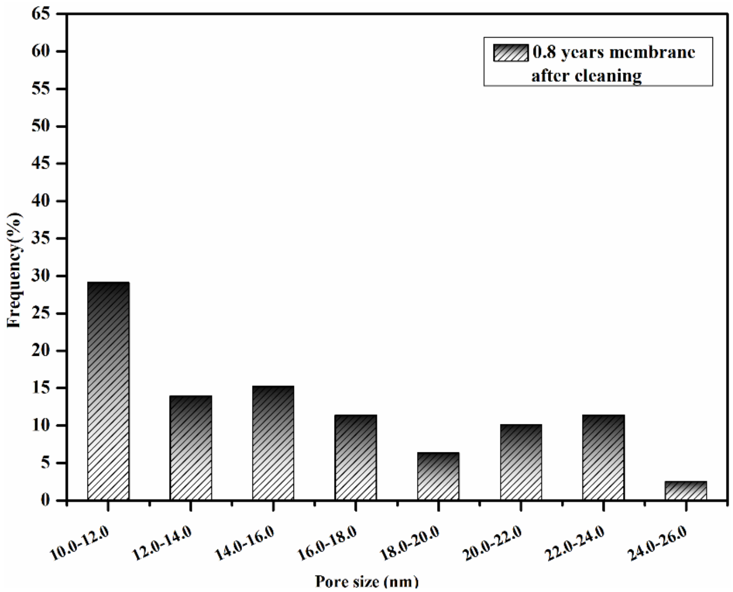
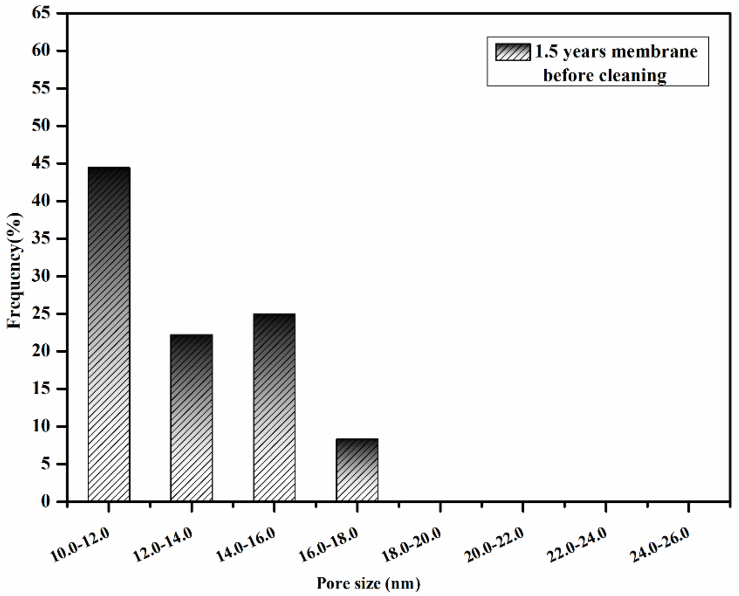


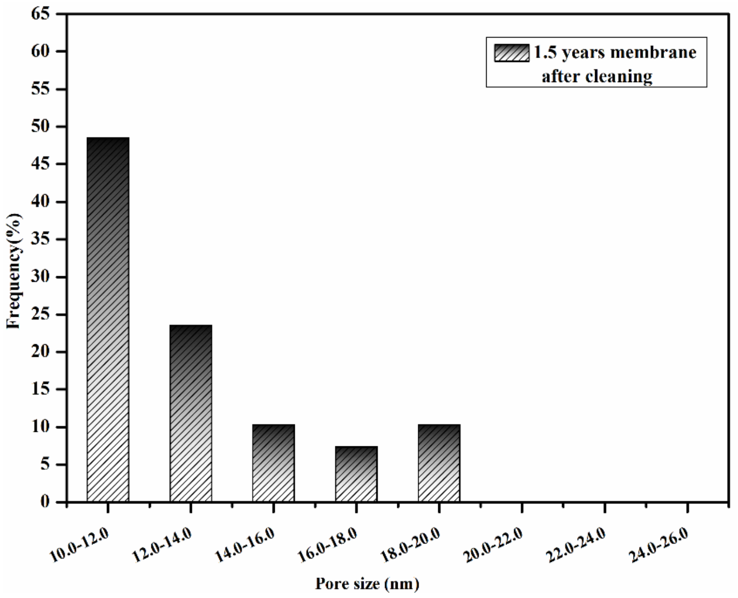
Fig. 3.4 (a) Pore size distribution of membranes (pore size from 5 nm)

One limitation of the pore size distribution study is that the relatively small pores (the size ranges from 4.0 nm to 10.0 nm) on the membrane surface observed from the current SEM images might be the dots of surface contaminates. To avoid this doubt, we cut off the pore sizes which are smaller than 10.0 nm and rearranged the pore size distribution in Fig. 3.4 (b). Fig. 3.4 (b) shares the same result with Fig. 3.4 (a) which is the range of the pore size distribution shrunk within the membrane age. Chemical cleaning extended the range at certain level due to the partial removal of foulants. Further studies should use a larger magnification of the SEM to verify if the small dots of the current SEM images (5-10nm) are real pores or contaminations.


0.8 years membrane
before cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


0.8 years membrane
after cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


1.5 years membrane
before cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0


1.5 years membrane
after cleaning
Frequency(%)
Pore size (nm)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
10.0-12.0
12.0-14.0
14.0-16.0
16.0-18.0
18.0-20.0
20.0-22.0
22.0-24.0
24.0-26.0

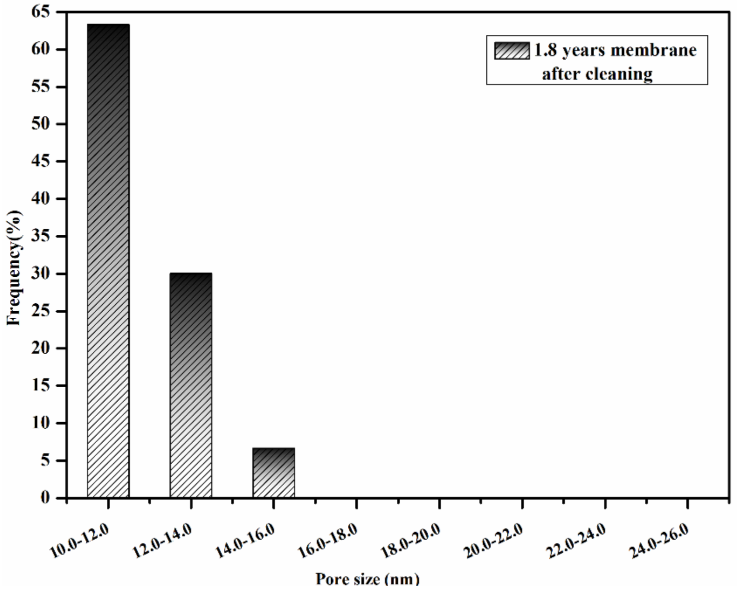


Fig. 3.4 (b) Pore size distribution of membranes (pore size above 10 nm)

3.3.3 Permeability

Pure water permeability is a direct indicator of membrane performance. The result is presented in Fig. 3.5. Membrane bundles of 0.8 years had the highest permeability either before cleaning or after chemical cleaning. The value of permeability had a dramatic drop when the membrane in the age of 0.8 years was compared to membrane at the age of 1.5 years (31.93%, before cleaning). Only a slight difference of permeability for membranes had been noticed between the age of 1.5 years and 1.8 years. Furthermore, results revealed that NaClO cleaning exerted a positive influence on membrane permeability recovery because of the removal of organic foulants on the membrane surface. The permeability recovery rates were 3.77%, 7.96%, and 4.74% for membranes of 0.8, 1.5 and 1.8 years, respectively. However, after citric acid cleaning, the permeability recovery rate could be neglected or even shown negative for 0.8 years membrane. Since citric acid is reported to be effective in removing inorganic foulants, it could suggest that foulants accumulated on the membranes in the study were not dominant by inorganic matter. It could also indicate that citric acid cleaning should be modified under optimal conditions.

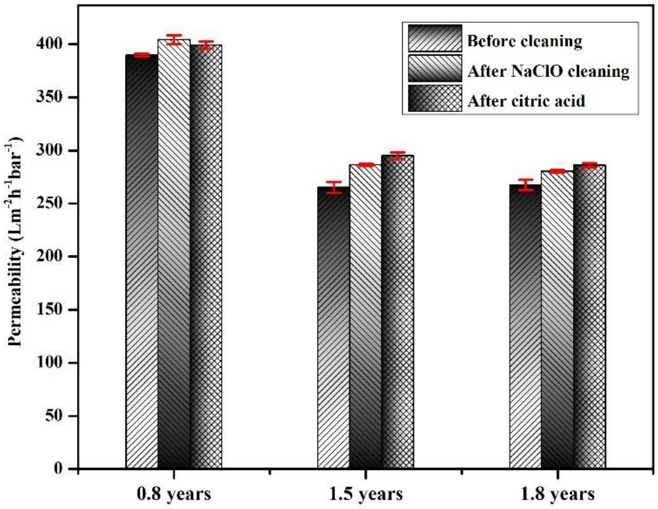


Fig. 3.5 Pure water permeability of membrane (ANOVA, P<0.05)

3.3.4 Dextran rejection

The dextran rejection of membrane bundles with different ages is depicted in Fig. 3.6. Dextran rejection shows a positive trend with the increase in membrane age yet a strongly negative trend with the treatment of chemical cleaning. For each age group of membrane bundles, considering the magnitude of the error bars, dextran rejection dropped very slightly after NaClO cleaning. Those results were due to the pores on the membrane surface were blocked thereby hindering transport of small deviations through pores. Dextran rejection decreased 3.14%, 2.06%, 5.72% for membranes in the age group of 0.8 years, 1.5 years and 2.5 years, respectively (ANOVA, P<0.05) after NaClO cleaning. Followed by citric acid cleaning, dextran rejection decreased 2.23%, 1.73%, 0.97%, respectively (ANOVA, P<0.05). Based on the results above, the main foulants accumulated onto the surface were probably organic matters. This could account for the reason why NaClO cleaning had a greater impact than citric acid cleaning on the dextran rejection test.

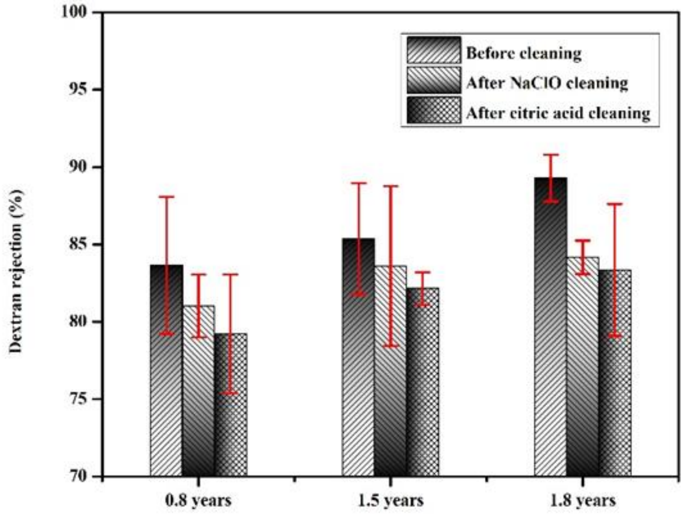


Fig. 3.6 Dextran rejection of membrane (ANOVA, P<0.05)

3.3.5 Porosity

Membrane porosity can be defined as the fraction of the void space in the membrane. As shown in Fig. 3.7, porosity decreased with the increase in membrane age. After foulants removed by NaClO and citric acid cleaning, membranes had higher porosity than before (75.82%-68.76% vs. 77.28%-68.76%) (ANOVA, P<0.05). That the degree of membrane fouling increased with membrane aging could explain the results. The results could explain the larger pore sizes and higher membrane permeability.

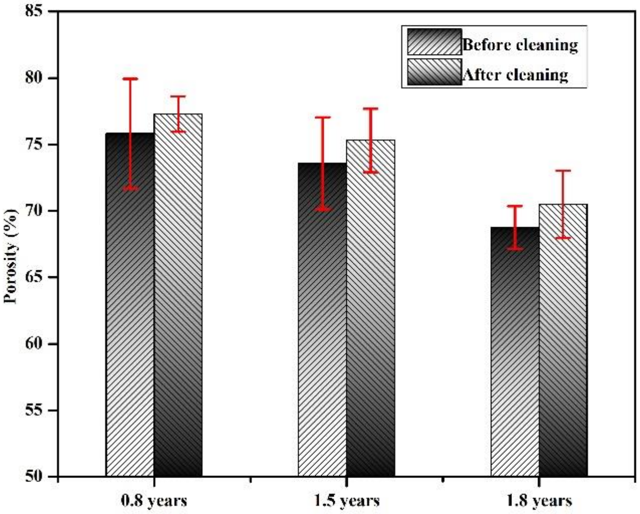


Fig. 3.7 Porosity of membrane fibers (ANOVA, P<0.05)

3.3.6 Hydrophilicity

The contact angle is a reliable method to determine the wettability of membrane surface. If the value is over 90°, then it is hydrophobic; if the value is below 90°, it considers as hydrophilic. Membranes used in the study are all hydrophilic and tend to adsorb water. As shown in Fig. 3.8, the contact angle dropped with age (from 73.01° to 62.88°) before cleaning while chemical cleaning procedures significantly decreased contact angle values (68.24° to 59.61°) (ANOVA, $P<0.05$). In conclusion, membrane aging and chemical cleaning improved the degree of PVDF membrane hydrophilicity. This phenomenon could be generated by the alteration in the membrane structure by aging and the exposure to chemicals like oxidants to remove foulants, which supported by Wolff and Zydney (2004) that bleach-treated membranes had larger effective pore sizes and greater negative charge that increased hydrophilicity.

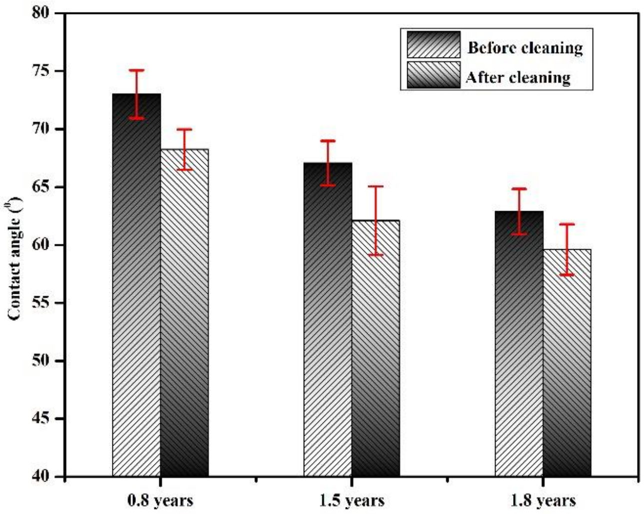


Fig. 3.8 Contact angle of membrane fibers (ANOVA, P<0.05)

3.3.7 Breaking strength

Breaking strength could tell the "tiredness" of the material after extensive cleaning and backwashing (Nghiem and Schafer, 2006). In the study, membrane fibers in the age of 0.8 years, 1.5 years and 1.8 years before cleaning and those after two-step chemical cleaning were both tested. The result is presented in Fig. 3.9. Breaking strength of membrane fibers decreased from 4.28 MPa to 3.87 MPa, which suggests membrane fibers became brittle with age. It was also noticed a slight drop in the breaking strength after two-step chemical cleaning (3.99 MPa to 3.76 MPa). Overall, breaking strength decreased with the cumulative operational times (expressed in years) and NaClO/citric acid cleaning performed in this study. The breaking of polymeric functional groups upon contact with cleaning chemicals leads a gradual deformation of the membrane structure and declination in mechanical strength (Lovinger 1982; Rabuni et al. 2015).

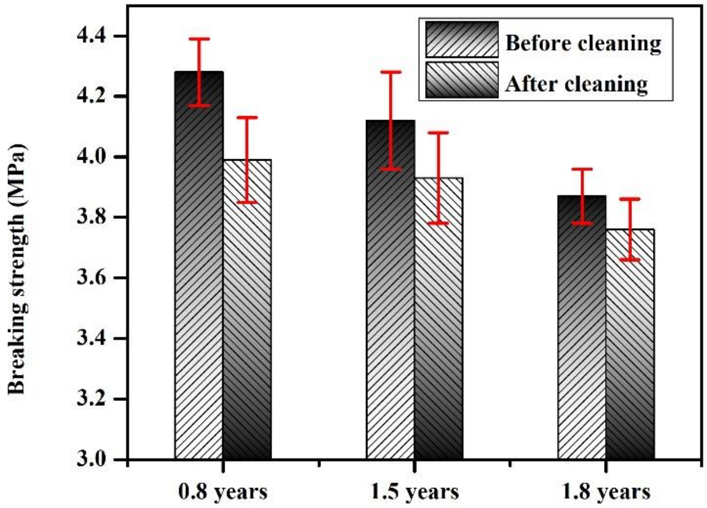


Fig. 3.9 Breaking strength of membrane fibers (ANOVA, $P<0.05$)

3.4 Discussion

The SEM morphology of membrane cross-section and inner surface structure showed no difference among all tested membranes (Fig. 3.2). Also, the membrane fiber wall thickness and lumen diameter had minor variations under experimental conditions (Table 3.2). Lumen diameter slightly decreased with membrane aging while thickness insignificantly increased with membrane aging. Since the membrane filtration plant located in the cold region of Canada, it is possible that cold water temperature (0.3-0.4°C) in feed water could have an impact on membrane structures, for example, causing the hollow fiber to shrink. So far, this study cannot verify the correlation between membrane structures and membrane aging, chemical cleaning, feed water temperature. Strictly controlled experiments need to be done to figure out their relationships.

Membrane fouling remains inevitable. During membrane filtration process, foulants such as colloidal particles and natural organic matter (NOM) of large molecular weight were attached on membrane surface forming a fouling layer. Fig. 3.3 showed that the outer surface was covered by foulants, while the inner surface was clear with no visible fouling (Fig. 3.2). This is because outer surface tended to expose to colloidal particles and NOM, while the inner surface was filled with permeate.

According to Fig. 3.5, the pure water permeability of membranes decreased with an increase in membrane age which suggests that membrane aging at least partially attributed to changes in membrane structure at three ages (Table 3.2 and Fig. 3.2, 3.3, 3.4, 3.6, 3.7). The decrease in pore size (Fig. 3.4), porosity (Fig. 3.7), lumen diameter (Table 3.2) with an increase in membrane age could be related to an increase in the hydraulic resistance or TMP and thus decreased permeability.

Membrane cleaning is accepted as a necessary procedure during the filtration operation to restore membrane flux and performance. Some foulants were successfully removed during NaClO cleaning. Thus, the increase in permeability appeared (Fig. 3.5). Liu et al. (2001) reported that organic fouling is dominant in membrane filtration if source water contained a relatively high level of natural organic matter (NOM). Furthermore, the internal pore plugging would cause greater hydraulic resistance than cake formation on membrane surface (Chang et al. 2015). Adsorption of NOM on the membrane remains a plausible mechanism considering that most NOM has smaller sizes than pore diameters of MF and UF used in drinking water filtration. Jucker and Clark (1994) mentioned that pore adsorption sites are preferentially filled before other sites on the membrane surface, and adsorption capacity varies with membrane material and foulants. From Fig. 3.3, surface fouling is the primary mechanism existed in membrane fouling. This seems confirmed by Fig. 3.4 that after two-step cleaning, the pore size is partially restored. On the other hand, sodium hypochlorite improved the permeability in degree while citric acid cleaning had minor influence (Fig. 3.5). This might suggest citric acid, as a chelating agent for Fe, was not effective in dissolving inorganic foulants containing Ca, Mg, Si, and S, etc. Further study can focus on the optimization of chemical cleaning to remove inorganic foulants.

The increased dextran rejection results for aged membranes were due to membrane pores blocked by the extension of membrane operation time (Fig. 3.6). The decreased membrane pore sizes could be explained by the membrane surface fouling (Fig. 3.3 and Fig. 3.4) and decreased membrane porosity (Fig. 3.7) caused by membrane shrinkage at cold temperature (0.3-0.4°C). Although for the same membrane, after NaClO cleaning membrane pore size partially restored, the dextran retention still decreased. Since solute rejection is primarily controlled by the membrane properties and pore structure, it is possible that foulants not only attached to the surface but could be filled inside the pores which could also account for why dextran rejection increased with the membrane aging. Likewise, after citric acid, the dextran rejection had a minor impact.

The porosity of membrane decreased with an increase in membrane age. This could be caused by membrane fouling on the membrane outer surface (Fig. 3.3) and reduced membrane internal pore sizes (Fig. 3.5). Furthermore, the porosity of all the membranes increased after chemical cleaning due to the foulants removal but kept decreasing with age. Internal pores clogging could be accepted.

Fig. 3.8 shows the contact angle decreased with the increase in membrane age which means membrane surface is getting more hydrophilic during filtration time. The presence of polar foulants accumulated on the membrane surfaces could explain that. After chemical cleaning, the contact angles for all the membranes maintained decreasing. This might explain by more hydrophilic sites were uncovered on the membrane surface after exposing to cleaning agents (hypochlorite) (Ravereau et al. 2016).

Breaking strength is negatively impacted by membrane aging. Membranes become less robust and more brittle with the “service time”. From Fig. 3.9, the mechanical strength of membranes deteriorated upon hypochlorite cleaning and led to the tendency for fiber breakage. Above findings fit with Arkhangelsky et al. (2007) and He et al. (2014). Possible reasons are that membrane aging aggravated chances of breakage in polymeric chains within PVDF membranes and daily operation in the plant coupled with periodic chemical cleanings exaggerated mechanical properties. (He et al. 2014).

3.5 Conclusions

Lab-scale studies investigated the effect of membrane aging on hollow fiber ultrafiltration membrane performances. Conclusions are listed as follows:

1. Pores on membrane surface were blocked heavily with the membrane aging. Optimized chemical cleaning (NaClO solution followed by citric acid) partially recovered pure water permeability.

2. The diameter of membrane lumen, membrane porosity, and membrane pore size decreased with membrane aging. Accumulation of membrane foulants and potentially cold temperature effect could explain the changes in membrane structure and properties.

3. The decrease in membrane permeability correlated well with the changes in membrane structure with an increase in membrane age.

4. Chemical cleaning could partially restore membrane permeability and porosity but deteriorate membrane breaking strength.

5. Membrane hydrophilicity increased with membrane aging and hypochlorite cleaning. Membrane surface alteration and mechanical deterioration could account for the results.

3.6 References

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Chapter 4. Assessing seasonal variation of NOM in raw waters, permeates and concentrates in a drinking water treatment plant

4.1 Introduction

Natural organic matter (NOM) is described as a highly heterogeneous mixture of organic compounds existed in ground and surface waters that vary spatially and temporally in NOM type and concentration (Sharp et al. 2006). Temporal changes at a single site remain uncertain due to Fearing's research in 2004, and he also suggested that understanding variations in NOM concentration should combine with NOM character.

Since bulk NOM has no readily identifiable structure, isolation of NOM is widely used to study NOM character (Kukkonen et al. 1990). Malcolm and MacCarthy (1992) developed a two-column resin adsorption technique based on hydrophobic-hydrophilic separation. Aquatic NOM consists of both hydrophobic and hydrophilic components where hydrophobic acids are believed to make up about 50% of the dissolved organic carbon (DOC) (Owen et al. 1993).

The Bare Point water treatment plant located in the city of Thunder Bay, ON, Canada which experiences four distinct seasons. The plant produces potable water by ultrafiltration for the city from Lake Superior. The research presented here investigated whether seasonal changes (winter and spring) affect the NOM entering the treatment plant and their fate through ultrafiltration.

4.2 Experimental section

4.2.1 Summary of treatment plant

All samples were taken from the Bare Point water treatment plant, located on the shores of Lake Superior and supplying drinking water to the city of Thunder Bay. The climate of the city has experienced a distinctively seasonal variation all year round.

4.2.1.1 Bare Point Water Treatment Plant

The Bare Point water treatment plant is a membrane filtration plant (producing 113.6 million liters per day) on the northeastern corner of the city using membrane ultrafiltration and post-chlorine disinfection. A fundamental treatment process schematic is shown in Fig. 4.1.

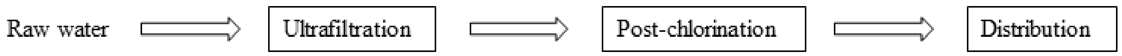


Fig. 4.1 Schematic of Bare Point water treatment plant

4.2.1.2 Water Samples

Each of 2 L raw water, permeates and concentrates was collected from the Bare Point Membrane Water Treatment Plant between 30/11/2016 and 29/03/2017 (six days) (three sets of samples for each season) to investigate NOM seasonality (18 samples in total). All samples were stored in plastic containers at -20°C before use.

4.2.2 Resin Fractionation

Raw waters, membrane permeates and concentrates were fractionated by XAD resin adsorption techniques into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPH) fractions using a method adapted from Piper (2010). The resins were XAD-7HP resin and XAD-4 resin (Amberlite, Rohm and Haas Co., PA, USA). XAD-7HP, acrylic based, macroporous, nonionic and moderately polar, is used to adsorb hydrophobic compounds. XAD-4, styrene-based, microporous, nonpolar, is used to adsorb transphilic compounds. A diagram of the fractionation method is shown in Fig. 4.2. Note that fractionation of membrane permeates, and concentrates shared the same procedures as of raw water.

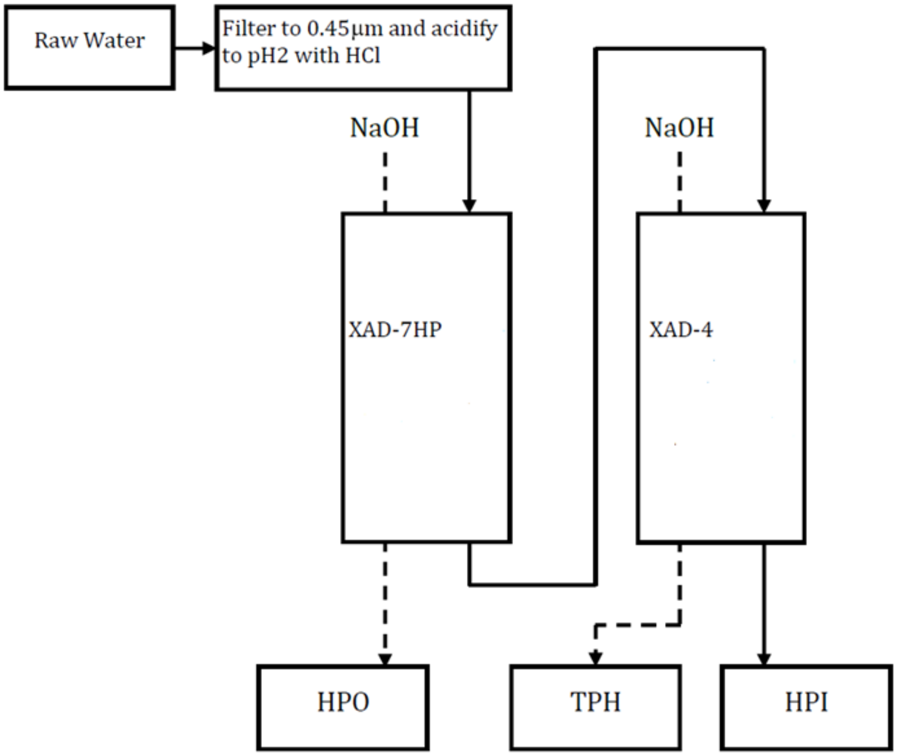


Fig. 4.2 A schematic diagram of the resin fractionation process

4.2.2.1 Resin preparation

XAD-7HP Resin (Amberlite)

All the resin preparation methods were modified from Goslan (2003) and Piper (2010). Approximately 150 mL of resin was slurried with 1 L of 0.1M NaOH solution and the solution was renewed daily for the first ten days. After decanting with NaOH solution, the resin was washed several times with deionized water. After ten days, the resin was rinsed three times with methanol and stored in methanol for 24 hours. Afterwards, the resin is ready for Soxhlet extraction. The resin was placed in the cellulose extraction thimble inside the Soxhlet chamber and was sequentially extracted for 48 hours each with 1.5 L of methanol, acetonitrile and again methanol. It is imperative that the resin should be carefully and thoroughly cleaned by those two steps because the new resin from the supplier is commercial grade with an abundance of impurities. Removing the fine resin particle is vitally significant to avoid clogging the resin column during the fractionation. All resins should be stored in methanol before use.

Before fractionation, two types of resin were packed into two chromatographic glass columns respectively and passed through the 8 L deionized water until the effluent DOC was no higher than 0.5 mg/L. It is critical to free the methanol from the resin because the sorptive properties of the resin are decreased for most solutes in the water-methanol mixture.

After washing out methanol, each column was passed through by 2.5-bed volumes of 0.1M NaOH followed by 2.5-bed volumes of 0.1M HCl several times to remove any hydrophobic solute contaminants in the deionized water. This base-acid rinse should be repeated right before daily resin column usage. The XAD resins should only be left standing in HCl solution in the column between daily usage of resin fractionation.

XAD-4 Resin (Amberlite)

XAD-4 resin preparation is the same as XAD-7HP Resin preparation.

4.2.2.2 XAD resins column capacity calculation

Both adsorption and elution of organic solutes on resins determine the hydrophobic-hydrophilic separation which is controlled by the polarity of the solute as well as the ratio of the resin to the solute passing through the resin bed. Leenheer (1981) mathematically defined the crossover of hydrophilic solutes into the hydrophobic fraction. Hydrophobic solutes are those that are greater than 50% retained on XAD-8 (XAD-7HP instead for factory discontinued) at a given ratio of resin to water passing through the column, while hydrophilic solutes are those that are greater than 50% eluted at the same ratio of resin to water eluent. Leenheer (1981) also introduced the column capacity factor k' (Eq. (4.1)):

k' = (mass of solute adsorbed on resin) / (mass of solute dissolved in water) Eq. (4.1)

In 1981, Thurman and Malcolm gave a final relation between k' and the breakthrough (elution) volume V_E (Eq. (4.2)):

$V_E = V_o \times (1 + k'_{0.5})$ Eq. (4.2)

where V_o = void volume

$k'_{0.5}$ means the effluent concentration is 50% of the influent concentration, the volume of sample applied to the resin column V is described by Eq. (4.3) (Leenheer 1981):

$V = 2\,V_E = 2\,V_o \times (1 + k'_{0.5})$ Eq. (4.3)

where $k'_{0.5} = 50$ is generally accepted in the literature.

In our research, the initial volume of each water sample for fractionation was 500 mL (V= 500 mL), $k'_{0.5} = 50$, solving from Eq. 4.3, Vo = 5 mL. As the void volume of XAD-7HP resin is ~65% of its bulk column volume, a 5- mL ÷ 0.65 = 8 mL column of XAD-7HP resin is required. XAD-4 resin column capacity calculation is the same as XAD-7HP Resin (8 mL).

4.2.3 Fractionation procedure

In this study, raw water, membrane concentrates and permeates are shared with identical fractionation methodologies including resin quantities and experimental sample volumes. Two adjustable permeation pumps and Teflon tubings were used to carry and pump all the testing samples from 500 mL graduated cylinders to resin columns in the course of the experiment. Column fractionations of each sample were triplicated. The following description of raw water fractionation is an example of the whole procedure.

Raw water (500 mL) from Bare Point water treatment plant was passed through a 0.45 µm cellulose acetate membrane filter (Sterlitech CO., WA, USA). 40 mL filtered raw water was collected for analysis of initial DOC content. The rest of 460 mL raw water was acidified to pH 2 (±0.2) using 0.1M HCl and ready for fractionation. Then the acidified filtered water was put through 8 mL of each XAD-7HP/ XAD-4 resin column in tandem. Flow speeds were maintained by the adjustable permeation pump at the lowest speed for two columns, respectively.

When 460 mL raw water sample was first passed through the XAD-7HP resin, the first 15 mL should be discarded. After the remaining 445 mL went through XAD-7HP, the effluent was collected in the 500-mL graduated cylinder, then pumped into XAD-4 resin column. Likewise, after passing through the XAD-4 resin, the first 15 mL should be wasted and 40 mL effluent was collected considered as the hydrophilic (HPI) fraction. 45 mL 0.1M NaOH was then passed through the XAD-7HP resin to desorb the hydrophobic (HPO) fraction in the same direction; first 5 mL was wasted and 40 mL effluent was collected as HPO fraction. Identically, after passing through the XAD-4 resin, 45 mL 0.1M NaOH was pumped into XAD-4 resin column to desorb and collect 40 mL transphilic (TPH) fraction. After 460 mL raw water sample had been passed through XAD-7HP/XAD-4 column pair, at least 1 L deionized water was passed through each column for returning the pH to neutral. Then, 20 mL 0.1M HCl reacidified the columns (pH=2) for the next procedure. Note that both resins can be reused for subsequent fractionations until resin run off with deionized water was above 1.0 mg/L tested by TOC analyzer.

4.2.4 Analytical methods

Dissolved organic carbon (DOC) was measured by a Vario TOC select (elementar, Americas). The measuring principle is based on the high temperature digestion of the sample in an air / O_2 stream at 850 °C. Totally bound carbon is oxidized to CO_2 which is quantitatively determined using a non-dispersive infrared (NDIR) detector. The DOC recovery calculated as follows:

$$\text{DOC recovery } = \frac{(DOC\ of\ concentrated\ sample)\times(Volumeof\ concentrated\ sample)}{(DOC\ of\ pretreated\ sample)\times(Volume\ of\ pretreated\ sample)}$$

$$= \frac{(DOC\ of\ HPO\ )\times 40mL+(DOC\ of\ TPH)\times 40\ mL\times\left(\frac{460}{445}\right)+(DOC\ of\ HPI)\times 445\ mL\times\left(\frac{460}{445}\right)}{(DOC\ of\ feed\ sample)\times 460\ mL}$$

4.3 Results

4.3.1 Bulk water analysis

Samples of raw, concentrated and permeated water samples collected on November 30, December 7, December 14, 2016, and March 15, March 20, March 29, 2017, were analyzed for pH, conductivity, and dissolved organic matter (DOC). These results are summarized in Table 4.1. Note that the word "feed" indicates as samples of raw water, concentrates, permeates before fractionation throughout the study.

Table 4.1 Characteristics of feed samples from the full-scale plant

Date	Source	pH	Conductivity (μScm^{-1})	DOC(mg/L)
30/11/2016	Raw water	6.88	68.38	3.141 ± 0.099
	Permeate	6.93	66.78	2.885 ± 0.595
	Concentrate	6.91	289.20	8.847 ± 2.450
07/12/2016	Raw water	6.88	63.73	4.735 ± 0.104
	Permeate	6.88	58.96	4.799 ± 0.865
	Concentrate	7.48	82.80	8.062 ± 0.739
14/12/2016	Raw water	6.24	60.47	3.637 ± 0.467
	Permeate	7.02	65.27	3.299 ± 0.225
	Concentrate	7.01	61.60	4.500 ± 0.129
15/03/2017	Raw water	7.27	56.12	2.871 ± 0.266
	Permeate	7.57	61.44	2.380 ± 0.897
	Concentrate	8.79	59.93	2.967 ± 0.196
20/03/2017	Raw water	6.83	72.27	2.680± 1.060
	Permeate	6.93	70.28	2.479 ± 0.000
	Concentrate	8.41	179.30	3.464 ± 0.466
29/03/2017	Raw water	6.82	71.06	2.538 ± 0.256
	Permeate	6.93	55.80	2.527 ± 0.160
	Concentrate	6.86	67.82	2.837 ± 0.596

The analysis of DOC concentration in feed samples before each of the fractionation procedures is shown in Figure. 4.3. The DOC concentration of raw water, permeate and concentrates were in the range of 2.538-4.735 mg/L, 2.38-4.799 mg/L, and 2.837-8.847 mg/L, respectively. The DOC concentrations in permeates were only slightly lower than that in raw water suggesting a relatively low efficiency of NOM removal in the treatment process. The DOC concentrations in concentrates were richer than that in raw water. Overall, the DOC concentrations in three types of samples during November and December 2016 were typically more abundant than samples from March 2017 (Figure 4.3).

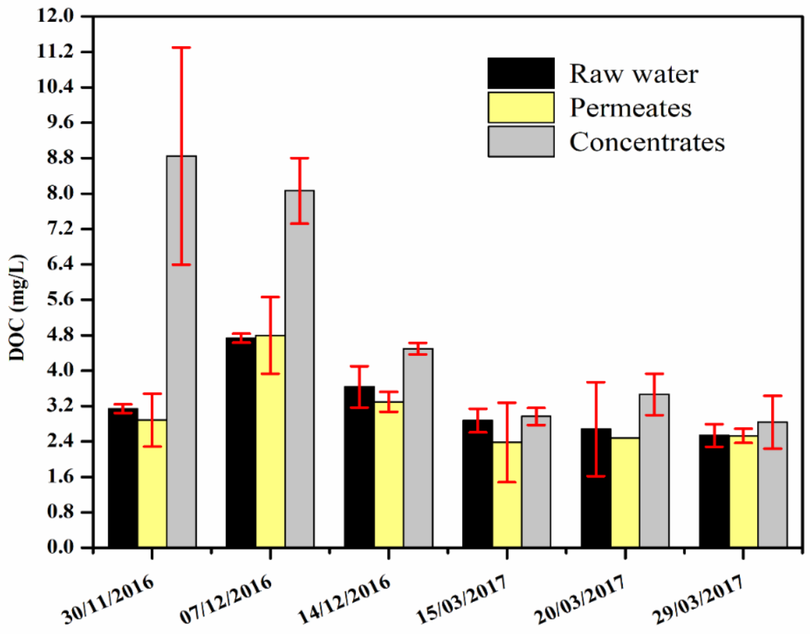


Fig. 4.3. The seasonal variation of NOM in full-scale plant, in mg/L of raw water, permeates and concentrates.

4.3.2 Fractionated water analysis

All above samples taken between 30/11/2016 to 29/03/2107 were fractionated using XAD resins to access the content of individual fractions of natural organic matter (NOM). Triplicate fractionations were conducted for each sample. In all fractionations, XAD-7HP resin contributed to the HPO fraction. XAD-4 resin contributed to the TPH fraction. The portion left in the final effluent named the HPI fraction. According to mass balance, the recovery of DOC was quantified by measuring both the DOC of feed and fractions and volume of the fractions produced. The NOM fractions recovered for each feed samples all derived from 100% DOC recovery (Fig. 4.4). The DOC Recoveries ranged from 36.5% (14/12/2016, raw water) to 115.8% (14/12/2016, permeates) with a mean recovery of 88.0% (Fig. 4.4).

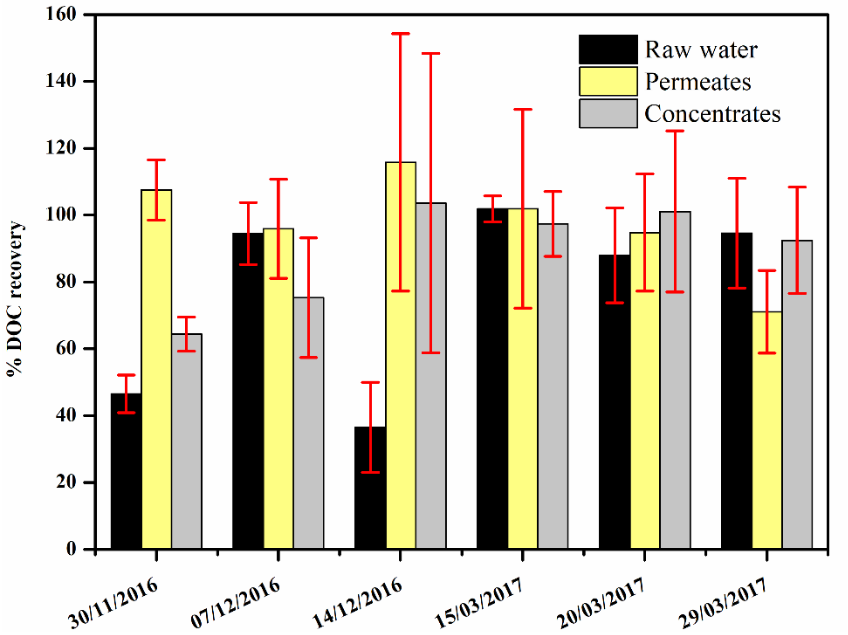
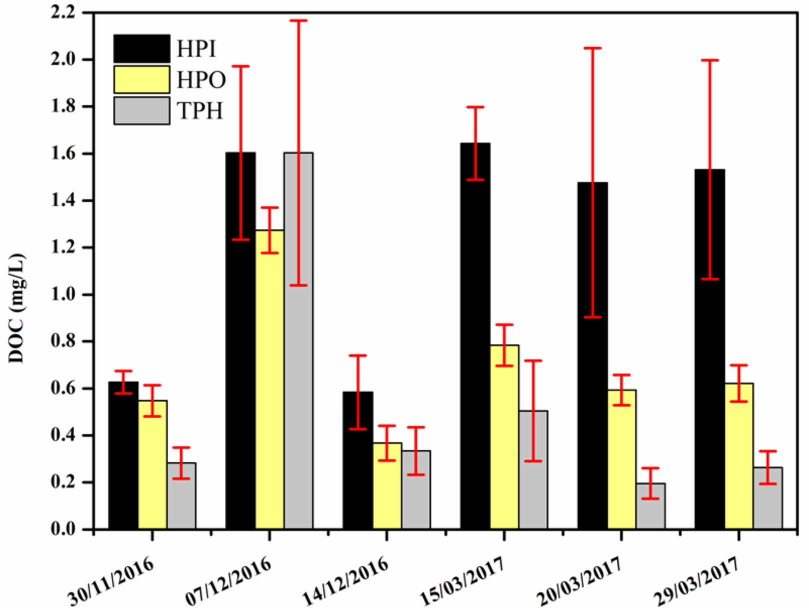


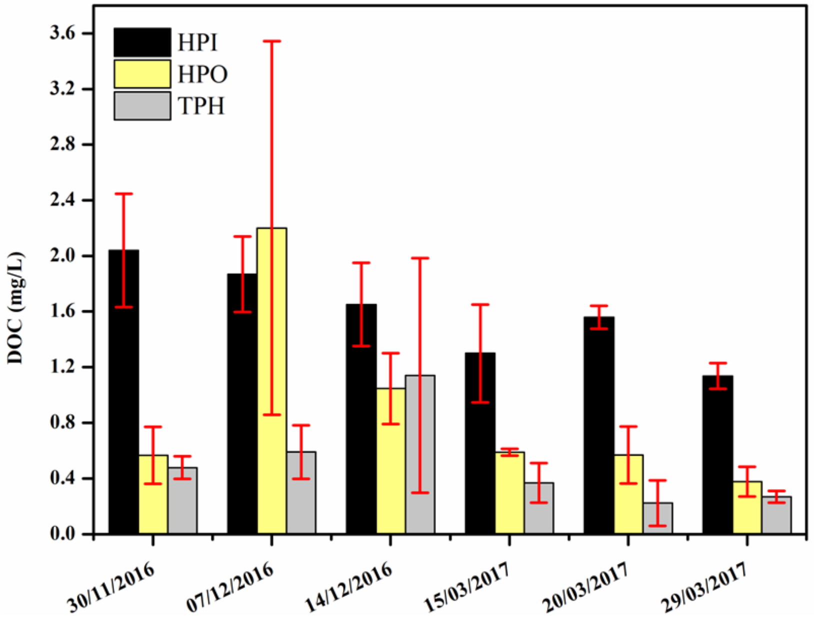
Fig. 4.4 The DOC recoveries from NOM fractions using XAD resins fractionation technique.

The trend of NOM fractions from three types of feed samples expressed as a concentration of DOC (mg/L) is shown in the Fig. 4.5. In general, the HPI fraction dominates the NOM types of all samples (except for the permeate on 07/12/2016 which the HPO fraction had the highest DOC concentration). The amount of the HPO fraction follows the HPI fraction in raw water over the time, while in the permeates and concentrates on 14/12/2016, the HPO fraction had the lowest DOC concentration. TPH fraction accounted for the least in most of the feed samples.

(a) Raw water



(b) Permeates



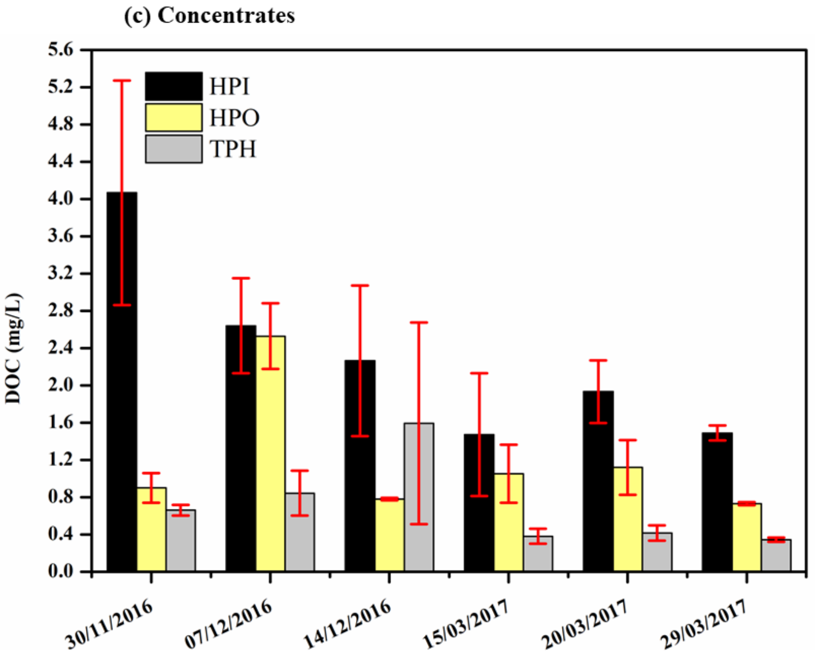


Fig. 4.5. The variation of NOM fractions in full-scale plant, in mg/L of raw water (a), permeates (b), concentrates (c).

However, due to the considerable variation between tested samples in DOC recoveries, comparing NOM seasonal variation by the measured DOC concentration of each fraction seemed unwise. The deviation from 100% recovery is a source of error. It is noticeable that during the fractionation procedure, the HPI fraction did not require NaOH solution elution and was calculated from the final effluent, which means this fraction does not share the same error as the HPO and TPH fractions and could not be quantified.

4.4 Discussion

The pH of raw water ranging from 6.24-7.27 with a mean of 6.82 (±0.33) suggested that the pH of source water from the sampling site was stable over the period (Table 4.1). The pH of permeates ranging from 6.88-7.57 with a mean of 7.04 (±0.26) and the pH of concentrates from

6.86-8.79 with a mean of 7.58 (±0.83) also suggested that the pH during the treatment process was only slightly fluctuating (Table 4.2). The operational guideline recommended in drinking water is to maintain a pH between 6.5 and 8.5 to promise water that is neither corrosive or producing incrustation (Ontario Drinking Water Standards, Objectives and Guidelines, 2006). The relationship between conductivity of solutions at 25°C (μs/cm) and total dissolved solids (TDS) (mg/L) is shown below (Table 4.2). As shown in Tables 4.1 and 4.2, TDS concentration of raw water and permeates were in the range of 37.28- 74.55 mg/L, far lower than the requirement in the Ontario drinking water standard (≤ 500 mg/L).

Table 4.2 Relationship between TDS of KCl standard solution and conductivity of solutions at 25°C (adapted from CHEMIASOFT.com)

TDS of KCl Solutions (mg/L)	Conductivity of Solution at 25 °C (uS/cm)
0	0
7.46	14.9
37.28	73.9
74.55	146.9
372.76	717.5
745.51	1412
1491.02	2765
3727.55	6667
7455.1	12890
14910.2	24800
37275.5	58670
74551	111900

The DOC concentration in raw water and permeates had an average of 3.267 (±0.817) mg/L and 3.062 (±0.916) mg/L, respectively, suggesting that natural organic matter (NOM) removal by ultrafiltration (UF) in the plant was not efficient (6.29%). Ultrafiltration (UF) is efficient in reducing turbidity, particles, and pathogens but NOM removal remains varied and conditionally ineffective. In general, NOM removal efficiency depends on NOM character and membrane molecular weight cut-off. The UF membranes with the cut-off ≥ 60 kDa, 10-60 kDa and ≤ 10 kDa had shown NOM removal from 14-49%, 20-75% and 38-87%, respectively (Metsämuuronen et al. 2014). NOM adsorption and gel-layer formation on membrane surfaces affect flux decline and the observed rejection characteristics (Cho et al. 2000). Geographic locations and climate lead to spatial and temporal changes in NOM character which made removal not consistent over time, even for a single site (Sharp et al. 2006). Also, it is interesting to notice that the DOC level of UF permeates was sometimes higher than of raw water as shown in Fig. 4.3. A similar finding was also reported by Chang et al. (1998) and Choo et al. (2005). However, neither of them gave a detailed explanation. It is not definite yet possible that concentration polarization of NOM at the membrane surface resulting in some fluctuations in the DOC level of permeate during UF (Choo et al. 2005). One limitation of the study is that the UF membrane process and NOM characterization had not been under the lab-scale control which means changes in the NOM character cannot be scientifically associated with the UF membrane performance.

According to Fig. 4.4, it is not unusual as recoveries under or above 100% when using resin column fractionation technique. Goslan et al. (2002) and Piper (2010) reported the recoveries ranging from 87-110% and 65-151%, both highlighting that this technique lacks accuracy and considerable compositional and structural alterations might take place due to the extreme pH conditions used in the fractionation procedure. However, Peuravuori and Pihlaja (1997) confirmed the fractions produced by XAD resins were not innate products of the procedure used to prepare them. The limitation of this technique should be considered when discussing the structure of the NOM in the further study.

The peak DOC concentration (4.735 mg/L) in raw water appeared on December 7, 2016, then went down afterward (Fig. 4.3). As expected, variations in climate can vary the NOM type and concentration, but there is no scientific consensus on explanations (Delpla et al. 2009). Some researchers studied the streams and lakes in UK, Scandinavia, Czech Republic, Northeastern USA and Canada. They reported that the increase in water temperature, rainfalls and snowmelt could lead to a higher DOC concentration (Hejzlar et al. 2003; Worral et al. 2004; Evans et al. 2005; Monteith et al. 2007; Clark et al. 2008; Prathumratana et al. 2008). Scott et al. (2001) came up with a theory that a microbially-driven mechanism of DOC release could result in the observed DOC variations throughout the year and then Hejzlar et al. (2003) concluded that soil leaching contributes to the principal source of NOM in surface waters. The aerobic microbial activity is more activated in a relatively warmer surface water temperature which links to an increase in the DOC concentration (Prathumratana et al. 2008). A rainfall event or snowmelt runoff would increase surface runoff thereby flushing the accumulated organics into the aquatic environment (Sharp et al. 2006). The historical Thunder Bay weather reports recorded that alternating rain and snow occurred from December 5 to December 7 ("Weather in December 2016," 2016). It is likely that weather in the days before December 7, 2016 influenced the DOC concentration in raw water. Plus, according to Great Lakes Statistics (2016-2017), the average surface water temperature in Lake Superior during November and December 2016 is higher than that during March 2017. This could account for the DOC concentration in raw water in December 2016 is higher than that in March 2017 (3.141 mg/L, 4.735 mg/L, 3.637 mg/L vs. 2.871 mg/L, 2.68 mg/L, 2.538 mg/L). Comparison with published data reveals variations in DOC concentration across seasons for river and lake systems. Sharp et al. (2006) observed the DOC concentration in raw water at a moorland water plant in the UK with a high of 14.5 mg/L in December 2002 to a low of 4.3 mg/L in September 2004. At McDonalds Branch freshwater fen in the U.S., Maurice et al. (2002) reported the NOM concentration rose from 3.4 mg/L during autumn drought conditions to 9.9 mg/L the following spring. Aiken et al. (2004) checked the DOC from intake in Santa Ana River in the U.S. that it varied between 2.2 mg/L to 9.0 mg/L during June 2000 and May 2002. Piper (2010) investigated the DOC concentration in Butterley reservoir in the UK that the two relatively high concentrations appeared in October and December 2009 then decreased afterward until May 2010. Published research articles shared an extended period monitor for DOC concentration (6 months to 36 months), thus concluded that NOM variability expressed as the DOC concentration changes can be associated with seasonal changes. Apparently, in our current study, samples were chosen randomly in 3 discrete months. More samples need to be analyzed in the following months.

As in this study, the raw water originates from Lake Superior is clear, low in DOC concentration (3.267±0.817 mg/L), and hydrophilic. This result is consistent with Li and Minor (2015). They analyzed the surface and deep-water from seven Lake Superior sites, open-lake and near-shore. They reported that nearshore sites exhibited a little higher DOC concentration than offshore sites but no significant difference due to the excess DOC input by snowmelt. Their DOC analyses showed that Lake Superior water is oligotrophic, low in concentration and very clear than most studied fresh-water systems. However, the technique and measurement units they used are different from our study (solid phase extraction; μM). It is impossible to compare the absolute DOC concentration values.

In addition, Lee et al. (2004), Leenheer 2004, and Wei et al. (2008) reported that lake and reservoir waters tend to have a greater hydrophilic (HPI) content than river waters. Contradictory results have also been reported the water taken from various source including surface waters, reservoir and highly coloured waters composed above 50% hydrophobic (Leenheer and Huffman 1976; Malcolm 1985; Croué et al. 1993a, b; Aiken et al. 2004; Sharp et al. 2006). Water bodies in low flowing rate result in the domination of hydrophilic content for autochthonous material (i.e., algae) while erosion in water potentially increases hydrophobic allochthonous material (Leenheer 2004). Moreover, lakes have an average DOC concentration of 2.2 mg/L; oligotrophic and eutrophic lakes are 2-3 mg/L and 9-16 mg/L (Wilderer 2011). Since Lake Superior is known as a dimictic and oligotrophic system, the results presented in our study are reasonable (Herdendorf 1982; Urban et al. 2005).

4.5 Conclusions

The results obtained in the analysis of NOM type and concentration in raw water, membrane permeates and concentrates at the drinking water membrane treatment plant, using the XAD resin fractionation procedures can be summarised by the following:

1. Peak DOC concentration in raw water occurred on December 7, 2016, and dropped in March 2017 over the period. The surface water temperature of Lake Superior and the weather condition

could explain the result. The DOC concentrations from water samples in Nov and Dec 2016 were generally higher than that in March 2017.

2. NOM type of most raw water, permeates, and concentrates from the drinking water treatment plant dominated by the hydrophilic fraction (HPI) and then followed by HPO fraction. The TPH fraction had the lowest concentration.

3. DOC removal by ultrafiltration in the Bare Point water treatment plant is inefficient. However, the measurement of bulk water parameters is not always sufficient to determine how the water will respond to a treatment process.

4.6 References

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Chapter 5. Summary and Further Work

5.1 Summary

Membrane aging is considered to deteriorate the membrane filtration performance and shorten membrane lifespan causing undesirable expense. Natural organic matter (NOM) is ubiquitous in all surface water and affects the water quality. This study has focused on the aging impact on structure and properties of ultrafiltration membrane as well as seasonal changes in NOM. Experiments of hollow fiber ultrafiltration membrane characterization and NOM characterization by XAD-7HP and XAD-4 resin column fractionation have been performed to achieve the research goal. All samples were provided by the Bare Point water treatment plant in the city of Thunder Bay. Results are summarized below.

1. Membrane aging aggravated pores that blocked membrane surface. This problem could partially resolve with the optimal chemical cleaning procedures (soaking in 200 ppm NaClO and 2000 ppm citric acid for 2 hours respectively) by observing an increase in the pure water permeability after cleaning.

2. Membrane aging deteriorated the membrane structures. The diameter of membrane lumen, membrane porosity, and membrane pore size all decreased with the membrane age. The accumulation of membrane foulants and cold temperature influence could explain above results.

3. Membrane aging correlated well with membrane pure water permeability, that is, permeability went down within the aging. Chemical cleaning improved the pure water permeability to some extent.

4. Membrane aging affected the breaking strength by becoming more brittle and less robust. This could be caused by periodic chemical cleaning for operational maintenance. Also, membrane aging could increase the chances of breakage in polymeric chains within PVDF membranes.

5. Membrane aging made membrane surface more hydrophilic as well as chemical cleaning. Surface alteration and mechanical deterioration could account for the reason.

6. Hydrophilic material (HPI) is dominant in raw water, and most samples of membrane permeates and membrane concentrates. Raw water from Lake Superior is hydrophilic, low in DOC concentration and clear.

7. Peak NOM content in raw water occurred on December 7, 2016, and reduced in March 2017 over the sampling period.

8. DOC mass balance analysis indicated that there is no ideal way of either analyzing or fractionating NOM. Separation of bulk NOM due to the extreme pH change might cause its alteration.

5.2 Future work

Many communities in Canada located in cold regions. Water producing by the drinking water treatment plants in those areas may experience difficulties under extreme weather condition. If membrane aging problems get worse by the cold feed water temperature, then an increase in capital and operating costs of membrane filtration plants would be expected in cold regions. Therefore, we suggest further work could focus on the temperature impact associated with membrane aging. Lab-scale membrane systems should be operated in the well-controlled cold room at a specific temperature as well as the same membrane systems identically being operated at the room temperature. Membrane aging assessment tools and techniques should be performed on both to check and compare the changes in membrane structure and properties.

Fouling behavior of NOM in ultrafiltration membranes from a full-scale drinking water treatment plant is worth to be considered. We suggest using natural fouled membranes from the plant. The feed water, the permeates and natural foulants extracted on the same membranes should be collected. Water quality analysis, characterization of membranes and foulants, NOM fractions structural and chemical analysis using HPLC-MS should be considered. Results would tell whether hydrophilic or hydrophobic NOM components contribute more to the membrane fouling.