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Preferential fouling of natural organic matter (NOM) fractions in submerged low-pressure membrane filtration

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ABSTRACT

The interactions between membrane fouling and natural organic matter (NOM) properties were investigated in a series of filtration experiments of raw and flotated water in a submerged low-pressure membrane system of hydrophobic and hydrophilic membranes. Norwegian surface water NOM was characterized by its electrostatic properties i.e., surface charge, charge density, and was fractionated with respect to its hydrophobic/hydrophilic characteristics. Hydrophobic/hydrophilic interaction was a more dominant mechanism compared to charge repulsion in membrane fouling as shown from the preferential adsorption of hydrophobic fraction with the highest charge density onto hydrophilic and hydrophobic membranes, and positively charged hydrophilic fraction onto hydrophilic membrane.

Keywords: Submerge low-pressure membrane; Natural organic matter; Membrane fouling; Hydrophobic/hydrophilic interaction; Charge repulsion

1. Introduction

Natural organic matter (NOM) is a ubiquitous and dynamic component of surface waters such as lakes, rivers, and oceans. The composition of NOM is strongly influenced by local biological sources such as plants and dominant microorganism environments. The fact that geochemical and physical processes occurring in the aquatic and surrounding environments play an important role in NOM formation results in a great complexity when classifying and defining NOM properties and characteristics [1]. Thus, NOM is really site specific and different from a water body to another. NOM is regarded as one of the major foulants in membrane filtration treating natural waters. The complexity of NOM and NOM fouling require a thorough study on NOM characteristics and their relation to membrane fouling [2]. This study was aimed to investigate the membrane fouling behavior by NOM fractions and the impact of pre-treatment on membrane filtration performance of submerge low-pressure membrane filtration. This paper discusses the basic properties of Norwegian surface water NOM, namely its electrostatic and hydrophobic-hydrophilic characteristics, and their relation to membrane fouling.

2. Theoretical background

As a heterogeneous mixture, NOM represents a complex solute that interacts with the membrane surface and pores. There are two possible effects resulting from membrane-NOM interaction, rejection and fouling. Three major rejection mechanisms can be put forward; size exclusion, electrostatic repulsion, and hydrophilic-hydrophobic interaction.

Foulant and membrane characterization techniques have been used to investigate the fouling tendencies of membrane systems. NOM can be characterized according to size, structure, and functionality, and moreover, to its characteristics that affect its interaction with the

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membrane, namely molecular weight distribution, hydrophobic-hydrophilic character, and functional group content [3]. Various adsorbent resins have been used to fractionate NOM, and the most common approaches and methods of fractionation always include macro resins to differentiate the NOM based on its hydrophobic-hydrophilic and charge characteristics [4–6]. Many studies have been conducted based on NOM fractionation to investigate which NOM fraction plays a dominant role in membrane fouling. The hydrophobic fraction of NOM was found to be the major foulant in hydrophilic nanofiltration (NF) of NOM in a study by Nilson and DiGiano [7]. Given that the hydrophobic fraction of NOM mainly consists of humic acid (HA) and fulvic acid (FA), Jucker and Clark [8] found that fouling was more irreversible for hydrophobic ultrafiltration (UF) membranes fouled by HA compared to that of membranes fouled by FA. This is due to the fact that HA has lower solubility and higher binding affinity to membrane materials. In contrast to the abovementioned studies, other researchers found that low UV absorbing, higher molecular weight hydrophilic neutrals are the major NOM foulants, as shown by Carrol et al. [9,10] and Lee et al. [10]. These findings support the premises of earlier studies conducted by Cho et al. [11] and Fan et al. [12] who claimed the magnitude of fouling potential of NOM fractions is in order of hydrophilic neutrals > hydrophobic acids > transphilic acids / slightly hydrophobic acids > charged hydrophilic.

Charge repulsion is believed to be a major mechanism to reduce NOM attachment to membrane surfaces. Amy and Cho [13] showed that membranes with higher zeta potential (negative charge) and higher molecular weight cut-off (MWCO) provided more effective NOM rejection compared to membranes with lower zeta potential and lower MWCO. The fact that NOM exhibits negative charge at natural pH provides the explanation of the dominance of electrostatic exclusion over size exclusion. However, one must realize that the charge densities of NOM fractions are different from one to another. Sharp et al. [14] employed a method developed by Kam and Gregory [15] to measure the charge densities of NOM fractions as a function of cationic polymer dose and to relate them with coagulation performance. They found that hydrophobic NOM fractions possessed a higher magnitude of charge density compared to that of hydrophilic fractions, and thus, controlled the effectiveness of the coagulation process.

3. Materials and methods

3.1. Membranes and reactor unit

Three types of membranes were used in a series of filtration experiments in a 40 l reactor. Total membrane area in the reactor was 0.013 m^2. The membranes used and their specifications are summarized in Table 1.

3.2.Analogue water

All experiments were conducted using an analogue feedwater which represents typical raw water sources commonly used in Norway for drinking water supply [16,17]. Analogue feedwater ensures that the same experimental conditions apply for all experiments conducted. The analogue water was produced by mixing NOM concentrate obtained from local full-scale ion exchange treatment plant with tap water; pH was adjusted by adding concentrated NaOH or HCl. The raw water properties are summarized in Table 2.

3.3. Filtration experiment setup

Two sets of filtration experiments were conducted for each membrane, namely feedwater consisting of direct raw water filtration and pretreated feedwater

Table 1
Membrane characteristics used in the experiments

Membrane type code	UF HFM-100 (Koch)	UF HFM-180 (Koch)	MF VCWP 29325 (Millipore)
Pore size/ MWCO	50 kDa	100 kDa	0.1 µm
Material	PVDF	PVDF	Mixed cellulose esters
Hydrophobicity	Hydrophobic	Hydrophobic	Hydrophilic
Contact angle	94.2	92.4	38.9

Table 2
Raw water characteristics

Parameter	Unit	Value	Parameter	Unit	Value
pH	–	6	TOC	mg C/l	6.90 ± 0.45
Colour	mg Pt/l	42.70 ± 0.50	DOC	mg C/l	6.78 ± 0.48
UVA$_{254}$	M^{-1}	28.4 ± 0.4	SUVA	l.m^{-1}mg^{-1}	4.19 ± 0.38

by flotation. Each filtration experiment lasted for 24 h under continuous operation without backwash or relaxation. A flux of 80 l.m^{-2}.h^{-1} was applied for both filtration experiments using the UF membranes (HFM-180 and HFM-100 in Table 1). Raw water filtration experiments for the microfiltration (MF) membrane VCWP 29325 were conducted at higher fluxes of 110 and 140 l.m^{-2}.h^{-1}, while filtration experiments for the pretreated feedwater was done at a flux of 110 l.m^{-2}.h^{-1}. The experimental configuration and setup is illustrated in Fig. 1.

Tap water and NOM concentrate were mixed to give a stable NOM concentration by adjusting Pump 1 (GALa 1602, ProMinent Doserteknik). pH of the analogue water (measured by SympHony SP70P, VWR) was maintained at pH 6 throughout the experiments. In the raw water filtration experiments, the raw water was fed directly to the membrane reactor by Pump 2 (Pumpdrive 5201, Heidolph), whereas in the flotation pretreated water experiments the raw water was first fed to a coagulation-flocculation-flotation unit (Severn Trent Service 2000) before being fed to the membrane reactor. Dissolved air flotation was achieved by pressurizing distilled water at 5.5 bar with a recycle rate of 10%. Alum sulfate (ALS, Kemira) was chosen as the coagulant and the optimal dose for flotation was found and set at 28 mg Al/l. The water level in the membrane reactor was kept constant by allowing a small amount of raw water overflow. The data from temperature (SEM203, Status Instrument) and pressure transducers (EW-68075-02, Cole-Parmer) were recorded using LabView 8.2 software and data acquisition system. Permeation was achieved by suction pump (Masterflex L/S, Cole-Parmer) and the amount of permeate was monitored by measuring the weight (PT 120, Sartorius) over time. Permeate samples were taken periodically (every 6–10 h) during each filtration experiment.

3.4. Analysis of NOM properties

NOM fractionation and charge density were determined using a fractionation technique [6] characterizing NOM in different groups i.e., Very Hydrophobic Acid (VHA), Slightly Hydrophobic Acid (SHA), Charged Hydrophilic (CHA), and Hydrophilic Neutrals (NEU) was employed to characterize the raw water, membrane permeate, and desorbed NOM from fouled membranes. NOM desorption from fouled membrane was done by soaking the fouled membranes in 0.1 N NaOH. Organic carbon concentrations were measured using a Dohrmann Apollo 9000, Teledyne-Tekmar laboratory analyzer. Charge density of bulk NOM and its fractions collected from the resin isolates were assessed by adding an increasing volume of 0.05 g/l cationic polymer solution (Fennopol K5060 Kemira, charge density of 1.6 meq/g dry weight) and by measuring the zeta potential [15] using a Beckmann-Coulter DelsaNano HC. Color and UV-absorption at 254 nm (UVA$_{254}$) were measured by Spectrophotometer U-3000, Hitachi.

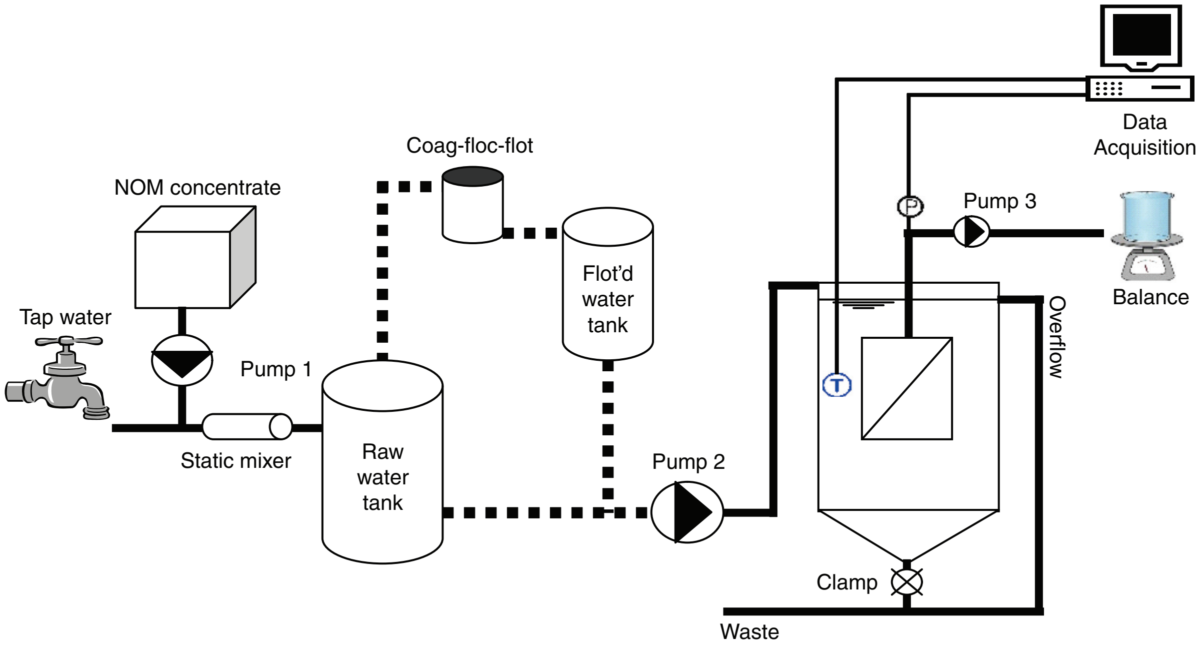


Fig. 1. Flow diagram of membrane filtration unit.

4. Results and discussion

4.1. Raw water and flotation pretreated water fractionation

SUVA value, which is the ratio between UVA_{254} over the DOC can be an indication of good NOM treatability in terms of DOC removal by coagulation processes [18]. A SUVA value of 4.19 ± 0.38 suggests that water inherited hydrophobic character. The results of the raw water fractionation confirm this interpretation in that up to 62% of the organic matter was found to be associated with VHA (Fig. 2a).

The applied pretreatment of coagulation-flocculation-flotation could achieve 73.7 ± 1.8% NOM removal thereby reducing the DOC concentration in the pretreated feedwater to the membrane reactor to 1.74 ± 0.07 mg C/l. From the results shown in Fig. 2a and with the information of NOM concentrations before and after flotation given above (values in the brackets), it is clear that the VHA and SHA fractions were removed to a large extent, while CHA almost completely disappeared from the picture and NEU became the only fraction with concentration similar to that of untreated raw water.

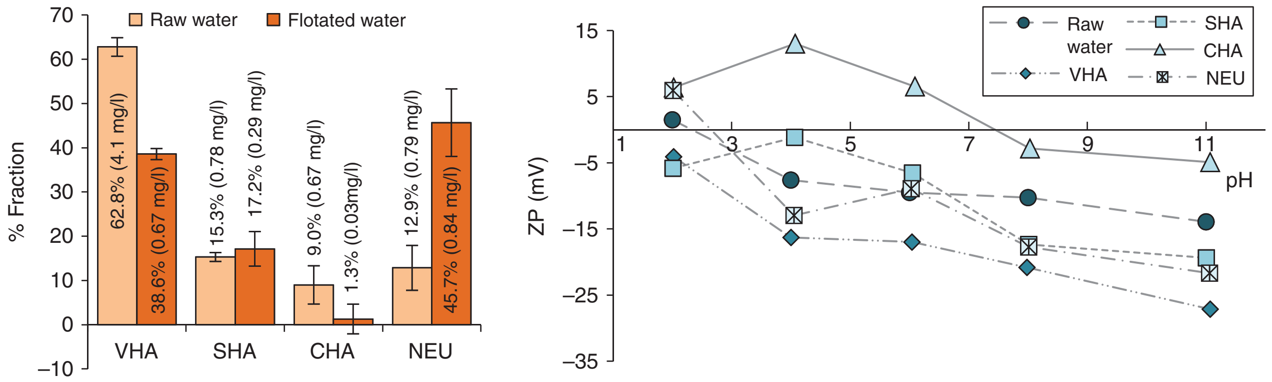
4.2. Zeta potential and charge density of bulk NOM and NOM fractions

Fig. 2b illustrates the behavior of zeta potential (ZP) of bulk NOM and its fractions as a function of pH. The two hydrophobic fractions, VHA and SHA, show no iso-electric point (IEP) over the pH range investigated. The bulk NOM and NEU show an IEP between pH of 2–3, while the CHA's IEP was observed between pH of 7–8. The ZP of SHA and NEU behaved in the same way over pH 6, while the VHA fraction inherited the highest negative charge over that pH range. At pH 6 the ZP of raw water, VHA, SHA, CHA, and NEU were around –9.5 ± 2.1 mV, –17 ± 1.4 mV, –6.6 ± 0.9 mV, 6.5 ± 5.8 mV, and –8.9 ± 1.0 mV, respectively. The CHA fraction was positively charged at the pH of the filtration experiments suggesting that charge repulsion might, in contrast to the other NOM fractions, be insignificant in the interaction of the respective NOM fractions with the membrane knowing that the membrane materials should reveal a negative charge in such moderate pH [19]. VHA demonstrated the highest charge density of all the fractions with an average of 0.25 meq/g DOC, followed by SHA (0.17 meq/g DOC) and NEU (0.024 meq/g DOC), respectively. Due to the positive charge of CHA, charge density of this fraction was not measurable simply because the polymer used (Fennopol) is positively charged as well.

4.3. Filtration performance

Fig. 3 shows the percentage of DOC removal as a function of sampling time for each membrane in the raw water filtration experiments. The percentage of DOC removal reflects the increasing tightness of the membranes with HFM–100 being the membrane with highest NOM removal. As shown in Fig. 3, the removal values vary over time indicating there is a dynamic within the system during the course of filtration. As fouling progresses, the properties of the membrane might change and, hence, this affects the separation ability. The HFM-100 was able to remove up to 30% of the NOM during the first stage of the filtration after which the removal stabilized around 11–13%. The other two membranes showed the dynamic of NOM removal percentage, but unlike the HFM-100, the removal was stable around the average values.

The NOM size is much smaller than the pore size of the VCWP 29325 membrane which is around 100 nm,



(a) Raw water NOM fractionation

(b) Zeta potential of raw water

Fig. 2. Raw water characterization.

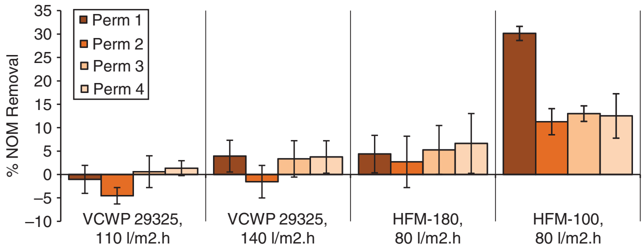


Fig. 3. % NOM removal of membranes fed by raw water.

however, the membrane still achieved a small percentage of DOC removal (up to 1.3%) at flux 110 l.m^{-2}.h^{-1}. The NOM rejection increased with when a higher flux was applied (flux 140 l.m^{-2}.h^{-1}) with a NOM removal of maximum 4% being achieved. This observation can be attributed to the concentration polarization phenomenon where the high concentration of materials above the membrane surface acts as dynamic layer that enhances membrane selectivity.

Fig. 4 illustrates the percentage of DOC removal as a function of sampling time for the membranes fed by pretreated water. It appears that after flotation the percentages of NOM removal were better for the previously less-performing membranes (VCWP 29325 and HFM-180) when fed with raw water directly. However, when interpreting the percentage removals one needs to take into consideration the initial concentration values for the two test conditions tested, i.e., raw water and pretreated water.

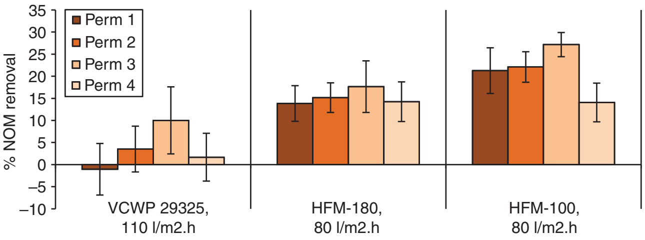


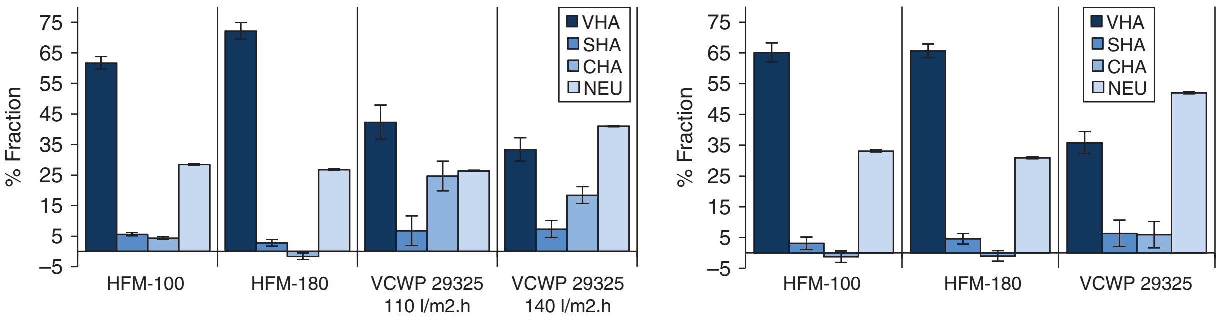
Fig. 4. % NOM removal of membranes fed by flotated water.

Taking into account total NOM removed, in the case of the HFM-180 membrane the removal efficiency for pretreated water is 15% which is equivalent to 0.26 mg C/l while for raw water filtration the average 5% equates to 0.32 mg C/l. This effect is more pronounced in the case of HFM-100 membrane that was able to reduce quite an amount of NOM during raw water filtration, indicating that the remaining fractions of NOM after flotation is too small to be efficiently removed by the membrane. The sole advantage of applying flotation is in terms of operating time since the membranes can operate longer given that the fouling rate is significantly reduced by the pretreatment.

4.4. Fractionation of desorbed NOM from fouled membranes

Figs. 5a and 5b represent the results of fractionation of desorbed NOM from the fouled membranes. The VHA fraction appears to dominate the fractions of NOM adsorbed by the membranes made from PVDF (HFM-100 / HFM-180) while in the case of the mixed cellulose esters (VCWP 29325) the NEU appears to dominates when treating both raw water at flux 140 l.m^{-2}.h^{-1} and flotated water at 110 l.m^{-2}.h^{-1}. In the case of the two hydrophobic PVDF membranes, there is a strong indication that hydrophobic interactions dominate over the charge repulsion as the fraction with the highest fractional charge and charge density (VHA) was adsorbed most by the membranes. This premise holds in the case of filtration of flotation pretreated water as well.

The CHA fraction is comprised of charged hydrophilic compounds. The fact that it is found only in small percentages on the desorbed NOM from the hydrophobic membranes, even though the ZP measurements revealed a positive charge at the pH of the filtration experiment, is interesting. As seen from



(a) Raw water filtration

(b) Flotated water filtration

Fig. 5. Fractionation of desorbed NOM.

Fig. 5a, the CHA fraction was found in significant percentage in the desorbed NOM from the hydrophilic VCWP 29325 membranes treating the raw water compared very low values when filtering the pretreated water. This can be accounted by the fact that the CHA fraction is almost completely removed by the pretreatment (see Fig. 2a). This leads to another indication of hydrophobic-hydrophilic interactions being the major mechanism of NOM attachment on the membrane materials. The only attachment of the CHA fraction to the hydrophobic membranes was in the case of filtration of raw water by the HFM-100 (5% of total fraction). It can be postulated that, as reflected by the lower MWCO compared to that of HFM-180, the pores of the HFM-100 are much smaller and consequently, sieving effect by the small pores on the CHA fraction could occur.

Hydrophilic membranes inherit, to a lesser extent, hydrophobicity in its structure [20]. Therefore, the wetting of hydrophilic membranes by hydrophobic compounds can still occur. This can be the rationale behind the fact that VHA fraction was found in abundance in the desorbed NOM from the hydrophilic VCWP 29325. The SHA fraction has a lesser degree of hydrophobicity and it is therefore logical to see a lesser amount of this fraction adsorbed by the hydrophobic and hydrophilic membranes. The NEU fraction was observed to dominant in VCWP 29325's raw water filtration experiment at the higher flux (140 $l.m^{-2}.h^{-1}$) while the VHA fraction dominated in the lower flux (110 $l.m^{-2}.h^{-1}$). This indicates that fouling is also influenced by the hydrodynamic condition within the system and not only the specific properties of the membrane or the various dominant foulants. In the case of filtration of pretreated water with the VCWP 29325 membrane, the dominance of the NEU fraction can also be accounted by the fact that it also has a higher concentration in the pretreated water compared to the other fractions (Fig. 2a). It is noteworthy that neither backwash nor relaxation was applied to the system during the filtration experiments. Therefore, reversibility of NOM fractions adsorbed on the membrane material is not discussed in this paper.

5. Conclusions

- The hydrophobic-hydrophilic interactions appear to be the dominant mechanism in NOM-membrane interactions and fouling. The VHA fraction, having the highest negative charge and charge density, was found to be the dominant fraction adsorbed to the membrane in almost all cases tested. Moreover, the CHA fraction, being positively charged at the pH of filtration experiments, was less adsorbed by the negatively charged hydrophobic membranes.
- The VHA, SHA and CHA fractions of the NOM were largely removed by flotation pretreatment, however, VHA was still the dominant fraction adsorbed by all membranes tested.
- For the hydrophilic membrane, the dominant adsorbed fractions were in the order of VHA/NEU>CHA>SHA, while for hydrophobic membranes the order was VHA>NEU>SHA>CHA.
- Pretreatment by flotation reduced the fouling rate significantly, indicating that the pretreatment was able to remove some of the main fouling-causing NOM fractions. However, in this configuration the membranes act merely as a polishing step with an even lower removal efficiency of NOM observed.

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