Ultrafiltration and nanofiltration membrane fouling by natural organic matter: Mechanisms and mitigation by pre-ozonation and pH

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ABSTRACT

The fouling of ultrafiltration (UF) and nanofiltration (NF) membranes during the treatment of surface waters continues to be of concern and the particular role of natural organic matter (NOM) requires further investigation. In this study the effect of pH and surface charge on membrane fouling during the treatment of samples of a representative surface water (Hyde Park recreational lake) were evaluated, together with the impact of pre-ozonation. While biopolymers in the surface water could be removed by the UF membrane, smaller molecular weight (MW) fractions of NOM were poorly removed, confirming the importance of membrane pore size. For NF membranes the removal of smaller MW fractions (800 Da – 10 kDa) was less than expected from their pore size; however, nearly all of the hydrophobic, humic-type substances could be removed by the hydrophilic NF membranes for all MW distributions (greater than 90%). The results indicated the importance of the charge and hydrophilic nature of the NOM. Thus, the hydrophilic NF membrane could remove the hydrophobic organic matter, but not the hydrophilic substances. Increasing charge effects (more negative zeta potentials) with increasing solution pH were found to enhance organics removal and reduce fouling (flux decline), most likely through greater membrane surface repulsion. Pre-ozonation of the surface water increased the hydrophilic fraction and anionic charge of NOM and altered their size distributions. This resulted in a decreased fouling (less flux decline) for the UF and smaller pore NF, but a slight increase in fouling for the larger pore NF. The differences in the NF behavior are believed to relate to the relative sizes of ozonated organic fractions and the NF pores; a similar size of ozonated organic fractions and the NF pores causes significant membrane fouling.

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1. Introduction

Ultrafiltration (UF) and nanofiltration (NF) technology have been widely applied as unit processes for the treatment of ground waters and surface waters as a consequence of their high degree of contaminant removal and relatively low capital investment costs (Mohammad et al., 2015). Owing to its smaller pore size compared to the lower pressure driven membranes of microfiltration (MF) and UF, NF can achieve a much greater removal of organic matter such as humic-like substances; and it has been widely recognized as a promising technology for the removal of organic components that act as precursors for disinfection by-products and problematic compounds such as hormones (Mohammad et al., 2015).

However, the phenomenon of membrane fouling continues to impede the application of membranes in water treatment, and its prevention or mitigation remains a subject of continuing research (Yu et al., 2016; Park et al., 2017). Membrane fouling by NOM has been reported for all membrane types (Wang and Tang, 2011b) and general information can be found in recent review publications (Tang et al., 2011; Shi et al., 2014). Some studies have reported that the fouling layer on NF membranes, caused by the filtration of surface water, was a combination of both colloids and natural organic matter (NOM) (Verhield et al., 2009; Mahlangu et al., 2015), and NOM adsorbed on the membrane was found to cause synergistic fouling effects (Contreras et al., 2009).

Other studies of membrane fouling have investigated the properties of the membrane and influent zeta potential, pH, hydrophilicity and molecular weight (MW). For negatively charged or
neutral organic matter, hydration forces have been shown to cause a decrease in the membrane fouling (Wang and Tang, 2011a; Miao et al., 2017). Substantial biofouling has been found to be present in full-scale nanofiltration and reverse osmosis installations (Vrouwenvelder et al., 2008), involving polysaccharide-like and protein-like substances, etc (Ivnitsky et al., 2010; Xu et al., 2010). In addition to the effect of biopolymers, membrane fouling is determined by the hydrophilicity/hydrophobicity and surface chemistry of the membrane (Mustafa et al., 2016). For hydrophilic membranes, the surface adsorbs water molecules, which weakens its binding efficiency to organic matter (Miao et al., 2017). Thus, a super-hydrophilic membrane showed resistance to fouling by hydrophobic substances and therefore achieved a high degree of removal, while conversely, a super-hydrophobic membrane showed resistance to fouling by hydrophilic substances and therefore had a high removal capacity for these substances (Xu et al., 2010).

Other characteristics of the influent water quality can influence fouling such as the presence of cations (e.g. Ca\(^{2+}\)) (Seidel and Elimelech, 2002; Li and Elimelech, 2004; Nghiem et al., 2008; Wang et al., 2016) and the pH, which affects the zeta potential/surface charge of both the organic matter and membrane. Thus, Ca\(^{2+}\) can complex with organic matter and increase its molecular size through aggregation, as well as altering the solution pH, resulting in a different extent of membrane fouling (Li and Elimelech, 2004; Wang and Tang, 2011a). Interaction force measurements have been used in some studies to predict membrane fouling by organic and inorganic colloids (Lee and Elimelech, 2006; Tang et al., 2009).

Various approaches have been employed to address the problem of fouling, such as the removal of fouling materials before membrane filtration. A range of pre-treatments have been used to mitigate membrane fouling, such as pre-coagulation, adsorption and oxidation. Several researchers have reported that ozone treatment was effective at degrading colloidal natural organic matter (or biogenic colloids) which were most likely responsible for the majority of membrane fouling (Lehman and Liu, 2009; Barry et al., 2014). A further study has shown that ozone oxidation caused a significant alleviation of membrane fouling for all investigated NF membranes in drinking water treatment (Van Geluwe et al., 2011b; Park et al., 2017). In contrast, other researchers have found that pre-ozonation may aggravate membrane fouling (Zhu et al., 2010). It is possible that the degradation of organic matter (e.g. bio-polymers) can result in products of a molecular size which are similar to the size of NF membrane pores, or substantially different, which can cause a different membrane fouling behavior.

In view of the foregoing, it is clear that the mechanisms of membrane fouling by surface water have not been explored fully to-date, including the impact of pre-ozonation. In this paper, we summarize the results of UF and NF membrane tests using samples from a representative surface water - a moderately contaminated lake - and a model HA water, in order to investigate in particular: 1) the effect of hydrophilicity/hydrophobicity of organic matter on membrane fouling and its removal, 2) the use of ozone pre-treatment to mitigate membrane fouling, 3) the influence of pH on membrane fouling, 4) the retention of organic matter on membranes during backwash (irreversible fouling).

2. Materials and methods

2.1. Surface waters and membranes

Samples of surface water were obtained from a nearby recreational lake in west-central London (Hyde Park); the lake is of moderate quality and subject to algal growth, and is described in our previous paper (Su et al., 2017). The principal quality parameters, including the TOC (4.3 mg/L) and pH (7.3), are summarized in Table S1. Humic acid solutions were prepared using a reference material, Suwannee River Humic Acid (HA) (25101H, International Humic Acid Substance Society, USA), which was dissolved in deionized (DI) water and NaOH to produce a HA concentration of 10 g/L (Nghiem et al., 2008). The stock HA solution was stored in the dark at 4 °C and brought to room temperature prior to the preparation of working solutions for subsequent tests. Before each experiment, the HA solution was diluted with 5 mM NaHCO\(_3\) to give a concentration of 10 mg/L (4.26 mg DOC/L). All chemicals used in the tests were analytical regent grade.

Two types of membrane were employed in the tests, namely a PVDF ultrafiltration membrane (100 kDa; Da = Dalton) and polyethersulfone (PES) nanofiltration membranes NF-3 (1 kDa) and NF-4 (800 Da), which were purchased from Ande membrane separation technology & engineering (Beijing) Co., Ltd, China. The physico-chemical characteristics of the membranes are listed in Table 1. It was evident from the results of the contact angle measurements that the two NF membranes were both substantially hydrophilic, and much more hydrophilic than the UF membrane.

2.2. Pre-oxidation of water and filtration experiments

As this paper is mainly concerned with the mechanisms of membrane fouling by organic matter in surface water, by pre-ozonation and pH, other forms of pre-treatment, such as coagulation, were not included in the experimental methodology. The pH of the surface water or HA solution (10 mg/L) was adjusted and maintained at 5.0, 7.0 or 9.0 by adding either 0.1 M NaOH or 0.1 M HCl (for the surface water the actual pH (7.3) was used instead of pH 7). For the surface water pre-treated with ozone before membrane filtration, the water was exposed to a range of ozone doses between 0 and 1 mg/L in a closed glass bottle with gas inlet and outlet (drechsel bottle), before being transferred to the pressure cell. The ozone was generated from air and the combined ozone/air flow bubbled through the solution for a specific time. The aqueous ozone dose was determined by mass balance of the gaseous inlet and outlet flows of ozone, with the gaseous ozone concentration measured by passing each flow through potassium iodide solution, and employing the potassium iodide/thiosulfate titration method (APHA, 2005) to quantify the equivalent ozone amount.

Dead-end flow experiments were undertaken using flat sheet, 76 mm diameter membranes in a stirred cell (Amicon 8400, Millipore) with a constant upstream pressure (1 bar for UF membrane and 4 bars for NF membranes) under nitrogen gas. Dead-end flow was used instead of cross-flow, which is more typically used in practice, in order to emphasize the fouling process and the impact of changing water and NOM properties on the mechanisms of fouling. The fouling characteristics of the UF and NF membranes were studied by filtration of the surface (Hyde Park) water and HA solutions (10 mg/L). In each test the performance of the membrane was evaluated by recording the variation of normalized flux, \(J/J_0\), as a function of time, where \(J_0\) is the initial membrane flux. Prior to use each membrane was placed in DI water for at least 24 h to remove impurities and production residues.

2.3. HPSEC

As indicated by Myat et al. (2014) size exclusion chromatography with UV detection (SEC-UV) can be used to identify bio-polymers that are sensitive to UV absorbance, as indicated by the apparent molecular weight (MW) distribution of UV-active substances in the sample waters (after 0.45 μm membrane filtration). Details of the equipment and method can be found in our previous
paper (Yu et al., 2015). In summary, SEC was performed using a BIOSEP-SEC-S3000 column (Phenomenex, UK) (7.8 mm × 300 mm) as well as a Security Guard column fixed with a GFC-3000 disc 4 mm (ID). A solution of 10 mM sodium acetate (Aldrich, USA) was used as the mobile phase. Analysis using High Performance Size Exclusion Chromatography (HPSEC) was achieved by the HPLC system (Perkin Elmer, USA) using the following instrumentation: Series 200 pump, UV/VIS detector operated at a wavelength \( \lambda = 254 \) nm and autosampler. The flow rate was set at 1 mL/min, and the injection volume of water samples was 100 \( \mu \)L. Prior to operation, the mobile phase was purged at a volumetric flow rate of 2 mL/min in order to clear any residual and wash out the column of any contaminants. Polystyrene sulfonate (PSS) standards (American Polymer Standard Corp., U.S.) of molecular weights 33500, 14900, 6530, and 1100 Da were employed to calibrate the relationship between the MW and the retention time.

2.4. XAD-4 and DAX-8

Resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany) were used to analyze the hydrophilic and hydrophobic organic components, by fractionating the NOM into three groups: strongly hydrophobic organic matter (adsorbed by DAX-8), weakly hydrophobic (or transphilic) organic matter (adsorbed by XAD-4) and hydrophilic organic matter (non-adsorbed by both resins) according to previously established methods (Aiken et al., 1992; Wang et al., 2009).

2.5. Other analytical methods

SEM images of membrane samples were obtained by a method where the samples were platinum-coated by a sputter and observed under a high resolution field emission gun scanning electron microscope (FEGSEM, LEO Gemini 1525, Germany). The

### Table 1
Characteristics of membranes.

| Parameter                        | UF     | NF-3   | NF-4   |
|----------------------------------|--------|--------|--------|
| Pore size (Da)                   | 100 kDa| 1000 Da| 800 Da |
| Contact Angle (°)                | 56.3 ± 3.8 | 15.2 ± 2.8 | 24.2 ± 0.9 |
| Initial flux/ permeability (DI water) L/(m².h.bar) | 855 ± 42 | 12.85 ± 0.74 | 5.50 ± 0.42 |
| Zeta potential (mV)              | −42.9 ± 3.2 | −22.5 ± 2.3 | −24.2 ± 2.8 |
| Materials                        | PVDF   | Polyethersulfone | Polyethersulfone |

Fig. 1. Removal of organic matter from HA solution and Hyde park surface water by UF and NF membranes as indicated by molecular weight distribution of HA (a) and surface water (b), and TOC for both waters (c) (samples were taken after membrane filtration of 300 mL); the hydrophilic/hydrophobic properties of both test waters (d).
dissolved organic carbon (DOC) concentration (after 0.45 μm membrane filtration) and zeta potential of water samples were determined using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan), and Zeta Sizer instrument (Nano-ZS90, Malvern Instruments Ltd, UK), respectively. The hydrophilicity/hydrophobicity of the membranes was indicated by measuring their water contact angles using an automated goniometer (Model 590) with DROPimage Advanced software (Ramé-hart instrument Co., USA).

3. Results

3.1. Organic matter removal

The removal of organic matter during water treatment processes is important in order to achieve drinking water quality objectives, such as minimizing the formation of disinfection by-products. Therefore, the separation of organic matter by different membranes was investigated in terms of changes in the MW distribution (by SEC) and TOC, using the HA solution and surface water (Fig. 1). For the HA solution, there was little organic matter removal by the UF membrane filtration evident from the SEC analysis, while in contrast the NF-3 and NF-4 membranes removed almost all of the UV-absorbing HA over the complete MW range, with a slightly greater removal by the NF-4 as a consequence of its lower MW cutoff. These results were confirmed by the TOC results, which showed a minor removal (≤10%) by the UF membrane, and near 90% removal by the NF membranes. For the surface water, the SEC analysis indicated the presence of bio-polymers (MW > 30 kDa), humic substances and other small MW organic matter. While the UF membrane retained most of the bio-polymers there was little removal of lower MW organic matter (<10 kDa). As expected, for the NF membranes there was extensive removal of organic matter across a wide MW range, in marked contrast to the UF, and the NF-4 achieved a substantially greater removal of organic matter in the MW range between 1 kDa and 4 kDa, compared to the NF-3 membrane.

Comparing the performance of the membranes for the two test waters, little organic matter was removed by the UF membrane for both waters, while the NF membranes were able to remove most of the organic material from the HA water, but less of the organic matter (<10 kDa) from the surface water. Also, the results indicated a greater removal difference between the NF-3 and NF-4 membranes for the surface water than for the HA water. The TOC results also confirmed that less organic matter was removed by the NF membranes for the surface water than for the HA water. Comparing the two test waters, it was evident that while the HA solution was mainly composed of hydrophobic components, the surface water comprised substantial quantities of both hydrophilic and hydrophobic substances (Fig. 1d). Overall, the results showed that physical size (MW) is not the sole parameter that determines the removal of organic matter by membranes, and that other characteristics are influential, such as the molecular charge/zeta potential and hydrophiliicity/hydrophobicity of the organic matter. As little organic matter was removed by the UF membrane (except bio-polymers), subsequent tests of water filtration were undertaken principally with the NF membranes.

3.2. Effect of pH and ozonation on the properties of organic matter

The variation of the zeta potential of the HA solution and surface water at different pH values, and with ozone oxidation (surface water) were determined in order to investigate the mechanism of charge interaction between the organic matter and membrane, and hence the potential for fouling. The results showed that the zeta potential of both waters decreased with increasing pH (Fig. 2a).

Comparing the results of the HA solution and surface water, it was clear that the zeta potential of the HA solution was substantially more negative than that of surface water, and decreased more markedly with pH, reflecting the presence of dissociating carboxylic and phenolic groups associated with the HA macromolecules. Also, the addition of ozone (Fig. 2b) decreased the zeta potential (more negative) of the Hyde park organic matter, by degrading or modifying organic matter through changes to their folding ability and tertiary structures, and increasing carboxylic acid groups (Hammes et al., 2006). In principle, decreasing the zeta potential of NOM should enhance electrostatic repulsion between the organic matter and the membrane surface (Du et al., 2009), thereby reducing fouling.

As well as the zeta potential/surface charge of the organic matter, other physico-chemical properties are also important, such as the presence and quantity of hydrophilic and hydrophobic components. The results showed that the proportion of hydrophobic components within the organic matter decreased with increasing ozone dose (Fig. 2b); in contrast, the hydrophilic and weakly hydrophobic organic components increased with ozone dose. Ozonation of NOM is known to attack carbon–carbon double bonds (e.g. in aromatic structures) and form low MW compounds such as aldehydes, ketones and carboxylic acids (Van Geluwe et al., 2011a), which is consistent with the observed conversion of hydrophobic to hydrophilic substances.
3.3. Effect of pH on membrane performance and fouling

The variation of NF membrane flux at different pH conditions was explored for both the HA solution and surface water (Fig. 3). The initial flux of the NF-3 membrane (1 kDa) and NF-4 membrane (800 Da) with HA solution decreased as pH increased. At all pH conditions the membrane flux decreased with filtration time, but for the HA solution the decrease was less than 12% ($J/J_0$) after 1600 s. As HA is generally hydrophobic in nature (Fig. 1d), it was expected that HA solution would cause little membrane fouling for the hydrophilic PES NF membrane. The greatest decrease of flux for both NF-3 and NF-4 membranes occurred at pH 5, and the flux decline diminished systematically with increasing pH (7 and 9). For the filtration of surface water, the initial flux of surface water also decreased as the pH value increased from 5 to 9, for both NF-3 and NF-4 membrane. As found with the HA solution, the greatest membrane fouling for the surface water was at pH 5, compared to pH 7 and pH 9, which may be a consequence of the lower repulsive force between organic matter and membrane at pH 5. The greater decrease of $J/J_0$ in the case of surface water, compared to HA solution, was probably related to the different characteristics and greater variety of organic matter (Yamamura et al., 2007).

Size exclusion chromatography was used to further characterize the dissolved organic matter in terms of MW distribution before and after membrane filtration and in membrane backwash effluents for different pH conditions (Fig. 4). The MW distributions displayed significant differences in the feed, filtrate and backwash samples, depending on pH. Lowering the feed water pH to 5 reduced the concentration of organic matter with MW between 2 kDa–6 kDa, but there was little change in the presence of biopolymers (Fig. 4a). As expected, there was a large reduction in organic matter between the influent (feed water) and permeate of the NF-3 membrane for both biopolymers (100% removal) and humic substances (>70%) at all pH values. The extent of the reduction, and influence of pH, was indicated by the presence of organic matter in the backwash effluent (Fig. 4c). It was evident that the mass of organic matter washed from the fouled NF-3 membrane increased with pH both for biopolymers and lower MW organic fractions, which was probably related to charge effects (increasing zeta potentials) between the organic matter and membrane, with higher pH leading to greater repulsive forces. For the NF-4 membrane, a greater extent of organic matter was removed from the surface influent water, especially fractions corresponding to an apparent MW > 2 kDa, compared to the NF-3 membrane (Fig. 4b and d). As observed with the NF-3 membrane, more organic matter was removed from the NF-4 membrane at higher pH conditions during the backwash process, including biopolymers and humic acid fractions (Fig. 4e).

3.4. Effect of ozonation on membrane performance for surface water

In order to investigate the impact of the ozonation on mitigating UF/NF membrane fouling by surface water, the variation of flux for the surface water pretreated with 0 mg/L or 1 mg/L ozone was determined (Fig. 5 and Figure S1). For the UF membrane without...
pre-ozonation, a substantial extent of pore blockage was expected (owing to similar size of biopolymers and membrane pores) and a corresponding severe flux decrease (~82%) was observed, while the application of ozone to the surface water reduced the membrane fouling (Fig. 5a); however, the decrease of flux was still substantial (70% for 300 mL permeate, compared to 80% without ozone pre-treatment). This behavior was probably related to the decrease in biopolymer concentration as a consequence of degradation by ozone oxidation. After backwash the flux immediately returned to its initial (clean membrane) value, and similar flux declines were observed during the second filtration operation as found with the first filtration operation.

For the NF-3 membrane the results were markedly different to the UF, and the addition of ozone had a slightly deleterious impact on relative flux (J/J0) decline (Fig. 5b). There was a much greater decrease of membrane flux (55% for 50 mL permeate), with or without ozone, compared to the UF membrane, as expected with the much smaller pore size of the NF membrane. In addition, for the NF-3 membrane the ozone oxidation of the surface water most likely had two effects that resulted in a slight increase in the flux decline; firstly, an increase in the organic fractions having a MW near to the NF-3 membrane pore size, and secondly, an increase in...
the hydrophilic fraction of the organic matter which is easier to be removed. However, this did not appear to cause irreversible fouling. Thus, after backwash the initial flux was fully recovered and the flux decline in the second filtration cycle was identical to the first cycle. For the NF-4 membrane, the extent of fouling was less than that of the NF-3 membrane in the absence of pre-ozonation (35% for 50 mL permeate), possibly because of a lower flux, and ozone had a slightly beneficial effect with a dose of 1 mg/L giving a corresponding flux decrease of 28%. Following backwashing, the flux appeared to fully recover and the subsequent decline was identical to the first cycle. Since only two cycles were conducted in these tests, it is unclear what effect the addition of ozone might have on the potential occurrence of irreversible membrane fouling in the long term, and this will be considered in future studies.

In general, with increasing ozone dose the presence of large biopolymers and smaller MW organic matter, including humic substances, decreased, and the resulting impact on membrane flux is believed to be related to the changes in the nature of these organic matter, such as zeta potential and hydrophobicity/hydrophilicity (Fig. 2), and MW distribution. The impact of ozone on the MW distributions before and after membrane treatment is summarized in Fig. 6. Whilst acknowledging that ozone may affect the UV absorbance of certain organic fractions, it is clear from the results for the UF permeate (Fig. 6b), there was little change in the organic matter with apparent MW < 10 kDa, but all the biopolymers were removed by the UF membrane. As the membrane pore size of NF-3 was much smaller than the UF, there appeared to be a corresponding increase in the removal of moderate-to-high MW organic matter (>1 kDa) by the NF-3 membrane, which was directly related to the ozone dose (Fig. 6c). These effects were also seen, but to a greater extent, with the NF-4 membrane, as shown in Fig. 6d.

To further characterize the foulants, the MW distributions of the organic substances in the samples from the membrane backwash were compared to the raw and filtrate water (Fig. 7), including the cases with 0 mg/L and 1 mg/L ozone pre-oxidation of the raw surface water (from Hyde park). The results showed that without the addition of ozone most biopolymers were successfully removed from the UF membrane by the backwash, but there was little removal of the smaller organic matter (<10 kDa), indicating that biopolymers determined the UF membrane fouling, at least the reversible form of fouling (Fig. 7a). Similarly, after pretreatment with 1 mg/L O3, some biopolymers (at a lower concentration) were evident in the backwash water from the UF membrane (Fig. 7b), which were associated with the lower membrane fouling (Fig. 5a). Pre-ozonation also had little impact on the retention or adsorption of humic substances (MW < 10 kDa) on the membrane (Fig. 7b).

For the NF-3 membrane, the organic matter recovered from the backwash water contained both biopolymers and lower MW fractions (1–10 kDa), with the latter generally absent in the backwash water from the UF membrane. Since the size of the lower MW fractions present in the backwash was closer to the membrane pore size, their collection on the membrane surface contributed to the greater membrane fouling than was found for the UF membrane. With the addition of 1 mg/L O3, although the amount of biopolymer was less than that without ozone, the content of lower MW organic matter after backwash was similar, which probably related to the same degree of NF-3 membrane fouling. For the NF-4 membrane, although there was a greater removal of organic matter in the 1–10 kDa MW range compared to the NF-3 membrane, the content of lower MW organic matter in the backwash waters was slightly greater. However, with the addition of ozone not only was there less biopolymer in the backwash water, as also observed with NF-3, but the smaller MW organic fractions were also much less than without ozone, which could explain the lower membrane fouling observed (Fig. 5c). The differences in the presence of organic matter in the backwash waters was most likely related to the membrane properties, as the NF-3 membrane (15.2 ± 2.8° contact angle) was more hydrophilic than the NF-4 membrane (24.2 ± 0.9° contact angle), and more hydrophobic organic matter was adsorbed on the
NF-4 membrane.

As the MW distributions of the organic matter in the UF and NF permeates for the first and second cycles were the same, it was evident that the membrane pores were unchanging after the backwashing operation. Since these tests were limited to only two cycles, further studies are recommended involving an extended period of continuous operation of the membranes in order to investigate the possible development of irreversible membrane fouling.

4. Conclusions

In this study the effect of pH and surface charge on membrane fouling during the treatment of samples of a representative surface water were evaluated, together with the impact of pre-ozonation. The results of the laboratory tests are summarized as follows:

1. While biopolymers in the surface water were extensively removed by UF, there was little removal of smaller MW fractions, such as humic acids. For the NF membranes the removal of smaller MW fractions (800 Da—10 kDa) was less than expected as suggested by the membrane pore size for the surface water, but there was a very high removal of organic matter from the HA solution (90%). These results indicated the importance of other properties influencing the membrane separation, such as the charge and hydrophilic nature of the NOM.

2. During the NF treatment of surface water, a greater membrane fouling was found compared to the HA solution. Membrane fouling could be mitigated by increasing the pH value of the surface water or HA solution, owing to increasing repulsive forces between organic matter and membrane surface, and highlighting the role of charge effects in membrane separation.

3. Pre-ozonation of the surface water systematically increased the hydrophilic fraction and anionic charge of NOM and altered their size distributions. For the UF membrane there was a corresponding increase in the flux systematically with ozone dose, which was probably related to the decrease of biopolymers concentration as a consequence of ozone oxidation. For the NF membranes, the impact of ozone on membrane flux was different, with a decreased fouling (flux decline) for the smaller pore NF, but a slight increase in fouling for the larger pore NF. This difference in the NF behavior is believed to relate to the relative sizes of the ozonated organic fractions and the NF pores.

4 The results of the NF tests indicated that the size/characteristics of the membrane pores were fully recovered after backwashing, and there was no evidence of irreversible membrane fouling. However, further tests involving continuous, long-term operation of the NF membranes is recommended, to investigate the occurrence and extent of irreversible membrane fouling.

Fig. 6. Effect of ozonation on the apparent MW distribution of organic matter from Hyde park surface water (a), the UF permeate (b), the NF-3 permeate (c) and NF-4 permeate (d) (residual ratio in sub-figure refers to the ratio of the absorption peak of the permeate to the raw water at 3000 Da).
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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.watres.2018.04.025.

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Fig. 7. Effect of ozonation on the apparent MW distribution of organic matter from Hyde park surface water over 2 filtration cycles: a) UF membrane without ozonation, b) UF membrane with ozonation, c) NF-3 membrane without ozonation, d) NF-3 membrane with ozonation, e) NF-4 membrane without ozonation, f) NF-4 membrane with ozonation (samples were taken after filtration, backwash and re-filtration).
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