Influence of ionic composition on NOM size and removal by ultrafiltration

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Abstract In this study, the effects of Na⁺ and Ca²⁺ on the apparent MWt distribution and removal efficiency of NOM by deadend ultrafiltration were investigated. NOM samples from Singapore (reservoir-based), IHSS (river-based standard) and Biohumic (soil-based) were used. The effective particle sizes and MWt distributions of the NOM, with and without ions, were analyzed by light scattering and HPSEC, respectively. The effective size of the NOM was significantly reduced by increasing the Na⁺ concentration. This was probably due to coil-to-globule conversion and polyelectrolyte interaction, changing the NOM conformation from linear to spherical. However, increasing the concentration of Ca²⁺ showed competing effects. At relatively low concentrations of Ca²⁺, the size of the NOM was reduced, presumably by the mechanism attributed to Na⁺. As the concentration of Ca²⁺ was further increased the NOM size increased, due to aggregation or chelation between humic acid in the NOM and Ca²⁺ becoming the dominant factor. Ion interactions with NOM also had a significant impact on removal by ultrafiltration. With addition of Na⁺, the Singapore NOM retention decreased from 52% to 29%. In contrast, the retention of Biohumic NOM increased from 45% to around 70% with an increase in Ca²⁺ concentration.

Keywords Ionic interaction; natural organic matter; ultrafiltration

Introduction
Natural organic matter (NOM), derived from the degradation and decomposition of organic substances by microorganisms, is widely present in surface waters. The main components in NOM are humic substances, which are a complex mixture of organic compounds such as humic acids, fulvic acids and other hydrophilic acids (Burgos et al., 2000; Chen et al., 2003). The humic substances have characteristic lengths around 1 nm to 10 nm and reported molecular weights from a few hundred to approximately 100,000 Da (Schaefer, 1998; Chang, 1996, 2003; Austin et al., 2001; Peuravuori and Pihlaja, 1997).

It is well recognized that the presence of the NOM in surface water has an adverse effect on the water quality. As a result the removal of NOM from drinking water has been extensively studied (Chen et al., 2003; Schafer, 1998; Chang, 1996; Chang and Benjamin, 2003). Among the various removal technologies, membrane ultrafiltration (UF) has the advantages of low pressure operation and relatively good removal efficiency, especially when the “tightest” UF membranes are employed (Schafer, 1998; Cho et al., 2000; Majewska-Nowak et al., 2002). However, NOM removal by UF not only depends on the membrane pore size but also on the hydrodynamic size of the NOM components. The source of NOM and solution conditions such as ionic composition, ionic strength and pH are important in determining the conformation of NOM species and subsequent filtration performance.

Previous studies have shown that multivalent ions such as Ca²⁺ and Mg²⁺ interact strongly with the humic substances, leading to the formation of stable complexes or aggregation brought about by the chelating effect of the divalent cations. Consequently, there is an increase in both size and apparent molecular weight of the humic substances (Gjessing et al., 1999; Pinheiro et al., 2000). The ionic environment can also have an impact on the molecular size of the humic substances which may become smaller at a high ionic strength.
or low pH. For example, it was suggested that the molecules of the humic substances tended to be linear at a low ionic strength of 1 mmol l⁻¹ NaCl, whereas the structure was fully spherical at 50 to 100 mmol l⁻¹ NaCl (Andersen et al., 2000). The hydrodynamic diameters of the humic substances were found to decrease from 15 to 1.7 nm when the concentration of NaCl changed from 0.4 mmol l⁻¹ to 1 mol l⁻¹ (Andersen et al., 2000; Margarida and Maria, 2002). The solubility of humic substances also varies with the concentration of multivalent ions and the pH because of charge neutralization or complexation effects. Humic acid is insoluble at a pH < 2 while fulvic acid is soluble over the pH range (Andersen et al., 2000; Margarida and Maria, 2002).

In this study, the effects of Na⁺ and Ca²⁺ interaction with NOM on the apparent molecular size distribution of the species and the NOM removal efficiency by UF membranes in a dead-end filtration cell were investigated over a wide range of ionic strengths. This is the first reported assessment of Singapore NOM, which is typical of a tropical catchment. It is compared with IHSS NOM (typically temperate) and Biohumic NOM (soil derived). This study is an attempt to obtain a better understanding of solute–solute interactions for further optimization and enhancement of UF for NOM removal.

**Materials and methods**

**Model NOM and other chemicals**

Three types of NOM were used in this study, namely Singapore NOM, IHSS and Biohumic NOM. The Singapore NOM was collected from the Kranji reservoir at a concentration of about 5.02 ppm TOC. It was then filtered by MF (Millipore 0.45 µm) and concentrated to 52.1 ppm by batch NF (Filmtex NF 270–400; measured retention of NOM was about 96%). The concentrated solution also contained 26.5 ppm Ca²⁺, 3.2 ppm Mg²⁺, 6.8 ppm K⁺ and 16.2 ppm Na⁺. IHSS NOM was made by mixing equal amounts of IHSS humic acid (HA) and IHSS fulvic acid (FA), which were purchased from the International Humic Substances Society. The use of this well-defined material allows comparison of the results with other laboratories. Biohumic NOM was obtained from Bioiberica S.A. and, as it is soil-based may contain species different from those in the NOM collected from surface waters. The Biohumic NOM contained 11% humic acids and 4% fulvic acids. Other chemicals used were purchased from Sigma-Aldrich at analytical grade.

**Solution preparation**

A series of NOM solutions containing the various NOMs and ions at different concentrations were prepared using high quality Milli-Q water. The Na⁺ strength in the solutions was adjusted to different levels with 0.1 mol l⁻¹ NaCl, while the Ca²⁺ concentration was adjusted by adding 20 mmol l⁻¹ CaCl₂. The pH value of the solutions was adjusted to between 5–7 by adding 0.1 mol l⁻¹ NaOH or 0.1 mol l⁻¹ HCl solutions. All the solutions were stirred for 1 hour prior to the experiments.

**Membranes and filtration protocol**

The membranes used were flat-sheet PBGC UF membranes, manufactured by Millipore Corp. The PBGC membrane is an asymmetric polyethersulfone membrane with 28 kDa MWCO, determined inhouse using Gel Permeation Chromatography and dextrans of various molecular weights. Prior to use, the membranes were washed thoroughly with MilliQ water to remove preservative and then compacted by permeation experiments with pure water at a pressure of 500 kPa for a period of 3 h. The operating temperature was kept at room temperature.

The filtration experiments were carried out in a 110 ml dead end cell, which accommodated 12.6 × 10⁻⁴ m² of membrane. The use of unstirred conditions was based on the
deadend mode (no crossflow) typically applied to membranes in water treatment to minimize energy usage. A feed reservoir of 1.5 L was connected to the dead end cell to provide extended filtration volumes and a PC-controlled electronic balance was employed to weigh collected permeates. The transmembrane pressure applied was 300 kPa using pressurized N$_2$. The permeates and retentates were sampled after 20 to 30 minutes. TOC retention was based on spot samples of retentate and permeate and defined by,

\[
\text{TOC retention} = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{retentate}}} \right) \times 100 \%
\]

The membranes were cleaned by soaking in 0.1 mol l$^{-1}$ NaOH for 30 minutes followed by soaking in MilliQ Water for 30 minutes two times; this protocol restored membrane permeability. The membranes were used up to five times and were stored in a 0.1 mol l$^{-1}$ EtOH solution at 4 °C.

**Analysis**

The total organic carbon (TOC) content was analyzed using a Shimadzu TOC-V CSH Total Organic Carbon analyzer and the analysis was conducted within one day of sample collection to avoid any changes in the NOM. The effective particle sizes of the NOM were measured using a 90plus/BI-MAS Multi Angle Particle Sizing Analyzer (Brookhaven Instruments Corporation USA). The light scattering particle size analyzer is capable of measuring concentrated suspensions of small particles or solutions of macromolecules over the range of 2 nm to 3 µm. The sizes reported are the mean particle sizes.

The relative molecular weight distribution of NOM was determined using a High Pressure Size Exclusion Chromatograph (HPSEC), with RI detector, which was manufactured by Waters. Ultrahydrogel columns types 120, 250 and 500 from Waters and a Shodex standard P-82 were used for HPSEC analysis. Prior to HPSEC measurement, water samples were filtered by a 0.45 µm microfiltration membrane to remove large particles and colloids. The filtered samples were then concentrated by low pressure RO membrane to reach around 200 ppm for analysis.

**Results and discussion**

**Effect of Na$^+$ interaction with NOM**

The influence of sodium concentration on the effective size of Singapore NOM and IHSS NOM are shown in Figure 1. The Na$^+$ concentration varied over the range 0-100 mmol l$^{-1}$. It was found that the effective particle size of Singapore NOM reduced significantly from about 700 nm to 80 nm when the concentration of Na$^+$ increased to 50 mmol l$^{-1}$. A similar trend was observed for IHSS NOM, HA and FA and Biohumic NOM.

![Figure 1](https://iwaponline.com/ws/article-pdf/4/4/197/417499/197.pdf)
This phenomenon was mirrored by the HPSEC analysis of the NOM solutions. It should be noted that the NOM analyzed is the non-particulate fraction after 0.45 μm microfiltration. Figure 2 illustrates the apparent molecular weight distributions of Singapore NOM with different NaCl concentrations. The original NOM without Na\(^+\) addition had a broad molecular weight distribution. With the addition of Na\(^+\) to the solutions, the distributions shifted gradually to narrower bands and the smaller NOM molecules accounted for the bulk. Similar phenomena were found in the cases of IHSS NOM and Biohumic NOM, but the effect of Na\(^+\) on Singapore NOM was found to be more pronounced than for IHSS or Biohumic NOM.

The observed effect of Na\(^+\) on NOM could be due to coil-to-globule conversion and polyelectrolyte interaction, which changes the conformation of NOM from linear to spherical as suggested previously (Pinheiro et al., 2000; Chen et al., 2003). Based on Flory’s average field theory (Bahattin, 2003; Luke et al., 2004), soft polymer chains can change from coils to globules when the conditions of the solution are altered. This conversion could be attributed to either ion addition or temperature change. For instance, the size of Poly-N-isopropylacrylamide (PNIPAM) can be reduced by 99% when the temperature is adjusted to 32°C. NOM, being a mixture of macromolecules or polymer, is normally in a state of random coils in a water solution. When a salt is added to the NOM solution, the NOM solubility would be affected. NOM could contract to small globules to adjust for the change in its environment.

An alternative viewpoint is that the NOM contains polar compounds which can be ionized in a water solution. The electrostatic forces of repulsion would result in an “open” conformation. With the addition of salts the interactions would become shielded resulting in a smaller effective size.

**Effect of Ca\(^{2+}\) interaction with the NOM**

The influence of calcium concentration on the effective size of Singapore NOM and IHSS NOM is presented in Figure 3. An opposite trend to the case of Na\(^+\) was found as the effective size of Singapore NOM increased with an increase in Ca\(^{2+}\) concentration. However, IHSS HA and IHSS FA responded differently to Ca\(^{2+}\) addition. Increasing Ca\(^{2+}\) showed competing effects on the size of IHSS HA. When 5 mmol l\(^{-1}\) Ca\(^{2+}\) was added to the 60 ppm IHSS HA solution, the effective size was reduced from 400 nm to 180 nm. However, with a further increase in Ca\(^{2+}\) concentration to 10 mmol l\(^{-1}\), the effective size of IHSS HA increased significantly to 1,800 nm. In contrast, the effective size of IHSS FA consistently decreased with Ca\(^{2+}\) loading over the range of concentrations. For IHSS NOM, being a mixture of IHSS HA and IHSS FA in equal portions, the effect of Ca\(^{2+}\) loading on the size of IHSS NOM followed the pattern of IHSS HA as the change in IHSS HA size was then more significant.
These observations were also verified using HPSEC analyses. The molecular weight distributions of IHSS NOM and Biohumic NOM with zero and low Ca\(^{2+}\) concentrations shown in Figures 4(a) and (b), respectively, confirm that there was a decrease in the NOM size at low concentration of Ca\(^{2+}\), as the original broad molecular weight distributions narrowed in the range of low molecular weights. However, this type of spectrum could not be obtained for Singapore NOM and other NOM solutions with higher Ca\(^{2+}\) loading, because the aggregated particles in the solutions tended to clog the guard column in the HPSEC leading to operational problems. Thus the sizes of the aggregated particles had exceeded the limitation of the guard column, which pretreated the solutions with a 0.45 \(\mu\)m microfilter.

It is presumed the same mechanism observed in the case of Na\(^+\) played a role in the case of Ca\(^{2+}\) interaction with IHSS NOM and Biohumic NOM at relatively low concentrations. However as the concentration of Ca\(^{2+}\) in the solution was increased, the size increase could be due to aggregation or chelation between the phenolic groups in humic acid and Ca\(^{2+}\) becoming a dominant factor. Similar mechanisms have been proposed in the literature (Bahattin and Frank, 2003).

**Effect of solution pH**

Figure 5 shows the size distribution of IHSS at different pH obtained by HPSEC. It was found that although there was no difference in the effective molecular size distribution of IHSS over the pH range 4–10, its measured size decreased significantly at low pH values (≤2) (lower molecular weights are to the right of the figure). The pH influence on Biohumic NOM is similar to that for IHSS NOM. It was also found that IHSS FA was not very sensitive to the pH change.
Ultrafiltration study

In addition to the above studies, the impact of ion interactions on NOM removal in an ultrafiltration process was investigated. As noted above, the measurements were done in unstirred conditions to more closely simulate the dead end mode typically used in the water industry. As a result the reported retentions are likely to be significantly lower than the intrinsic retention of the membranes used. Future studies are planned to examine the influence of hydrodynamic conditions on retention. Figure 6 shows the retentions of Singapore NOM and Biohumic NOM solutions with/without NaCl addition, respectively using the PBGC membrane. With the introduction of Na\(^+\), the Singapore NOM retention decreased from 52% to 29% and Biohumic NOM retention decreased from 45% to 29%. Moreover,
the HPSEC chromatograms shown in Figure 7 demonstrate that the molecular sizes of Biohumic NOM permeates became smaller with Na\(^+\) addition.

In contrast, the retention of the PBGC membrane for Singapore NOM increased by adding about 1 mmol l\(^{-1}\) Ca\(^{2+}\) into the solution as shown in Figure 8. The retention of Biohumic NOM increased from 45% to around 70% when more than 0.5 mmol l\(^{-1}\) Ca\(^{2+}\) was loaded.

For IHSS NOM, the combined effect of 20 mmol l\(^{-1}\) NaCl and 0.5 mmol l\(^{-1}\) CaCl\(_2\) on the filtration was examined. As the relative concentration of Ca\(^{2+}\) to NOM was quite low, the interactions of both Ca\(^{2+}\) and Na\(^+\) with the NOM resulted in a decrease in NOM size. As a consequence, the NOM retention decreased from about 50% to 30% for the PGBC membranes. This result illustrates the complex interactions that can influence membrane performance. Further work is planned to improve our understanding of NOM-solute interaction in order to optimize and enhance NOM filtration performance.

Conclusions
This study deals with NOM sourced from a Singapore reservoir, which is compared with Standard humic substances and a commercially produced NOM. The influences of Na\(^+\) and Ca\(^{2+}\) concentrations as well as solution pH on the NOM molecular size and removal efficiency in membrane ultrafiltration processes were investigated. The effective size of the NOM was significantly reduced by adding Na\(^+\) to the NOM solution due to the coil-to-globule conversion and polyelectrolyte interaction. In contrast, increasing Ca\(^{2+}\) showed two possible effects on the size of the NOM. At relatively low Ca\(^{2+}\) concentrations, NOM size was reduced presumably by the same mechanism observed in the case of Na\(^+\). However, when the concentration of Ca\(^{2+}\) was increased, there was an increase in NOM size, possibly due to an aggregation or chelation between the humic acid in NOM and Ca\(^{2+}\). The NOM also reduced its size when the solution pH was below 2.

These observations were further confirmed by NOM ultrafiltration experiments. The NOM retentions by the PBGC membranes decreased when Na\(^+\) was added into the solution, whereas increasing Ca\(^{2+}\) concentration increased the NOM retentions of PBGC membranes. Therefore, it is important to have a good understanding of solute–solute interaction to optimize and enhance NOM filtration performance.

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References


