Characterization of micro-flocs of NOM coagulated by PACl, alum and polysilicate-iron in terms of molecular weight and floc size

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ABSTRACT

Micro-flocs of NOM coagulated by polyaluminium chloride (PACl), alum and polysilicate-iron (PSI) were characterized by flocs size, HPSEC-based molecular weight and the captured content of coagulants-based aluminium and iron. Changes in floc composition with respect to the mass ratios of captured NOM to Al and Fe were examined. Lowering water pH to optimum levels was found to be capable of removing small NOM constituents that are generally difficult to be precipitated at neutral pH levels. For PACl and PSI, the distribution of micro flocs (0.1–5.0 μm) reached steady stage after rapid mixing for 30 seconds, with NOM being found existent within the non-coagulated fraction (d < 0.1 μm) and the coagulated fraction with floc sizes above 5.0 μm (d > 5.0 μm). For alum, however, the existence of NOM inside intermediate floc fractions of d = 0.1–1.0 μm, 1.0–3.0 μm and 3.0–5.0 μm was confirmed.

Key words | coagulation, floc size, humic substance, molecular weight, NOM

INTRODUCTION

Natural organic matter comprising mainly humic molecules is the predominant organic matrix present in most natural river and lake water systems. NOM is getting increasingly concerned in light of its high potential in forming carcinogenic disinfection byproducts. Enhanced removal of NOM is expected also because even if not targeted for removal, its constituents can adversely affect the performance of other water treatment processes, for instance, the adsorption process for removing some specifically targeted synthetic organic chemicals (SOCs) via site competition and pore blockage (Ebie et al. 2001; Li et al. 2003a). NOM is also found to be capable of interacting with heavy metals, SOCs as well as natural hormones to form various types of complexes, thus regulating the fate and behavior of such micropollutants during physicochemical and biological treatment as well as in natural water environments.

Literature review revealed that removals of dissolved organic matter in drinking water sources by conventional rapid sand filtration system, where coagulation is the core process, differ broadly in about 10–90%, with an average removal of approximately 30% (Sharp et al. 2006a). In addition to the differences of NOM in its physicochemical features (including molecular weights, hydrophobic strengths, charge densities, etc.), coagulation conditions involving such parameters as coagulant types and dosage, water pH, and the stirring strength and time could also greatly affect the structures and properties of flocs (Masion et al. 2000; Jarvis et al. 2006). Effective formation of micro-flocs in the rapid mixing stage is the key since it affects the performance of some particle separation processes that deal directly with micro-flocs (such as direct sand filtration and membrane filtration), and also the features of settling flocs formed aftermath during the succeeding slow mixing stage. Characterization of micro-flocs of NOM based on their physical sizes and constituents (in regard of the captured amounts of aluminium or ferric, and the NOM molecules of varied molecular weights) is thus important for better
understanding the involved coagulation mechanisms and for optimization of coagulation conditions.

Accordingly, the main objective of this study is to characterize micro-flocs of a representative aqueous NOM coagulated under varied pH and coagulant dose conditions with polyaluminium chloride (PACl), alum and polysilicate-iron (PSI) based upon floc sizes and the HPSEC-based molecular weights of NOM constituents captured within respective flocs. The composition of flocs in relation to the mass ratios of captured NOM to coagulants-based Al and Fe was also examined, and the impacts of such parameters as pH, stirring strength and stirring time on enhanced coagulation of NOM were discussed.

MATERIALS AND METHODS

Water source

A groundwater collected from a shallow well in the Kitamura village of Hokkaido, Japan was used as the source of NOM for study. This water was chosen because it contains higher content of NOM (about 10 mg/L-DOC) originated mainly from peat, and the physicochemical features and treatability by such processes as coagulation and activated carbon adsorption were found very close to organic matrices encountered in most river water sources (Matsui et al. 1993; Li et al. 2003b). The collected water was filtered through a 0.1 µm membrane filter for removing suspended particles and dilution was made as desired, before subjected to coagulation experiments.

Coagulants

Three coagulants, namely polyaluminium chloride (PACl), alum and a polysilicate-iron complex (PSI) were used for comparison. The used type of PACl contains 10.5% of Al₂O₃ and has been well applied in drinking water treatment plants in Japan. For alum, a reagent grade product, Al₂(SO₄)₃.14-18H₂O, from Wako Pure Chemicals (Japan) was purchased. In regard of PSI, a synthesized type having the molar ratio of Fe: Si = 1:1 was chosen (Wang et al. 2002).

Jar test experiments

Two series of jar test experiments were conducted. The first series used water samples, whose initial pH before the addition of coagulants was controlled at 7.0 and 5.5, respectively, and was performed by varying the coagulant dose in 0–10.0 mg/L-Al (for PACl and alum) and 0–19.5 mg/L-Fe (for PSI) for assessing the coagulant-dose effects. Rapid mixing was conducted at the G value of about 660 s⁻¹ for 5 minutes, followed by slowing mixing at G = 150 s⁻¹ for 15 minutes and subsequent settling for 30 minutes. The associated performance was assessed based upon the lumped NOM removals, changes in apparent molecular weight (MW) distribution and the removal behavior of each MW fraction divided based on relative HPSEC chromatograms. The second series of experiments were performed for examining the characteristics of micro-flocs formed under pH = 5.5 and pH = 7.0 with different rapid mixing (G = 660s⁻¹) lengths: t = 0.5, 1, 3 and 5 minutes, respectively. For comparison, experiments by introducing 15 minutes of slow mixing after 5 minutes of rapid mixing were also performed.

For the second jar test series, pH was controlled throughout corresponding experimental runs to designated levels of 5.5 and 7.0 by addition of HCl or NaOH when necessary. After coagulation, water fractionation was implemented by filtering each coagulated water sample through membrane filters having openings of 5.0, 3.0, 1.0 and 0.1 µm, respectively. Then, following the process of breaking micro-flocs contained in each water fraction by elevating water pH to above 11 and strong stirring, the content of NOM and its MW distribution as well as the coagulants-based Al or Fe were quantified. By doing so, micro-flocs were characterized into five size fractions: d < 0.1 µm (un-coagulated fraction), d = 0.1–1.0, d = 1.0–3.0, d = 3.0–5.0 and d > 5.0 µm; and the molecular weights of NOM constituents as well as Al and Fe captured within each floc fraction were determined.

The content of NOM was assessed by total dissolved organic carbon (DOC) and ultraviolet absorbance at 260 nm (UV260). The apparent MW distribution was analyzed using a HPSEC system calibrated with polystyrene sulfonates (PSS) (Li et al. 2003). The coagulants-based Al (for PACl and alum) and Fe (for PSI) were measured using the Agilent 7500 series ICP-MS system (ICP-MS 7500).
RESULTS AND DISCUSSION

Effect of coagulant dose on removal of NOM

Figures 1 and 2 show the effect of coagulant dose on residual UV260 and DOC at the initial pH of 7.0 and 5.5, respectively. For comparison, the decreasing trend of water pH with increases in coagulant dose is also displayed. For the case of initial water pH at 7.0, as shown in Figure 1 (a, b) that for all three coagulants, UV260 and DOC decreased with increases in coagulant dose over the ranges of 0–10 mg/L-Al for PACl and alum and 0–19.5 mg/L-Fe for PSI. Increasing coagulant dose over these ranges resulted in decreases of water pH from its initial value of 7.0 to the lowest value of 6.0 observed for alum; however, there were no signs of worsening in the coagulated water quality regarding both UV260 and DOC.

In validation of previous indications, coagulation started from the lower water pH (pH5.5 in this study) seemed to be more effective for removal of NOM. As shown in Figure 2,
although the residual UV260 and DOC increased when coagulant dose excelled certain levels, about 2 mg/L-Al for alum, 6 mg/L-Fe for PSI, which indicated deteriorations in the coagulation performance, comparisons with the results shown in Figure 1 revealed clear that enhanced removal of NOM could be achieved no matter which coagulant was used. This effect was particularly obvious for PSI. With this coagulant, the residual DOC could be lowered to about 20% by dosing 6 mg/L-Fe, which was a furthered reduction of NOM by about 40% as compared to a value of about 60% residual achieved when coagulation was initialized from pH 7.0. This effect has significant implication for enhanced removal of NOM and is conceived to be mainly attributed to the combined effects achieved by lowering water pH: (1) reductions in the charge density of NOM molecules since disassociation of humic molecules exhibiting the features of weak acids could be inhibited by lowering water pH; and (2) increases in the existing percentages of aluminium and ferric species possessing greater charge neutralization capabilities (Sharp et al. 2006b). The first effect was also inferred to be involved in confirmed effect of enhanced adsorption capacity of NOM onto coal-based activated carbons (Li et al. 2002).

Effect of coagulant dose on SEHPC chromatograms of NOM

The effect of coagulant dose on the apparent MW distribution of NOM is displayed in Figure 3 for the case of PACl as examples. Increasing coagulant dose resulted in a general shift of the HPSEC chromatogram towards the right side, indicating that larger NOM constituents were preferentially coagulated, with those having smaller molecular weights being remained for the case of the initial water pH 7.0 (Figure 3a). By lowering initial water pH to 5.5, the shift extent of the MW distribution was significantly enhanced (Figure 3b).

Based on the peak number of HPSEC chromatogram at Dose = 0, the NOM studied was divided into five fractions. The apparent molecular weights and partition percentages of these fractions are given in Table 1, and their residuals under different coagulant doses are displayed in Figure 4. It seemed that for all MW fractions, enhanced removal at lower coagulant doses was achieved for the case of initial pH5.5. For smaller MW fractions F3, F4 and F5, enhanced removal by lowering pH was also apparent, especially for PACl and alum. The results thus suggested that, to enhance the removal for NOM, lowering water pH be effective due to its capability in promoting aggregation of small NOM molecules that are generally difficult or nearly impossible to be coagulated at neutral pH levels around 7.0.

<table>
<thead>
<tr>
<th>MW fraction number</th>
<th>Retention time (min)</th>
<th>Mw (Dalton)</th>
<th>Partition ratio (%)</th>
</tr>
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<tbody>
<tr>
<td>F1</td>
<td>30.4</td>
<td>5000</td>
<td>37.1</td>
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<tr>
<td>F2</td>
<td>31.0</td>
<td>4600</td>
<td>20.9</td>
</tr>
<tr>
<td>F3</td>
<td>32.2</td>
<td>4000</td>
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</tr>
<tr>
<td>F4</td>
<td>34.3</td>
<td>3000</td>
<td>15.4</td>
</tr>
<tr>
<td>F5</td>
<td>39.3</td>
<td>1500</td>
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</table>
Coagulation jar tests conducted by varying the coagulation pH in the range of about 3–9.5 confirmed that for all three tested coagulants, larger NOM removals occurred at pH levels below 6.0, with the optimum pH ranges for coagulation with PSI and PACl (about 4.0–5.9) being broader than alum (about 4.9–6.0) (figures not shown here).

Characteristics of micro-flocs formed at coagulation pH of 7.0 and 5.5

The distribution changes of NOM constituents after coagulation by 5 minutes of rapid mixing under controlled pH (pH = 7.0) throughout the experimental runs are displayed in Figure 5. For comparison, the distribution changes obtained under controlled pH (pH = 5.5) throughout related runs are displayed in Figure 6. The presence of NOM was classified in terms of five floc size fractions: $d < 0.1\, \mu m$, $0.1 \leq d < 1.0\, \mu m$, $1.0 \leq d < 3.0\, \mu m$, $3.0 \leq d < 5.0\, \mu m$, and $d \geq 5.0\, \mu m$, and five MW fractions having apparent molecular weights of 5000, 4600, 4000, 3000 and 1500, respectively. The fraction with floc sizes of $d < 0.1\, \mu m$ was defined as the non-coagulated fraction that did not interact with coagulants to form precipitates with sizes above 0.1 $\mu m$.

For the case of coagulation at pH 7.0, compared to the NOM constituents before coagulation (Figure 5a), the proportions of NOM constituents after coagulation aggregated in varied proportions to sizes above 0.1 $\mu m$ (Figure 5b, c, d). With PACl and PSI, NOM constituents were distinctly divided into two size fractions: the not-coagulated fraction ($d < 0.1\, \mu m$) and the coagulated fraction with sizes above 5 $\mu m$ ($d > 5.0\, \mu m$); with alum, however, the existence of some intermediate size fractions ($1.0 \leq d < 5.0\, \mu m$) was confirmed. Given $G = 660\, s^{-1}$, the distribution of NOM constituents reached its steady state almost within 30 seconds for both PACl and PSI. For alum, however, observable distribution variation continued until the end of 300 seconds of rapid mixing even if the total content of NOM captured within flocs above 0.1 $\mu m$ was found relatively stable (about 52%), showing little changes with the studied rapid mixing lengths of 0.5, 1, 3 and 5 minutes (data not shown).

These phenomena also appeared for coagulation at pH 5.5 as illustrated in Figure 6. However, the proportions of
Figure 5 | The distribution changes of NOM constituents after coagulation by 5 minutes of rapid mixing at pH = 7.0.

Figure 6 | The distribution changes of NOM constituents after coagulation by 5 minutes of rapid mixing at pH = 5.5.
NOM constituents captured in flocs with intermediate sizes between $d < 0.1 \mu m$ and $d > 5 \mu m$ increased, with the increases being more obvious for coagulation with alum than with PACl and PSI. The characteristics of flocs formed by subsequently introducing 15 minutes of slow mixing after 5 minutes of rapid mixing were also studied for all three coagulants used. The results obtained resembled those shown in Figures 5(d) and 6(d), indicating that the introduced slow mixing did not bring about furthered growth/aggregation of micro flocs to sizes above $5 \mu m$ (data not shown). For floc particles above $5 \mu m$, since further fractionation was not conducted, it is unclear on how slow mixing affected their characteristics in regard of the sizes, and the captured content and species of NOM and coagulants-based Al and Fe, a topic of concern for further studies.

Changes in the mass ratio of UV260/Al (for PACl and alum) and UV260/Fe (for PSI) within the faction of flocs having sizes above $5.0 \mu m$ are displayed in Figure 7. Similarly, the changes in the mass ratio of DOC/Al and DOC/Fe are displayed in Figure 8. In both these figures, except for data plotted at the mixing time of 20 minutes, which were obtained through jar tests conducted by including 15 minutes of slow mixing after rapid mixing for 5 minutes, all remaining data were obtained from jar tests by applying rapid mixing alone. The above $5 \mu m$ floc fraction was singled out for discussion because, of the total quantities of dosed Al and Fe ($5 mg/L$-Al for PACl and alum and $10 mg/L$-Fe for PSI at pH 7.0; and $3 mg/L$-Al for PACl and alum and $6 mg/L$-Fe for PSI at pH 5.5), markedly larger proportions were captured within flocs of this size fraction, with the proportions remaining in dissolved forms ($d < 0.1 \mu m$) being very small. For instance, after five minutes of rapid mixing, dissolved Al and Fe concentrations in water after coagulation with PACl, alum and PSI were measured as 0.002, 0.02, 0.02 mg/L (for pH 7.0), and 0.19, 0.16 and 0.11 mg/L (for pH 5.5), respectively.

As shown, for coagulation with alum at pH 7.0, the DOC/Al ratio increased with mixing time, indicating the need for longer coagulant-NOM interactions when this coagulant type was employed (Figure 8a). Besides, compared to the ratio values at pH 7.0 (Figures 7a and 8a), those at pH 5.5 (Figures 7b and 8b) were generally larger for both polymerized coagulants PACl and PSI. This supports the
earlier indication that lowering water pH was probably an effective way for enhanced coagulation of aqueous NOM.

CONCLUSIONS

Coagulation experiments were performed to investigate the coagulation behavior of a representative aqueous NOM contained in a shallow groundwater by PACl, alum and PSI, respectively. The differences in the characteristics of the formed micro-flocs were assessed based on measurements of the lumped NOM content indices of UV260 and DOC, HPSEC-based MW distribution and coagulants-based Al and Fe. The composition changes of micro-flocs with pH, coagulant dose and rapid mixing time were also grasped. The findings obtained are considered important as they could be used as reference for benefitting enhanced coagulation removal of NOM encountered in drinking water treatment.

ACKNOWLEDGEMENTS

Experimental contribution from Mr. Hiroshi Hoshino, a former graduate of Gifu University, is highly appreciated.

REFERENCES


