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Coagulation of surface water: Observations on the significance of biopolymers

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ABSTRACT

Although the treatment of natural surface waters by coagulation has been investigated extensively, the detailed interaction between natural organic matter and alum is still not adequately understood or predictable, owing to the complexity of different components of the organic matrix and the conditions during coagulation. In this paper, we present the results of a novel approach to the study of the topic, which involved the progressive separation of organic components according to size, followed by coagulation of the filtrate solution, in order to expose the influence of particular organic fractions. Using two natural water sources, representative of lake and river waters, solutions of different organic content were obtained by progressively filtering the source waters using membranes of decreasing pore size; viz. microfiltration (MF), ultrafiltration (UF), and two grades of nanofiltration (NF). While MF had little impact on the range of organics present, UF was able to separate biopolymers (MW > 100 kDa), and NF had a substantially impact on the separation of medium-high MW (1–10 kDa) substances. The results of the coagulation tests showed that the size of flocs was substantially greater when biopolymers were present, suggesting their beneficial role in bridging precipitated $Al(OH)_3$ nanoparticles. For the smaller organic fractions (<10 kDa), the results showed a trend of increasing floc size with decreasing organic MW and concentration, but the trend was minor and may be explained by charge effects. Very similar results were found with both water sources, which support the main finding that biopolymers have an important influence on floc formation.

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1. Introduction

The composition of natural organic matter (NOM) in surface waters, such as rivers and lakes, which are commonly used as the source waters for drinking water supply, is a complex matrix of substances (Ritson et al., 2014). The NOM can be classified into two types: (1) autochthonous NOM, including high molecular weight (MW) compounds originating from algae and other microorganisms, such as biopolymers and extracellular polymeric substances (EPS), and (2) allochthonous low molecular weight NOM of terrestrial origin dominated by humic substances (Pivokonsky et al., 2015). During treatment it is desirable to remove as much of the NOM as possible since its presence can lead to drinking water quality issues, such as disinfection by-product (DBP) formation and microbial activity in distribution networks (Fabris et al., 2008), and reductions in treatment performance and efficiency (e.g. membrane separation) (Lee et al., 2004).

Coagulation-flocculation is generally considered to be an effective and economically feasible option for achieving an adequate degree of NOM removal, compared with other alternatives such as oxidation and membrane filtration (Schafer et al., 2001; Bond et al., 2010; Bagastyo et al., 2011). The removal efficiency is greatly dependent on the nature of the NOM, including the properties of the constituents such as their electrostatic charge, chemical species and structures, molecular weight and hydrophobicity (Swietlik and Sikorska, 2004; Cao et al., 2011). The consensus of previous studies is that the hydrophobic and high MW fractions of NOM are more easily removed than the hydrophilic fractions and low MW compounds (Jarvis et al., 2008; Matilainen et al., 2010). However, despite substantial advances in recent years in the understanding

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of NOM complexity, the removal mechanisms of different NOM species during coagulation have not yet been fully, or adequately, explained (Imai et al., 2002; Her et al., 2008; Yu et al., 2016b).

Hydrophobic NOM mainly consists of humic substances, principally humic and fulvic acids, and is rich in aromatic carbon, phenolic structures and conjugated double bonds (Stenson, 2008). A lot of attention has been paid previously to the interaction between coagulants and humic substances, and the reaction mechanism also has been studied extensively based on hypothetical molecular structures of humic acid (HA) (Duan and Gregory, 2003). In the lower pH range of 4.0–5.0, HA can be neutralized by cationic hydrolysis species of the coagulant, while with increasing pH, the aluminium/ferric cations may still react with HA but are unable to neutralize the surface charge completely, and HA removal is caused by enmeshment within metal hydroxide flocs (Cheng and Chi, 2002). In the study of ferrate, the dual action of ferrate (oxidation and coagulation) appeared to enhance the hydrophilic and anionic nature of HA leading to an extended region of charge neutralization; ferrate achieved much larger HA-flocs compared with ferric chloride (coagulation only) at pH 7, but a substantially lower degree of HA removal (Graham et al., 2010). Also, larger alum-humic flocs have been reported by employing a two-stage dose strategy, rather than a single point dosing (Liu et al., 2011), and details of the connection mechanism of humic flocs have been revealed in another study (Yu et al., 2010).

With respect to large MW organic substances, the significance of biopolymers in drinking water treatment has attracted increasing attention in recent years, owing to the ambiguity of their role in coagulation and particular treatment processes, such as membrane filtration (Kimura et al., 2014; Tabatabai et al., 2014; Yu et al., 2016a). For example, the interaction between algal organic matter (AOM) and HA during the coagulation process has been investigated, and the results indicated a positive effect of AOM on coagulation in the presence of HA (Pivokonsky et al., 2012). However, other researchers have found that the presence of HA exerted a negative influence on the AOM coagulation efficiency (Jiang et al., 1993). It is evident, therefore, that the interaction between AOM/EPS and HA during the coagulation process still remains unclear and needs further exploration, especially in terms of physico-chemical mechanisms, such as floc formation.

In comparison, small MW organic substances are commonly recognized as the fraction of NOM that is poorly removed by conventional coagulation in drinking water treatment, and this fraction can correspond to 80% or more of the dissolved organic carbon (DOC) in surface water when the temperature is relatively low (<4 °C) (Yan et al., 2009; Yu et al., 2013). Consequently, the relatively poor removal efficiency of small MW organics may contribute to several undesirable consequences, including the formation of disinfection byproducts (DBPs) during chlorination, and severe fouling of membranes in nanofiltration (Hong and Elimelech, 1997; Liang and Singer, 2003; Bessiere et al., 2009). Although much attention has been paid to this topic in recent years, there is still a dearth of literature concerning the detailed mechanisms of coagulation (Szlachta and Adamski, 2009; Wang et al., 2012).

In this paper, we summarize the results of coagulation tests undertaken with samples of surface waters representative of lake and river waters, containing a wide range of NOM, in order to understand more clearly the influence of organic substances of different MW on coagulation performance. The tests involved separating the organic content of the surface water samples into different MW ranges using membrane filtration. Floc formation was studied using a continuous optical sensor, a photometric dispersion analyzer (PDA), and scanning electron microscopy (SEM) was undertaken to investigate the structure of flocs from a micro-scale perspective. In addition, molecular weight distribution, functional group and hydrophobicity analyses were conducted to provide further information concerning the contribution of different organic MW fractions to coagulation.

2. Methods and materials

2.1. Water samples and reagents

Two types of surface water samples (15 L) were collected every two days from nearby locations in London during the experimental period (September/October 2016), these being the Serpentine recreational lake in Hyde Park and the river Thames. The water from Hyde Park was representative of a moderately contaminated urban lake, while the river Thames is a major lowland river and source of drinking water in London and southeast England; typical values for the quality of both waters are summarized in Table S1. Water samples were collected and then settled overnight in the laboratory to remove large particles, particularly for the samples of the river Thames, and were maintained at room temperature (~25 ^{O}C) before use.

Aluminum sulfate hydrate ($Al_2(SO_4)_3 \cdot 16H_2O$; Fisons, >96%) was employed in this study as coagulant, and stock solutions were prepared using deionized (DI) water at a concentration of 0.1 M, and renewed every two weeks.

2.2. Separation of organics before coagulation

Filtrates of the surface waters with natural organic matter (NOM) of various MW ranges were prepared using a proprietary dead-end filtration equipment incorporating a stirred cell (Amicon 8400, Millipore), as referred to in previous studies (Li and Elimelech, 2004). A series of flat sheet membranes were purchased from Ande Membrane Separation Technology & Engineering (Beijing) Co., Ltd, China, comprising four representative sizes of membrane pores; in decreasing size these were 0.2 μm, corresponding to microfiltration (MF), and nominal molecular weight cutoff values of 100 kDa, 1 kDa and 0.8 kDa, corresponding to ultrafiltration (UF), nanofiltration (NF-3) and nanofiltration (NF-4), respectively. The operational pressures of MF and UF were maintained at 1 bar, and those for nanofiltration were set up to 4 bars. For consistency in the testing (e.g. filtrate quality), new membranes were employed after every 300 mL of use for the MF and UF filtration, and after every 100 mL for the nanofiltration (NF-3 and NF-4).

Filtrates (1200 mL) separated using the membranes of different pore sizes were divided into a volume employed in a consistent sequence for coagulation tests (800 mL) and the remainder (400 mL) subjected to a range of analytical techniques to determine the characteristics of the organic substances present, such as their molecular weight distribution and hydrophobicity, etc. These techniques are described in the following sections.

2.3. Jar test and PDA measurement

For the coagulation tests, a Flocculator 2000 (Kemira Kemi, Helsingborg, Sweden) jar test apparatus was programmed and used. On the basis of previous studies, the samples were mixed rapidly at a speed of 200 rpm (corresponding to an average velocity gradient of 184 s^{-1}) for 1 min, and followed by slow mixing at 50 rpm (23 s^{-1}) for 20 min. The effect of coagulant dose (0.05 mM–0.4 mM) on charge neutralization capability (zeta potential) was initially evaluated and the optimal dose was determined to be 0.1 mM. Thus, a predetermined amount of alum to give a resulting concentration of 0.1 mM was added to the test water (800 mL) at the beginning of the rapid mixing stage. During the

whole period of tests, the temperature of samples was maintained at 25 ± 1 °C, in order to avoid undesirable effects on the coagulation process arising from temperature fluctuations, as reported elsewhere (Gregory and Nelson, 1986).

The coagulation kinetics and floc formation were monitored using a photometric dispersion analyzer (PDA-3000, Rank Brothers, UK), which is a well-established laboratory instrument for observing rapidly changing particle suspensions via an optical technique that analyses the light transmitted through a flowing suspension (Gregory and Nelson, 1986). The basis of the method involves the measurement of two indicative parameters, namely the average transmitted light intensity (dc value) and the root mean square (rms) value of the fluctuating component. Thus, a sensitive particle aggregation measure is provided by the ratio of the two signals (rms/dc), designated as the Flocculation Index (FI). The value of FI has been found to have a close relationship to floc size and increases when floc formation is proceeding (Yu et al., 2015b). The FI value was recorded automatically by computer at an interval of 1 s.

2.4. HPSEC

The molecular weight distribution of NOM in samples of source waters, membrane filtrates and backwash waters, were determined by high performance size exclusion chromatography (HPSEC). As reported previously, SEC with UV detection at 254 nm (SEC-UV254) can be an effective indicator of biopolymers (Myat et al., 2014). HPSEC was performed using an HPLC system (Perkin Elmer, USA) carried out with the following components: a BIOSEP-SEC-S3000 column (Phenomenex, UK) (7.8 mm × 300 mm), together with a Security Guard column fixed with a GFC-3000 disc 4 mm (ID), a Series 200 pump, a UV/VIS detector operated at a wavelength of 254 nm and auto-sampler. A solution of 10 mM sodium acetate (Aldrich, USA) was applied as the mobile phase at the flow rate of 1 mL/min, and the injection volume per sample was 100 μL. Prior to measurement, the mobile phase was purged at a flow rate of 2 mL/min so that any contaminants in the column would be cleared. Polystyrene sulfonate (PSS) standards (American Polymer Standard Corp., U.S.) corresponding to molecular weights of 33,500, 14,900, 6530, and 1100 Da were employed to calibrate the relationship between compound MW and the peak retention time.

2.5. Other analytical methods

The hydrophilic and hydrophobic organic fractions of the source waters were separated using resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany) into three categories: strongly hydrophobic (adsorbed by DAX-8), weakly hydrophobic (or transphilic) (adsorbed by XAD-4) and hydrophilic (passing through both resins) (Wang et al., 2009). To ensure the resins were free of any organic matter prior to use, they were washed using methanol and deionized water until the total organic carbon (TOC) of the wash solution approached that of DI water. Samples of 200 mL (pH adjusted to 2) was firstly pumped into the DAX-8 adsorption column (at a rate of 5 mL/min) and then into the XAD-4 resin (at 15 mL/min). The quantities of the three different components were calculated by the difference from the TOC of samples before and after the DAX-8 and XAD-4 resins.

Samples of flocs were taken below the surface of the suspension at 5 min before the end of the slow stirring period of jar tests, using a hollow glass tube with an inner diameter of 5 mm. After air-drying, the flocs were platinum-coated by a sputter, and images of the flocs were observed under high resolution field emission gun scanning electron microscope (FEGSEM, LEO Gemini 1525, Germany).

Samples of the source waters and filtrates were freeze-dried and then the specific functional groups of organics were analyzed by Fourier Transform Infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA) with Quest ATR Accessory (SPECAC Ltd, UK).

Dissolved organic carbon of samples were determined after filtration (0.45 μm) using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan) (TOC for raw water was measured after rapid centrifugation (3000 rpm)), and the zeta potential of flocs was measured using a Zetasizer Nano ZS90 (Malvern, UK).

3. Results and discussion

3.1. Zeta potential of filtered waters

In order to study the role of different organic substances in the coagulation process, water samples from the river and lake sources were filtered sequentially by membranes of decreasing pore size and coagulation tests were undertaken with each filtrate. Fig. 1 shows the variation of zeta potential of the flocs with the coagulant dose, and the change in solution pH. No zeta potential values

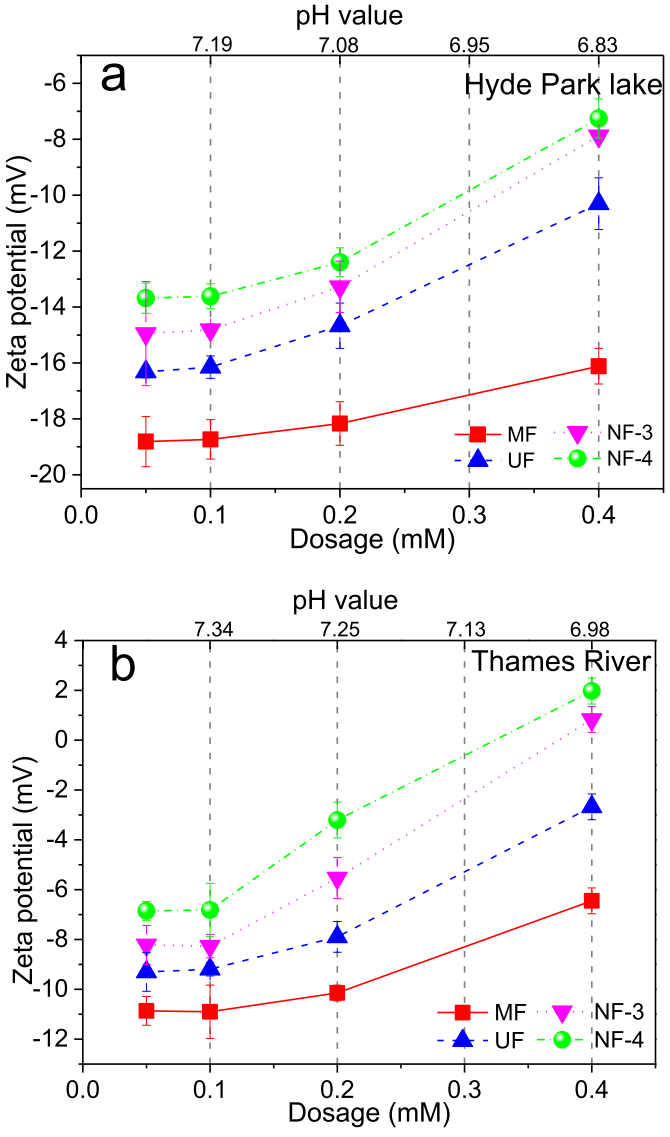


Fig. 1. Effect of alum dosage on zeta potential of flocs coagulated in filtrates from different membranes: (a) lake source (Hyde Park) and (b) river source (Thames River).

were available for uncoagulated filtrates (no alum dosage) owing to the instrument sensitivity (only water containing particles could be measured); however, the zeta potential values of uncoagulated source waters are given in Table S1.

As can be seen in Fig. 1a, the zeta potential of the dissolved and colloidal organic matter in the filtrates was systematically less negatively charged with decreasing pore size, as more organic components were rejected by the membrane with smaller pore size. With coagulation, the zeta potential of flocs in the filtered waters from the lake sample (Hyde Park) generally increased (less negative) with the increasing coagulant dosage, and the increase was relatively greater for the lower pore size filtrates. Thus, for the MF filtrate the zeta potential increased only slightly from −18.8 mV to −16.1 mV as the alum dose increased from 0.05 mM to 0.40 mM, while in the case of the UF filtrate (MW < 100 kDa) the zeta potential increased from −16.3 mV to −10.3 mV, for the same increase in alum dosage. This phenomenon can be explained by the nature and amount of the organic matter in the different filtrates and will be discussed in the Section 3.2. It is noted that at the lowest alum doses (0.05 and 0.1 mM) there was little change in zeta potential for each filtrate, but above 0.1 mM the zeta potential increased significantly. This 'increase' can be explained by the increasing ratio of (positively charged) alum floc to (negatively charged) organic substances with higher alum dosages, as a certain quantity of organic matter could be adsorbed at low alum dosage and there is residual NOM in the water (Yu et al., 2012).

Similar results were obtained for the river sample, as summarized in Fig. 1b, showing a consistent behavior for the two types of surface water, although the absolute value of zeta potentials was different. It was also evident that the zeta potential of coagulated flocs was insensitive to alum dose below 0.1 mM, but increased systematically with alum dosage above 0.1 mM.

In these tests, and as subsequently described in this study, the pH was in the narrow range of 6.8 and 7.4 for both source waters (Fig. 1). Under these conditions ([Al] $\geq$ 0.5 mM) it is assumed that following the dosing of alum the Al^{3+} hydrolysis proceeds rapidly to the formation of amorphous $Al(OH)_3$, and for an alum dose of 0.1 mM the amount of floc formed can be estimated to correspond to 26.5 mg/L (Hudson, 1965). This can be compared to the quantity of NOM present of 3–5 mg/L (as TOC), which suggests a mechanism of adsorption/enmeshment of the organics within a comparatively larger volume of $Al(OH)_3$ floc. Based on the results summarized in Fig. 1a and b, it can be deduced that an alum dose of 0.1 mM alum was able to provide an adsorption/neutralization saturation balance between the $Al(OH)_3$ floc and the negatively charged organics. Consequently, 0.1 mM was selected as the alum dosage for all subsequent coagulation tests with the two source waters in this study.

3.2. Floc formation and its relationship with TOC

Fig. 2a shows the process of floc growth with the filtered waters from Hyde Park at the alum dosage of 0.1 mM. It is clear that the FI value of flocs/aggregates formed in the MF filtrate was much larger than in the other filtrates. As reported by previous researchers, a greater FI value invariably indicates larger aggregates are present (Yu et al., 2016c). In contrast, the FI values of flocs formed in the filtrates from the UF, NF-3 and NF-4 membranes, were considerably smaller but similar to each other (Fig. 2a), although the peak FI of the NF-4 filtrate appeared to be greater than that of the NF-3 and UF filtrate.

In addition to the FI values (flocs sizes), the comparative TOC results for the filtrates are summarized in Fig. 2b. In general, the reduction of TOC for the Hyde Park waters was relatively minor (15–20%) but consistent with that predicted by previously established empirical coagulation models (Tseng and Edwards, 1999). With decreasing membrane pore size (Fig. 2b from left to right), the concentration of organics in the filtrates also decreased, and there was a significant reduction (up to 52%) after nanofiltration (NF-3 and NF-4 filtrates), as it was expected because of the lower MW cutoff. In terms of the FI values, there was a major difference between the MF and UF filtrates, but very little difference in the TOC values, both before and after coagulation (Fig. 2b). This is a novel finding that has not been reported previously. It is speculated that this can be attributed to the presence and role of biopolymers in the coagulation, which is discussed in detail in the next section.

Identical tests were conducted using samples of the river water (Thames River) and the corresponding results are displayed in Fig. 2c and d. Very similar results were obtained to the lake water (Fig. 2a), both in terms of the FI values and the relative coagulation performance of the 4 filtrates. Thus, the maximum FI value of the flocs formed in the MF filtrate was approximately 0.16, which was substantially greater than that for the other filtrates that were in the range of 0.09 and 0.11. Although the FI values for the UF, NF-3, and NF-4 filtrates were only slightly different, the differences between them were greater for the river samples than the lake, and demonstrated that the floc size of the NF-4 filtrate was consistently greater than those of the NF-3 and UF filtrates, even though the TOC of the NF-4 filtrate was the lowest. In general, the results for the UF, NF-3 and NF-4 filtrates indicated floc formation in the absence of the larger MW organics (biopolymers), which had been removed by the UF membrane. Additionally, the increase in floc sizes with decreasing size of the organics (i.e. NF-4 > NF-3 > UF) may be because of a more favourable interaction of the $Al(OH)_3$ with low MW substances, despite being present at a lower overall concentration, but possibly because of their lower negative charges (Fig. 1). This trend in coagulation behavior was discussed further in the following section (analysis of MW distributions).

3.3. Analysis of MW distributions

To provide further insight into the coagulation behavior of the different membrane filtrates, the MW distributions of the organic fraction in the source waters, filtrates, backwash waters and settled water after coagulation, were determined by HPSEC (Fig. 3 and Fig. S1).

Fig. 3a shows the MW distribution of the NOM in the water samples from Hyde Park lake and the corresponding membrane filtrates. The organic composition in the source water displayed a major peak at 2–5 kDa and other peaks of lower MW (~1.7 and 1 kDa), and in particular a much larger peak at 30–80 kDa; this large MW fraction is suggested to correspond to biopolymers like polysaccharides and proteins (Yu et al., 2015a). Fig. 3a shows that the MW distribution of the MF filtrate was almost identical to the source water, confirming that the size of the majority of organic substances was below the MF pore size of 0.2 μm. The results also demonstrated that the concentration and molecular size of organics in the filtrate waters decreased systematically with the decrease in the membrane pore size (i.e. MF → UF → NF-3 → NF-4). The MW distributions of organic matter in the backwash waters also confirmed that there were no biopolymers/high MW substances retained by the MF membrane, in clear contrast to results indicating the presence of these in the backwash of the three lower MW cutoff membranes (Fig. S1a). Coagulation was able to reduce the biopolymers/high MW substances in the MF filtrate by approximately 50% (peak value reduced from 0.36 to 0.19 by coagulation); while for the other organic components (MW < 10 kDa) there was no discernible change after coagulation. For the UF, NF-3 and NF-4 filtrates, although there was a small but measurable reduction in TOC (Fig. 2b), there appeared to be no

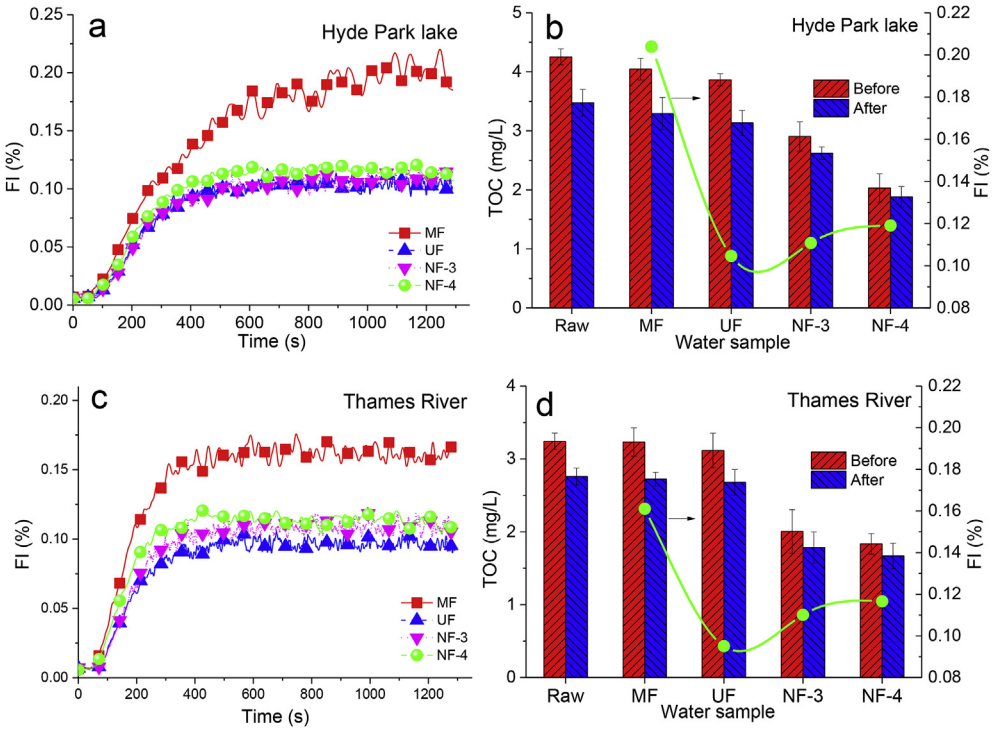


Fig. 2. Floc formation and TOC of filtrates before/after coagulation (0.1 mM alum): (a) temporal variation of FI value for filtrates from Hyde Park lake, (b) TOC and peak floc sizes (maximum FI value) for filtrates from Hyde Park lake, (c) temporal variation of FI value for filtrates from Thames River, (d) TOC and peak floc sizes (maximum FI value) for filtrates from Thames River.

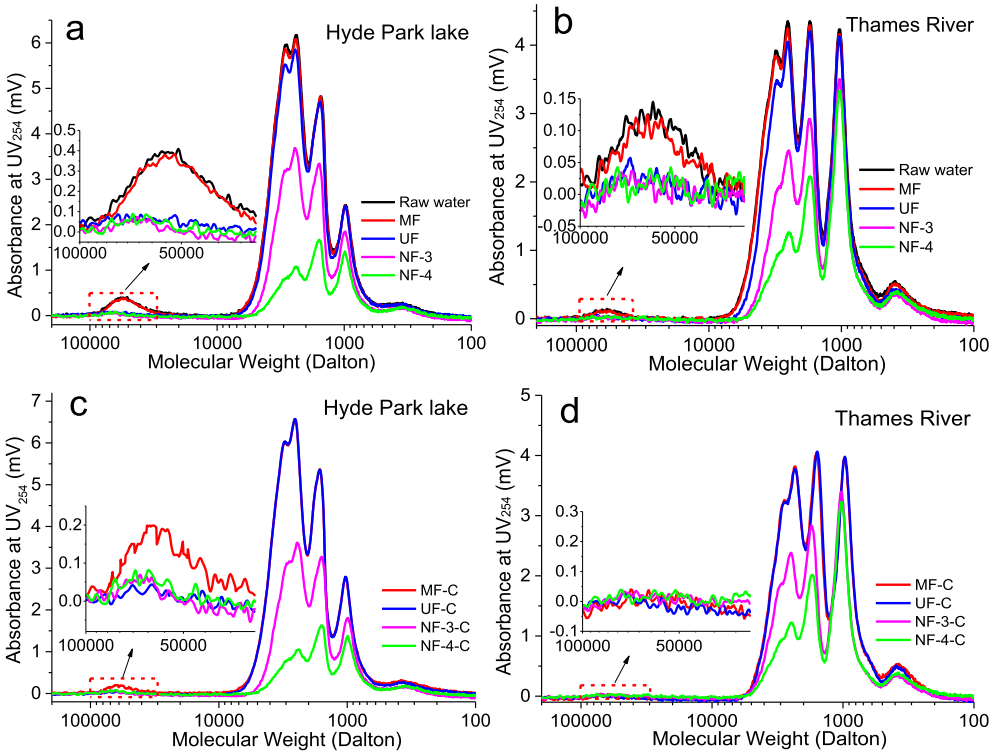


Fig. 3. Influence of coagulation on the MW distributions of organic substances for the two surface water samples: uncoagulated lake water and filtrates (a), uncoagulated river water and filtrates (b), settled lake water after coagulation (c), and settled river water after coagulation (d).

significant change in the MW distributions after coagulation (Fig. 3c), indicating that there were very minor reductions of organic substances across the whole MW range. This result is consistent with previous findings, which suggested that DOC

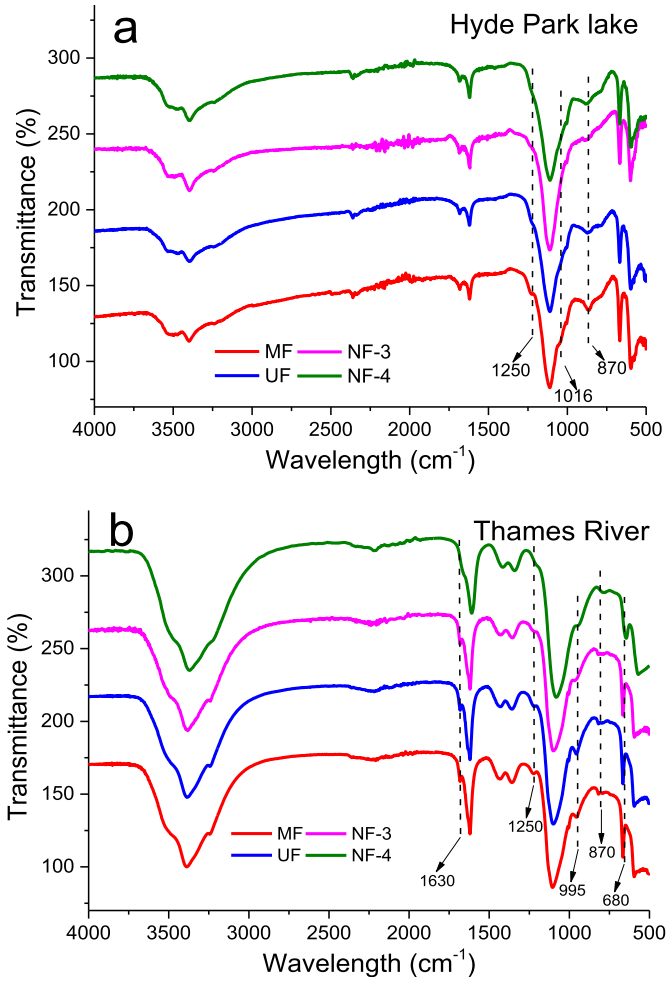


Fig. 4. FTIR spectra of organic matter in the different filtrates: (a) Hyde Park lake; (b) Thames River (no results are shown for the raw waters owing to the presence of particulate matter).

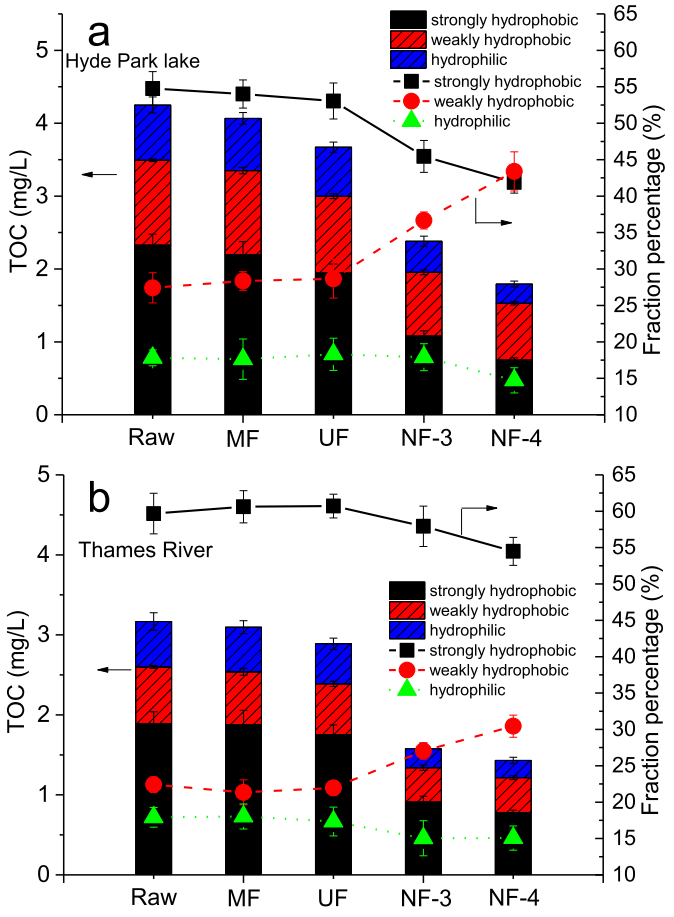


Fig. 5. Hydrophilic and hydrophobic components of NOM in the source waters and filtrates: (a) Hyde Park lake; (b) Thames River.

removal by coagulation was size-dependent with a bias toward larger MW organic matter and that low MW organic matter could not be precipitated by coagulation (Sinsabaugh et al., 1986).

The corresponding results for the river water (Thames River) are presented in Fig. 3b and d, and Fig. S1b. As shown in Fig. 3b, biopolymers were only observed in the raw water and the MF filtrate presented an absorbance peak at 40–90 kDa; in this case the UV absorbance peak was less than half that of the lake water. It is evident that the concentration of low MW organic matter (≤1 kDa) in the river water was significantly greater than that in the lake water, as indicated by the absorbance peaks shown in Fig. 3a and b. However, this difference between the two natural waters may be site-specific and vary in different cases; for example, a recent study observed a larger proportion of low MW constituents (<1 kDa) in Lake Michigan, compared to that in the Fox River (Xu and Guo, 2017). After coagulation, the biopolymers/high MW substances (>30 kDa) were substantially removed (Fig. 3d). Since, again, there was a substantial difference in the FI values of the MF filtrate and the other filtrates (as shown in Fig. 2c). It can be deduced that biopolymers were a major contributor to the formation of larger floc size in the MF filtrate, with the biopolymers acting as flocculant aids, and that the flocs were barely influenced by other organic components in the source waters. In accordance with this, the FI values were not substantially different among the UF, NF-3 and NF-4 filtrates (Fig. 2d) when the biopolymers were absent. Furthermore, the obvious differences in the concentration of medium MW organics (1 kDa −10 kDa) did not appear to exert a significant influence on floc size (Fig. 3d). Given that the MW distributions of the UF, NF-3 and NF-4 filtrates did not change too much after coagulation, it can be concluded that the minor decrease in TOC observed by coagulation was not influenced by any particular MW fraction.

3.4. FTIR and hydrophilicity/hydrophobicity of organic matter

In order to provide further information about the nature of the organic substances in the filtrate waters, and thus a better understanding of the mechanism of floc formation, determination of FTIR spectra and hydrophilicity/hydrophobicity were undertaken and the results are summarized in Figs. 4 and 5. The FTIR results indicate clearly that the peaks at wavelengths of 870 cm^{-1}, 1016 cm^{-1} and 1250 cm^{-1} decreased with the pore size of the membrane, as shown in Fig. 4a and b. As reported previously, the peak at 870 cm^{-1} (and at 680 cm^{-1} in the river water) corresponds to CH_2 chemical bonds (Fukushima et al., 2001; Park et al., 2012), and it is suggested that a reduction in CH_2 bonds can help promote floc formation; this is consistent with the results discussed earlier showing that the FI values of flocs formed in the UF, NF-3 and NF-4 filtrates increased with decreasing pore size of the membrane (Fig. 2b and d) (the results for the MF filtrate are different from this trend owing to the major impact of biopolymers present in the filtrate as described in Section 3.2). In addition, it was also evident that peaks at 995, 1250, and 1630 cm^{-1}, corresponding to alcohol or

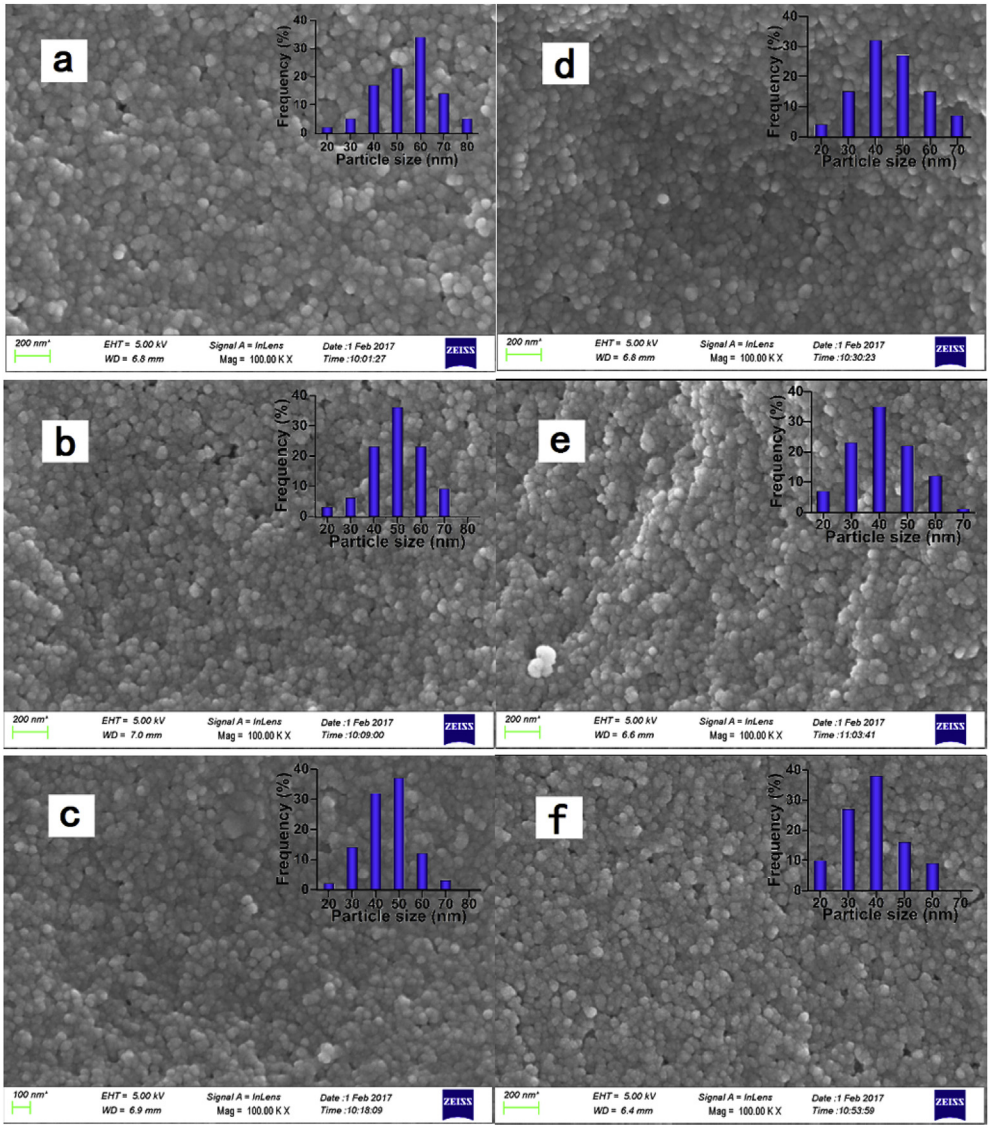


Fig. 6. SEM images of floc structure formed in Hyde Park lake: (a) MF, (b) UF and (c) NF-3 filtrates; Thames River: (d) MF, (e) UF and (f) NF-3 filtrates.

carboxylic acid groups, decreased with the pore size of the membranes (Duong et al., 2014). This indicated that alcohol or carboxylic acid groups, like the presence of CH_2 bonds, exerted a negative influence on the floc formation.

As reported previously, hydrophilic and hydrophobic components of NOM exert different influences on coagulation performance (Gray et al., 2007). The relative constituents in the raw waters and four kinds of filtrates were separated and the results are displayed in Fig. 5. With regard to the organic composition in the lake water samples (Hyde Park) shown in Fig. 5a, there was little change in the proportions of strongly and weakly hydrophobic, and hydrophilic organic matters for the raw water, MF and UF filtrates. However, a significant reduction was observed in the amount and proportion of strongly hydrophobic organic matter in the NF filtrates, which could be related to the hydrophilic nature of the membrane used here (PES membrane) (Mustafa et al., 2016); in contrast, the weakly hydrophobic (or transphilic) and hydrophilic fractions remained approximately unchanged in the NF filtrates. Similar results were found with the river water and filtrates (Fig. 5b, Thames river). As discussed previously, the size of flocs was progressively larger with decreasing pore size of the membranes (Fig. 2), which may suggest an association with the relative proportion of strongly hydrophobic substances, as this also decreased with decreasing pore size, for both source waters. With regard to biopolymers, it was difficult to identify their precise characteristics by TOC since they represented only a small proportion of the total TOC content in the raw and MF filtrate waters.

3.5. SEM images of flocs

Visual information concerning the nature of the flocs formed by the various source waters and filtrates was provided by scanning electron microscopy (SEM) (Fig. 6). For the lake water, Fig. 6a, b and 6c show the floc structure formed by coagulation of MF, UF and NF-3 filtrates, respectively. The images demonstrated that a floc was formed from nano-scale primary particles, and the size distribution of these particles was analyzed using 'Image J' (version 1.48) open source software. The results indicated that the common sizes of flocs were within the range of 20–80 nm (Fig. 6a, b and 6c), based on at least 100 particles counted. Compared to the UF and NF flocs (Fig. 6b and c), the MF floc particles (Fig. 6a) appeared to be larger, especially the percentage of particle size between 60 and 80 nm,

and the mean sizes for the three filtrates (MF, UF, NF-3) were 52, 48.3 and 43.4 nm; also, no particles > 80 nm were found in the UF and NF-3 filtrates (Fig. 6b and c). These results are consistent with the PDA (Fig. 2a) observations indicating the presence of larger flocs in the MF filtrate.

Analysis of the floc particle size distribution for the river water (Thames River, Fig. 6d, e and 6f), showed similar results. For this water the average size of particles indicated by the SEM images were 43.6, 40.3 and 38.2 nm for the MF, UF and NF-3 filtrates, respectively. Also, the images indicated that larger particles, those greater than 70 nm, were only visible in the MF filtrate (Fig. 6d). Overall, the PDA and SEM results support the role of biopolymers in the formation of larger flocs, in which they can act as a bridge to connect sub-nanoparticles and/or nanoparticles (micro-flocs) (Kalia and Averous, 2011).

4. Conclusion

In this study, a new experimental methodology has been used to gain a greater insight into role of natural organic matter in the coagulation of surface water with alum. Progressive filtration of samples of two representative surface waters by membranes with decreasing pore sizes has revealed a close, beneficial association between the presence of biopolymers and floc size. Although the biopolymers did not represent a significant proportion of the organic content of the surface waters (~5%), their presence led to an approximate doubling in the rate and magnitude of floc formation. In contrast, the presence of lower MW (<10 kDa) organic substances had limited influence on floc formation, but the results indicated that floc formation increased with decreasing MW fraction, possibly because of charge effects and a reduction in the proportion of strongly hydrophobic substances. Future work will examine in more detail the main finding of this study that biopolymers have an important influence of floc formation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2017.09.022.

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