Effect of pH and Floc Property on Disinfection By-products Precursors Removal by Coagulation in Treating Low Organic Matter Surface Water

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ABSTRACT
Two pre-hydrolyzed coagulants, polyaluminum chloride (PAC) and polyferric chloride (PFC) were used to treat the low organic matter (OM) surface water. The coagulation performance, disinfection by-products (DBPs) precursors removal and floc properties at pH 4, 6 and 8 were investigated. The results showed that the best DOC, UV$_{254}$ and DBPs precursors removal was achieved at pH 6, while the DOC and UV$_{254}$ trend were different from the chlorine demand results for the low OM surface water. At pH 8, the DBPs precursors were not effectively removed as DOC and UV$_{254}$ because the conditions were not favorable for precipitate formation. The differences of the PFC-flocs size were not significant in the pH range while the PAC-flocs were larger at pH 6. The flocs strength decreased with the increasing pH. The compact flocs tend to be generated at alkaline solution in the study. The preliminary study of the relationship between the floc properties and DBPs precursors removal showed that the small flocs were not favorable for DBPs precursors removal. Similarly, the compact flocs may not provide high removal efficiency on the DBPs precursors.

Keywords: Organic matter; disinfection by-products; floc property; coagulation

1. INTRODUCTION

Chlorination of water can lead to the formation of disinfection by-products (DBPs) by the reaction of free chlorine and DBPs precursors. The most known DBPs are trihalomethanes (THM) and haloacetic acids (HAA). Many of the DBPs are suspected carcinogens (Zhang et al., 2012). Due to the concerns over the health effects of the DBPs, several countries have established limits for DBPs in drinking water (Golfinopoulos and Arhonditsis, 2002; Richardson et al., 2007). Thus, in the recent years, drinking water treatment has significantly focused on reducing DBPs formation (Uyak et al., 2005).

In order to control DBPs formation in drinking water, DBPs precursors should be removed. The main DBPs precursors in natural waters were generally considered to be organic matter (OM) (Chen et al., 2008) which is often divided into dissolved (DOM) and particulate organic matter (POM), based on filtration through a 0.45 µm filter. Generally, DOM is more abundant than POM, accounting for approximately 90% of the total organic carbon in most waters. Singh et al. (2010) previously reported that dissolved organic matter (DOM) acts as a major precursor of undesirable DBPs.
Enhanced coagulation has been proposed as the best available technology for controlling DBPs precursors in conventional water treatment plants (Yan et al., 2008a). And it is known that the characteristics of the source water, including the DOC and SUVA (Chow, 2006) are the factors that affect the DOM removal and DBPs formation (Ates et al., 2007). Coagulation is usually used to treat waters with large concentration of OM (Moncayo-Lasso et al., 2008) and the UV absorbance is generally shown to correlate well with DBPs formation in waters with relatively high DOC concentration and high SUVA values (Ates et al., 2007). However, there is limited information in the literature on the DBPs precursors removal for waters with low concentration of OM. These waters may be characterized by having hydrophilic OM which is difficult to be removed and showed appreciable DBPs yields (Kitis et al., 2002). Therefore, more attention should be paid on DBPs precursors removal from the waters with low concentration of OM.

As the OM removal by coagulation has been researched, more and more interests have been focused on the floc properties, such as the flocs size, strength and structure. The size and strength of flocs has a significant effect on the efficiency of solid/liquid separation process (Chau, 2004; Yu et al., 2009), such as sedimentation, flotation and filtration. In addition, fractal dimension characteristic of flocs is the other particularly important operational parameter that deserves special attention. Recently, many studies have investigated the floc properties and the coagulation efficiency (Jarvis et al., 2006; Lin et al., 2008; Wei et al., 2009), but there have been few documents published on the relationship between the flocs properties and the removal of DBPs precursors.

Moreover, the removal of DBPs precursors is related to the solution pH because pH affects not only the surface charge of OM molecule but also the hydrolysis of the coagulant, which influences the interactions of coagulant – OM (Tseng et al., 2000). The variation of solution pH yields different floc characteristics. The estimation of pH effect on DBPs precursors removal and floc properties is valuable and necessary.

Pre-hydrolyzed coagulants, polyaluminum chloride (PAC) and polyferric chloride (PFC) which minimized the extent of pH depression (Yan et al., 2008b) were chosen to treat the low OM surface water. Overall, the goal of this paper was to compare the effect of solution pH on natural organic matter (NOM) and DBPs precursors removal from the low OM surface water through a chlorine model. The size, strength and fractal nature of flocs at different pH values were investigated by use of a laser diffraction particle sizing device. The effect of floc properties on DBPs precursors removal was preliminarily studied.

2. MATERIALS AND METHODS

2.1. Preparation of coagulant

PFC was prepared with FeCl$_3$·6H$_2$O (A.R.) and Na$_2$CO$_3$ (A.R.). Firstly, FeCl$_3$·6H$_2$O (A.R.) (24 g) was dissolved in distilled water (70 mL), then slowly mixed with Na$_2$CO$_3$ powder (5 g) at room temperature to obtain the desired [OH]/[Fe] (ratio denoted as B). The solution was stirred until foam disappeared and became transparent. Then, Na$_2$HPO$_4$ (A.R.) (1 g) was added to the solution as a stabilizer. According to Fe(III) hydrolysis/polymerization, Fe(III) species can be differentiated by Ferron assay into three categories: Fe$_a$, monomeric species such as Fe$^{3+}$, Fe(OH)$^{2+}$, Fe(OH)$_2^{2+}$, Fe(OH)$_3$ (molecule) and Fe(OH)$_4$$^-$. A dimer and trimer (Fe$_2$(OH)$_2^{4+}$ and Fe$_3$(OH)$_4^{5+}$), some small polymers, and instantaneous reacted species are usually classified into this category; Fe$_b$, polymeric species with medium and high molecular mass; Fe$_c$, larger polymer or colloidal species, no reaction species. The
characteristics of PFC are as follows: $\text{Fe}_a=17.4\%$, $\text{Fe}_b=29.8\%$, $\text{Fe}_c=52.8\%$, $\text{pH}=0.7$, $B=0.5$. The dosages of PFC were calculated as mg/L of Fe during coagulation experiments.

PAC with a basicity value ($B$, OH/Al molar ratio) of 2.0 was synthesized by adding pre-determined amount of $\text{Na}_2\text{CO}_3$ (13 g) slowly into $\text{AlCl}_3$ (29 g) solution under intense agitation. The temperature was kept at 80.0 $\pm$ 0.5°C by using recycling water bath. The properties of PAC were indicated as follows: $\text{Al}_a=24.8\%$, $\text{Al}_b=32.1\%$, $\text{Al}_c=43.1\%$, $\text{pH}=2.85$. The dosages of PAC were calculated as mg/L of Al during the coagulation experiments.

2.2 Raw water

All experiments were carried out on the raw water collected from Queshan reservoir, an important drinking water source in Jinan, China. The raw water characteristics are shown in Table 1, along with the methods of measurement. The raw water had DOC values < 3 mg/L which can be regarded as low OM water.

2.3 Coagulation tests

Coagulation experiments were performed on a program-controlled jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). After dosing, the water samples (1.0 L) were mixed rapidly at 200 rpm for 1 min, followed by 15 min of slow stirring at 40 rpm. The flocs were allowed to settle for 25 min, and the supernatant sample was withdrawn by a syringe from about 2 cm below the water surface for analysis. The effect of pH on the coagulation efficiency was investigated by using 1 mol/L NaOH and 1 mol/L HCl for pH adjustment under the same procedure stated above. The pH correction was done before coagulation tests were performed.

2.4 Chlorine decay experiments

Chlorine decay experiments were conducted in dark brown bottles to prevent light penetration or algal growth. Thereby the decay of chlorine was due to reducing compounds present in water samples. Two treated samples (500 mL) were transferred into the bottles and dosed with 2.0 and 2.5 mg/L chlorine (as Cl$_2$) to keep the free residual chlorine no less than 0.3 mg/L after 30 min contact. Free and total chlorine concentrations were measured continuously for 7 days with a Free & Total chlorine measuring meter HI93711 (Hanna, Italy).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
<th>Methods of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved organic carbon (DOC) (mg/L)</td>
<td>1.495–2.571</td>
<td>Prefiltered sample measured on a TOC analyzer (Shimadzu, Japan)</td>
</tr>
<tr>
<td>Ultraviolet light absorption at 254 nm (UV$_{254}$) (cm$^{-1}$)</td>
<td>0.049–0.057</td>
<td>Prefiltered sample measured on a UV-754 UV/VIS spectrophotometer (Shanghai Jinhua Group Co., Ltd., China)</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.03–7.56</td>
<td>Turbidimeter 2100P (Hach, America)</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>-13.2–-11.8</td>
<td>Zetasizer 3000HSa (Malvern Instruments, UK)</td>
</tr>
<tr>
<td>Specific UV absorbance (SUVA) (L/(mg·m))</td>
<td>2.2–3.4</td>
<td>SUVA=$\frac{\text{UV}_{254}}{\text{DOC}} \times 100$</td>
</tr>
</tbody>
</table>

Table 1 Raw water characteristics and methods of measurement
2.5 Chlorine decay model

The chlorine decay data were analyzed by using AQUASIM software. The details of chlorine decay model have been described elsewhere (Jegatheesan et al., 2009). The general chlorine decay model includes the following reactions between chlorine and other constituents in the water (Bell-Ajy et al., 2000):

\[ Cl_2 + \text{Fast reducing agents (organic compounds)} \rightarrow \text{inert products} \quad (1) \]

\[ Cl_2 + \text{Fast reducing nitrogenous compounds} \rightarrow \text{combined chlorine} \quad (2) \]

\[ Cl_2 + \text{Slow reacting agents (organic compounds)} \rightarrow \text{inert products} \quad (3) \]

\[ Cl_2 + \text{Slow reacting nitrogenous compounds} \rightarrow \text{combined chlorine (CC)} \quad (4) \]

\[ \text{Combined chlorine} \rightarrow \text{inert products} \quad (5) \]

In this study, the experimental chlorine decay data were used to estimate values of chlorine demand for FRA and SRA, respectively. DBPs formation with OM was a function of chlorine demand (Gang et al., 2003). Thus the amount of total chlorine demand which is the sum of chlorine demand for FRA and SRA can be used as an indication of the DBPs precursors concentration in the water.

2.6 Floc size distribution

The floc size distribution was measured by a laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK). At the end of the slow-mixing process, the effluent was monitored by drawing water through the optical unit of the Mastersizer and back into the jar by a peristaltic pump at a flow rate of 2.0 L/h. Size measurements were taken and logged onto a PC.

2.7 Floc strength factor

Floc strength experiments were performed using the laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK). Experiments were carried out on a cylindrical jar tester with a 50 × 40 mm flat paddle impeller. Briefly, all the jar tests were carried out under the following conditions: a rapid mix at 200 rpm for 1 min, followed by a slow stir phase at 40 rpm for 15 min, then a 5 min breakage phase at 200 rpm. Dynamic floc size was measured every 0.5 minute during growth and breakage of the flocs. Floc strength factor, which has previously been used to compare the relative breakage of flocs in different flocculated systems (Jarvis et al., 2005a, 2006) was calculated as follows:

\[ \text{Strength factor} = \frac{d_2}{d_1} \times 100 \quad (6) \]

Where \( d_1 (\mu m) \) is the average floc size of the steady phase before breakage, \( d_2 (\mu m) \) is the floc size after the floc breakage period. The strength factor value indicates the ability of flocs to withstand shear. A larger value of strength factor suggests that flocs are stronger than the flocs with a lower factor.

2.8 Floc fractal dimension

Light scattering method was used here for the determination of aggregate mass fractal dimension. Details in the theory of the mass fractal dimension have been reported in a few literatures (Bushell et al., 2002; Guan et al., 1998). The light scattering technique involves measurement of light intensity \( I \) as a function of the scatter vector \( Q \). The vector is defined as the difference between the incident and scattered wave vectors of the radiation beam in the medium (Guan et al., 1998), which is given as follows:
\[ Q = \frac{4\pi n \sin(\frac{\theta}{2})}{\lambda} \] (7)

Where \( n \), \( \theta \), and \( \lambda \) are the refractive index of the medium, the scattered angle, and the wavelength of radiation in vacuum, respectively.

For independently scattering aggregates, the relationship among \( I \) and \( Q \) can be represented by:

\[ I \propto Q^{-D_f} \] (8)

\( D_f \) is the fractal dimension and can be determined by the slope of a plot of \( I \) as a function of \( Q \) on a log-log scale. High \( D_f \) means the primary particles in an aggregate are arranged compactly, while low \( D_f \) results from highly branched and loosely bound structures.

3. RESULTS

3.1 Coagulant dosage optimization

Through jar testing procedures, the optimum dosages for PFC and PAC under the raw water condition were 14 mg/L (Fe) and 12 mg/L (Al), respectively. The optimum UV\(_{254}\) removal efficiencies were 36% and 39%, respectively. And the corresponding values for DOC removal were 31% and 38% for PFC and PAC, respectively.

3.2 OM removal efficiency by coagulation

The effect of pH value on DOC and UV\(_{254}\) removal by PFC and PAC was shown in Figure 1. The UV\(_{254}\) removal efficiency increased with the increase of pH value. After reaching the optimal pH, the UV\(_{254}\) removal efficiency was decreased. Compared with PAC, PFC showed a steeper increase and decrease in UV\(_{254}\) removal. In the pH range of 5-6, PFC was favorable to remove UV\(_{254}\), while PAC was favorable in the pH range of 7-9. In the term of DOC removal, PFC showed high removal efficiency in pH 4-6. As the pH increased from 6 to 9, the removal efficiency began to decrease rapidly. The DOC removal by PAC was first increased with the pH increased to 6 and then slightly decreased as the pH further increased. In the acid solution, DOC was removed more efficiently by PFC than by PAC. At higher pH range, the result was reverse. The highest DOC and UV\(_{254}\) removal efficiency was obtained around pH 6 which was in accordance with previous studies that the alum and ferric salt coagulants provide optimal organic matter removal at low pH values (Yan et al., 2008b).

3.3 DBPs precursors removal by coagulation

The chlorine decay data as a function of pH value were modeled by AQUASIM. Values of chlorine demand for fast and slow organic compounds which could react with chlorine were provided in Table 2. As shown in Table 2, the water quality, in term of the total chlorine demand, improved significantly after coagulation. For PFC and PAC coagulation, the highest removal efficiency in total chlorine demand (\( FRA \) and \( SRA \)) was achieved at pH 6 which indicated the lowest DBPs precursors concentration in the water.

3.4 Zeta potential of flocs

The variations of zeta potential of PFC and PAC at different pH conditions were shown in Figure 2. In terms of PFC, the zeta potential of the flocs decreased with the increasing pH across the pH study range. For PAC, the zeta potential of the flocs first increased and then slightly decreased when the pH was greater than 7. The zeta potential of PFC-flocs was higher than that of the PAC-flocs at the pH range 4-6 which indicated that PFC gave stronger charge neutralization. This might be responsible for the higher DOC removal efficiency of PFC at the pH 4-6. It is also
worth noting that the zeta potential of the PAC-flocs was still high and almost constant for the pH range of 7-9. So the DOC and $\text{UV}_{254}$ removal efficiency by PAC did not decrease rapidly and became higher than that of PFC in the alkaline range.

![Figure 1](image)

**Figure 1** Coagulation performance of PFC and PAC as a function of pH

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Raw water</th>
<th>PFC</th>
<th>PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.3</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>$FRA$ (mg/L as $\text{Cl}_2$)</td>
<td>0.0514</td>
<td>0.0027</td>
<td>0.0100</td>
</tr>
<tr>
<td>$SRA$ (mg/L as $\text{Cl}_2$)</td>
<td>1.563</td>
<td>0.675</td>
<td>0.337</td>
</tr>
<tr>
<td>Total chlorine demand ($FRA$ and $SRA$)</td>
<td>1.614</td>
<td>0.678</td>
<td>0.347</td>
</tr>
</tbody>
</table>
Figure 2  Zeta potentials of coagulated water as a function of pH

Figure 3  Floc size distributions as a function of pH at the end of the slow stirring phase

Lower pH can reduce the charge density of OM, making them more hydrophobic and easy to be removed. This may be one reason for the high OM removal at around pH 6. Additionally, the removal of OM is related to the solution pH because pH not only determines the surface charge of OM molecule but also significantly affects the hydrolysis of the coagulant. István (1993) proposed that the hydrolysis of metal ions occurred immediately after contacting with water. For PAC coagulation process, according to the flocs’ zeta potential, the positive charge of aluminum increased when pH increased from 4 to 6. In other words, with increasing pH from 4 to 6, contribution of the charge neutralization to OM removal increased. After pH 7, the zeta potential slightly decreased and other mechanisms performed. However, a bit decreasing contributions of charge neutralization led to a slight decrease in OM removal. The mechanism of charge neutralization predominated for OM removal
by PAC, which was in accordance with Sontheimer (1978) and Qin et al. (2006). Similarly, for PFC at the acid range, the removal of OM was due to charge neutralization which formed the complex of PFC-OM. In the high pH range, the negatively charged flocs of Fe(OH)$_3$ or the Fe(OH)$_4^{2-}$ ions formed. In short, the increase of pH favored the hydrolysis of PFC, and decreased the formation of positively charged ions. Thus the ability to neutralize the negative charge on OM became small, and adsorption and enmeshment was assumed to play an important role in the coagulation of OM.

3.5 Floc property

3.5.1 Floc size

The floc size distribution formed by PFC and PAC as a function of pH was shown in Figure 3 for the flocs at the end of the slow stirring phase. In terms of PFC-flocs, the peak height of the size distribution in the steady-state phase was highest at pH 4, and lowest at pH 8. A large fraction at floc size of 700-1200 µm was seen for the pH studied. As shown in Figure 3, the major size peak of the PAC-flocs at pH 4 was in a low value and the $d_{50}$ was 197 µm. When the pH was 6, the major size peak shifted to a higher size value, indicating the dominance of the large particles within the size distribution. However, when the pH increased to 8, the floc size presented a decrease.

After the slow stir phase, PFC-OM flocs had reached a $d_{50}$ floc size of 880 µm, 870 µm and 730 µm at pH 4, 6 and 8 respectively. These were approximately double or triple the size of the PAC-OM flocs. This agrees with the findings that the Fe-OM flocs were larger than Al-OM flocs (Jarvis et al., 2005b).

3.5.2 Floc strength

In order to characterize the floc breakage progresses, strength factor was calculated as in Equation (6). The results were summarized in Table 3. It is evident that different coagulation conditions yielded different strength factors. However, the strength factor decreased with the increasing pH in all cases, suggesting that the break-up behavior of the flocs on exposure to an increasing shear was very low at acidic pH conditions.

The influence of pH on flocs breakage can be interpreted from the point of different coagulation mechanisms at different pH conditions. When pH was 4, charge neutralization dominated the removal of OM flocs. As pH increased, metal ions were hydrolyzed and possibly less positive charge. Consequently, charge neutralization was weakened and a combination of charge neutralization and sweep flocculation might occur. It has been reported that the flocs formed by entrapment and adsorption of NOM onto metal precipitates are considered weak and fragile (Aguilar et al., 2003). Therefore, the strength factors significantly decreased as pH increased. For PAC-flocs, the differences between the zeta potential at pH 6 and 8 were small, which indicated the differences in the charge neutralization at the two pH conditions were not significant. Therefore, the strength factor of PAC-floc was the same at pH 6 and 8.

In addition, the strength factors of PAC flocs were larger than that of PFC flocs at the same pH value. This may due to the different floc size formed in the coagulation process. Larger flocs became more affected by the microscale eddies that are attributed to floc breakage. Smaller flocs are more likely to become entrained within the eddies rather than being broken by them (Jarvis et al., 2005b). PFC-flocs were larger than the PAC-flocs which were more affected by the microscale eddies that were attributed to floc breakage. PAC-flocs were smaller which generally were not broken to the same extent as larger flocs.
Table 3  Strength factors of flocs ($d_{50}$) after 5 min of breakage as a function of pH

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFC</td>
<td>40</td>
<td>31</td>
<td>29</td>
</tr>
<tr>
<td>PAC</td>
<td>48</td>
<td>39</td>
<td>39</td>
</tr>
</tbody>
</table>

Figure 4  Relationship between the scattered light intensity ($I$) and the wavenumber ($Q$) on a log-log scale in the steady-state phase as a function of pH

3.5.3 Floc Fractal Dimension

The floc fractal dimension is recognized as the crucial physical property that has impact on DBPs precursors removal (Chau, 2004). The derivation of floc fractal dimension at different pH values from the scattered light intensity ($I$) as a function of wavenumber ($Q$) was shown in Figure 4 for flocs after 15 min slow stir when the flocs had reached their maximum steady state size. There was good linear correlation for all of the data and all of the fractal dimensions were between 2.2 and 2.6. The fractal dimension increased with the increasing pH. It was apparent that the fractal dimension was much lower at pH 4 when compared to that at pH 6 and 8, implying the looser structures of flocs formed at pH 4. Besides, the fractal dimensions were also dependent on the characteristic of coagulant. It can be deduced that the PFC flocs were denser than PAC flocs at pH 4 and 6, reflected by the higher values of fractal dimensions. However, the PAC flocs were denser at pH 8 compared to the PFC flocs formed at pH 8.

At pH 4, PFC-flocs gave more compact structures compared with PAC-flocs. A possible explanation was that PFC could perform stronger charge neutralization during coagulation, which led to a high degree of compaction. Likewise, at pH 8, the stronger charge neutralization of PAC led to a high degree of compaction (Figure 2). The increased fractal dimension of the flocs as a function of pH indicated that at high pH value polymer bridging gives rise to the most compact structures. This agrees with the findings for the NOM flocs, which show a general increase of fractal dimension as polymer bridging is increased (Jarvis et al., 2005b).
4. DISCUSSION

Some investigations indicated that THM and HAA had different precursors (Hua and Reckhow, 2007; Liang and Singer, 2003). Aliphatic structures played a more important role in THM formation than HAA formation, while HAAs had more aromatic structures as their precursors than THMs. So the aliphatic compounds and aromatic compounds are all considered as the DBPs formation precursors. Studies showed that aromatic matter could strongly react with chlorine and be responsible for the initial chlorine demand (Zhang et al., 2009). Kitis et al. (2002) showed that aromatic matter was more directly related to reactivity than other compounds. Thereby, most FRA was probably aromatic compounds and hydrophobic. Chlorine reactions with aliphatic organic compound were generally slow or negligible (Deborde and Gunten, 2008). Hence, most SRA were considered as aliphatic organic compounds. It is believed that by reducing the amount of total FRA and SRA chlorine required, DBPs formation potential will be reduced. So the optimum pH for DBPs precursors removal was 6. At pH 6, FRA and SRA removal efficiency was 80% and 78%, respectively for PFC, and 88% and 69%, respectively for PAC. FRA was more effective removed than SRA. These results support the observation that coagulation generally removes more HAA precursors than THM precursors because it preferentially removes hydrophobic organic matter over hydrophilic organic matter (Liang and Singer, 2003).

It was reported that negative charges on DBPs precursors were partly neutralized by hydrogen ions in acidic conditions (Cheng, 2002; Shi et al., 2007). Because of electrostatic effects of DBPs precursors decreasing, DBPs precursors precipitated through self-aggregation and charge neutralization with aluminum or iron species in the acid conditions (Cheng, 2002). So the total chlorine demands at pH 4 and 6 were lower than that at pH 8. The alkaline conditions of coagulation were not favorable for precipitate formation. So the DBPs precursors were not effective removed at pH 8. This was in accordance with the find that high pH favored the formation of THMs and HAAs (Hua and Reckhow, 2007).

By referring to Figure 1, it can be found that the effluent had the lowest DOC value at pH 6 compared with pH 4 and pH 8. Meanwhile, SRA and FRA were reduced to the lowest extent at pH 6 which indicated more DBPs precursors were removed. For PFC, the residual DOC was lower at pH 4 than that at pH 8 which was in accordance with the chlorine demand results. For PAC, the DOC results were not in accordance with the chlorine demand. The UV$_{254}$ trends by PFC and PAC were different from the chlorine demand results in this study, although DOC and UV$_{254}$ have been widely used as indicators of DBPs precursors of NOM. It is likely that the DBPs precursors removal from the low OM water was not easily obtained from the DOC or UV$_{254}$ results. Different from DBPs precursors, the organic matter represented by DOC and UV$_{254}$ had less fundamental groups with negative charges than DBPs precursors, such as -COOH or -OH (Zhao et al., 2008). Therefore, much less organic matter represented by DOC and UV$_{254}$ was removed through charge neutralization at pH 4, whereas much more organic matter represented by DOC and UV$_{254}$ precipitated through adsorption at pH 8.

The approach adopted by this investigation of the floc properties could provide preliminary indication on the DBPs precursors removal. The PAC-floc was small at pH 4 and 8 compared with that at pH 6. And the DBPs precursors were not effectively removed at pH 4 and 8. It is likely that small flocs were not favorable for DBPs precursors removal. This may be that OM was insufficiently coagulated into the flocs for small flocs. Though the PFC-flocs were decreased with the increased
pH, the difference between the floc sizes was not significant. \(d_{50}\) was in the range of 730 µm-880 µm. And the PFC-flocs were all larger than PAC-flocs under the pH investigation. But it is found from Table 2 that the DBPs precursors removal for PFC varied with the pH changes. It is likely that the floc size was not a limiting factor that influenced the DBPs precursors removal. It may be that if the floc size increased to a certain extent, there are other floc properties except the floc size that affected the DBPs precursors removal for large flocs.

It is noted that the floc strength decreased with the increasing pH. The flocs were stronger under acidic conditions due to the strong charge neutralization of PFC, which reduced the interior repulsion of flocs (Wei el at., 2009). However, excessive charge caused the flocs to repel with each other which resulted in decreasing DBPs precursors removal. Flocs formed by entrapment and adsorption of OM onto metal precipitates in alkaline range was weak and fragile (Bache el at., 1997) and the DBPs precursors removal efficiency was low. Thus, weak flocs which attributed to a lack of bridging bonds holding these flocs together (Jarvis el at., 2005b) were not favorable for DBPs precursors removal.

According to the fractal dimension analysis, flocs generated at pH 8 were dense and compact compared with pH 4 and 6. It is surprising that the DBPs precursors removal rate was low. It seems that the compact flocs may not provide a high removal efficiency on the DBPs precursors. However, there has not been a clear explanation on the degree of compaction and the DBPs precursors removal. Further research will be carried out in our subsequent work.

CONCLUSIONS

OM removal was favored at lower pH. OM was mainly removed by charge neutralization for PAC, whereas the adsorption and entrapment played important roles in OM removal in the alkaline solution for PFC. The optimum pH for DBPs precursors removal was 6 due to the self-aggregation and charge neutralization in the acid range. The alkaline conditions of coagulation were not favorable for precipitate formation and the DBP precursors were not effectively removed. The flocs properties varied with the pH values. PFC-flocs’ size was decreased as the pH increased, while the PAC-flocs were increased first with the increasing pH and then decreased. The flocs strength decreased with the increasing pH. The compact flocs tend to be generated at alkaline solution in the study whilst the flocs formed in acid solutions were loose. The small and compact flocs were not favorable for DBPs precursors removal in treating the low OM surface water.

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