Roles of coagulant species and mechanisms on floc characteristics and filterability

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HIGHLIGHTS

• The effects of Al species on floc filterability were studied.
• Al species of nano-Al13 were more abundant than that of alum at neutral pH level.
• Higher MW Al species could improve coagulation performance and floc filterability.
• The floc formed by charge neutralisation mechanism has better floc filterability.

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ABSTRACT

In full scale water treatment operation, the rapid filtration process, as the last step of solid–liquid separation, is largely influenced by floc characteristics. In this study, aluminium sulphate (alum) and nano-Al13 were investigated to understand the influence of coagulant species on the formation and filterability of flocs. At neutral pH, it was found that nano-Al13, a high MW polymer, showed better floc filterability than alum. This is because of the densely compacted and well-distributed size flocs from nano-Al13, even though floc sizes of alum were generally bigger. Al specie distributions of the two co-agulants at different pH levels were compared by using electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) to further elucidate the reasons for the superiority of nano-Al13 in floc filterability. Depolymerisation/re-polymerisation of nano-Al13 occurred as pH changed, and Al species from nano-Al13 were more abundant than that from alum, especially for the high molecular weight (MW) oligomers such as Al11, Al12, Al13 and Al14. Under the charge neutralisation mechanism, higher MW Al species was found to improve coagulation performance and floc filterability. In addition, breakage resistance and regrowth ability of nano-Al13 was better than alum, at weak acid condition. Flocs formed by the charge neutralisation mechanism readily regenerated after being thoroughly broken up. The floc regrowth ability of nano-Al13 at high shear rates (200 rpm and 300 rpm) was much better than at low shear and better than any shear applied to alum, and the flocs after breakage at 200 rpm and 300 rpm also showed better filterability than other conditions.

1. Background

Filtration is an important process being the last solid–liquid separation step in the primary purification of water (Boiler and Blaser, 1998). Its performance determines the amount of residual turbidity in drinking water before its distribution. The filtration process is greatly affected by coagulation which is the most common preceding treatment process (Xiao et al., 2009a; Jiao et al., 2014). Coagulation performance determines the amount of residual particles that need to be separated by filtration. Similarly, the characteristics of coagulation floc also strongly influence the filtration efficiency, as poor coagulation can result in floc which cannot settle readily due to low weight or weak strength. These can lead to floc breakage under hydraulic shear force (Jarvis et al., 2005a). Residual floc can be challenging to remove in media...
filtration because the floc may pass straight through the filter bed, detach from the filter media, or overload the filter (Fabrizi et al., 2010). Therefore, floc characteristics that result in efficient filtration and high quality drinking water are of high importance.

In recent years, the physical characteristics of flocs in water treatment have been taken into consideration in treatment efficiency assessment for tap water (Yang et al., 2012; Cao et al., 2011; Liu et al., 2011). The formation of floc depends on many factors including type and dosage of coagulants, applied shear force and the characteristics of the particles (Yu et al., 2010b; Ehrl et al., 2008). Of these factors, the influence of coagulant type on floc formation has received more attention, especially for the monomeric and polymeric aluminium coagulants. Xu et al. (2011) compared the floc characteristics of two coagulants, pre-hydrolysed Al13 and AlCl3, applied for coagulation of humic acid (HA). They used a laser diffraction particle sizer. They found that floc formed by pre-hydrolysed Al13 contributed to flocs of larger fractal dimension than AlCl3. In the study of Yu et al. (2009), the formation, breakage, and re-growth of flocs were investigated using alum and polyaluminum chloride (PACl) to explore floc strength and regrowth. It was observed that the strength factor of floc formed by alum was higher than PACl, regardless of coagulant dose or frequency of breakage.

Coagulant type strongly influences coagulation mechanisms. Coagulation mechanisms are also affected by coagulant dose and the characteristics of target particles, which directly determine the formation of flocs. Therefore, coagulation mechanisms are considered as the basic factor affecting floc characteristics (Kim et al., 2001; Xiao et al., 2009b). For example, Yu et al. (2011) compared the floc formed by charged neutalisation and sweep flocculation by using alum, and found flocs formed by charge neutralisation were much stronger than by sweep flocculation. Similarly, Li et al. (2006) studied alum and cationic polyacrylamide, and ranked the floc strength formed by different mechanisms, showing that bridging is stronger than charge neutralisation, which is stronger than sweep flocculation.

Although a number of studies have been conducted on the factors impacting on floc formation and its characteristics, to date, researchers have paid little attention on the direct relationship between floc characteristics and filterability. The aim of the work reported here was to investigate the influence of coagulant species and mechanisms on floc characteristics and filterability, using alum and nano-Al13. Floc characteristics before and after breakage and the impact of these on floc filterability under different mechanisms were also studied in order to gain greater insight into the relationship between floc properties and filterability.

2. Materials and methods

2.1. Raw water samples

Raw water was collected from the Happy Valley water treatment plant/Reservoir which is located 15 km south of Adelaide, South Australia. The water is sourced from the River Murray and supplemented by the Mt Bold catchment. During the period of this study, the turbidity of the source water was 4.7 ± 0.1 nephelometric turbidity units (NTU), with raw water dissolved organic carbon (DOC) of 10 ± 0.5 mg L−1. Moreover, the UV254, colour and pH were 0.26 ± 0.01 cm−1, 36.4 ± 0.5 mg L−1 and 7.8 ± 0.1 (in 20 °C), respectively.

2.2. Jar testing

Jar testing was performed using a PB-900 programmable six-paddle gang mixer (Phipps and Bird, USA). Two sets of jar tests were carried out. For the first set, initial flash mixing of coagulants was performed at 200 rpm for 1 min with the addition of coagulant at t = 30 s. This was followed by 14 min slow mixing at 40 rpm and then followed by 15 min of sedimentation. For the second set, fast mixing was the same as the first set, however, the slow mixing was only 14 min with 40 rpm, and then the flocs were subjected to increased shear for 1 min at 80 rpm, 120 rpm, 200 rpm and 300 rpm, respectively. This was followed by 14 min slow mixing at 40 rpm to allow time for possible re-growth of floc and then settling for 15 min.

In terms of different aluminium (Al) species, two Al-based coagulants were selected to evaluate their coagulation behaviour. These coagulants are Al2(SO4)3 (alum) and nano-Al13. By using a Ferron colorimetry (Xu et al., 2003), the main Al species of Al2(SO4)3 and nano-Al13 are Alα (92.7%) and Alβ (86.5%) respectively. Aluminium sulphate hydrate (Al2(SO4)3·18H2O) was used in this experiment. Stock alum solutions were prepared at a concentration of 20,000 mg/L and kept cool at 5 °C. According to previous studies, the preparation of nano-Al13 was carried out by sulphate precipitation from a PACl with basicity of 2.2. According to previous studies, the preparation of nano-Al13 was carried out by sulphate precipitation from a PACl with basicity of 2.2. PACl and Na2SO4 were mixed in the molar ratio (SO4/Al) of 0.6−1. The precipitation was then filtered, and the supernatant was aged for 48 h. Next, the aged solution was filtered again, and the nano-Al13 sulphate crystal was produced. After, the crystal was dried, and the solution made from the sulphate powder was mixed with BaCl2. The supernatant was nano-Al13 with the concentration of 0.1 M. The characteristics of prepared coagulants were shown in a previous study (Jiao et al., 2015).

2.3. Filterability index

A filterability index unit was used to assess the floc filterability. The structure of the apparatus is shown in the supporting information Fig. 1 (S-Fig. 1). In experiments, dual media, anthracite and sand were chosen to model the full-scale filter process (S-Fig. 2).

The filterability index can be calculated as shown in Eq. (1):

\[
\text{Filterability Index} = \frac{H - C}{C_0 \cdot T \cdot V}
\]

In this formula, \(H\) is the Head loss (cms) that can be calculated by comparing the difference of initial and final values of the water manometer, \(C\) and \(C_0\) are the bench filter turbidity (NTU) and the turbidity (NTU) after conventional coagulation and sedimentation, respectively. \(T\) is the filter time (min). \(V\), obtained by the flow rate (cm² min⁻¹) over the area of the filter column (cm²), giving the velocity of filtration (cm min⁻¹). In experiments, the flow rate was 50 cm² min⁻¹, so \(T\) was constant; meanwhile, \(V\) was a constant with the value of 4.41 cm min⁻¹. Thus the other three parameters, \(C_0\), \(C\) and \(H\) determined the value of filterability index. The higher the value of filterability index, the more difficult the floc can be filtered. In actual water treatment process, low \(H\) and low ratio of \(C/C_0\) are desired to minimize value of filterability index and the increase of floc filterability.

In experiments conducted, the filterability indexes of different water samples were determined by using the supernatant water after sedimentation, which has been treated by coagulation.

2.4. Floc characteristics

The photometric dispersion analyser (PDA2000, Rank Bros Ltd, Cambridge, UK) was used for floc monitoring (Gregory and Nelson, 1986). During the entire process of floc formation and
sedimentation, sample was siphoned from the stirred jar at 22 mL min\(^{-1}\) through a 3 mm internal diameter transparent plastic tube and continuously passed between a high-intensity light source and photo-diode. The pump was located after the PDA to avoid the breakage of the generated floc before measurement. The experimental procedure was similar to that of Braun et al. (2014). In this study, three parameters, initial floc aggregation (IFA), the relative settling factor (RSF) and variance, were extracted from the flocculation index (FI) results in order to better understand flocs characteristics (Braun et al, 2014; Staaks et al., 2011). IFA and RSF represent the floc growth speed and sedimentation ability respectively; while variance indicates the size distribution and variation of floc.

### 2.5. Electrospray ionization time-of-flight mass spectrometry

Electrospray ionization time-of-flight mass spectra (ESI-TOF-MS) were recorded with a micromass hybrid quadrupole time-of-flight (Q-TOF) mass spectrometer (2695XE Micro, Waters, USA) equipped with an electrospray ion source. All ESI MS data were obtained in positive ion mode (Feng et al., 2015), \([\text{Al}_x\text{O}_y(\text{OH})_z(\text{H}_2\text{O})_m]^{2+}y^{-1}z^{-1}m^{-1}\) was used as the general formula to calculate all species. The percent concentration of each species was determined by the ratio of the peak intensity for each species to the total intensity of all of the species (Feng et al., 2015, 2012). The samples were injected into the spectrometer at a flow rate of 10 L min\(^{-1}\). The mobile phase was ultrapure water. The instrumental conditions were as follows: capillary voltage 3500.0 V, sample cone voltage 70 V, Fflens 200 V, extraction cone voltage 5 V, source temperature 120 °C, cone gas (N\(_2\)) flow rate 300 L h\(^{-1}\), mass range of 80–1000.

In this study, ultra pure water was used as the black sample, and the mass spectra of black sample is shown in S-Fig. 3.

### 2.6. Analyses of water quality

Analysed parameters included pH, turbidity and DOC. Turbidity measurements were conducted on a 2100AN Laboratory Turbidimeter (Hach, USA) with results given in NTU. DOC samples were filtered using pre-rinsed 0.45 μm membranes and analysed with a Sievers 900 Total Organic Carbon analyser (GE Analytical Instruments, USA). pH was determined by using a pH meter (MP220, Mettler-Toledo, Switzerland).

### 3. Results and discussion

#### 3.1. Impacts of dosages on coagulation performance and floc filterability

Dosage effect on the coagulation performances of alum and nano-Al\(_{13}\) were comparatively investigated in this study. The pH was controlled at 7.0 ± 0.2 by pre-adding HCl (0.5 M) or NaOH (1 M). The pH was continuously measuring after adding coagulants for keeping the pH level consistent during the dosage determination process.

Comparison of the two coagulants in terms of turbidity as well as DOC removal efficiencies is shown in S-Fig. 4. For turbidity removal, alum showed superiority in minimizing the dosage requirement. Based on the criteria for minimizing the residual turbidity, the optimum dosage of alum was just 0.15 mM while nano-Al\(_{13}\) was 0.18 mM. However, the residual turbidity of treated water by nano-Al\(_{13}\) was lower than that by alum, and the removal rate ((Turbidity\(_{\text{removed}}\)/Turbidity\(_{\text{raw water}}\) × 100%) at the optimum dosages for two coagulants were 43.6% and 61.5%, respectively. Although the turbidity removal rates were visibly different, the difference of DOC removal by the two coagulants was slight. DOC declined as the dosage increased for both coagulants with the highest removal rate of 39.5% (alum) and 37.6% (nano-Al\(_{13}\)) at the highest dosages.

At pH 7.0, sweep flocculation is usually considered as the main mechanism occurring when alum is used (Hu et al., 2006); however, due to the high positive charge of nano-Al\(_{13}\), the neutralisation mechanism is always prominent at neutral pH condition (Wu et al., 2007). In previous study, natural particles typically carry negative charges over a pH range of 5–9 (Duan and Gregory, 2003). The raw water used in this study had relatively low turbidity and high DOC. Consequently, sweep flocculation mechanism might not be efficient for the removal of turbidity because of the lack of solid particles (nucleation sites); while charge neutralisation could remove particles readily once the coagulant positive charge was sufficient. Results of turbidity and DOC removal suggested that nano-Al\(_{13}\) was more effective for solid particle (turbdity) removal while the DOC removal was equivalent to alum.

Fig. 1 compares the floc filterability of two coagulants as dosages increased. In actual full-scale operation, eliminating the residual flocs after sedimentation is the main goal for the filtration process. Floc filterability which was described by filterability index was used to indicate the efficiency of the floc filtration process. The filterability index is not only correlated to residual turbidity, but is also related to the head loss. Minimizing the filterability index (Eq. (1)) will contribute to good filtration performance. From Fig. 1, it can be seen that the filterability index declined as the dosage increased and this result was in accordance with the coagulation performance of the two coagulants (S-Fig. 4). However, in both cases, the optimum dosages required to minimise the filterability index were higher than that necessary to maximise turbidity removal. The optimum dosages determined by filterability index for alum and nano-Al\(_{13}\) were 0.18 mM and 0.24 mM, respectively which were similar to the coagulants dosages of maximizing DOC removal, especially for nano-Al\(_{13}\) (S-Fig. 4). This may be because DOC has much smaller size which will further affect the depth filtration process. In addition, from S-Fig. 5, flocs formed by these two optimum dosages were also found having high FI value which is positively correlated to floc size (Yu et al., 2010a, 2010b). Therefore, in actual operation, a relatively higher dosage than what determined by turbidity removal seemed to enhance the filter efficiency and improve the treated water quality. In addition, because of less residual (settled water) turbidity, the filterability index of nano-Al\(_{13}\) at the optimum dosage was notably lower than that of alum.

![Fig. 1. Filterability Index by different dosages (mM as Al).](image-url)
3.2. Variation of floc characteristics and filterability with pH changes

Coagulation pH is one of the most important factors that will affect the coagulant species, which will further determine the coagulation mechanisms that occur. Monomeric coagulants are considered more unstable species. Hydrolysis occurs immediately after dosing and the active aluminium exists in the form of alumino-hydroxy complexes before interacting with particles (Yang et al., 2010; Yan et al., 2007). Therefore, the influence of the pH on coagulation mechanisms was correlated with the hydrolysed species of alum (Hu et al., 2006; May et al., 1979). Although nano-Al13 is the pre-hydrolysed coagulant, its species may still change as the pH is varied. It is therefore essential to consider the pH influence on coagulation performance.

In actual water treatment processes, pH is usually maintained around neutral conditions in order to minimise the pH adjustment necessary post-coagulation and prior to disinfection. For this reason, pHs within the neutral range (6.5, 7.0 and 7.5) were applied in this study. Dosages of 0.18 mM (alum) and 0.24 mM (nano-Al13) were chosen, respectively. S-Fig. 6 showed turbidity and DOC removals under varied pH. Similar to the results from S-Fig. 4, there were significant differences for turbidity removal between two coagulants but only slight difference for DOC removal at pHs 6.5 and 7.0. The residual turbidity of nano-Al13 was lower than that of alum until pH reached 7.5.

Floc formations at different pH levels, indicated by FI, are shown in Fig. 2. From these results, it was found that alum had a much higher FI value than nano-Al13 at each pH level, meaning the floc size of alum were generally bigger than that of nano-Al13. Additionally, the parameters IFA, RSF, and variance, extracted from FI, would better describe the characteristics of floc. The goal of conventional coagulation is to maximize IFA and RSF while minimizing variance of floc, which means increasing the floc growth speed and improving both floc sedimentation ability and floc density (Braun et al., 2014). The results are shown in Table 1. Corresponding to the FI value, the IFA and RSF indices of alum at each pH was also higher than nano-Al13, indicating that the relatively large floc was formed with fast floc formation speed as well as relatively good settling ability. However, a lower value of variance by nano-Al13 was an indication that floc formed by nano-Al13 have denser structure and well-distributed sizes. This might be the result of the high positive charge of nano-Al13 which leads to charge neutralization mechanism is predominant, especially at low pH level. Meanwhile, charges on the particle surface would be high at low pH level, so nano-Al13 showed better turbidity removal at pH 6.5 and pH 7.0.

Fig. 3 exhibits the result of the influence of pH on filterability index. Findings indicated that the filterability index was closely correlated with turbidity removal and was also related to the floc characteristics. The floc filterability of nano-Al13 was better than that of alum at pH 6.5 and pH 7.0, while the result reversed when pH reached 7.5. According to S-Fig. 6, nano-Al13 showed lower residual turbidity value at pH 6.5 and 7.0 than that of Alum. Consequently, the turbidity removal efficiency was the key factor that determined the filtration efficiency at the neutral pH range for both alum and nano-Al13. For nano-Al13, the residual turbidity were similar at pH 6.5 and 7.0, however, floc formed at pH 7.0 had lower variance value (Table 1), and small size distribution of floc would be more favourable to partitioning through a media filter, so it could be shown that filterability of residual nano-Al13 floc at pH 7.0 was the most efficient rather than pH 6.5.

From the results detailed above, the impact of pH on the particles removal and floc filterability were significant. For alum, charge neutralisation occurs at low pH level, while sweep floculation mechanism will substitute when pH is higher than 6.5. Therefore, sweep floculation mechanism should be dominant for alum in this study. In addition, owing to its high positive charge, nano-Al13 was considered to be mainly dependent on the charge neutralisation mechanism at neutral pH levels. The coagulation mechanisms should be consistent at the set pH range; however pH 7.0 was found as the turning point for nano-Al13. Consequently, the coagulants species variation as pH changes was deduced as an important factor that affected the coagulation performance.

Therefore, it is necessary to detect the change in coagulant species at the set pH range. Recently, ESI-TOF-MS has been applied in metal ions species identification for determination of molecular mass (Feng et al., 2015; Feng et al., 2011; Bi et al., 2012). In this study, two coagulants at the same concentration of 0.2 mM were used to detect the Al species distributions. Table 2 summarizes the signals in the ESI-TOF-MS spectra and the corresponding Al species. Compared with nano-Al13 without pH adjusted (S-Fig.7), nano-Al13 depolymerised/re-polymerized when pH was changed. Thus, more species like Al4, Al7 and Al14 could also be found in the solution. In addition, it was found that nano-Al13 has more Al species compared with alum, especially for the high charge hydrolysates. This clearly demonstrated the charge neutralisation ability of nano-Al13 at neutral condition. The ESI-TOF-MS spectra at different pH levels are shown in Fig. 4. For alum at pH 6.5, eight peaks appeared which indicated the existence of Al6,...,Al13, and Al13. Among them, the most intensive peaks were m/z 165 and 307, representing Al10 and Al8 respectively. Similar to pH 6.5, hydrolysis species of alum at pH 7.0 changed slightly. Seven main peaks could be found at pH 7.0, and they represent Al4, Al7, Al10, and Al13.

<table>
<thead>
<tr>
<th>pH 6.5</th>
<th>pH 7.0</th>
<th>pH 7.5</th>
</tr>
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<tbody>
<tr>
<td>Alum</td>
<td>IFA</td>
<td>0.1712</td>
</tr>
<tr>
<td></td>
<td>RSF</td>
<td>0.8382</td>
</tr>
<tr>
<td></td>
<td>Variance</td>
<td>0.0209</td>
</tr>
<tr>
<td>Nano-Al13</td>
<td>IFA</td>
<td>0.1323</td>
</tr>
<tr>
<td></td>
<td>RSF</td>
<td>0.6806</td>
</tr>
<tr>
<td></td>
<td>Variance</td>
<td>0.0147</td>
</tr>
</tbody>
</table>

Table 1 Comparison of initial floc aggregation (IFA), relative settling factor (RSF) and variance of flocs formed by Alum and nano-Al13 at different pH.
Therefore nano-Al_{13} has greater charge neutralisation ability than alum at neutral pH conditions. Due to the instability of alum, it quickly hydrolysed into precipitate or species with negative charge that could not be detected at the set pH range investigated. As a consequence, pH change rarely affected the Al species distribution of alum. However, the positive charge Al species distribution of alum was not important near neutral pH because sweep flocculation mechanism was predominant. For nano-Al_{13}, it was found that the greater variety of Al species below pH 7.5 contributed to good coagulation performance and floc filterability. Thus, the result of turbidity removal and filterability index diminished when pH reached 7.5, as the variety of highly charged species reduced.

3.3. The analysis of floc strength and filterability after breakage by alum and nano-Al_{13}

Unlike laboratory jar-testing, which represents a batch process, in operational water treatment plants, coagulation is a continuous (flow) process where flocs can break due to shear forces after for-

Comparatively, the species that existed at pH 7.5 were almost the same as at pH 6.5 and 7.0, but very low concentrations of Al_{14}^{3+} were also found. In general, the Al species of alum were slightly affected by pH at neutral level. Low MW polymeric Al species, Al_{6}^{3+}, Al_{7}^{3+} and Al_{9}^{3+}, were the main species for all the three pH levels. In contrast to alum, Al species distribution of nano-Al_{13} was distinctly influenced by pH changes. As pH increased, the amount of Al species increased first, and then decreased at weak alkaline condition. Ten Al species, including Al_{4}^{3+}, Al_{7}^{3+}, Al_{8}^{3+}, Al_{9}^{3+}, Al_{11}^{3+}, Al_{12}^{3+}, Al_{13}^{3+}, Al_{14}^{3+} and Al_{14}^{3+} appeared at pH 6.5. When the pH reached 7.0, the variety of Al species was most abundant with three more species (Al_{11}^{3+}, Al_{12}^{3+} and Al_{14}^{3+}) compared to pH 6.5. However, as pH further increased to 7.5, there were just eight species formed, although significant amounts of the most effective high MW polymeric species remained.

The information obtained by ESI-TOF-MS well explained the differences of floc filterability at varied pH level. Al species of nano-Al_{13} were more abundant than that of alum, especially for the high MW polymers (Al_{11}, Al_{12}, Al_{13} and Al_{14}); furthermore, the high polymer nano-Al_{13} has more diverse electric charges than alum. This will further affect the coagulation efficiency and floc filterability in practice. Thus, the strength and regrowth ability of floc has been considered as one of the most important factors to realistically estimate the coagulant performance (Yu et al., 2010a).

Floc physical properties, such as size, density, and strength have been shown to influence the regrowth ability of broken floc in previous studies (Jarvis et al., 2005b, 2006). In addition, the stirring speed during floc breakage is known for having a major effect on the size of broken floc. In order to further investigate floc strength and regrowth ability by different coagulants, jar tests with four levels of shear, achieved through stirring speed were used, and the dosages were 0.18 mM (alum) and 0.24 mM (nano-Al_{13}). Form the results obtained from the earlier tests, pH 6.5 was chosen, at which similar performance on floc filterability was observed for the two applied coagulants.

S-Fig. 8 shows the Floc Index Results at different stirring speeds for the two coagulants. Generally speaking, up to the point of floc breakage, the results were very similar to the corresponding Floc Index values, shown in Fig. 2 for both coagulants. After breakage, the

![Fig. 3. Comparison of filterability of flocs from different coagulants.](image-url)
minimum FI reached was strongly affected by the breakage stirring speed, and was generally inversely proportional with floc sizes, which was in agreement with previous studies (Serra et al., 2008). Subsequently, the FI value began to increase again when the stirring speed increased.
speed was restored to 40 rpm and the regenerated floc showed a noticeably lower Fl value than prior to breakage. It is convenient to quantify the breakage and regrowth of floc in terms of the following factors (Yukselen and Gregory, 2002):

\[ F_1 = \frac{V_2}{V_1} \]  

(2)

\[ F_2 = \frac{V_3 - V_2}{V_1 - V_2} \]  

(3)

Where \( F_1 \) and \( F_2 \) are the strength factor and recovery factor; \( V_1 \) is the maximum Fl value before floc breakage; \( V_2 \) is the minimum Fl value when floc is broken, and \( V_3 \) is the maximum Fl value after regrowth of broken floc.

Comparison of breakage and regrowth factors was shown in Fig. 5. \( F_1 \) of both coagulants decreased with increasing shear. In general, \( F_1 \) of alum was considerably lower than that of nano-Al\(_{13}\) which meant the breakage resistance of alum was relatively poor. When comparing \( F_2 \), floc regrowth ability of nano-Al\(_{13}\) was also better than alum. It is worthy of note that the regrowth ability of alum at different stirring speeds did not change appreciably. Although \( F_2 \) at 80 rpm was slightly greater than that at higher breakage strength, \( F_2 \) at the three other stirring speeds were almost the same. The floc regrowth ability was not reduced as the breakage strength increased in this study. However, it could be shown that the floc regrowth ability of nano-Al\(_{13}\) at high shear rates (200 rpm and 300 rpm), conversely, was better than at low shear rates. The result is similar to the study of Xu et al. (2010). The floc differences observed between low and high shear rates might be related to the mechanisms of the two coagulants. Floc formed by alum depended on sweep flocculation. Therefore, as the stirring speeds increased, floc was broken thoroughly and no mechanism existed by which they could recover again. However, for nano-Al\(_{13}\), the charge of particles was retained more readily at high shear rates as floc was broken, so the floc has better opportunity for regrowth through the charge neutralisation mechanism.

The results correspond well to the floc filterability after breakage which was also shown in Fig. 5 (bar graph). Ultimately, regenerated floc with bigger size had better filterability. As a consequence, the filterability index of nano-Al\(_{13}\) at 200 rpm and 300 rpm were much lower than alum.

4. Conclusions

(1) At pH 7.0, nano-Al\(_{13}\) which mainly depends on the charge neutralisation mechanism was more effective in particle (turbidity) removal than alum for which sweep flocculation mechanism is predominant. However, the difference in DOC removal by the two coagulants was minimal.

(2) Floc filterability of nano-Al\(_{13}\) at the optimum dosage was lower than that of alum treating low turbidity raw water. In addition, the optimum dosages determined by filterability index were higher than that determined by turbidity removal for both coagulants. Therefore, in actual operation, relatively higher dosages are needed to enhance the filter efficiency and improve the treated water quality.

(3) Floc sizes of alum were generally bigger than that of nano-Al\(_{13}\) within a neutral pH6.5 to 7.5. However, nano-Al\(_{13}\) showed better turbidity removal at pH 6.5 and pH7.0 because floc had a denser structure and smaller size distribution variation. High turbidity removal rate contributed to good filtration performance at neutral conditions. Furthermore, small size distribution would be more favourable for consistent filtration.

(4) Al species of nano-Al\(_{13}\) were more abundant than that of alum, especially for the high MW oligomers. Under the charge neutralisation mechanism, higher Al-containing species improved coagulation performance and floc filterability.

(5) Under weak acid condition, breakage resistance of alum was relatively inferior to nano-Al\(_{13}\). In addition, floc regrowth ability of nano-Al\(_{13}\) at high shear rates (200 rpm and 300 rpm) was better than at low shear rates, because floc formed by charge neutralisation mechanism readily regenerated after complete breakage (dissociation).

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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.chemosphere.2016.02.030.

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