JOURNAL OF ENVIRONMENTAL SCIENCES 57 (2017) 338–345

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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Influence of coagulation mechanisms and floc formation on filterability

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A R T I C L E I N F O

Article history:
Received 12 September 2016
Revised 9 January 2017
Accepted 10 January 2017
Available online 27 January 2017

Keywords:
Coagulation mechanisms
Floc characteristics
Filterability
Turbidity

A B S T R A C T

Minimizing particles in water is a key goal for improving drinking water quality and safety. The media filtration process, as the last step of the solid–liquid separation process, is largely influenced by the characteristics of flocs, which are formed and controlled within the coagulation process. In a laboratory-based study, the impacts of the physical characteristics of flocs formed using aluminum sulfate on the filtration treatment of two comparative water samples were investigated using a photometric dispersion analyzer and a filterability apparatus. In general, the optimum dosage for maximizing filterability was higher than that for minimizing turbidity under neutral pH conditions. For a monomeric aluminum-based coagulant, the charge neutralization mechanism produced better floc characteristics, including floc growth speed and size, than the sweep flocculation mechanism. In addition, the charge neutralization mechanism showed better performance compared to sweep flocculation in terms of DOC removal and floc filterability improvement for both waters, and showed superiority in turbidity removal only when the raw water had high turbidity. For the different mechanisms, the ways that floc characteristics impacted on floc filterability also differed. The low variation in floc size distribution obtained under the charge neutralization mechanism resulted in the flocs being amenable to removal by filtration processes. For the sweep flocculation mechanism, increasing the floc size improved the settling ability of flocs, resulting in higher filter efficiency.

Introduction

Minimizing the particles in treated drinking water is fundamental to the successful operation of a water treatment facility. In water treatment processes, media filtration is the final solid–liquid separation step, (Boller and Blaser, 1998) and its performance is mainly evaluated by filtered water qualities (turbidity and dissolved organic carbon (DOC)), head loss development (rate and time to backwash) and water production (unit filter run volume). Parameters that determine the

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http://dx.doi.org/10.1016/j.jes.2017.01.006

filtration performance include particle size, particle concentration and the surface chemical properties of particles, and these are usually influenced by pre-treatment methods. Coagulation, applied for the removal of turbidity and natural organic matter (NOM), is the most common treatment process prior to the filtration process (Xiao et al., 2009; Jiao et al., 2014).

During coagulation treatment, most natural particles can be effectively aggregated in floc formation and then removed by sedimentation. However, a certain amount of flocs will not settle readily due to small size, low density and/or weak floc strength that leads to floc breakage under hydraulic shear forces (Jarvis et al., 2005). These flocs can then break up through the filtration process. Typically, small fine particles with the size of 1–10 μm have been considered the most challenging elements to be removed in media filters. This is because particles of this size range can pass straight through the filter bed, detach from the filter media, or overload the filter (Fabrizi et al., 2010; Kim and Tobiason, 2004). Therefore, the development of floc characteristics that result in efficient filtration and high quality drinking water is of high importance.

To date, in studies on floc characteristics, researchers have focused on the evaluation of the physical characteristics of flocs under different coagulation conditions. For example, studies found that the formation of flocs depends on the type and dosage of coagulant, applied mixing shear, and the concentration and characteristics of the floc particles, *e.g.*, size (Yu et al., 2010a; Ehrl et al., 2008). Besides hydraulic conditions, coagulation mechanisms are largely influenced by the coagulant type, the demand for coagulant and the characteristics of particles. From a control point of view, coagulation mechanisms determine the characteristics of flocs. For the commonly used hydrolyzing coagulants, the removal of particles mainly depends on two mechanisms (charge neutralization and sweep flocculation) that have been widely studied (Duan and Gregory, 2003; Yu et al., 2010b). Some studies have described the influence of coagulation mechanisms on floc characteristics (Kim et al., 2001; Li et al., 2006). For example, Yu et al. (2011) compared the floc strength and reforming of broken flocs from aluminum sulfate formed at pH 5 and pH 7 using a photometric dispersion analyzer (PDA). They found that the flocs formed by charge neutralization were much stronger (resistant to breakage) than those by sweep flocculation (Yu et al., 2011). In the study of Xu et al. (2011), the floc characteristics of two different coagulants, pre-hydrolyzed Al_{13} and $AlCl_3$, in humic acid (HA) coagulation were compared using a laser diffraction particle sizer. It was found that flocs formed by preformed Al_{13}, where formation mainly depends on the neutralization mechanism, contributed to flocs with larger fractal dimension than those formed using $AlCl_3$ (Xu et al., 2011).

Previous studies have mostly focused on floc characteristics during the coagulation stage. However, the impacts of the physical characteristics of flocs on filtration treatment have often been overlooked. Therefore, the aim of the study reported here was to investigate the influence of different raw water turbidities on coagulation mechanisms and floc properties, plus the relationships between floc characteristics and filterability under different mechanisms. In many laboratory-based studies, paper filters have been used for filtration of coagulant-treated waters (in jar tests) in the evaluation of floc filterability. However, filter papers used for filtration have smaller pore sizes than those present in sand filtration in full-scale operations. Further, it is not feasible to evaluate full-scale rapid sand filter head losses by the use of paper filtration under laboratory conditions. In this study, sand filtration was used under laboratory conditions to better simulate the practical water treatment process.

1. Materials and methods

1.1. Raw water

Two waters, of low and high turbidity (spiked with clay) were used in the experiments. The first (Water I) was collected from the Happy Valley Reservoir at the inlet to the water treatment plant (WTP), located 15 km south of Adelaide, South Australia. The Happy Valley Reservoir water is sourced from the River Murray and from the Mt. Bold catchment. During the period of study, the turbidity of the reservoir water was 4.6 ± 0.5 nephelometric turbidity units (NTUs), and DOC was 9.7 ± 0.3 mg/L. For the second water (Water II), clay was added into Water I to significantly elevate the turbidity. The clay was obtained from a zero order catchment (grassland) of the Myponga Reservoir (a drinking water reservoir located 50 km south of Adelaide). The clay sample was sieved to less than 420 μm. The elemental composition of the clay was determined by a field emission scanning electron microscope (FE-SEM) and is shown in Fig. 1 of the supplementary information (Appendix A Fig. S1). The turbidity of Water II was 46 ± 2 NTU, with raw water DOC of 9.5 ± 0.5 mg/L.

1.2. Jar testing

Jar testing was performed using a PB-900 programmable six-paddle gang stirrer (Phipps and Bird, USA). Flash mixing of the alum coagulant was performed at 200 r/min for 1 min with the addition of coagulant at t = 30 sec. This was followed by 14 min slow mixing at 40 r/min and then 15 min of sedimentation. Samples of settled water were then analyzed for turbidity and DOC.

Aluminum sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$) obtained from a full-scale water treatment plant (WTP) was used as the coagulant. Stock solutions were prepared at a concentration of 20,000 mg/L. All coagulant doses are expressed as mg/L $Al_2(SO_4)_3{\cdot}18H_2O$ in this study.

Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) of 0.5 mol/L were used to adjust the pH level.

1.3. Filterability index

A filterability index was used to assess flocs. The structure of the apparatus is shown in Appendix A Fig. S2. In the experiments, dual media comprising anthracite and sand was chosen to model a full-scale filter process (Appendix A Fig. S3). The filterability index can be calculated as follows:

$$\text{Filterability Index} = \frac{H \cdot C}{C_0 \cdot T \cdot V} \quad (1)$$

where, H (cm) is the head loss, which can be calculated by comparing the difference between the initial and final values

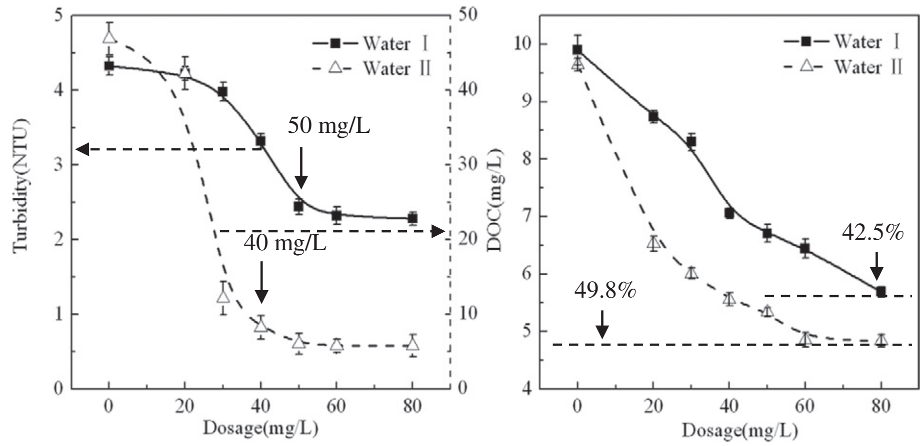

Fig. 1 – Effect of coagulant dosage on the turbidity and DOC removal. Water I: turbidity 4.6 ± 0.5 NTU, DOC 9.7 ± 0.3 mg/L; Water II: turbidity 46 ± 2 NTU, DOC 9.5 ± 0.5 mg/L.

of the water manometer. *C* (NTU) and C_0 (NTU) are the bench filter turbidity and the turbidity after conventional coagulation and sedimentation, respectively. *T* (min) is the filter time. *V* (cm^3/min), which was obtained from the rate of flow divided by the area (cm^2) of the filter column, is the velocity (cm/min) of filtration. In the experiment, the flow rate was 50 cm^3/min, thus *V* is a constant with the value of 4.41 cm/min.

In this experiment, the filterability indices of different water samples were determined by using the supernatant of the coagulated water after 15 min of sedimentation.

1.4. Floc monitoring

A photometric dispersion analyzer (PDA2000, Rank Bros Ltd., Cambridge, UK) was used for floc monitoring (Gregory and Nelson, 1986). During the entire process of floc formation and sedimentation, a water sample was siphoned from a jar stirred at 22 mL/min through a 3 mm transparent plastic tube and continuously monitored. The methodology described was based on the 'turbidity fluctuation' technique (Yu et al., 2010b). The pump was located after the PDA to avoid the breakage of the generated flocs. The experimental procedure was similar to that of Braun et al. (2014).

In the PDA method, the average transmitted light intensity through the flowing suspension (DC value) and the root-mean-square value (RMS) of the fluctuating component are determined. The ratio of RMS to DC, which is termed the FI, is positively correlated with floc size. Thus, the value generated is used to characterize flocculation and aggregation during the coagulation process (Gregory and Nelson, 1986). In this study, in order to better understand the floc characteristics, three parameters (the Initial Floc Aggregation (IFA), the Relative Settling Factor (RSF) and the variance) were extracted from the FI results according to previous studies (Braun et al., 2014; Staaks et al., 2011). IFA and RSF represent the floc growth speed and sedimentation ability, respectively, while the variance indicates the size distribution and variation of flocs. Generally, relatively large and consistently sized flocs with good settling ability will contribute to good coagulation performance. Therefore, the objective of conventional coagulation should be to maximize IFA and RSF, while minimizing the variance of flocs (Braun et al., 2014).

1.5. Analyses of water quality

Analyzed parameters included pH, turbidity and DOC. Turbidity measurements were conducted using a 2100AN Laboratory Turbidimeter (Hach, USA) with results given in NTU. pH was determined by using a pH meter (MP220, Mettler-Toledo, Switzerland). DOC was determined for filtered water samples using pre-rinsed 0.45 μm membranes and analyzed using a Sievers 900 Total Organic Carbon analyzer (GE Analytical Instruments, USA). In this study, the % DOC removal was determined using the formula

$$\text{DOC removal} = \frac{\text{DOC}_{\text{raw-residual}}}{\text{DOC}_{\text{raw water}}} \times 100\%. \tag{2}$$

2. Results and discussion

2.1. Relationship of floc formation and filterability with coagulant dosage

Jar tests were performed to determine optimal coagulant dosages based on the minimum filtered water turbidity. Dosages tested were chosen based on an empirically determined concentration range. In previous studies, pH has been considered to be one of the most important factors affecting the interactions between coagulants and particles as well as the floc species (Jiao et al., 2015). Thus, keeping the pH conditions consistent during coagulant dosing is important for better insight into the influence of coagulant dosage on particle removal. To achieve this, pH was controlled at 7 during the whole coagulation process.

Fig. 1 shows the removal efficiencies of turbidity and DOC from Water I and Water II. Water I showed a higher coagulant dosage requirement to reduce turbidity compared with Water II, and the optimum dosages for turbidity removal were 50 mg/L

and 40 mg/L, respectively. In addition, Water I showed worse turbidity removal efficiency than Water II, with the turbidity removal rates of 47.3% (Water I) and 87.7% (Water II), respectively. Consistently, the DOC removal of Water II was higher than that of Water I. The highest removals were 42.5% for Water I and 49.8% for Water II. Over the usual pH range of natural water (pH 5–9), particles, colloids and NOM generally carry a negative surface charge (Duan and Gregory, 2003). The interaction between natural organic matter and clay in water is considered to result in particles having a negative surface charge that enhances colloid stability, and which inhibits coagulation behavior (Elfarissi and Pefferkorn, 2000; Kam and Gregory, 2001). The addition of clay to Water II did not decrease the overall removal efficiencies of turbidity and DOC in this study. It appears that under charge neutralization conditions only, increasing the number of particles contributed to poor coagulation performance. For $Al_2(SO_4)_3$, because of its instability, fast hydrolysis processes at high pH encouraged sweep flocculation, entrapment and adsorption as the main mechanisms of coagulation (Yang et al., 2010; Frommell et al., 2004). The addition of clay to Water II increased the particle density, which increased the inter-particle collision rate. This aided aggregation and the growth of flocs, thus improving coagulation performance.

This phenomenon is demonstrated in Fig. 2, which shows floc formation. FI is an index that is correlated to floc size and increases as flocs grow in size (Yu et al., 2010b). It was found

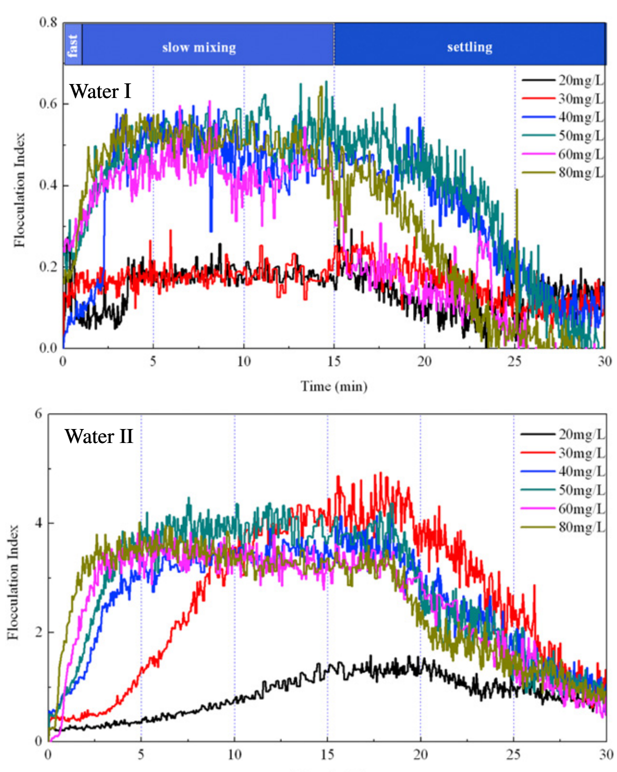

Fig. 2 – Effect of coagulant dosage on the floc formation indicated by Flocculation Index (FI). Coagulation conditions: 200 r/min for 1 min with the addition of aluminum sulfate at 30 sec (flash mixing); 40 r/min for14 min (slow mixing); 0 r/min for 15 min (sedimentation).

that Water II had a much higher FI value than Water I. Correspondingly, the Initial Floc Aggregation (IFA) indices (Fig. 3) of dosages of Water I were also significantly lower than those of Water II. This indicates that relatively small sized flocs were formed, with slow formation rate, and this led to poor performance in turbidity and DOC removal. Under sweep flocculation, floc aggregation and growth were mainly determined by the particle concentration in the water. The Relative Settling Factor (RSF) is an index that reflects the settling ability of flocs. Both IFA and RSF were correlated to the dosages. This means that increasing the dosage will accelerate floc aggregation, lead to an increase in the weight of flocs and accelerate the rate of settling.

The filtration process, as the final physical treatment after coagulation, is pivotal for maintaining good water quality. In actual operation, there are often residual flocs after sedimentation that require removal, and this is the main goal of filtration. Floc characteristics, such as size and density, affect filter efficiency, which not only correlate to residual turbidity, but also relate to the filter head loss. In this study, the filterability index was used to assess the filterability of flocs. The aim in conventional coagulation should be to obtain the minimum filterability index, which represents the highest filterability of flocs and lowest head loss.

Among all the factors, coagulant dosage has the most profound influence on floc characteristics and the filterability index. Fig. 4 compares the changes in filterability indices as dosages were increased for both water samples. Dosages for optimum filterability indices were higher than that required for turbidity removal, with values of 60 mg/L and 50 mg/L, respectively. Importantly, the optimal dosages obtained from RSF results closely coincided with the results of filterability indices. It is usually considered that the higher the RSF value, the heavier the floc, and then the better the settleability of the floc.

In order to better understand the relationship between filterability index and RSF, correlation analysis was performed. Fig. 4a shows a significant inverse correlation between RSF and filterability index ($R^2 = 0.7324$), meaning that under neutral pH conditions, good settling ability will contribute to good filterability of flocs. In other words, when the sweep flocculation mechanism is predominant, if there are fewer residual flocs left in the supernatant because of more efficient settling of large and heavy flocs, the filtration will achieve the highest turbidity removal efficiency and lowest head loss. Therefore, the sedimentation process is the determinant step that controls filter efficiency under the sweep flocculation mechanism. However, different coagulation mechanisms will affect the formation and growth of flocs differently (Jiao et al., 2015) and, correspondingly, the floc characteristics will also be different. The way that coagulation mechanisms impact the floc filterability is discussed further below.

2.2. Impact of pH on the floc filterability

As observed by other researchers, the mechanisms to explain coagulation include charge neutralization, adsorption and sweep coagulation (Gregor et al., 1997; Cheng et al., 2008). Under different conditions, the different mechanisms or their

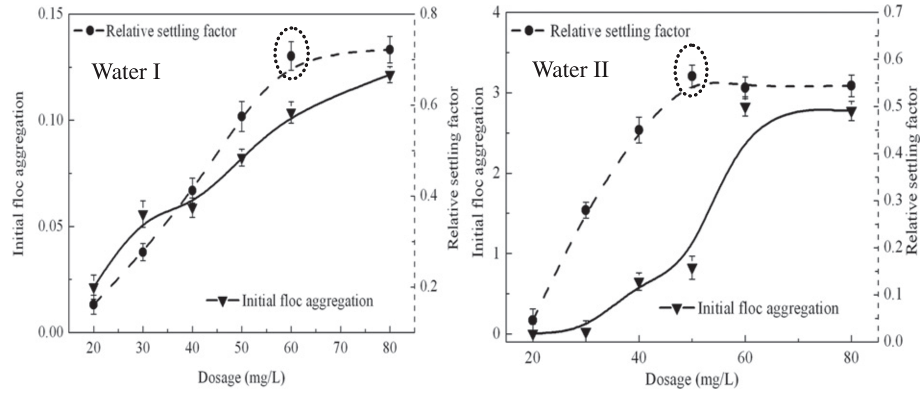

Fig. 3 – Photometric dispersion analyzer parameters measured at different coagulate dosages.

combination may be dominant. pH is the most important factor that affects the mechanisms of coagulation. For the monomeric coagulant $Al_2(SO_4)_3$, the influence of pH on coagulation mechanisms is correlated with the hydrolyzed species of the coagulant (May et al., 1979; Hu et al., 2006). Under raw water conditions, $Al_2(SO_4)_3$ would hydrolyze immediately after dosing and exist in the form of hydroxides before reacting with organic matter. According to the previous studies (Duan and Gregory, 2003; Yang et al., 2010), at pH lower than 5, positively charged hydrolysis products of Al^{3+}, including $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, and $Al_3(OH)_4^{5+}$ become the main species. However, Al species with high positive charge decrease as pH increases, and the concentration of dissolved Al reaches a minimum at pH 6.0–6.5 because of the formation of $Al(OH)_3$. Therefore, charge neutralization is dominant when pH is lower than 6.5. As the pH continues to increase, high polymeric hydrolysis products increase, and the particles are easily adsorbed and co-precipitated. Thus, sweep flocculation is dominant until pH reaches 8.0, when $Al(OH)_4^-$ becomes the main species.

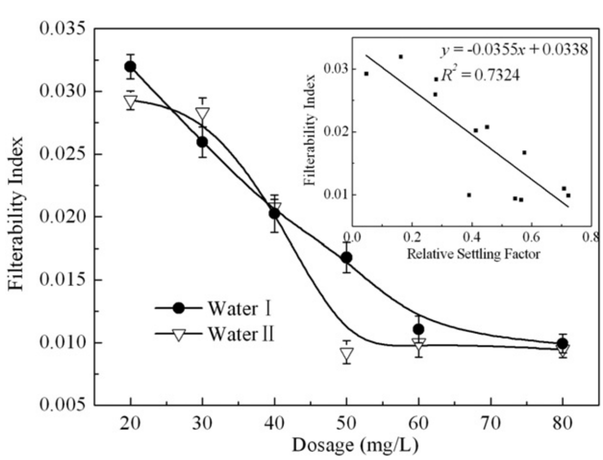

Fig. 4 – Influence of coagulant dosage on filterability index. The filterability index was obtained using the apparatus with dual media comprising anthracite and sand. In the experiment, the flow rate was 50 cm^3/min.

Given that pH has a key influence on coagulation performance, experiments with different pH values from 5.5 to 8.0 were performed. Doses of 60 mg/L (Water I) and 50 mg/L (Water II) were chosen according to the optimum floc filterability results. Fig. 5 shows the turbidity and DOC removals at different pH levels. By comparing these two water samples, clear differences in turbidity variation were observed as pH increased. For Water I, the optimum pH to reduce turbidity was pH 6.5. By comparison, the optimal pH was pH 5.5 for Water II. The results supported the theory that coagulation mechanisms change as the pH level changes. At low pH, charge neutralization plays an important role in particle removal. For Water II, addition of clay increased the negative charge, requiring more positively charged alumina-hydroxyl complexes to neutralize, while Water I, with lower negative charge, required less positive charge input (coagulant dose), and the optimum pH condition was found to be higher (Jiao et al., 2015). Due to the large amount of particles present in Water II, another turbidity minimum can be seen at pH 7.0 (coagulation mechanism changed from charge neutralization to sweep flocculation). Although better turbidity removal could be found for Water II at high pH level, the DOC removal efficiency of the two raw waters was similar in general. This may be because the raw water samples had the same DOC level. Moreover, both of the water samples showed a positive correlation between DOC and pH value. Generally, the charge neutralization mechanism showed better performance compared to sweep flocculation in the DOC removal (dissolved particle removal) process, while for turbidity removal (undissolved particles) the charge neutralization mechanism showed superiority only when raw water had high turbidity.

The FI at different pH levels was examined, and results are shown in Fig. 6. For Water I, the FI at pH lower than 7.0 (under the charge neutralization mechanism) was higher than at high pH level (under the sweep flocculation mechanism), which suggests that the floc size resulting from charge neutralization was larger. For Water II, the differences in FI at different pH were slight. From the results of IFA (Fig. 7), it was found that the flocs formed by charge neutralization also developed faster than those by sweep flocculation. For different applied coagulant dosages, RSF was positively correlated to IFA. The results at different pH followed different trends. When the pH is under 6.5, indicating charge neutralization is predominant, RSF is negatively correlated with

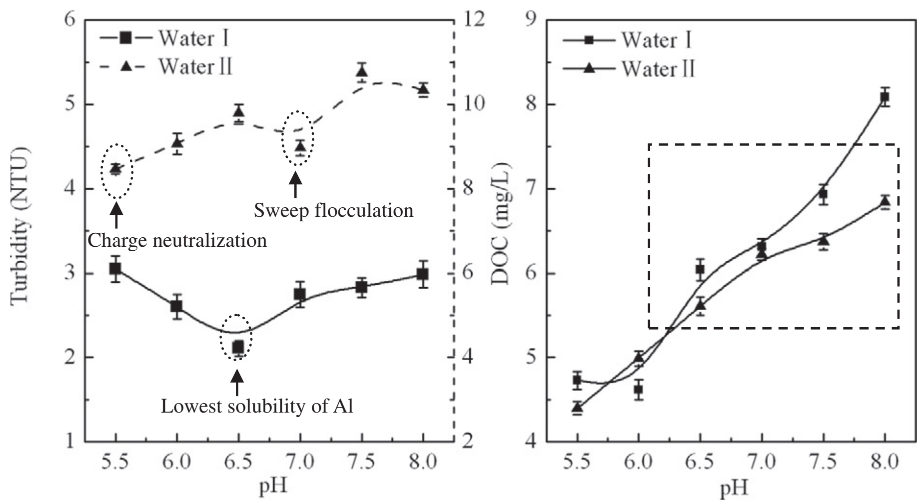

Fig. 5 – Effect of pH on residual turbidity and DOC. Coagulation dosages were 60 mg/L (Water I) and 50 mg/L (Water II).

IFA. This illustrates that the flocs formed by charge neutralization grow large rapidly but have relatively poor settling ability. Conversely, RSF, which is positively correlated to IFA at pH 7.0 and 7.5, corresponded well to the results of different dosage. At pH 8.0, the results reversed again, possibly because $Al(OH)_4^-$ complexes predominated.

Fig. 8 shows the influence of pH on the filterability index. This showed that the filterability index varied in accordance with turbidity removal. The optimum pH condition for minimizing the filterability index was pH 6.5 and pH 5.5/pH 6.0 for Water I and Water II, respectively, which were the same pH values required to maximize the reduction of turbidity for both water samples.

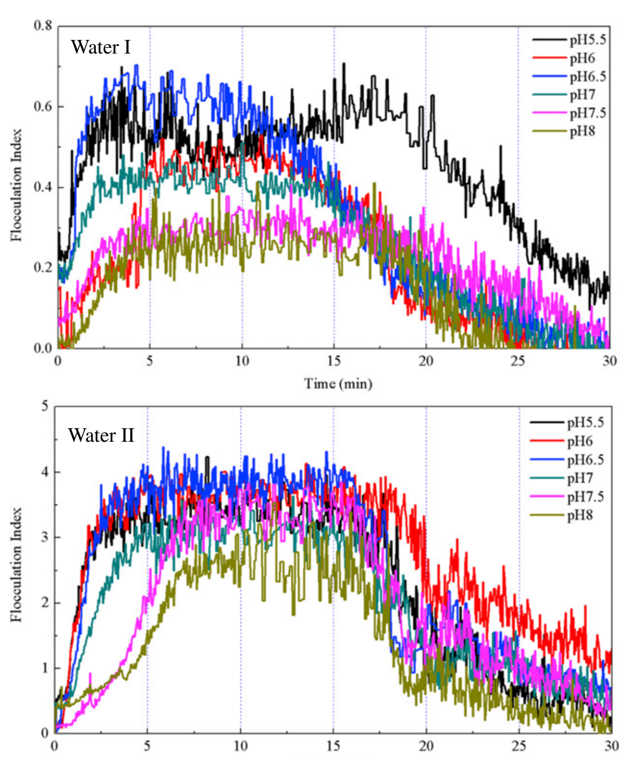

Fig. 6 – Effect of pH on Flocculation Index.

When comparing the RSF with the filterability index, poor correlation was found, and the relationship between these two factors followed the trend between RSF and IFA discussed previously. Therefore, the settling ability of flocs will only determine the filterability of flocs under the sweep flocculation mechanism. By analyzing another parameter, the variance, which represents the size distribution of flocs at equilibrium, it was found that the changes of variance along with the filterability index at various pH values were almost the same under the neutralization mechanism. Consequently, when the charge neutralization mechanism is dominant, the uniformity of the floc size distribution is a key factor that affects the filterability of flocs. This may be because the fractal dimension of flocs formed by charge neutralization is usually lower than those by sweep flocculation, even though the flocs appear large in size (Li et al., 2006). Thus, at low pH, when the flocs are slow to settle, similar sized flocs will be prone to form a filter cake layer, which promotes turbidity removal and minimizes the head loss; while at high pH conditions, larger but more variably sized flocs are formed, improving settling, which decreases the residual flocs introduced to the filter and which can also enhance the floc filterability.

3. Conclusions

This paper has evaluated the influence of two different raw water turbidities on coagulation mechanisms and floc properties using $Al_2(SO_4)_3$ as coagulant. In addition, the relationships between floc characteristics and filterability under different mechanisms were also studied.

(1) The optimum dosage for turbidity removal was lower than that for minimizing the filterability index, while the optimum pH for both turbidity removal and floc filterability was the same.
(2) Different turbidities in raw water will affect both the growth rate and size of flocs. Generally, flocs formed from water with higher turbidity grew faster and larger. In addition, under the sweep flocculation mechanism,

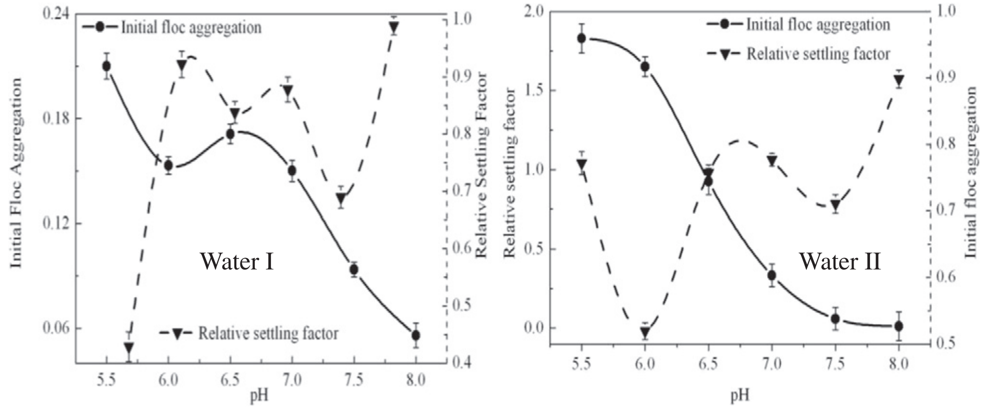

Fig. 7 – Effect of pH on PDA parameters.

higher turbidity contributed to greater DOC removal and better filterability of flocs.

(3) The charge neutralization mechanism showed better performance compared to sweep flocculation in dissolved particle removal and floc filterability improvement for both waters, and showed superiority in undissolved particle removal only when raw water had high turbidity.

(4) Under sweep flocculation, improving the settling ability of flocs and reducing the residual flocs after the sedimentation process is an alternative means to promote the filtration efficiency. However, when the charge neutralization mechanism is predominant, decreasing the floc size distribution will be favorable for floc removal by filtration processes.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51308008, 51179099), SA Water Visiting International Academics, Graduates, Researchers and Affiliates (VIAGRA) Fund and UniSA Visiting Researcher Fund are gratefully acknowledged.

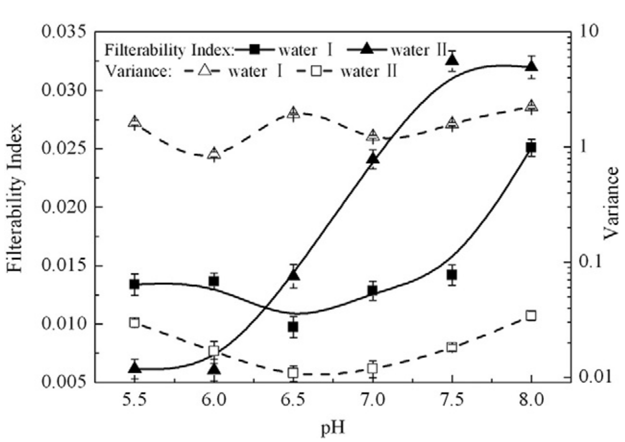

Fig. 8 – Influence of pH on filterability index and variance.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.01.006.

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