

Effects of Coagulation pH and Mixing Conditions on Characteristics of Flocs in Surface Water Treatment

* Zhun Ma¹⁾, Jian-Jun Qin²⁾, Cui-Xian Liou³⁾, Lifeng Zhang²⁾,
Suresh Valiyaveettil ⁴⁾

¹⁾ *NUS Environmental Research Institute, National University of Singapore,
5A Engineering Drive 1, T-Lab Building #05-03, Singapore 117411*

²⁾ *PUB, Singapore's National Water Agency,*

³⁾ *School of Civil and Environment Engineering, Nanyang Technological
University, Singapore*

⁴⁾ *Materials Research Laboratory, Department of Chemistry, National
University of Singapore, 3 Science Drive 3, Singapore 117543*

¹⁾ erimz@nus.edu.sg

ABSTRACT

This work aims at investigating the effects of coagulation pH and mixing conditions such as rapid mixing time, slow stirring speed and breakage period on characteristics of flocs during coagulation of surface water. Jar tests were systematically conducted in lab scale under different pH (5-7) and alum dosage (2.5-10 mg/L as Al). The formation, breakage and re-growth of flocs were evaluated by a continuous monitoring technique PDA 2000 in order to better understand the coagulation mechanism.

It was found that flocculation index was very significantly related to the floc size attribution. The flocculation index after breakage and re-growth was much smaller than before breakage when the coagulation mechanism was dominated by the charge neutralization. Coagulation rate, floc strength and recovery factor were calculated and the results showed that the coagulation rate was in the order of pH 5 > pH 7 > pH 6. However, the strength and recovery factor were higher at pH 6 than other pH, which indicated that the ability of flocs to resist the breakage at pH 6. Moreover, the coagulation rate and recovery factor decreased with an increase in alum dosage. It was concluded that the flocs generated at low pH demonstrated a much better recoverability (i.e. the ability of the broken flocs to re-grow to the size before breakage), which has not been reported so far.

Keywords: alum; floc strength; floc re-growth; charge neutralization

1. Introduction

Coagulation is a widely applied unit process for removing particles and organic matter present in water treatment works (WTW) (Jarvis 2005). One property that may have a significant impact at water treatment works is characteristics of flocs, which cause a critical effect on solid/liquid separation process (McCurdy 2004; Yu 2009). Therefore, flocs formed are strong enough to resist rupture under exposure to shear force and have a good recovery capacity.

Floc properties, such as floc size, strength and regrowth, play a crucial role during coagulation process. Boller and Blaser (1998) found that small particles generally had lower removal efficiencies in solid/liquid separation process following flocculation, since smaller particles generally settled down more slowly than larger particles of similar density. Generally, floc would be broken into smaller clusters in the regions of higher shear forces. Flocs must resist these stresses to prevent being broken up. Some researchers also reported that broken flocs were difficult to regrow, because their surface charge may be altered and partially re-stabilized (McCurdy 2004; Petzold 2004). Therefore, floc strength and recoverability are considered as a particularly important operational parameter in solid/liquid separation techniques for the efficient removal of aggregated particles. Floc characteristics of coagulants were comprehensively influenced by not only characteristics of water source and coagulants, but also various water quality parameters, such as applied shear force, solution pH, breakage period, etc. (Yukselen 2004; Hu 2006).

In this study, the major objectives were to investigate the breakage and regrowth properties of flocs formed by alum under different conditions in terms of different rapid mixing time, solution pH. The relationship between floc properties and coagulation mechanisms was also discussed.

2. Materials and method

2.1. Raw water and coagulant

Source waters for coagulation performance examination were withdrawn from Choa Chu Kang Water Works (CCKWW) in Singapore. The water was collected in March 2010 and the water temperature was at 29-31 °C. The raw water characteristics are shown in Table 1.

Table 1 Raw water characteristics

Characteristic	Value
Turbidity (NTU)	12.9-14.2
Total alkalinity as CaCO ₃	27.4-41.3
Ultraviolet light absorption at 254 nm (UV254) (cm ⁻¹)	0.101-0.181
Total organic carbon (DOC) (mg/L)	3.7-6.43
Zeta potential (mV)	-18.1—-20.1
pH	6.9-7.4

Aluminum sulfate hydrate (alum), analytical reagent, was used as coagulant. Stock alum solution was prepared at a concentration of 1 g/L and kept at 4 °C in a refrigerator.

2.2. Jar test

All reagents used were of analytical grade, and the solution pH was adjusted to 5, 6 and 7 by addition of 0.1 M NaOH or HCl. The experiments were conducted at a temperature of 24±1°C

Coagulation was conducted using a jar tester (JLT-6, VELP Scientifica, Milano, Italy) at different coagulant dosages and different pHs. As coagulant was added, stirring of the suspension was started at 200 rpm, which was chosen as the rapid mixing speed throughout this work. For different rapid mixing times, the stirring speed was maintained at 200 rpm for periods between 10 and 60 s, followed by a slow stirring speed of 50 rpm for 10 min, to allow flocs to grow. After this, the breakage phase at fixed 200 rpm for 30 s was operated to break the flocs and then restored to 50 rpm for 10 min and followed by a 30min settling period. The supernatant samples after settling were collected using a pipette from about 2 cm below the water surface for the measurements of turbidity, UV254 absorbance, zeta potential and TOC. The samples were prefiltered through a 0.45µm fiber membrane before testing for UV254 (absorbance at 254nm using a UV-754 UV/VIS spectrophotometer) and DOC (measured by a Shimadzu TOC-VCPh analyzer), while the turbidity was measured without microfiltration using a 2100Q01portable turbidimeter (Hach, USA) and zeta potential was analyzed with a Zetasizer Nano90S (Malvern Instruments, UK).

2.3 Floc formation, breakage and regrowth measurement

Experiments on the kinetics of formation, breakage and subsequent re-growth of flocs were carried out using a Photometric Dispersion Analyzer (PDA-2000, Rank Brothers, UK). The experiment process was similar to that of Yukselen and Gregory (2004). The PDA 2000 measures the average transmitted light intensity (dc value) and the root mean square (rms) value of the fluctuating component. The ratio (rms/dc) provides a sensitive measure of particle aggregation (Gregory 1986). The ratio value is strongly correlated with floc size and always increases as flocs grow larger. The ratio value is often called the Flocculation Index, FI. It significantly increases as aggregation occurs, and decreases when aggregates are broken. In this work, after the FI value reached an initial steady value, coagulant was added into the suspension and the FI value was recorded by a PC data acquisition system (Pico ADC-20, Pico Technology, UK) at 1 s intervals.

In this study, the coagulation rate is here defined as the rate of change of the FI value since this is directly related to the rate of change of floc size. It was

calculated in the same way as previously described (Xiao 2010).

$$C.R. = \frac{\Delta FI}{\Delta time} \quad (\text{coagulation rate}) \quad (1)$$

In order to characterize the efficiency in formation of flocs before breakage and after re-growth under different solution pH and dosage of coagulant, and to compare the shear resistance in different conditions, strength factor and re-growth factor were induced. The formulae were shown as follows (Yukselen 2002; Wei 2010).

$$F_1 = \frac{FIb}{FIa} \quad (\text{strength factor}) \quad (2)$$

$$F_2 = \frac{FIc - FIb}{FIa - FIb} \quad (\text{recovery factor}) \quad (3)$$

where FIa is the average flocculation index of the plateau before breakage, FIb is the flocculation index after floc breakage period, and FIc is the flocculation index after regrowth to the new plateau.

3. Results and discussion

3.1. Effect of pH and coagulant dose on coagulation performance

Fig. 1 presented the coagulation performance (including residual turbidity, UV254 and TOC removal efficiencies as well as zeta potential) of alum under different coagulant concentrations and pHs. The various doses for alum were 2.5, 5.0, 7.5, 10.0 and 12.5 mg/L as Al and solution pH was range from 5 to 7, respectively.

The coagulation with alum has been studied for decades, which suggests that it is achieved by charge neutralization, the bridge formation and sweep coagulation mechanism (Duan 2003; Gao 2005). As shown in Fig. 1a, the residual turbidity decreased significantly at a low alum dosage less than 2.5 mg/L under different pHs, and then remained approximately constant (<1.0 NTU) as the alum dosage further increased. From Fig. 1b and c it could be observed that the NOM removal efficiency increased with dosage increasing and reached steady value, which accompanied the increasing zeta potential (Fig. 1d). As the alum concentration increased, the negative charge of colloidal particles decreased and an isoelectric point appeared at about 2.5mg/L Al in pH 6. It was worthwhile to note that the relative coagulation efficiency at low dosages corresponded well with the neutralization ability of coagulant. Sharp (2006) and Wei (2010) also reported that the flocculation phenomenon was likely to be attributed to simple charge neutralization. As the coagulant dosage further increased, the positive charge became more dominant, which led to

electrostatic repulsion between particles. According to the zeta potential results, charge neutralization is believed to play a major role during the flocculation process using alum coagulant.

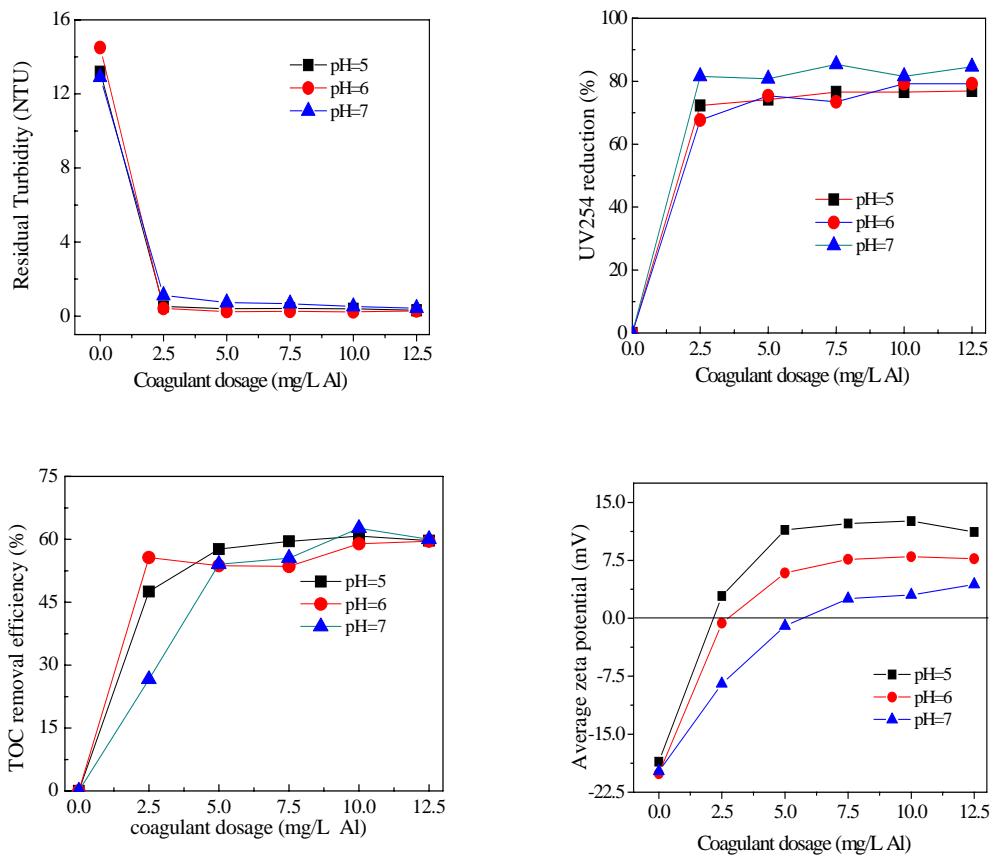


Fig. 1. Coagulant dosage and solution pH effect on the coagulation performance: (a) residual turbidity (b) UV254 removal efficiency (c) TOC removal efficiency (d) zeta potential

3.2. Effect of coagulant dosage on floc properties

As suggested by Wang (2009), the coagulation rate was adopted to investigate the floc formation process. The variation of coagulation rates as a function of coagulant dosage and pH was shown in Fig. 2. It implied that flocs formed quickly at lower solution pH, which was in the order of pH 5 > pH 7 > pH 6. As more coagulant was added, more particles could be destabilized throughout charge neutralization and efficient collisions, which led to the increase of aggregation at the initial aggregation. However, there was a various drop in the coagulation rate when the dosage was up to 7.5 mg/L under lower pH.

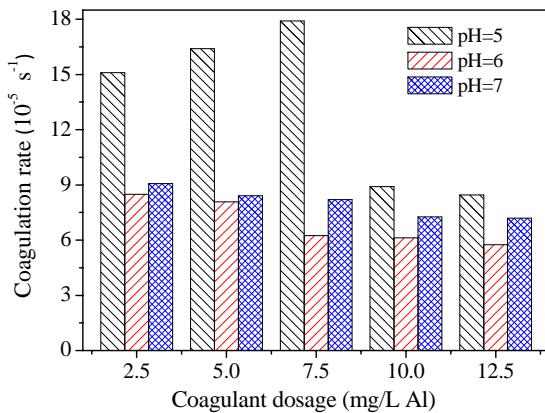


Fig. 2. Coagulation rate as a function of coagulant dose and pH

In order to analyze the floc breakage and re-growth, strength factor and recover factor were calculated as in Eq. (2) and Eq. (3), respectively. Figs. 3 and Fig. 4 presented the strength and recovery factors in surface water varied with coagulant doses and solution pHs. It could be seen that the strength and recovery factors were greatly impacted by solution pHs. The order of the strength factor was observed as follows: pH 6 > pH 7 > pH 5. Moreover, it was worthwhile to note that the strength factor was higher at a low dose of coagulant than that of high dose. As we known that the floc strength is closely related to the balance of attraction and repulsion between the particles (Boller 1998). When the dosage was low, there was not enough energy between the particles, which resulted in weak flocs. It could also be seen from Fig.4 that there was a significant drop in recovery factor at low dosages (2.5 and 5.0 mg/L) within the pH range investigated, and then a gradual decline followed as the dosage further increased. It should be noted that the re-growth factor was higher than 100% at low dose when charge neutrality dominates the coagulate mechanism. As the alum dosage increased, conditions become favorable for aluminum hydroxide precipitation. And the coagulation mechanism transformed to sweep flocculation. The results agreed well with the previous studies, which elucidated that flocs formed by charge neutralization can fully reform, while sweep flocs are irreversible after breakage (Yukselen 2004; Yu 2009).

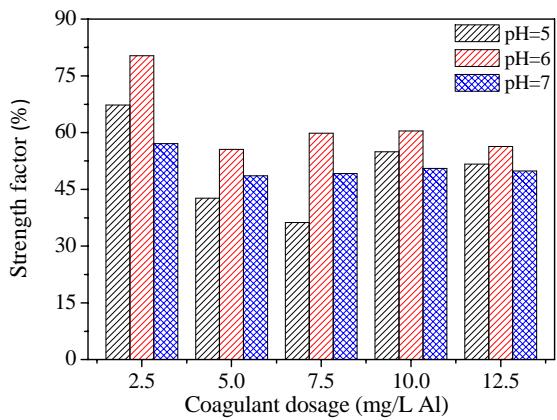


Fig.3 Strength factor of flocs at different coagulant dosage and solution pH

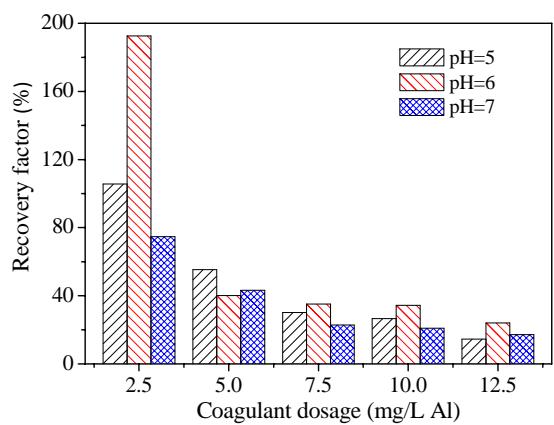


Fig.4 Recovery factor of flocs at different coagulant dosage and solution pH

3.3. Effect of rapid mixing on floc properties

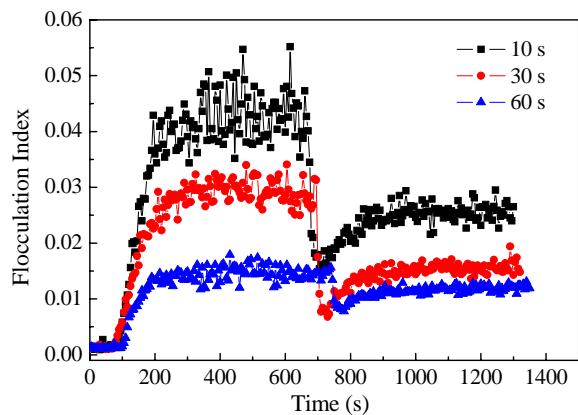


Fig. 5. Floc formation, breakage and re-growth for different rapid mixing times.
coagulation condition: pH=6 and 2.5mg/L Al as coagulant dose

Fig.5 presented the influence of different rapid mixing times on the increase of flocs size throughout the period of formation, breakage and re-growth. The FI values increased to a plateau during the slow stirring period, indicating a steady-state floc size, which implied there was a dynamic balance between floc growth and breakage. It was found that the FI value was greatly affected by the duration of rapid mixing. The plateau FI values before breakage decreased as the duration of rapid mixing increased from 10 s to 60s, perhaps because the longer exposure to high shear deteriorated the bonding forces between primary particles and reduced collision efficiency for small flocs. Amirtharajah and Mills (1982) suggested a fast destabilization process (less than 1 s) after alum dosage, so it is unlikely that mixing times greater than 10 s would give any change in the degree of destabilization. Actually, There would have large numbers of flocs collided mutually under long rapid mixing time. However, the balance between floc formation and breakage was broken and the nature of the floc surface was changed by the repeated breakage and reconnection of floc fragments (Yu 2010).

After breakage, the FI value was smaller than that before breakage and the regrowth of flocs had the same tendency as before breakage. It implied that the sizes of the broken and re-grown flocs were dependent not only on the applied shear conditions during breakage and re-growth and but also on the conditions during the initial floc growth. This was likely that the initial floc growth influence on the surface properties of flocs.

4. Conclusions

The formation, breakage and re-growth nature of flocs formed by alum laws comparatively investigated with CCKWW reservoir water under different operating parameters such as solution pH, coagulant dose and initial mixing time. The correlation of floc properties and coagulation mechanisms were also discussed. The main conclusions of this work are:

1. The coagulation rate was in the order of pH 5 > pH 7 > pH 6. However, the strength and recovery factor were higher at pH 6 than other pH,
2. Longer rapid mixing speed will cause lower plateau FI value, and the limited regrowth of flocs after breakage was occurred. This implied that the flocs not only were formed charge neutralization mechanism and but also might be held together by a chemical bonding rather than the physical bond.

Acknowledgement:

The authors thank the Environment and Water Industry Programme Office (EWI) under the National Research Foundation of Singapore (PUBPP 21100/36/2, NUS WBS NO. R-706-002-013-290, R-143-000-458-750, R-143-000-458-731) for financial support of the work.

Reference

- Amirtharajah, A., Mills, K.M., (1982), "Rapid-mix design for mechanisms of alum coagulation," *J. Am. Water Works Assoc.* 74, 210-216.
- Boller, M., Blaser, S., (1998), "Particles under stress," *Water Sci. Technol.* 37, 9-29.
- Boller, M. Blaser, S. (1998), Particles under stress, *Water Sci. Technol.* 37, 9-29.
- Duan, J., Gregory, J. (2003), "Coagulation by hydrolysing metal salts," *Adv. Colloid Interface Sci.* 100-102, 475-502.
- Gao, B.Y. Chu, Y.B. Yue, Q.Y., Wang, B.J., Wang, S.G., (2005), "Characterization and coagulation of a polyaluminum chloride (PACl) coagulant with high Al₁₃ content," *J. Environ. Manage.* 76, 143-147.
- Gregory, J., Nelson, D.W. (1986), "Monitoring of aggregates in flowing suspensions," *Colloids Surf.* 18, 175-188.
- Hu, C.Z., Liu, H.J., Qu, J.H., Wang, D.S., Ru, J. (2006), "Coagulation behavior of aluminum salts in eutrophic water significance of Al₁₃ species and pH control," *Environ. Sci. Technol.* 40 (1), 325-331.
- Jarvis, P., Jefferson, B., Parsons, S.A. (2005), "Breakage, re-growth, and fractal nature of natural organic matter flocs," *Environ. Sci. Technol.* 39 (7), 2307-2314.
- McCurdy, K., Carlson, K., Gregory, D. (2004), "Floc morphology and cyclic shearing recovery: comparison of alum and polyaluminium chloride coagulants," *Water Res.* 38 (2), 486-494.
- Petzold, G., Geissler, U., Smolka, N., Schwarz, S., (2004), "Influence of humic acid on the flocculation of clay," *Colloid. Polym. Sci.* 282, 670-676.
- Sharp, E.L., Jarvis, P., Parsons, S.A. Jefferson, B. (2006), "The impact of zeta potential on the physical properties of ferric-NOM flocs," *Environ. Sci. Technol.* 40 (12), 3934-3940.
- Wang, Y., Gao, B.Y., Xu, X.M., Xu, W.Y. Xu, G.Y. (2009), "Characterization of floc size, strength and structure in various aluminum coagulants treatment," *J. Colloid Interface Sci.* 332, 354-359.
- Wei, J.C., Gao, B.Y., Yue, Q.Y., Wang, Y. (2010), "Strength and regrowth properties of polyferric-polymer dual-coagulant flocs in surface water treatment," *J. Hazard. Mater.* 175, 949-954.
- Xiao, F., Ma, J., Yi, P., Huang, Ju.H. (2008), "Effects of low temperature on coagulation of kaolinite suspensions." *Water Res.* 42, 2983-2992.
- Xiao, F., Yi, P., Pan, X.R., Zhang, B.J., Lee, C. (2010), "Comparative study of the effects of experimental variables on growth rates of aluminum and iron hydroxide flocs during coagulation and their structural characteristics," *Desalination* 250, 902-907.
- Yu, W.Z., Li,G.B., Xu,Y.P., (2009), "Breakage and re-growth of flocs formed by alum and PACl," *Powder Technol.* 189 (3), 439-443.
- Yu, W.Z., Li, G.B., Xu, Y.P. and Yang, X. (2009), Breakage and re-growth of

- flocs formed by alum and PACl, Powder Technol. 189, 439-443.
- Yu, W.Z., Gregory, J., Campos, L., (2010) "The effect of additional coagulant on the regrowth of alum-kaolin flocs," Sep. Purif. Technol. 74, 305-309.
- Yukselen, M.A., Gregory, J. (2004), "The reversibility of floc breakage," Int. J. Miner. Process 73 (2-4), 251-259.
- Yukselen, M.A. Gregory, J. (2002), "Breakage and reformation of alum flocs," Environ. Eng. Sci. 19, 229-236.
- Yukselen, M.A., Gregory, J. (2004), 'The effect of rapid mixing on the break-up and reformation of flocs,' J. Chem. Technol. Biotechnol. 79, 782-788.