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Study of the Coagulation Property of Polyaluminum Silicate Chloride Coagulants Prepared with Ultrasonic-Assisted NaOH Dosing

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Abstract: Polyaluminum Silicate Chloride (PASiC) is a new water treatment coagulant. It contains silica that can be hydrolyzed to produce SiO_2 as coagulant aid. Hence, this coagulant consumes little alkalinity and is effective at low dosages. It is, therefore, especially suitable for treating water of low alkalinity and low turbidity. When manufacturing PASiC, the alkalinity solution involved in the polymeric reaction must be added slowly to the aluminum salt solution to avoid local over-saturation which enhances the production of high-valence medium polymer species (Alb) (e.g. $Al_{12}AlO_4(OH)_{24}^{7+}$, Al_{13}). In this research, the use of an ultrasonic vibrating system to assist the alkalinity dosing during the formation of PASiC was studied. The ultrasonic vibrating system breaks up the NaOH solution into fine mists so that the latter can be more evenly dispersed into the aluminum silica solution to avoid local over-saturation. This ultrasonic-assisted NaOH dosing method leads to a more stable polymerization of aluminum changing ratios of Ala, Alb, and Alc in the final product and raising the Alb portion in the coagulant. Long-term observations also show that PASiC prepared with the ultrasonic-aided NaOH dosing at 0.25 mL/min is more effective in removing turbidity.

Keywords: PASiC, ultrasonic, coagulation, Al-Ferron test, stability

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INTRODUCTION

Inorganic aluminum polymer coagulants such as polyaluminum chloride (PACl) are most commonly used in coagulation and flocculation in modern water treatment plants. According to recent research aluminum polymeric coagulants are composed of (Al^{3+}), $Al(OH)^{2+}$, $Al(OH)_{3(am)}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{12}AlO_4(OH)_{24}^{7+}$ (1). Also, the Al(III) in polymeric aluminum species, e.g. polyaluminum chloride (PACl), and polyaluminum silica chloride (PASiC), can be classified according to its degree of polymerization into three categories using the Al-Ferron test (2–5). The categories are: the monomeric (Ala), medium polymer (Alb) (e.g. $Al_{13}0_4(OH)_{24}^{7+}$, Al_{13}), and sol or gel species (Alc). The distribution of these Al(III) species in the coagulants depends on the solution basicity (B, $B = OH^-/Al^{3+}$) and also the dosing velocity of the NaOH solution into the aluminum salt solution when the polymeric coagulant is manufactured. Lowering the dosing rate will reduce the local over-saturation of ions to avoid a high ratio of gel aluminum (Alc) (5). However, no matter how low the alkaline dosing rate is, the size of the alkaline solution drops cannot be effectively controlled which still causes some over-saturation. Hence, the medium polymer (Alb) being the major species to proceed electrical neutralization during coagulation. Therefore, raising the Alb proportion in the coagulant imparts higher positive charges to the coagulant and enhances its hydrolysis stability (6). Of the various manufacturing methods that significantly influence the composition of the resulting coagulant, two methods, the separated and purified process and the electrolysis process have been extensively studied (6–9) in an attempt to raise the Alb proportion in the coagulant. The objective of this study was to use an alternative, simple, ultrasonic-assisted method to achieve a slow alkaline dosing solution during PASiC coagulant manufacturing. The NaOH solution was added with a peristaltic pump at the tip of an ultrasonic vibrator that instantaneously broke up the NaOH drops into finer microdrops. Hence, it was possible to disperse the OH^- ions evenly into the aluminum salt solution to react with the Al^{3+} ions without causing local super-saturation, which lead to the formation of $Al(OH)_3$ without coagulation capability. The coagulant manufactured using the ultrasonic-assisted NaOH dosing method was subjected to the Al-Ferron test to analyze its composition. Jar tests were also done to investigate its long-term stability.

MATERIAL AND METHODS

Method for Manufacturing PASiC

The PASiC coagulants used in this study were prepared in the laboratory according to a method developed by Gao et al. (10). The final PASiC solution, with a basicity (B) of 1.5 and an Al/Si ratio of 5, was prepared by adding 23.5 mL 1.5 M HCl solution into 50 ml 0.5 M SiO_2 solution while stirring rapidly. The mixture's pH was adjusted to 2 to yield a 0.329 M polysilicate (Psi). Another aliquot of 40 mL 0.25 M $AlCl_3$ solution was diluted with de-ionized water of a pre-determined volume. Based on the required Al/Si ratio, the prepared $AlCl_3$ solution was added to 6.28 mL of the Psi solution. Using the setup shown in Fig. 1, 30 mL 0.5 M NaOH solution was dosed with a peristaltic pump at flow rates of 3 mL/min and 0.25 mL/min respectively through the tip of an ultrasonic vibrator into the aluminum silica solution for the polymerization of aluminum and silica. The dosing durations were 10 minutes for 3 mL/min rate and 2 hours for 0.25 mL/min rate. After the addition of the NaOH solution, the final volume was 100 mL containing 0.1 M Al. The SONIFIER 450 Ultrasonic Vibrator (Branson Co. USA) was set at 150 Watt output power. Additionally, the coagulant was also prepared by dosing the NaOH solution without ultrasonic assistance at a rate of 0.05 mL/min for a 10-h dosing duration and a rapid direct NaOH dosing.

Al-Ferron Test

(a) Ferron solution: Prepared by dissolving 0.4 g Ferron (8-hydroxy-7iodo-quinoline-5-sulfonic acid) (Fluka) in 200 mL de-ionized water.
(b) HOAc/NaOAc buffer solution: Prepared by mixing 100 mL 4 M sodium acetate solution with 100 mL 1 M acetic acid solution. It was prepared

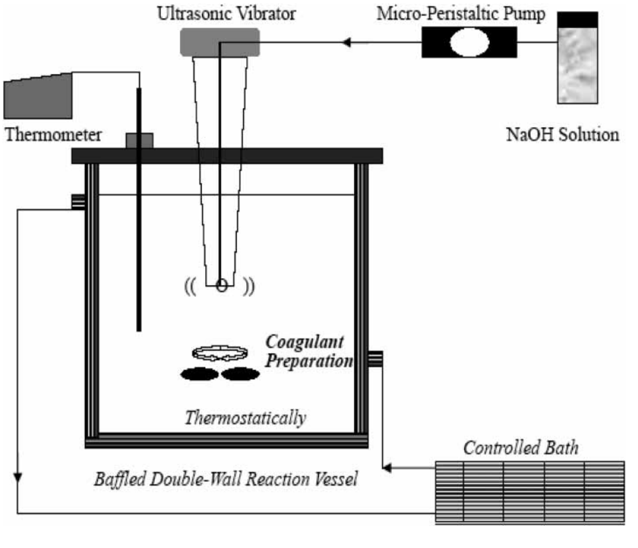

Figure 1. Schematic diagram of the ultrasonic-aided NaOH dosing setup for preparing PASiC.

before the experiment by mixing the aforementioned Ferron solution into the acetate buffer.

To analyze the aluminum concentration, 10 μL sample was added to 5 mL water that had the same pH value as the sample thus diluting the aluminum concentration to within the aluminum calibration curve range ($5 \times 10^{-5} \sim 2.5 \times 10^{-4}$ M); 5 mL Ferron reagent was immediately added to the diluted sample. The mixture was placed in a 10-mm quartz cell to measure the absorbance at 370 nm wavelength in a DR/4000U Spectrophotometer (Hach Co. USA). The absorbance measurements were made after 1 min for 2 h. The 1 min absorbance as Ala, the absorbance increase from 1 min to 2 h as Alb, and Alc was obtained as the total Al minus Ala and Alb.

Jar Test and Stability Test

Synthetic water samples were prepared in the laboratory by mixing SiO_2 in 1 L de-ionized water and adding 0.072 g $NaHCO_3$ and 1.2244 g $NaClO_4$ to yield a final alkalinity and turbidity of raw water with 10 NTU, 50 mg/L as $CaCO_3$ and 0.01 M ion strength. Jar tests were performed in a sequence of 40-sec rapid mixing at 100 rpm, 15-min flocculation at 20 rpm, and 15-min settling. Samples were taken from 3 cm below the surface of the water and the HACH-2100 turbidity measuring meter was used to measure the residual turbidity. The residue of the dissolved aluminum in the filtrates that had been filtered through a 0.45 μm membrane was determined by absorption at 535 nm using the ERC (Eriochrome Cyanide R) method (11). The coagulation was repeated with the coagulants that had been aged for 30, 90, and 120 days to test stability.

Floc Distribution Curve

During the slow mixing period, flocs that were formed from the polymeric coagulant had various sizes; the time for forming flocs and their sizes was influenced by slow mixing. In order to prove that the coagulant prepare by ultrasonic-aided method would speed up the floc formation and increase the floc size, samples were collected at 5, 10, and 15 minutes after the onset of the slow mixing 3 cm below the liquid surface for analysis of floc numbers and size distribution using a particle size analyzer (Pacific Scientific, 8000A HRLD-400HC). The results were used to calculate the volume of flocs with various diameters; the floc distribution curve was obtained by plotting floc volume versus floc diameter.

RESULTS AND DISCUSSION

Influence of the Manufacturing Processes on PASiC

In general, the dosing rate of the NaOH solution should not be too fast when manufacturing the inorganic polymeric coagulant. If so, the resulting polymerization of aluminum and silica will not be uniform. Therefore, the NaOH dosing is usually carried out under 0.05 mL/min. In this research, the four coagulant polymers were prepared by

1. using the rapid direct NaOH dosing
2. ultrasonic-aided NaOH dosing at 3 mL/min for 10 minutes
3. ultrasonic-aided NaOH dosing at 0.25 mL/min for 2 hours, and
4. traditional NaOH dosing at 0.05 mL/min for 10 hours.

Table 1 shows that the PASIiC produced using the rapid NaOH dosing method contained 51.52% aluminum monomer (Ala) because of incomplete polymeric reaction between the aluminum and OH^- ions. Additionally, the rapid reaction between NaOH solution drops and aluminum silica solution resulted in over-saturation leading to the formation of 13% gel or $Al(OH)_3$. Using the ultrasonic-aided dosing at 3 mL/min, the Al-Ferron test results indicated that compositions of the polymer were similar to those obtained using the direct rapid NaOH dosing method. This observation demonstrated that if the NaOH dosing rate was not low enough, the over-saturation problem could not be avoided either with or without the use of ultrasonic dosing. With ultrasonic-assisted NaOH dosing, the resulting aluminum chloride polymer contained higher medium aluminum polymer (Alb) and lower gel aluminum (Alc). Using a 0.25 mL/min NaOH dosing rate for 2 hours, the resulting polymeric aluminum chloride contained 61.61% medium polymer (Alb) and only 0.003% gel aluminum. Thus, the ultrasonic vibration for more than 2 hours will be effective in reducing the production of gel aluminum (Alc). In comparison, the aluminum silica polymer prepared using the traditional 0.05 mL/min NaOH dosing rate contained 51.34% medium (Alb) but still 11.85% Alc indicating that without ultrasonic

Table 1. Distribution of the various components of the aluminum chloride polymers prepared with the different NaOH dosing methods

	0.05 mL/min without ultrasonic	directly without ultrasonic	3 mL/min with ultrasonic	0.25 mL/min with ultrasonic
Ala%	36.8	51.52	49.75	38.05
Alb%	51.34	35.5	37.54	61.61
Alc%	11.85	13	12.71	0.003

assistance, the lowest practical NaOH dosing rate could not avoid over-saturation. These results revealed that the ultrasonic vibration-assisted method greatly reduced the NaOH dosing duration while raising the percentage of medium polymer in addition to reducing the aluminum gel percentage.

The time-dependent turbidity variation, shown in Table 2, revealed that the polymeric coagulant produced with the ultrasonic-aided 0.25 mL/min NaOH dosing method did not show obvious turbidity while other polymers did. The direct rapid NaOH dosing method, especially, caused un-even dispersion of NaOH leading to unstable polymers to form a large quantity of gel or $Al(OH)_3$. Thus, the turbidity change of the polymer solution revealed that the polymer had been produced under stable conditions that caused a stable hydrolysis.

Jar Test on Polymer Stability

Jar tests to study the stability of the prepared polymers that had been left undisturbed for 0, 30, 90, and 120 days were performed; the results are shown in Fig. 2(a). Without aging, the polymer was not effective in flocculating turbidity as mentioned in the literature; the polymeric coagulant has to be left un-disturbed for a certain period to age (10, 12). The aging process makes the polymer molecules grow and become stable (13). After one month of aging, the results of the beaker test, as shown in Fig. 2(b), indicated that all four coagulants achieved turbidity removal; the PASiC prepared using ultrasonic-aided NaOH dosing at 0.25 mL/min and the direct rapid NaOH dosing showed good turbidity removal with the residual turbidity less than 1 NTU. After 90 and 120-day aging, as shown in Figs. 2(c) and (d), the PASiC prepared using the ultrasonic aided NaOH dosing at 0.25 mL/min produced the best results in the removal of turbidity to less than 1 NTU at low dosages. The other three PASiC polymers did not show such a good stability. Results of the Jar tests demonstrated that the ultrasonic-aided NaOH dosing at 0.25 mL/min resulted in the more stable PASiC polymer being used for treating water of low turbidity at lower dosages than the other three methods studied in this research.

Table 2. Aging of the aluminum silica polymer

	Change of turbidity			
Aging time	0.05 mL/min without ultrasonic	Directly without ultrasonic	3 mL/min with ultrasonic	0.25 mL/min-with Ultrasonic
No aging	230	17.7	159	277
30 Days	260	259	246	233
90 Days	365	485	383	234

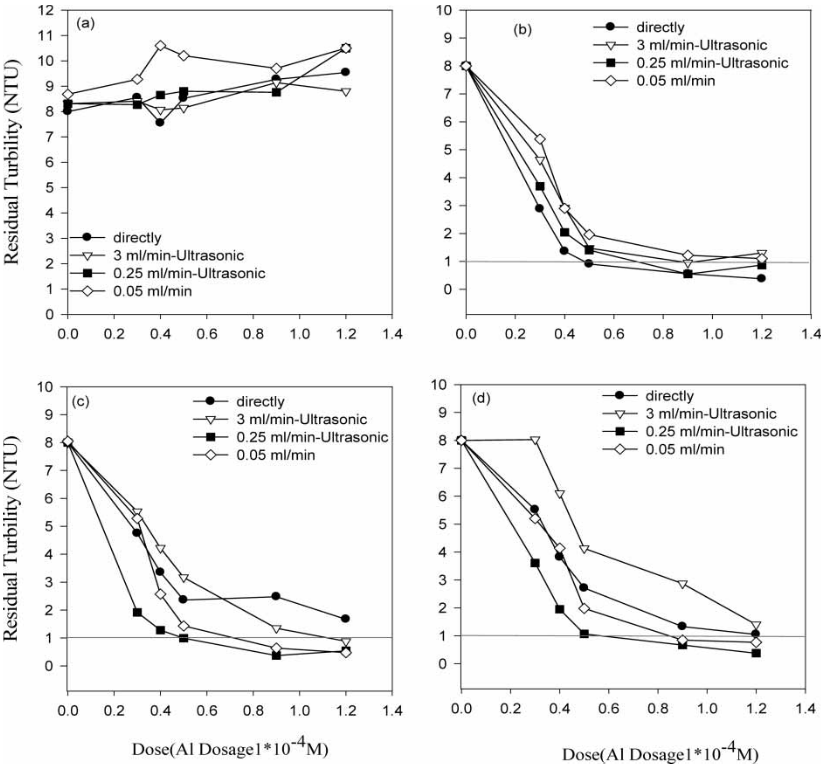

Figure 2. Comparison of the stability of polymeric coagulants produced with the different NaOH dosing methods for (a) 0 days, (b) 30 days, (c) 90 days, and (d) 120 days aging.

The efficiency for treating water of low turbidity was evidenced, not only by the coagulant stability in the jar tests, but also by the speed of aluminum floc formation; the Alc value played an important role in the coagulation efficiency. As shown in Fig. 3, without aging, all four coagulants contained low Alc leading to insufficient aluminum silica flocs to supplement the low turbidity and hence the coagulation efficiency was not satisfactory. After 30-day aging, all four coagulants contained 40–50% Alc and exhibited satisfactory coagulation efficiencies. Figure 3 also reveals that the Alc was proportional to the aging time but the Alc increasing rates were different for coagulants produced using different NaOH dosing methods. After aging 90–120 days, the PASiC produced with the ultrasonic-added 0.25 mL/min NaOH dosing rate showed a lower Alc increasing rate than the other three coagulants. This was mainly because the aluminum and alkaline solutions were evenly mixed reducing local super-saturation that controled the aluminum polymeric formation speed and maintained the best hydrolytical

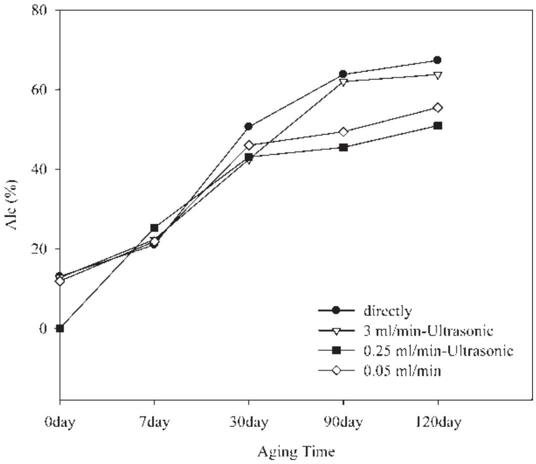

Figure 3. Variation of Alc for different aging times.

stability. A low dosage of the coagulant led to the formation of sufficient aluminum flocs to compensate for the insufficient turbidity resulting in satisfactory coagulation; the residual solution aluminum in the coagulated water was also low. Since the residual soluble aluminum in the coagulated water could have an adverse health impact causing Alzheimer disease, WHO and USEPA limit the residual aluminum in drinking water to below 100 ppb (14). The results shown in Fig. 4 indicate that after 30-day aging, the PASic produced with the ultrasonic-aided 0.25 mg/min dosing rate produced good coagulation with doses of below $0.3-0.9 \times 10^{-4}$ M. Although the coagulant prepared with the rapid NaOH dosing method also had good coagulation, the coagulated supernatant contained 80 ppb soluble aluminum concentration as measured on the filtrate through 0.45 μm filter paper; it was twice as much as that obtained with the coagulant prepared with the ultrasonic-aided 0.25 mL/min NaOH dosing method. This observation clearly demonstrated the instability of the coagulant prepared with the rapid NaOH dosing method.

Floc Size Distribution Curve

The size of flocs formed during the coagulation process and their formation time influenced the subsequent water treatment operations and processes. When relatively large flocs were formed during the flocculation period, less time was needed for the slow mixing and the quiescent periods. The number and volume of flocs formed in the coagulation process with addition of 0.9×10^{-4} M for the four coagulants produced using different NaOH dosing methods were investigated. Samples were collected at 5, 10,

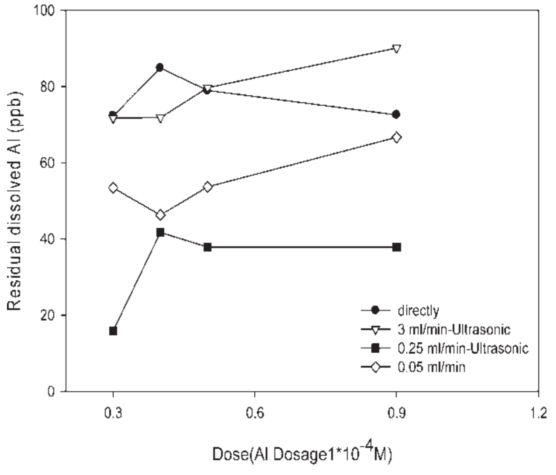

Figure 4. Variation of the residual aluminum concentration after 30 days.

and 15 minutes of the slow mixing period at 3-cm depth below the water surface for the floc particle size analyzer to determine the floc size distribution and formation time. For coagulants with no aging, Figs. 5(a), 6(a), and 7(a) show that there was no obvious floc formation in all cases. Small flocs with diameters below 10 μm were observed to appear but they do not agglomerate to form large settleable flocs. In comparison, after aging for 30 days, jar tests indicated that all the coagulants coagulated satisfactorily and that there was no change in the residual turbidity for higher coagulant dosages. Samples of floc

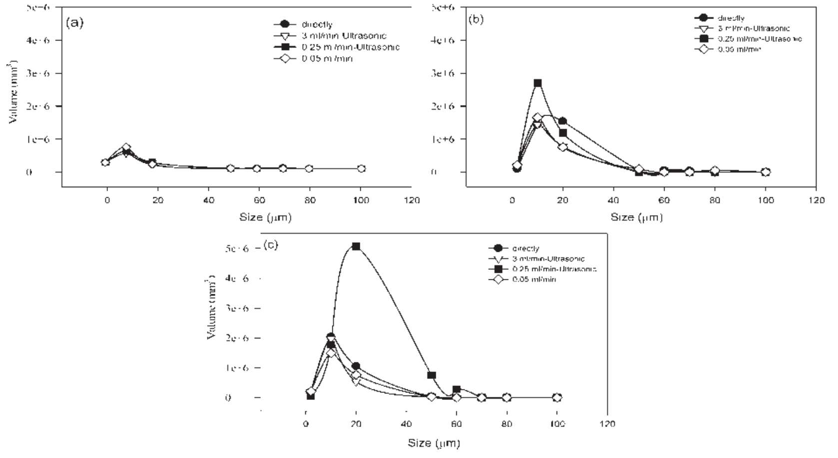

Figure 5. Floc distribution for samples collected after 5 minutes of the slow mixing period; (a) no aging, (b) 30 days aging, and (c) 90 days aging.

distribution collected at different times of the slow mixing period showed exaggerated differences in floc agglomeration capability for the various coagulants. Figure 5(b) shows that 5 minutes into the slow mixing period, small flocs started forming for the coagulant manufactured with the ultrasonic-aided 0.25 mL/min NaOH dosing method. Figure 6(b) shows that in the 5 and 10 minute samples, obvious large flocs had been formed for all coagulants with a diameter distributed mainly between 20 to 50 μm. Only the sample treated with the coagulant produced with the rapid NaOH dosing method showed no obvious changes. Samples collected at the end of the slow mixing period, as shown in Fig. 7(b), showed large flocs for all coagulants. The flocs formed with the ultrasonic-aided 0.25 mL/min aluminum dosing coagulant were the largest with diameters ranging from 20 to 80 μm; the volume was about 3 times that of the other coagulants. After aging for 90 days, Figs. 5(c) and 6(c) show that the coagulant prepared using the ultrasonic-aided 0.25 mL/min NaOH dosing method formed flocs within 5 minutes, which is faster than for the other three coagulants. Additionally, all coagulants aged for 30 days produced large flocs at 10 minutes of slow mixing as shown in Fig. 6(b). But, with 90-day aging, Fig. 7(c) shows that, except with the coagulant prepared using the ultrasonic-aided 0.25 mL/min NaOH dosing method, all coagulants had to be slowly mixed for at least 10–15 minutes before floc formation. The aforementioned results clearly demonstrate that the ultrasonic-aided 0.25 mL/min NaOH dosing method produced a coagulant with good stability as well as an enhanced floc formation time.

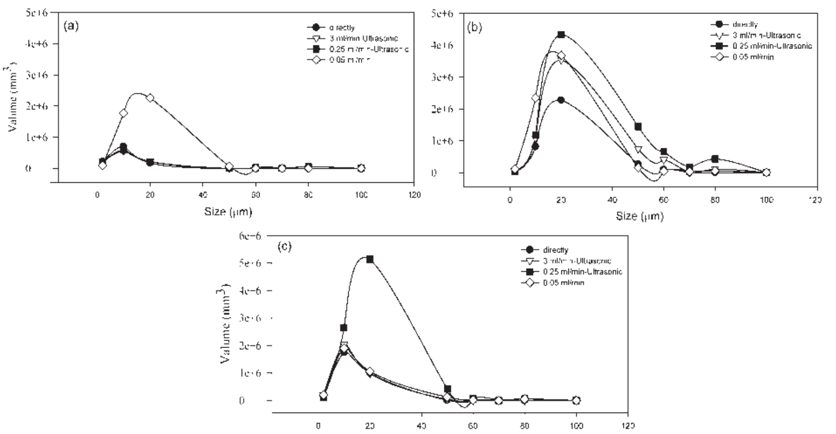

Figure 6. Floc distribution for samples collected after 10 minutes of the slow mixing period; (a) no aging, (b) 30 days aging, and (c) 90 days aging.

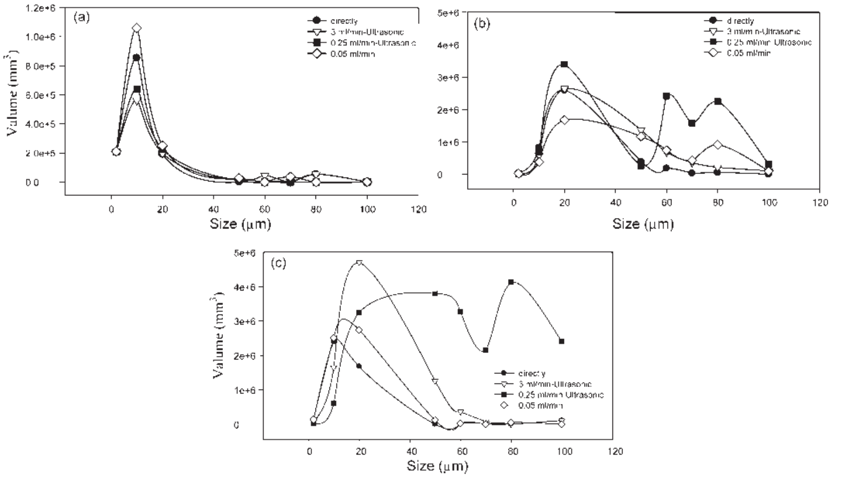

Figure 7. Floc distribution for samples collected after 15 minutes of the slow mixing period; (a) no aging, (b) 30 days aging, and (c) 90 days aging.

CONCLUSION

Results of the Al-Ferron test confirmed that the ultrasonic-aided NaOH dosing method greatly reduced the NaOH dosing time in the preparation of PASiC coagulant; this method also raised the Alb and reduced the Alc ratios. The resulting PASiC of the ultrasonic-aided NaOH dosing method had a relatively higher portion of positively charged polymeric aluminum and was more stable than the coagulants prepared without it; this PASiC, after a long period of aging, also coagulated more effectively than the other PASiC solutions. Additionally, using coagulants that had been aged for 1 to 4 months in kaolinite synthetic water, the PASiC prepared with the ultrasonic-aided 0.25 mL/min NaOH dosing method formed relatively larger flocs with relatively lower residual aluminum concentrations in the treated water than other coagulants.

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REFERENCES

1. Gao, B.Y., Chu, Y.B., Yue, Q.Y., Wang, B.J., and Wang, S.G. (2005) Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al_{13} content. *Journal of Environmental Management*, 76: 143–147.

2. Smith, R. W. (1971) Reactions among equilibrium and non-equilibrium. *Adv. Chem Ser.*, 106: 250–257.
3. Jardine, P.M. and Zelazny, L.W. (1986) Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with ferron. *Soil Sci. Soc. Am. J.*, 50: 885–900.
4. Parker, D.R. and Bertsch, P.M. (1992) Identification and quantification of Al13 tridecameric polycation using ferron. *Environ. Sci. Technol.*, 26 (5): 908–914.
5. Wang, D.S., Sun, W., Xu, Y., Tang, H.X., and Gregory, J. (2004) Speciation stability of inorganic polymer flocculant-PACl. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 243: 1–10.
6. Chu, Y.B., Gao, B.Y., Yue, Q.Y., Wang, S.G., and Wang, Y. (2005) Purification of Al_{13} species in polyaluminum chloride (PAC) by column chromatography and the character of the fractions. *Environmental Science*, 26 (3): 87–91 (In Chinese).
7. Liu, H.J., Qu, J.H.; Hu C. Z., and Zhang, S.J. (2003) Characteristics of nanosized polyaluminum chloride coagulant prepared by electrolysis process. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 216: 139–147.
8. Qu, J.H. and Lin, H.J. (2004) Optimum conditions for Al_{13} polymer formation in PACl preparation by electrolysis process. *Chemosphere*, 55: 51–56.
9. Xu, Y., Wang, D.S., Liu, H., Lu, Y.Q., and Tang, H.X. (2003) Optimization of the separation and purification of $Al_{13.}$. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 231: 1–9.
10. Gao, B.Y., Hahn, H.H., and Hoffmann, E. (2002) Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment. *Water Research*, 36: 3573–3581.
11. APHA-AWWA-WEF (1998) *Standard Method for the Examination of Water and Wastewater*; APHA: Washington, DC.
12. Gao, B.Y., Yue, Q.Y., and Wang, B.J. (2002) The chemical species distribution and transformation of polyaluminum silicate chloride coagulant. *Chemosphere*, 46: 809–813.
13. Cheng, W.P., Chi, F.H., and Yu, R.F. (2006) Evaluation the ability of polyaluminum silicate chloride coagulants for turbidity removal efficiency. *Separation Sci. Technol.*, 41 (2): 297–308.
14. Twort, A.C., Ratnayaka D. D., and Brandt, M.J. (2000) *Water Supply*, 5th edn.; Arnold: London.