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Electrokinetic characteristic and coagulation behavior of flocculant polyaluminum silicate chloride (PASiC)

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Abstract: The electrokinetic characteristics and coagulation behaviors of polyaluminum silicate chloride (PASiC) and polyaluminum chloride (PAC) were studied and compared by streaming current (SC) measurement and jar test method. The experimental results showed that the interaction between polysilicic acid characterized negative charge and hydrolyzed aluminum species result in a decrease of the charge-neutralizing ability of PASiC, compared to PAC. The decrease has a close relationship with the basicity (*B*) and Al/Si molar ratio in PASiC. The less the *B* value and the Al/Si molar ratio, the lower the charge-neutralizing ability of PASiC is. In contrast, the preparation technique for PASiC affects the charge – neutralization of PASiC to a smaller extent. In addition, compared with PAC, PASiC may enhance aggregating efficiency and give better coagulating effects.

Keywords: flocculant polyaluminum chloride (PASiC); streaming current (SC); electrokinetic characteristics; coagulation effect

Introduction

The study on the coagulation-flocculation process of inorganic polymer coagulant in water and wastewater treatments generally involves two aspects. One is the study of the hydrolysis-polymerization process, the species and their transformation of inorganic metal salt in water, and the other is the study of the colloidal particle destabilization process caused by hydrolyzed products of the coagulant acting on colloid particles. Since the destabilization of colloidal particles in water is closely related to the density of electrical charges of coagulant added in water, the electrokinetic characteristic of coagulant itself is usually taken as a very important aspect during the research on the colloidal destabilization. At present, streaming current (*SC*) and micro-electrophoresis are two important methods to investigate the electrokinetic characteristics of coagulant and to judge the flocculation (Black, 1965; Tang, 1995). The micro-electrophoresis measurement is a technique to observe the moment velocity of charged particles in electric field and then to calculate the zeta potential of colloid particles. Since zeta potential is an important parameter to illustrate the electrokinetic characteristics of colloid, it can be regarded as an effective indicator to judge the destabilization degree of colloid particles during coagulation/flocculation after the coagulant is added in the water, and is also very useful to investigate coagulation/flocculent mechanism. However, there exist following disadvantages when measuring zeta potential: lower precision, poor repeatability, and impossible to be used in on-line monitoring and successive detection. In order to overcome these disadvantages, SC has recently become widely used to investigate the electrokinetic characteristics of coagulant and the charge neutralization effect of coagulant on the surface of colloid particle (Qu, 1997). Further, the zeta potential reflects the charge condition of colloid diffuse layer, which is thought to be equal to the potential of diffuse layer, and SC results from the separation of the diffuse layer and fixed layer. Therefore, zeta potential and SC are linearly related theoretically (Dentel, 1991), and may quantitatively reflect the charge of inorganic coagulant in water and the charge neutralization of inorganic coagulant on colloid particle surface.

In this paper, poly-aluminum-silicate-chloride (PASiC) is prepared by two procedures, and the electrokinetic characteristic and coagulation behavior of PASiC has been examined by SC measurement and jar test method in comparison with polyaluminum chloride (PAC), respectively. The initial results of the conditional experiments will be very useful for further investigating on the flocculating effect of PASiC and its coagulation/flocculation mechanism.

1 Materials and methods

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1.1 The preparation of PASiC coagulant

The preparation of PASiC coagulant was carried out as described earlier(Gao, 1999). Briefly, stock solution of 1.0781 mol/L $AlCl_3$ was diluted with deionized water into 0.25 mol/L $AlCl_3$ before preparing the PASiC coagulant. Two approaches were used to prepare PASiC: (1) Slowly titarate quantitatively diluted $AlCl_3$ solution with 0.5 mol/L NaOH solution to obtain the desired [OH]/[Al] ratio PAC solution using 655 dosimat micro-titration apparatus. The [OH]/[Al] ratio was denoted as B, where [OH] and [Al] is the total concentration of OH and Al added in solution, respectively. During the titration at a rate of 0.05 ml/min NaOH solution, the 655 dosimat micro-titration apparatus was used to record the change of pH, and it was thoroughly stirred ($\approx$ 300 r/min) to obtain homogeneous solution, with a final aluminum concentration (denoted by Al_T) of PAC solution at 0.1 mol/L. Then, the PAC was combined with polysilicic acid aged for 2 hours at Al/Si ratio $\geqslant 5$ to obtain poly-aluminum-silicate-chloride (PASiCm) coagulant, with an Al_T of 0.094 ~ 0.098 mol/L; (2) mix the diluted $AlCl_3$ solution and fresh polysilicic acid at different Al/Si ratios before adding base. Then, the 0.5 mol/L NaOH solution was slowly added (0.05 ml/min) and thoroughly stirred to obtain desired *B* value and different Al/Si ratio poly-aluminum-silicate-chloride (PASiCc) coagulant with 0.1 mol/L Al_T. Also, during titrating, the 655 dosimat micro-titration apparatus was used to record the change of pH, and vigorously stir the solution ($\approx$300 r/min) to make it homogeneous. Finally, cope, seal and store the prepared coagulant samples overnight at 20℃ prior to any analysis.

1.2 SC measurement method

SC value was successively determined by a SC-30S streaming current detector (SCD). During experiments, different coagulant doses were added into 2.0L test water made of 1.0L deionized water and 1.0L tap water. Then, the water was rapidly stirred by a magnetic stirrer; and the *SC* values under different experimental conditions were recorded. Also, the pH value was adjusted with 0.1 mol/L hydrochloric acid or 0.1 mol/L sodium hydroxide solution.

1.3 Jar test procedures

Using jar testing on a six-paddle gang stirrer carried out coagulation experiments. The test water was drawn from Wohu Mountain Lake in Jinan City of China. The 500 ml test water was dosed with different coagulant to give final concentrations in the range of 0.5—8.5 mg/L (as Al_2O_3 + SiO_2). The solutions were stirred rapidly at 120 r/min for 2 min during coagulant addition, followed by slow stirring at 60 r/min for 8 min and 10 min sedimentation. After sedimentation, a supernatant sample was withdrawn for study.

2 Results and discussion

2.1 Comparison of *SC* value between PASiC and PAC

The changes of *SC* value with respect to the dosage of coagulant at different *B* values and Al/Si ratios for PASiC and at different *B* values for PAC, respectively, were summarized in Figs. 1 to 4. It can be seen that the *SC* value gradually becomes larger with the increase of dosage in both PASiC and PAC, but is always larger in PAC than PASiC at the same *B* value and the same dosage. As for PASiC, the higher the Al/Si molar ratio, the larger the *SC* value is. Also, at $B = 1.5$, the *SC* value of PASiCm is slightly higher than that of PASiCc, but, at $B = 2.0$, the situation is reversed. However, the differences of *SC* value between PASiCc and PASiCm gradually becomes smaller as the *B* value increases. The findings above indicate that the charge neutralization occurs when the negatively-charged polysilicic acid is combined with positively-charged aluminum salt, which reduces the *SC* value of PASiC. And, the more the polysilicic acid content, the lower the *SC* value of PASiC is. The results also show that preparation technique of PASiC has some effects on the charge of PASiC, but, it becomes smaller with the increase of *B* value.

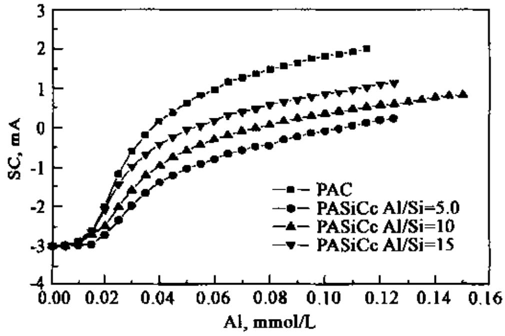

Fig.1 Variation of *SC* value of PASiCc and PAC with the dosage at *B* = 1.0

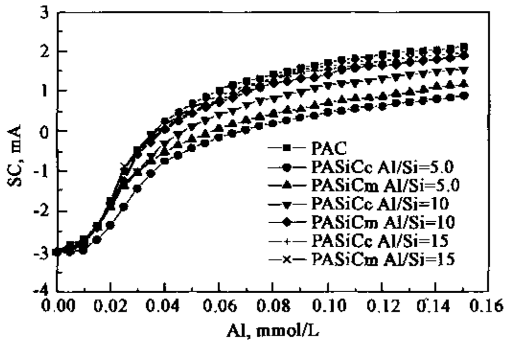

Fig.2 Variation of *SC* value of PASiC and PAC with the dosage at *B* = 1.5

In addition, the effects of *B* value, Al/Si molar ratio and preparation technique on the *SC* values of the coagulants discussed above may also be expressed by the required dosage to make *SC* reach zero (Table 1). It can be found in Table 1 that the required dose at *SC* = 0 for all the coagulants gradually becomes smaller when the *B* value becomes larger. On the other hand, at the same *B* value, the higher dose for PASiC than PAC is required to make *SC* = 0, and in PASiC the lower the Al/Si molar ratio, the higher dose requires. However, the difference of required dose between PAC and PASiC at *SC* = 0 becomes smaller when the *B* value increases. Further, the preparation technique has a larger effect on the charge-neutralizing capacity of PASiC with a lower Al/Si molar ratio, but a smaller effect on the charge-neutralizing capacity of PASiC with higher Al/Si molar ratio.

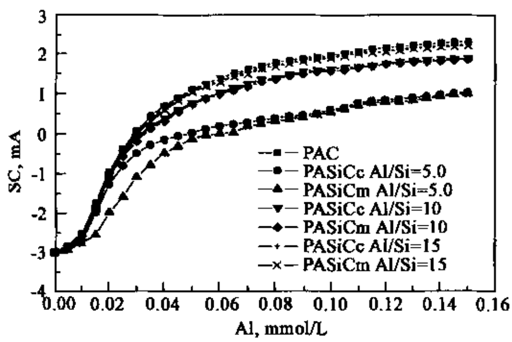

Fig.3 Variation of *SC* value of PASiC and PAC with the dosage at *B* = 2.0

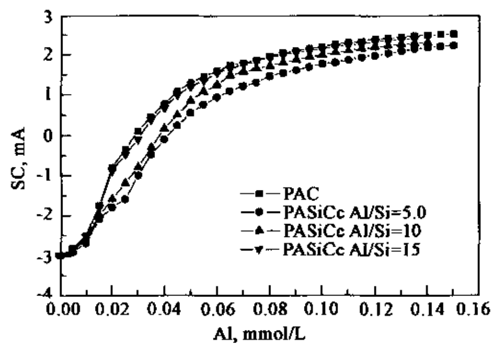

Fig.4 Variation of *SC* value of PASiCc and PAC with the dosage at *B* = 2.5

2.2 The relationship between *SC* values of coagulants and pH value of the test water

The change of *SC* value of PASiC and PAC is illustrated in Fig. 5 and Fig. 6, with respect to pH value of the test water when the dose of the coagulants is fixed at Al = 0.15 mmol/L during experiment. It can be observed that in every case, a similar pattern is obtained for the change of *SC* over a wide range of pH, but the curves of *SC* vs pH for PASiC are all lower than that for PAC. With increasing value of pH from very acidic side, the *SC* value for all tested coagulants take a maximum value at a pH range from 5.0 to 6.0 on the positive side, then monotonically decreases to zero at slightly higher pH than the neutral, and finally moves into the negative side.

Table 1 Required dose for PASiC and PAC at $SC = 0$

Sample	B	Al/Si	Dose, mmol/L	Sample	B	Al/Si	Dose, mmol/L
PAC	1.0		0.04	PAC	2.0		0.028
PASiCc	1.0	5	0.107	PASiCc	2.0	5	0.048
PASiCc	1.0	10	0.070	PASiCm	2.0	5	0.060
PASiCc	1.0	15	0.053	PASiCc	2.0	10	0.034
PAC	1.5		0.035	PASiCm	2.0	10	0.036
PASiCc	1.5	5	0.067	PASiCc	2.0	15	0.031
PASiCm	1.5	5	0.058	PASICm	2.0	15	0.032
PASiCc	1.5	10	0.046	PAC	2.5		0.024
PASiCm	1.5	10	0.039	PASiCc	2.5	5	0.041
PASiCc	1.5	15	0.037	PASiCc	2.5	10	0.033
PASiCm	1.5	15	0.036	PASiCc	2.5	15	0.030

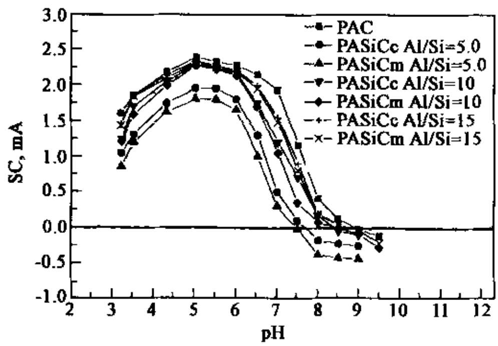

Fig. 5 Variation of *SC* value of PASiC and PAC with pH value at $B = 2.0$

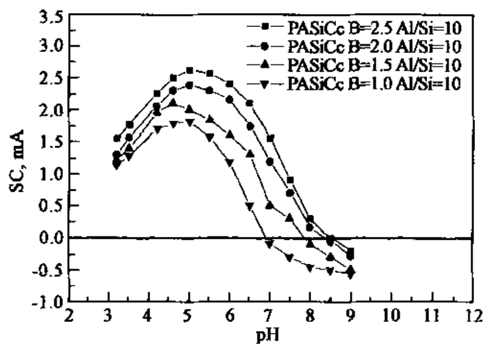

Fig. 6 Variation of *SC* value of PASiCc with pH value at Al/Si = 10 and different B value

As shown in Fig. 5, for PASiC coagulants with $B = 2.0$, the lower the Al/Si ratio, the lower the curve of *SC* vs pH is. For PAC, the *SC* value reaches zero at pH 8.9 approximately, however, the *SC* values for all tested PASiC coagulants equal to zero at lower pH value. As the Al/Si ratio changes from 15 to 5, the point on the curve with $SC = 0$ moves toward the acidic side of pH for both PASiCc and PASiCm. Also, compared to PASiCm, PASiCc has higher *SC* value at the same Al/Si ratio and pH. However, the difference of *SC* value between PASiCc and PASiCm becomes smaller with the increase of Al/Si ratio. From Fig. 6, it can be seen that for PASiCc with a fixed Al/Si ratio of 10, the *SC* value increases while B value increases. And, corresponding to B = 1.0, 1.5, 2.0 and 2.5, the *SC* value reaches zero at pH = 6.9, 7.9, 8.4 and 8.5, respectively. In summary, the findings demonstrate that B value, Al/Si molar ratio and preparation technique all have impact on the charge quantity of hydrolyzed products of PASiC coagulant.

2.3 Application of PASiC to coagulation of the water from the Wohu Mountain Lake in Jinan City

The water was taken from the Wohu Mountain Lake, Jinan City in China. The pH value, turbidity, UV_{254}, and COD_{Mn} of the water is 7.86, 22.0 NTU, 0.130 and 7.95 mg/L, respectively. The coagulation efficiency of PASiC with $B = 2.0$ and different Al/Si molar ratio and PAC with $B = 2.0$ is shown in Fig. 7. It can be seen from Fig.7 that PASC gives more removal of turbidity, UV_{254} and COD_{Mn} than PAC. For

PASiC with different Al/Si molar ratio, the lower the Al/Si molar ratio, the better the coagulation efficiency. The results above means that the interaction between the hydrolyzed aluminum species and polysilicic acid can enhance the coagulation efficiency of the composite coagulants PASiC and reduce the content of disinfecting byproducts in the treated water, and the more the content of polysicic acid in PASiC is, the more obvious the enhancement is, during the tested Al/Si molar ratio range. Because the PASiC with low Al/Si molar ratio has higher molecular weight(Gao, 1999) and lower positive charge, it can be thought that PASiC achieve the removal of turbidity and natural organic matter (NOM) by charge - neutralization and absorption-bridging action.

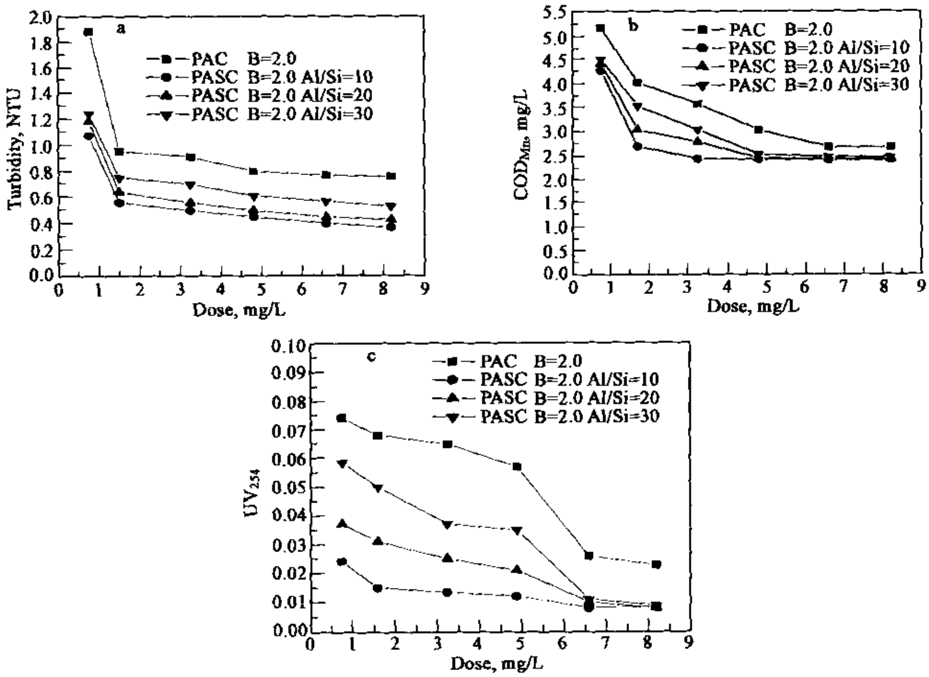

Fig.7 Comparison of coagulation efficiency between PASiC and PAC for water from the Wohu Mountain Lake in Jinan City

3 Conclusions

The results showed that PASiC is a cationic inorganic polymer coagulant. However, PASiC gives a less positive charge than PAC because of the interaction between negatively charged polysilicic acid and positively charged hydrolyzed aluminum species. The Al/Si ratio and the *B* value have great effects on the electrokinetic characteristics of PASiC. The less the *B* value and the Al/Si ratio, the lower the positive charge of PASiC is. In contrast, the preparation technique has a little effect on the electrokinetic characteristics of PASiC. The differences of *SC* value between PASiCc and PASiCm at the same *B* value and Al/Si ratio become smaller with the increase of Al/Si ratio. Therefore, the appropriate Al/Si ratio should be controlled when developing PASiC coagulant. Otherwise, the larger proportion of polysilicic acid in PASiC would dramatically lower the positive charge of PASiC too much, which would weaken charge effectiveness in coagulation process. In addition, compared with PAC, PASiC may enhance aggregating efficiency and give better coagulating effects. For PASiC, the lower the Al/Si molar ratio, the better the coagulation efficiency, during the tested range of Al/Si molar ratio of 10—30.

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