

Article ID: 1001-0742(2000)02-0232-04

Properties of polyferric-silicate-sulfate(PFSS) coagulant

GAO Bao-yu¹, YUE Qin-yan¹, ZHAO Hua-zhang¹, SONG Yong-hui²

(1. Department of Environmental Engineering, Shandong University, Jinan 250100, China; 2. Department of Chemical Engineering, Shandong Institute of Mining and Technology, Jinan 250031, China)

Abstract: Polyferric-silicate-sulfate(PFSS), as a new type of coagulant, was prepared by using sodium silicate, sulfuric acid and ferric sulfate as materials. The zeta potential of hydrolyzate of PFSS under different pH values was investigated. The effects of Fe/SiO₂ molar ratio and dosage of PFSS on turbidity removal were studied. The relation between the optimum coagulation pH range and Fe/SiO₂ molar ratio was found and the coagulation mechanism of PFSS was discussed. The experimental results showed that Fe/SiO₂ molar ratio has an effect on the zeta potential of hydrolyzate, the coagulation performance and the optimum coagulation pH range of PFSS and that PFSS gives the best turbidity removal effect when its Fe/SiO₂ molar ratio was 1.5.

Key words: inorganic polymer coagulant; polyferric-silicate-sulfate; polymerization of silicic acid; zeta potential; turbidity removal
CLC number: X703 **Document code:** A

Introduction

With metal ions, the highly polymerized polysilicic acid can give an excellent coagulation performance in water treatment (Takao, 1990). This kind of coagulant prepared by introducing the metal ions into polysilicic acid (PSA), is called metal-polysilicate coagulant. Because the average molecular weight of this species is estimated to be as high as 200000 (Takao, 1989), it is possible for it to take part places of composite organic polymeric coagulant to escape toxicity. Usually, ferric ion or aluminum ion can be used as the introduced metal ion, and its molar ratio to silicic acid can be adjusted for different needs. Using ferric ion, the authors prepared PFSS coagulant and its properties were studied.

1 Experimental method

1.1 Instruments and reagents

JS94E micro-electrophoretic mobility detector, 722 grating spectrophotometer, ZD-1 turbidimeter, J6-1A agitator, PHS-2 pH meter, sodium silicate (industrial products, modulus was 3.21), kaolinite (chemical purity grade), other chemicals were analytical reagent grade.

1.2 Preparation of PFSS

An amount of sodium silicate was diluted to a certain concentration, and then its pH value was adjusted with sulfuric acid. When silicic acid was polymerized to a certain degree, a certain amount of ferric sulfate was added and the mixture was heated to make ferric sulfate dissolved. After aging for 2h, PFSS coagulant (liquid) containing 2.0% of SiO₂ was prepared. Changed the amounts of ferric sulfate and repeated the above procedure. Then PFSS coagulants with varied Fe/SiO₂ molar ratios were obtained.

1.3 Coagulation method

The test water was prepared with kaolinite and distilled water. After adding 1g of kaolinite into 1 liter of distilled water, 0.032g of Na₂CO₃ was added to make the alkalinity of test water at 0.8 to 1.0 meq/L. In 500ml of the test water, a certain amount of PFSS was added. After that, the test water was rapidly stirred at 120 r/min for 2 min, slowly stirred at 60 r/min for 7 min, and then took rapidly 50 ml from the test water to measure its zeta potential. After the rest had settled quiescently for 10 min, a supernatant sample was withdrawn from a position of about 2 cm below the water surface and its turbidity was measured. In the process of measurement, distilled water was used as blank and the turbidimeter was calibrated by standard hydrazine solution. The pH value of test water was adjusted with dilute HCl solution or NaOH solution.

1.4 Measurement of zeta potential

The zeta potential of colloidal particles was measured by JS94E micro-electrophoretic mobility detector (co-made by Normal University of East China and Shanghai Jiecheng Industrial Company Ltd.). In the detector, a 0.5 cm-thick-electrophoresis tank made of glass was used and the electrodes were placed in the tank. The sample needed was very little, only about 0.5 ml every time. The time needed to shift from positive to negative to could be adjusted continuously from 0.30s to 1.20s. Gathering samples only needed from 3s to 10s. The voltage between the electrodes could be adjusted according to experimenter's need (usually 10 mV). A probe was used to gather automatically and continuously environmental temperatures, and the information was return to computer to adjusts automatically the parameters to compute zeta potential. In the computing process, multimedia technique was used: the microparticles (with a radius range from 0.5 μm to 10 μm) which had been magnified 1500 times already were automatically and continuously "photographed", and four pseudocolor "photos" in double directions were provided to compute and analyze.

2 Results and discussion

2.1 Size distribution of kaolinite particle

The molar ratio of silicon to aluminum of kaolinite reagent was 1.43, measured by scanning electron microscope (SEM). Its size distribution measured by size distribution detector is shown in Table 1. The results showed that the radii of most (about 60%) of the kaolinite particles were in the range from 4 μm to 9 μm , and the radii of 75.70% of them were smaller than 10 μm . This was similar to the condition of natural water (most of the soil particles which can bring about turbidity were smaller than 10 μm in radius (Xu, 1990)).

Table 1 Size distribution of kaolinite particles

Radius, μm	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	>10
Size distribution, %	1.50	3.90	6.50	9.86	12.25	14.25	15.64	9.80	2.45	24.30

2.2 Zeta potential of PFSS under different pH values

The PFSS samples were diluted (about to 100) to make the ferric concentration in the range from 1.67×10^{-3} to 3.34×10^{-3} mol/L (the ferric concentration was too high or too low would lead to too many or too small colloidal particles in the diluted samples. Both of them were detrimental to measurement of zeta potential). The pH values of diluted samples were adjusted with dilute HCl solution or NaOH solution before the measurement. Because a certain amount of dissolved hydrolyzate of PFSS was adsorbed on the surface of sediment of PFSS hydrolyzate, zeta potential of the sediment could provide an information similar to the change of zeta potential of PFSS hydrolyzate. Fig. 1 showed that zeta potential of PFSS coagulant under different pH values and the comparisons between PFSS and $\text{Fe}_2(\text{SO}_4)_3$ solution (containing 3.34×10^{-3} mol/L of ferric) and between PFSS and PSA solution (containing 3.33×10^{-4} mol/L of SiO_2), when Fe/ SiO_2 molar ratio of the PFSS was 0.5 and 1.0, respectively. In PFSS coagulant, the introduction of ferric salt into PSA had an effect on the zeta potential values of ferric salt and PSA. The zeta potential value of PFSS coagulant was greater than that of PSA solution and less than that of $\text{Fe}_2(\text{SO}_4)_3$ solution at the same pH value, and it was coming to that of PSA solution with decreasing Fe/ SiO_2 molar ratio and was coming to that of $\text{Fe}_2(\text{SO}_4)_3$ solution with increasing Fe/ SiO_2 molar ratio. So PFSS has a characteristic that zeta potential varies with Fe/ SiO_2 molar ratio. For PFSS coagulants with various Fe/ SiO_2 molar ratios, the characteristic makes it possible to have different optimum coagulation pH ranges.

2.3 Effect of Fe/ SiO_2 molar ratio on coagulation performance of PFSS

The dose of PFSS was expressed by volume. In 1 liter of sample, 0.25 ml of PFSS was added (in PFSS the SiO_2 concentration was fixed at 20 g/L and the ferric concentration was adjusted according to Fe/ SiO_2 molar ratio). The pH value of the sample was adjusted at about 8.0. Fig. 2

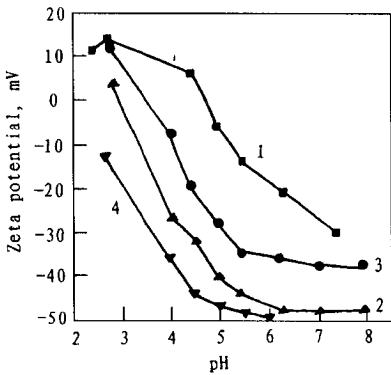


Fig. 1 Zeta potential of PFSS vs. pH value
1. $Fe_2(SO_4)_3$; 2. PFSS $Fe/SiO_2 = 0.5$;
3. PFSS $Fe/SiO_2 = 1.0$; 4. PSA

shows that Fe/SiO_2 molar ratio had a great effect on coagulation and turbidity removal. The coagulation performance of PFSS was improved with increasing Fe/SiO_2 molar ratio and was the best when Fe/SiO_2 molar ratio was about 1.5. When $Fe_2(SO_4)_3$ was used as coagulant in the above procedure, the residual turbidity of kaolinite suspension was 98.1 mg/L. So the results also shows that PFSS with suitable Fe/SiO_2 molar ratio has a much better coagulation performance than $Fe_2(SO_4)_3$.

2.4 Effect of PFSS dose on coagulation performance

Fig. 3 shows the experimental results of PFSS samples whose Fe/SiO_2 molar ratios were 0.5, 1.0 and 1.5, respectively. The results demonstrate again that the greater Fe/SiO_2 molar ratio is, the better coagulation performance PFSS has. By doing 0.19 ml/L, the PFSS with a Fe/SiO_2 molar ratio 1.5 gave the best turbidity removal effect. The excessive dose could not make kaolinite suspension

restabilized. For PFSS whose Fe/SiO_2 molar ratio was 1.0, dose of 0.375 ml/L was needed to make the supernatant very clear. To get the same effect, higher dose was needed for PFSS when its Fe/SiO_2 molar ratio was 0.5

2.5 Discussion of suitable pH value for PFSS and its coagulation mechanism

Fig. 4 shows the results of the experiments in which the doses were fixed at 1 mg/L (as SiO_2). It was found that Fe/SiO_2 molar ratio had an effect on the suitable pH value for turbidity removal. PFSS with a low Fe/SiO_2 molar ratio would give an excellent coagulation performance in a low pH range. With Fe/SiO_2 molar ratio increasing, the optimal pH value for coagulation increases slightly and the increment of the optimal pH value grows with the increasing of Fe/SiO_2 molar ratio. The property of PFSS can be applied to water treatment and suitable PFSS coagulants for different water can be prepared by adjusting Fe/SiO_2 molar ratio.

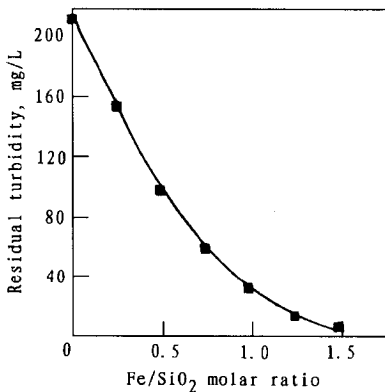


Fig. 2 Effect of Fe/SiO_2 molar ratio on coagulation performance

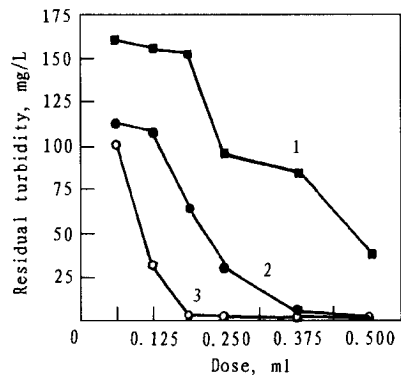


Fig. 3 Effect of PFSS dose on coagulation performance
1. $Fe/SiO_2 = 0.5$; 2. $Fe/SiO_2 = 1.0$; 3. $Fe/SiO_2 = 1.5$.

In Fig. 4, the curves of relation between zeta potential and pH value demonstrate that PFSS coagulant can give an excellent turbidity removal to kaolinite suspension, when the surfaces of kaolinite particles are charged by relatively more negative electrons. So it can not correctly reflect the truth in coagulation process if charge neutralization is considered the main criterion of coagulation performance. The coagulation mechanism depends on the kinds and the properties of

coagulants.

When discussing the coagulation mechanism, we should consider all the respects: (1) the general characteristics of PSA as a polymer; (2) the general characteristics of ferric salt; (3) the interaction between silicon hydroxyl of PSA and ferric (ferric ion and ferric hydrolyzates). After PFSS is added as coagulant into the water, on the one hand: (1) the change of hydrolytic degree and the transformation of species of ferric salt will be brought about by the dilution and the increase of pH value; (2) the ferric hydrolyzate will incorporate into PSA; (3) the increase of pH value will lead to further polymerization of PSA until gelation; on the other hand: (1) all kinds of ferric hydrolyzates will be adsorbed on the suspended particles in mixing process and then destabilize the particles; (2) after ferric hydrolyzates were adsorbed on the suspended particles, large molecules or gel of PSA will bridge and stick the particles to form large floc, and then the water will be cleaned. The two processes above can proceed at the same time and be finished rapidly. In the optimum pH range for turbidity removal, the agglutinated suspended substance having relatively more negative electrons shows that the coagulation mechanism of PFSS is obviously different from that of conventional ferric salt coagulants. PFSS coagulant takes on typical characteristics of adsorption-bridge formation and stick-scavenging action.

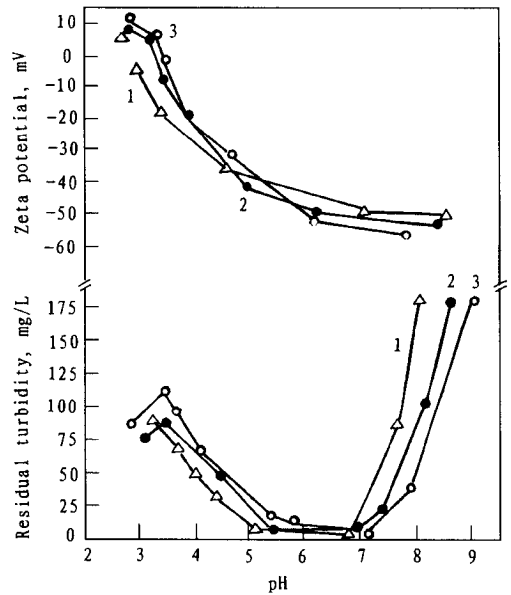


Fig. 4 Zeta potential and residual turbidity of supernatant under different pH value
1. Fe/SiO₂ = 0.5; 2. Fe/SiO₂ = 1.0; 3. Fe/SiO₂ = 1.5

3 Conclusion

PFSS is a new type inorganic polymer coagulant which an excellent coagulation performance. The Fe/SiO₂ molar ratio has great effect on the coagulation performance, zeta potential of hydrolyzate and the optimum pH range for turbidity removal. The kind of coagulant can be simply prepared, has non-toxicity and a significant coagulation performance. Furthermore, an even satisfactory coagulation performance will be achieved, by adjusting the ingredients of PFSS to change Fe/SiO₂ molar ratio according to the pH values of different water. So with the deeper research of this kinds of coagulant, its value will be found and accepted by more and more people.

References:

- Takao Hasegawa, 1990. Method and flocculant for water treatment[P]. US patent, 4923629. 1990-05-08.
Takao Hasegawa, Takuya Onitsuka, Minoru Suzuki, 1989. Water Nagoya'89[R]. ASPAC IWSA. 31S-05-A8. 152—161.
Xu Baojiu, 1990. Principle of applied and waste water treatment at present time[M]. Beijing: Advanced Education Press. 165.

(Received for review December 8, 1998. Accepted May 10, 1999)