



## Preparation and coagulation efficiency of polyaluminium ferric silicate chloride composite coagulant from wastewater of high-purity graphite production

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### Abstract

The aim of the present work was to produce a polyaluminium ferric silicate chloride (PAFSiC) coagulant from acidic and alkaline wastewater of purifying graphite by roasting, and subsequently to evaluate coagulation efficiency of the reagent by treating surface water from the Yellow River as well as municipal wastewater in comparison with the conventional coagulant polyaluminium chloride (PAC). The PAFSiC coagulant was prepared by co-polymerization. The effects of (Al+Fe)/Si molar ratio, OH/(Al+Fe) molar ratio (i.e.,  $\gamma$  value), coagulant dosage and pH value of test suspension on the coagulation behavior of PAFSiC and the stability of the PAFSiC were also examined. Results showed that PAFSiC performed more efficiently than PAC in removing turbidity, chemical oxygen demand (COD), and total phosphate (TP). The PAFSiC with a  $\gamma$  value of 2.0 and (Al+Fe)/Si ratio of 5 (PAFSiC 2.0/5) showed excellent coagulation effect for both turbidity and COD, while PAFSiC 1.0/5 was the best for TP. The optimum coagulation pH range of PAFSiC 2.0/5 was 5.0–9.0, slightly wider than that of PAC (6.0–8.0). The process can be easily incorporated into high-purity graphite production plants, thereby reducing wastewater pollution and producing a valuable coagulant.

**Key words:** polyaluminium ferric silicate chloride; industrial minerals; recycling; coagulant; wastewater

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### Introduction

Graphite mineral floats easiest as a rougher concentrate, but it is very difficult to upgrade it further by flotation or other mechanical processing methods. By scrubbing and two-step cleaning flotation (Lu and Forssberg, 2001), a fine graphite concentrate containing 87%–88% carbon can be upgraded to about 95% carbon, but further upgrading by flotation is difficult. Therefore, chemical purification is always essential to produce high purity graphite. Alkali roasting effectively eliminates impurities from graphite ores and has traditionally been conducted at high temperatures ranging from 500 to 900°C (Liu et al., 2000; Sun, 1995). Recent research showed, however, that alkali roasting purification was effective even at low temperatures of 200–300°C and confirmed that the main impurities of graphite ores were SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> (Lu and Forssberg, 2002; Niu et al., 2007). The whole process includes alkali roasting, water washing, acid leaching, and drying. Figure 1 shows the flow chart of purification of high-purity graphite. First, mixtures of NaOH solution and

raw graphite powder are roasted in a furnace. The roasted materials are then washed until neutral (pH = 7) under a vacuum filter to remove both the soluble roasting products and the extra alkali. The washed materials are treated with 10% HCl to further remove the insoluble compounds (mainly hydroxide and oxides). Finally, the acid leached materials are washed until neutral (pH = 7) and dried. During this process, the acidic oxide of SiO<sub>2</sub> is washed into alkaline wastewater, and the alkaline oxides of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are washed into acidic wastewater.

Acidic and alkaline wastewater (AAW) is an important water pollution problem in high-purity graphite production. In China, conventional treatment of AAW involves mixing the two kinds of wastewater and coagulation. High-purity graphite manufacturers in China mostly use polyaluminium chloride (PAC) or polyferric sulphate (PFS) as coagulants. The coagulation precipitates are removed in settling ponds and dissolved air flotation units (Du, 2000; Chen and Zhao, 2006). Although this treatment can provide effective remediation, it has problems related to disposal of the bulky sludge along with waste chemicals, which are, in fact, useful.

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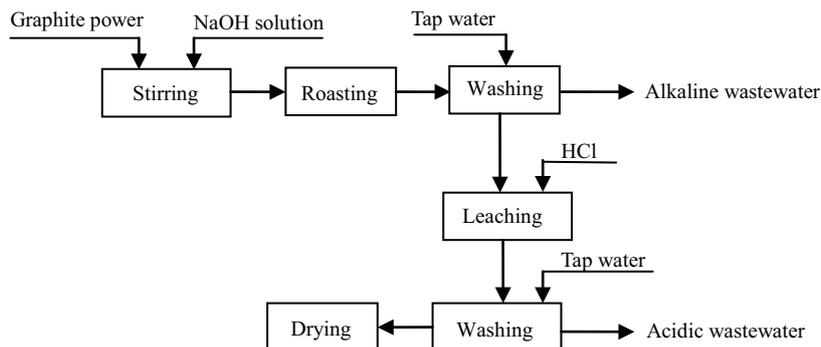


Fig. 1 Flow chart of purification of high-purity graphite.

The AAW contains high concentrations of silicon, iron, and aluminum. One potential way to extend the use of natural resources is to recover potentially valuable materials, such as these from the AAW.

The most widely used coagulant for water treatment is PAC (Bratby, 1980). In the past decade, increasing attention has been paid to aluminum toxicity to human health (Jiang and Liang, 1999; Becaria et al., 2006). Recently, a new kind of water treatment coagulant has been developed. By introducing metal ions into polymerized silicic acid solution, the molecular weight of the product is increased and the respective stability and coagulation performance are further improved (Hasegawa et al., 1990, 1991). Moreover, polysilicate (PSi) has several advantages such as facileness, abundance and non-toxicity. Extensive studies on polysilicate coagulant combined with ferric salt and aluminum salt have been conducted by researchers all over the world (Luan and Song, 1997; Gao et al., 2003; Zouboulis and Moussas, 2008; Tzoupanos et al., 2009).

Along these lines, the aim of the present study was to produce a polyaluminium ferric silicate chloride (PAFSiC) coagulant from AAW of purifying graphite by the roasting method. Additionally, we evaluated coagulation efficiency of the reagents in comparison with the conventional coagulant.

## 1 Materials and methods

### 1.1 Wastewater samples

The first AAW wastewater sample was collected from a high-purity graphite plant near Zhengzhou City, Henan Province, China, and sealed in high-density polyethylene bottles. The solids and debris in the water samples were removed by settling and the remaining suspended solids were removed by filtration through a 0.45  $\mu\text{m}$  membrane and stored at 4°C. The general characteristics of the acidic wastewater were  $\text{Al}^{3+}$  0.16 mol/L,  $\text{Fe}^{3+}$  0.14 mol/L, HCl 0.55 mol/L, while for the alkaline wastewater were  $\text{SiO}_2$  0.248 mol/L, NaOH 0.48 mol/L, and  $\text{Na}_2\text{CO}_3$  0.57 mol/L. The analytical results show that the concentrations of iron and aluminium in the acidic wastewater were higher, while the concentration of  $\text{SiO}_2$  in the alkaline wastewater was higher. The sodium carbonate is formed due to oxidation of graphite in the air and alkali roasting. These metals and silicon can be recovered and used as the raw materials for

preparing coagulant PAFSiC.

The second wastewater sample was surface water taken from the Zhengzhou section of the Yellow River. The pH, water temperature, and turbidity of the sample were 7.22, 25°C and 430 NTU, respectively.

The third aqueous sample was municipal wastewater collected from the outflow of the Municipal Wastewater Treatment Plant of Zhengzhou. The main characteristics were: initial concentration of chemical oxygen demand (COD) 387 mg/L, total phosphate (TP) 9.32 mg/L, and pH 8.01.

### 1.2 Reagents

Commercial PAC was obtained from the GW Aluminum Corporation of China. The reagents used for acid concentration adjustments were analytical grade NaOH or HCl.

### 1.3 Materials recovery and preparation of PAFSiC coagulant

Iron, aluminum, and silica were recovered from the wastewater and PAFSiC was prepared by copolymerization (Yang et al., 2004; Gao et al., 2002a). First, under magnetic stirring (60 r/min) and pH control using an acidity meter, a certain amount of alkaline wastewater was added at a flow rate of 1.0 mL/min into the acidic wastewater at a predetermined (Al+Fe)/Si molar ratio, i.e. 5, 10, 15. During titration, the pH of the mixture was recorded and adjusted to 2.0, which was chosen to obtain the most stable polysilicate. Under vigorously stirring (300 r/min) at room temperature, 0.5 mol/L NaOH was then slowly titrated at a flow rate of 0.3 mL/min into the above solution to obtain the desired  $\gamma$  value, where  $\gamma = C_{\text{OH}}/C_{\text{Al+Fe}}$  in which  $C_{\text{OH}}$  and  $C_{\text{Al+Fe}}$  are the total concentrations of OH and Al+Fe in the solution, respectively. During titration, the solution was vigorously stirred and the base was dosed slowly to ensure that a homogeneous solution was obtained. The achieved solutions were PAFSiC coagulants with various  $\gamma$  values and (Al+Fe)/Si values. Finally, the prepared PAFSiC samples were capped, sealed, and stored at room temperature for at least 3 hr before use.

According to the basicity and (Al+Fe)/Si molar ratio, the coagulants were as follows: PAFSiC with  $\text{OH}/(\text{Al+Fe}) = 2.0$  and (Al+Fe)/Si = 5 as PAFSiC 2.0/5, while PAC with  $\text{OH}/\text{Al} = 2$  as PAC2. The basicity =  $(\text{OH}/(\text{Al+Fe}))/3 \times 100$  (Zouboulis and Tzoupanos, 2009).

## 1.4 Coagulation experiments

Coagulation tests were performed using samples of surface water or wastewater. All water treatment experiments were carried out in 1.0 L plexiglass beakers with conventional Jar Test apparatus (SC656, Hubei Meiyu, China). Eight hundred milliliters of raw water was dosed with different coagulants. The suspension was stirred rapidly at 150 r/min for 3 min during coagulant addition, followed by slow stirring at 30 r/min for 10 min. The samples were then left undisturbed without any agitation for 30 min to allow settling of the solids. After sedimentation, supernatant samples were taken from a point 2–3 cm below the surface of the test water sample for analysis. The experiments were repeated two to three times and the average values are reported; the variance between the separately obtained values was within 2%–3%. The pH adjustment (when needed) was accomplished by the addition of 0.5 mol/L of HCl or NaOH solution in the sample under stirring.

## 1.5 Analytical methods

Metal analyses were carried out by inductively coupled plasma (ICP) spectroscopy using a 2100 Spectrometer (PerkinElmer, USA). Determination of silicon dioxide content was performed by molybdenum blue photometry (SL 91.2-1994) (SP-751, Shanghai Optical Instrument, China). Determination of TP was carried out by ammonium molybdate spectrophotometry (GB/T 11893-1989) (SP-751, Shanghai Optical Instrument, China). Sodium hydroxide and sodium carbonate contents were determined by double-indicator method. Turbidity was measured by a Turbidimeter (WGZ-100, Shanghai Precision Instrument, China). The COD was determined with potassium dichromate method (GB/T 11914-1989).

## 2 Results and discussion

### 2.1 Application of PAFSiC to coagulation of surface water from the Yellow River

#### 2.1.1 Effects of OH/(Al+Fe) ratios and (Al+Fe)/Si ratios on coagulation performance

Coagulation experiments were conducted and the results are shown in Fig. 2. Results from the impact of OH/(Al+Fe) ratios on the coagulation performance, indicated that the most suitable OH/(Al+Fe) molar ratio was 2.0. This was based on the evaluation of best performance, e.g. the lowest residual turbidity, which may be attributed to the higher polymerization degree that PAFSiC with OH/(Al+Fe) = 2.0 (Zouboulis and Moussas, 2008). When polymeric species are predominant in a coagulant's composition, coagulation efficiency increases due to the adsorption of polymeric species onto particles, which enables a coagulant bridge to form between adjacent particles and facilitates the subsequent formation of easily settled flocs. When the OH/(Al+Fe) ratio is too high ( $\gamma = 2.5$ ), however, due to decreased stability of the prepared coagulant, coagulation efficiency decreases. Moreover, with increasing (Al+Fe)/Si molar ratio, coagulation performance tends to slightly worsen, which might be attributed

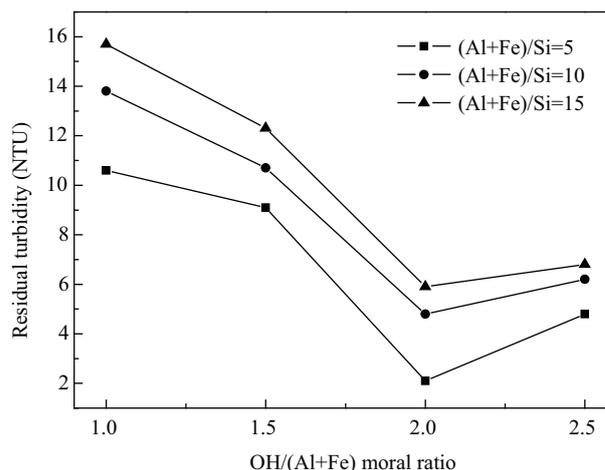


Fig. 2 Effects of OH/(Al+Fe) ratios and (Al+Fe)/Si ratios on coagulation performance. Concentration of coagulants was 4 mg/L.

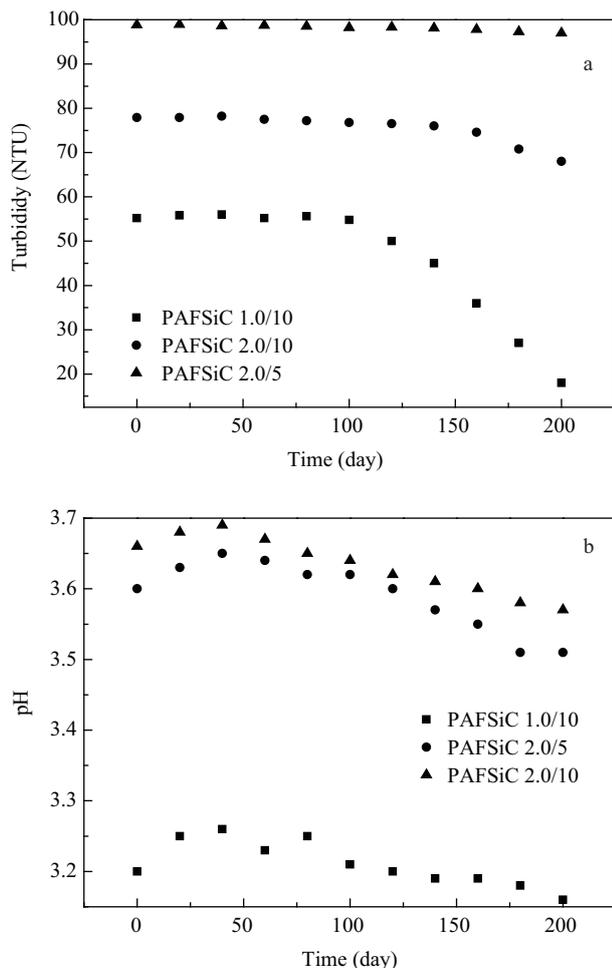
to the decreased concentration of polysilicic acid constraining the formation of large polymeric species with high molecular weight, thus compromising coagulation efficiency. Accordingly, we observed that low (Al+Fe)/Si ratios and high OH/(Al+Fe) ratios formed larger and more rapidly precipitated flocs.

#### 2.1.2 Stability of prepared coagulants

Coagulant stability is a very important parameter as it affects treatment performance. When stored over a long period of time, usually at room temperature at the treatment facilities, their coagulation/flocculation abilities can deteriorate. Figure 3 shows the turbidity and pH variations with time for selected coagulants. The examination period was over six months and the samples were stored at room temperature.

As shown in Fig. 3a, all prepared coagulants are quite stable for at least 3 months. The turbidity tended to decrease for all coagulants at different rates for the various reagents after approximately 100 days. This indicated that stability improved with increased OH/(Al+Fe) and decreased (Al+Fe)/Si molar ratios. In other words, the stability of composite coagulants improved with increased polymerization degree and silicate content. Furthermore, the composite coagulants prepared with higher polymerization degree and silicate content exhibited higher initial turbidity values. An exception was samples with OH/(Al+Fe) = 2.5, which were shown to be quite unstable. After one month, the appearance of suspended solids and a sudden increase in turbidity were observed, followed by a decrease in coagulation efficiency. Therefore, the respective data were excluded.

When increasing the degree of polymerization and silica content, the increase in macromolecular compounds, due to the formation of Al–O–Si, Fe–O–Si or Al–Si–Fe complexes, may be responsible for the higher turbidity values (Tzoupanos et al., 2009). The decrease in turbidity after time can be attributed to the depolymerization of polymeric silicates. Depolymerization is higher in alkaline solutions, slower in acidic solutions, and is strongly affected by silica concentration and the presence of other ions (Fu et al., 2007). Depolymerization can be, in fact, retarded



**Fig. 3** Investigations on the stability of prepared coagulants. (a) turbidity variation with time, (b) pH variation with time.

by the presence of metal cations (Dietzel and Usdowski, 1995). Furthermore, the increase in silica content can inhibit depolymerization. Hence, due to the presence of aluminum and ferric species, the decomposition of silicates was retarded after about 100 days for the majority of composite coagulants. In addition, the silica concentration in the prepared coagulants varied with (Al + Fe)/Si molar ratios. With increased silica concentration, the stability of silicates was improved. Thus, composite coagulants with higher silica content tended to preserve their stable characteristics for a longer time period.

Regarding pH variation over time, a slight increase was observed for all coagulants during the first 30 days (Fig. 3b), but with longer aging time the pH values decreased. This result also suggests that there are some interactions among hydrolyzed aluminum species, ferric species, and polysilicic acid. These interactions affected hydrolysis of aluminum and ferric ions, which resulted in the light increase and decrease of pH in different regions. The higher initial pH values were exhibited in coagulants with higher OH/(Al+Fe) molar ratio, which was attributed to increasing base content. The introduction of silica resulted in a small decrease of pH for the reagents with the same OH/(Al+Fe) molar ratio, which may be the neutralization of a small remaining free acid.

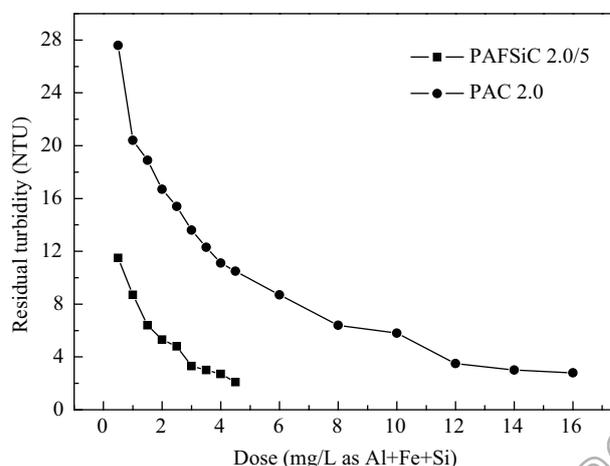
### 2.1.3 Effects of dosage on turbidity removal

Considering stability and coagulation efficiency, PAFSiC with  $\gamma = 2.0$  and (Al+Fe)/Si = 5 was used to investigate the effect of dosage on coagulation performance in treating surface water from the Yellow River in comparison with PAC with  $\gamma = 2.0$ . The results are shown in Fig. 4, which indicate that PAFSiC exhibited lower residual turbidity than PAC at the same dosage, especially at lower dosages. Compared with PAC (16 mg/L), a lower PAFSiC dosage (4 mg/L) was required to reach a residual turbidity of 2 mg/L. These results demonstrate that the removal efficiency of PAFSiC was much higher than that of PAC, as PAFSiC has a higher molecular weight (Gao et al., 2002a), which results in much stronger bridge-formation and very tough flocs when used in water treatment.

### 2.1.4 Effects of pH on turbidity removal

pH is one of the main factors that influence gelation time. To investigate pH influence on coagulation performance, the PAFSiC 2.0/5 sample was used, which was compared with the performance of commercially available PAC 2.0. The initial pH of the raw water varied between 4.0 and 9.0, the dosage of examined coagulants was 4 mg/L and the other experimental conditions remained as per Section 2.1.3.

The effect of initial pH on turbidity removal is shown in Fig. 5, which was consistent with previous reported results (Amuda and Amoo, 2007), i.e., initial pH had an important effect on coagulation behavior of PAFSiC and PAC. As indicated in Fig. 5, when initial pH was lower than 6.0, turbidity removal efficiency increased obviously as pH value increased with the magnitude of about 95.8% and 90.5% for PAFSiC and PAC, respectively. When initial pH was between 7.0 and 9.0, the performance of PAFSiC tended to worsen slightly. Overall, PAFSiC worked efficiently in a pH range of 5.0 to 9.0, which was slightly wider than the suitable range of PAC (6.0–8.0). Thus, PAFSiC was significantly better than the PAC, especially in slightly acidic and neutral pH values. The best performance was observed at pH 6.0. Furthermore, the results presented above demonstrate that the composite coagulant PAFSiC was superior to the traditional coagulants.



**Fig. 4** Comparative coagulation performance of PAFSiC and PAC.

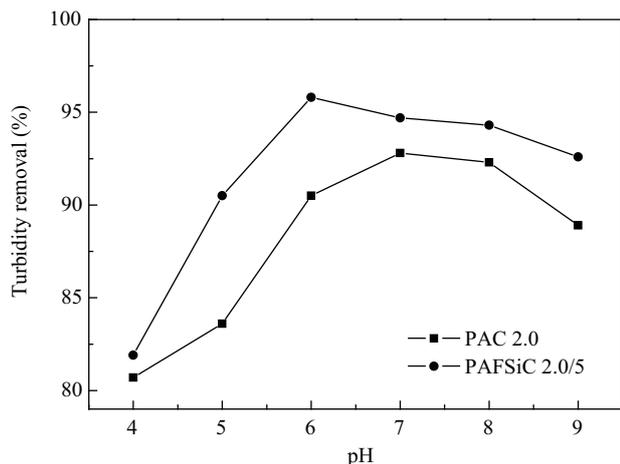


Fig. 5 Effect of coagulation pH on turbidity removal.

The effect of initial pH on turbidity removal was correlated with the coagulant hydrolyzates. When pH is less than 5.0, the primary hydrolyzates of PAC are  $\text{Al}(\text{OH})_2^{2+}$ ,  $\text{Al}(\text{OH})_3^+$ ,  $\text{Al}_2(\text{OH})_4^{2+}$ , and  $\text{Al}_3(\text{OH})_5^{3+}$  (Yang et al., 2010). These positive hydrolyzates easier neutralize the exterior negative charges of colloids and further destabilize them. Meanwhile, they also benefit the physical or chemical adsorption of the destabilized colloids, which lead to flocs growth. When the initial pH range is between 6.0 and 8.0, there are some high polymeric positive hydrolyzates and  $\text{Al}(\text{OH})_3$  forms in solution (Yang et al., 2010). The colloids are easily adsorbed and co-precipitated by the hydrolyzates, which have low solubility and large surface area. When pH is higher than 8.0, the suspension system is difficult to destabilize because the hydrolyzates are transformed to  $\text{Al}(\text{OH})_4^-$  (Yang et al., 2010).

It has been reported that the addition of silicates into PAC with certain OH/Al molar ratios can result in the decrement of medium Al polymers content (Gao et al., 2002b). Therefore, PAC has a greater polymerization degree than PAFSiC, although with the same OH/Al molar ratio. The formation of aluminosilicate complexes seems to play a significant role; it may be the presence of silica enhances the resistance of aluminum species for further hydrolysis. Hence, the change of pH had little effect on the coagulation performance of PAFSiC, and the optimum pH range can broaden to pH values 5.0–9.0 from 6.0–8.0 for PAC.

## 2.2 Application of PAFSiC to coagulation of municipal wastewater

Figure 6 shows the effect of  $\gamma$  value on the efficiency of COD removal by PAFSiC. The COD removal efficiency of PAFSiC increased with increasing  $\gamma$  value. The dosage of PAFSiC also affected COD removal efficiency. The optimal dosage for PAFSiC with different  $\gamma$  values was 9.0 mg/L.

All PAFSiC samples with  $\gamma = 2.0$  were tested and compared to the commercially available PAC. Figure 7 shows the effect of (Al+Fe)/Si molar ratio on the coagulation performances of PAFSiC and PAC.

The PAFSiC coagulants, except PAFSiC with  $\gamma = 2.0$

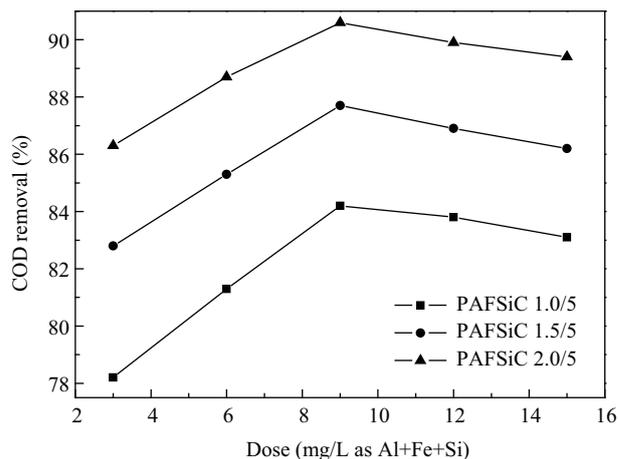


Fig. 6 Variation of COD removal efficiency with  $\gamma$  values and dosages of PAFSiC.

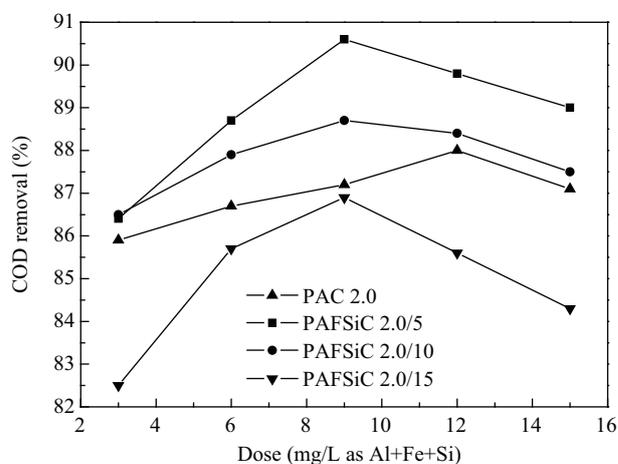


Fig. 7 Effects of (Al + Fe)/Si ratios on COD removal by PAFSiC and PAC.

and (Al+Fe)/Si = 15, were more effective than PAC in COD removal (Fig. 7). Coagulant dosage needed for optimal COD removal was lower for PAFSiC than that for PAC. The optimal dosage for PAFSiC with different (Al+Fe)/Si ratio was 9.0 mg/L, while the optimal dosage for PAC was 12 mg/L. This is because PAFSiC has a larger molecular size and higher positive charge, which results in stronger bridge-formation and charge-neutralizing capability than PAC for treating municipal wastewater (Yang et al., 2004). Less (Al + Fe)/Si molar ratios (the higher the concentrations of polymeric silicic acid) resulted in better coagulation efficiency. The PAFSiC 2.0/5 exhibited the highest COD removal efficiency.

Figure 8 shows the results of TP removal by PAFSiC with different  $\gamma$  values for initial coagulant concentrations 10–50 mg/L. It can be noted that removal efficiency increased as  $\gamma$  values decreased, corresponding also to the decrease of polymerization degree (Gao et al., 2002b). The most efficient reagent in this case was PAFSiC with the least  $\gamma$  value ( $\gamma = 1.0$ ). The relevant explanation is based on the mechanism of phosphate removal through the addition of coagulants. Jiang and Graham (1998) reported that the removal of phosphates by the application of coagulation-flocculation involves the following two major mechanisms: (a) the interaction of phosphates with soluble metal forms

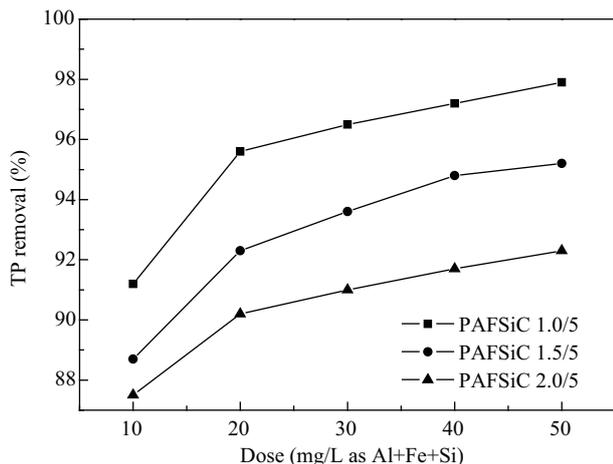


Fig. 8 Variation of total phosphate (TP) removal efficiency with  $\gamma$  values and dosages of PAFSiC municipal wastewater.

(chemical complexation), or with non-soluble (charge neutralization) complexes, which can either adsorb onto the positively charged hydrolysis species, or may act as cores for the precipitation of metal hydrolysis products. (b) The direct adsorption of phosphates on metal hydrolysis products, mainly referred to precipitation with insoluble  $M(OH)_3$  (sweep flocculation). Additionally, Ratnaweera et al. (1992) suggested that with lower basicity coagulants (i.e. those with low  $\gamma$  values) the dominant mechanism is co-precipitation with  $M(OH)_3$  (sweep flocculation), while with high basicity coagulants (i.e. those with high  $\gamma$  values) the dominant mechanism is the formation of  $M-PO_4$  complexes. Based on our experimental results and the aforementioned possible mechanisms, it is suggested that the dominant mechanism during phosphates removal was sweep flocculation.

Figure 9 shows the effect of  $(Al+Fe)/Si$  molar ratios on the coagulation performances of PAFSiC and PAC at the same  $\gamma$  value ( $\gamma = 1.0$ ). The PAFSiC sample with  $(Al + Fe)/Si = 5$  had the best coagulation performance, which was better than the performance of PAC. This result was also found in previous research on phosphates adsorption using alum and polyaluminium silicate sulfate samples (Boisvert et al, 1997). They concluded that the presence of

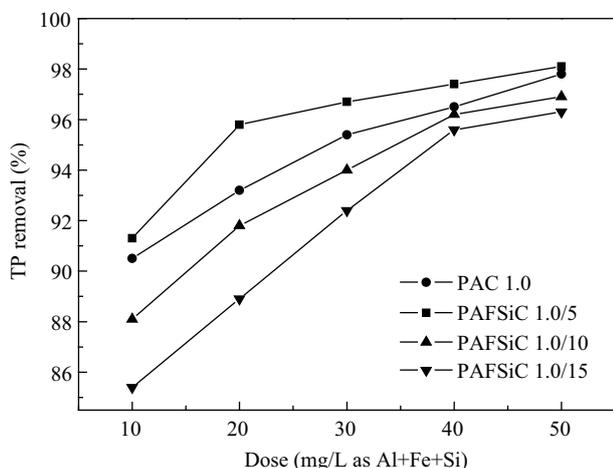


Fig. 9 Variation of TP removal efficiency with  $(Al + Fe)/Si$  ratio and dosage of PAFSiC and PAC.

silicate at low levels ( $(Al+Fe)/Si$  ratio 25) did not present any notable effect on phosphates adsorption.

At a dosage of 20 mg/L or more, TP removal efficiency of municipal wastewater treated by PAFSiC with  $\gamma = 1.0$ ,  $(Al+Fe)/Si = 5$  was more than 95% (residual TP < 0.5 mg/L), which is below the demand (0.5 mg/L) of the discharge standard of pollutants for municipal wastewater treatment plants in China (GB18918).

### 3 Conclusions

This study found that the co-polymerization process of producing PAFSiC coagulant was an effective method. Water treatment tests proved that this inexpensive coagulant was more efficient than the conventionally used PAC in water treatment. The process of producing such a coagulant can be easily adopted in high-purity graphite production plants, thereby reducing the wastewater pollution and producing a valuable chemical reagent.

The experimental results showed that the coagulating performance of PAFSiC was dependent upon  $(Al+Fe)/Si$  ratio and  $OH/(Al+Fe)$  ratio ( $\gamma$ ). The optimum  $Al+Fe/Si$  ratio and  $\gamma$  value depended on the water and wastewater composition. In general, the coagulation efficiency of PAFSiC was better at greater  $\gamma$  values (except for TP) and lower  $(Al + Fe)/Si$  ratios. However, PAFSiC became unstable during aging at very high  $\gamma$  values (2.5). The PAFSiC 2.0/5 showed high coagulation effect, superior to that of PAC for both turbidity and COD, while PAFSiC 1.0/5 was the best for TP. The optimum coagulation pH range of PAFSiC 2.0/5 was 5.0–9.0, slightly wider than that of PAC (6.0–8.0).

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