



## Speciation characterization and coagulation of poly-silica-ferric-chloride: The role of hydrolyzed Fe(III) and silica interaction

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### Abstract

The highly efficient inorganic polymer flocculants (IPFs) of the ferric-silica system is a new and promising coagulant. Interactions between ferric species and silica play a large part in the coagulation of suspensions. These effects are quite distinct from those associated with polymeric or colloid silica. However, although these species are key to coagulation efficiency, they have not been comprehensively discussed. A new type of coagulant, poly-silica-ferric-chloride (PFSC), was synthesized by co-polymerization and characterized by time complexation spectroscopy and photon correlation spectroscopy. Compared with traditional ferric salt, the results indicated that PFSC had a higher molecular weight, lesser positive charge, lower  $Fe_b$  and higher  $Fe_c$ . The higher the Si/Fe ratio, the higher the silica and lower the silica<sub>c</sub> found. The PFSC with appropriate polysilica acid not only obtained better coagulation/flocculation efficiency in turbidity removal, enhanced the flocculation index (FI) and provided less residual ferric, it also lowered water treatment costs compared to traditional ferric salt. Results showed that PFSC could remove colloid particles in water by charge neutralization and sweeping, adsorption bridging mechanism.

**Key words:** coagulation; inorganic polymer flocculant; PFSC; species distribution; residual ferric

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### Introduction

An important step in drinking water treatment is coagulation/flocculation, in which small particles are combined into larger aggregates to remove suspended particles (Zouboulis and Moussas, 2008a). Conventional coagulants based on hydrolyzing metal salts are widely used, including aluminum and ferric salts such as aluminum sulfate and ferric chloride. The metal salts of such coagulants hydrolyze rapidly to form various cationic species, which are adsorbed by negatively charged particles resulting in charge reduction. Three mechanisms, that is, charge neutralization, sweeping, and bridging, exist during coagulation (Packham et al., 1965; Snodgrass et al., 1984; Ray and Hogg, 1987; Bolto, 1995; Yukselen and Gregory, 2004). While coagulant species are essential to coagulation/flocculation efficiency, however, they can form rapidly during dilution and the formation of hydrolysis species can not be controlled. To overcome these problems, a relatively new type of coagulants, inorganic polymer flocculants (IPFs) like poly-ferric chloride (PFC) and poly-aluminum chloride (PAC), have been widely developed

(Parthasarathy and Buffle, 1985; Jiang and Graham, 1998; Cheng, 2001). Compared with traditional coagulants, IPFs have higher efficiency and lower cost. They contain hydrolysis and polymeric species, which can slow hydroxide precipitation upon dilution and consequently allow polymeric species to be maintained for longer. In addition, IPFs generally carry high positive charge with high molecular weight, while colloidal particles in water and wastewater are often negatively charged and suspended in water by mutual electronic repulsions. As application of aluminum-based coagulants has been questioned in regards to their potential toxicity (IAWQ, 1998), the need for ferric-based coagulants has increased. Currently, however, the coagulation efficiency of IPFs are still lower than organic polymeric coagulants (Zeng et al., 2008; Wang et al., 2008). The performance of IPFs can be improved by increasing the proportion of polymeric species in the original composition or by adding extra components to produce a new composite coagulant, such as polysilicic acid.

The influence on coagulation processes can affect the choice of coagulants or coagulant aids. Since Baylis (1937) found that silica in its colloidal form can considerably

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enhance coagulation by alum, extensive work has been done on this aspect (Packham and Saunders, 1966). As the silica species can not be controlled, there is a need for precise control of the preparation method to give optimum results. Although activated silica was not widely used, it can improve the effectiveness of coagulation, increase density of flocs and improve performance at low water temperatures. Some of the effects of activated silica in enhancing coagulation are explained in terms of its behavior as an anionic polymer, however, little is known about the effects of silica size and species distribution on the coagulation properties of metal salts.

Although a few studies have been conducted on the preparation of the PFSC at the laboratory scale (Tang and Stumm, 1987; Tian and Tang, 1989; Zouboulis and Traskas, 2007, 2008b), very few articles have considered the characterization and particle size of PFSC. Herein, we synthesized PFSC and analyzed its species distribution by direct and indirect speciation methods and particle size by light scattering goniometer. Moreover, the coagulation behavior of PFSC was assessed by the reduction of residual turbidity and residual hydrolyzed Fe(III) in water. Although a number of methods have been developed to measure floc strength, no techniques experimentally characterize floc strength without damaging them to some extent. The coagulation process of particulate matter can be reflected by a flocculation index (FI) value. As such, we also examined the relationships between the Si/Fe ratio and floc size and settling ability.

## 1 Materials and methods

All chemical reagents were of analytical grade (China). Deionized water was used to prepare all solutions.

### 1.1 Synthesis of PFSC

Before the preparation of PFSC, better speciation of activated silica for coagulation was carried out. Best activated silica speciation was obtained by using water glass as the main material, and 0.6 mol/L of silica at basicity of 65%, pH 10.3 and temperature of 15°C maintained at stable conditions for 10 hr. The activated silica prepared under these conditions improved the effect of the coagulation remarkably. A series of ferric poly-silicate chlorides with different Fe/Si molar ratios, were prepared by adding poly-silicic acid to ferric chloride solutions with different Fe/Si molar ratios. Speciation results using Si-Mo assay and ferron assay show that: (1) species distribution of the activated silica  $Si_a\%$ ,  $Si_b\%$  and  $Si_c\%$  were 16.0%, 31.3%, 52.7%, respectively; and (2) species distribution of commercial hydrolyzed Fe(III) chloride  $Fe_a\%$ ,  $Fe_b\%$  and  $Fe_c\%$  were 76.1%, 18.7% and 5.2%, respectively.

### 1.2 Morphology and size analysis

#### 1.2.1 Characterization methods

Two main kinds of speciation methods (i.e., the timed complexation spectroscopy and particle size and counting

(PCS) analysis) were applied. Timed complexation spectroscopy used ferron to differentiate Fe(III) species and Si-Mo to differentiate silica species.

#### 1.2.2 Particles size

The PCS measurements (BI-200SM, Brookhaven, USA) with the servomotor-controlled light scattering goniometer (BI-9000AT auto-correlator, Brookhaven, USA) were applied. The incident light source was a 35-mW He-Ne laser operating at 632.8 nm wavelength with vertical polarization. The instrument alignment was checked by the BI-IST software, and the deviations were less than 2% over the angular range.

### 1.3 Coagulation experiments

A stock suspension of clay particles was first prepared by dispersing powder kaolin in deionized water to a concentration of 50 g/L and then preserved in a refrigerator. The size distribution of the kaolin suspension was measured by a particle counter. The results showed that the particles in the suspension had a mean volume diameter of 2.28  $\mu\text{m}$  with a relatively narrow size distribution. The specific surface area of kaolin was 30.2  $\text{m}^2/\text{g}$  measured by an accelerated surface and porosity system (2000AP, Micrometrics, USA). Electrophoretic mobility (EM) of the kaolin particles was measured by a laser zeta potential analyzer (Zetaplus, BIC, USA). It was found that the particles were negatively charged at all pH values measured (from 3.0 to 11.0). The stock suspension was finely mixed prior to use. Then under rapid stirring a certain quantity was transferred to test water, which contained  $5 \times 10^{-4}$  mol/L of  $\text{NaNO}_3$ . Thus, the effect of bicarbonate ion was controlled at a constant range.

For the purpose of evaluating coagulation efficiency, the conventional jar test was applied using a standard bench-stirrer (PB-700 Jar tester, Phipps & Bird, USA). The jar test was carried out in beakers of 600 mL. The target pH was adjusted by adding 0.1 and 0.02 mol/L of HCl or NaOH to the suspension. During the rapid mixing, coagulants were dosed by a milli-injector. Initial rapid mixing at 160 r/min for 2 min was used to obtain swift homogeneous dispersion, followed by slow mixing at 40 r/min for 8 min. The suspension was left to settle for 10 min, then a sample was collected at 2.0 cm beneath the surface for residual turbidity (RT) measurement using a model turbid meter (2100N, Hach, USA). Zeta potential was measured 30 sec after alum dosing (Zeta Sizer 2000, Malvern, UK). The flocculation index (FI) was measured by a Photometric Dispersion Analyser (PDA2000, Rank brothers, UK).

#### 1.4 Determination of flocculation index (FI)

Variation in FI reflects particle aggregation, and to some extent indicates the special coagulation mechanism. The difference of FI produced in given conditions is the value, the retard time, the range of variation, and the increasing speeds. A photometric dispersion analyzer (PDA) was used to control the coagulation process.

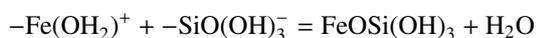
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## 2 Results and discussion

### 2.1 Morphology

#### 2.1.1 Speciation by ferron assay

The speciation of all samples was run after 24 hr aging. Results (Fig. 1) obtained from the ferron assay showed that as the Si/Fe ratio increases, the amount of  $Fe_a$  increases while the amount of  $Fe_b$  and  $Fe_c$  decrease. With a composition of 70%–85%, however, the  $Fe_a$  species is still the main component. Thus, the hydrolysis of Fe(III) can be inhibited at certain amounts of silica. Hence, introduced silica has a significant effect on species distribution of PFSC depending on the Si/Fe ratio. Monomeric silica is more active than polymeric silica in preventing the hydrolysis of Fe(III), through strong complexation or stereo combination with Fe(III) species by interaction of type:



However,  $silica_a$  appears to be inert to the hydrolysis of Fe(III) due to its bigger particle size and smaller amount of surface-active SiOH groups available in comparison with monomer silica. By increasing the Si/Fe ratio, more Fe(III) was complexed as indicated from the increase of  $Fe_a$ , which may interfere with subsequent polymerization and particle growth.

#### 2.1.2 Speciation by molybdic acid assay

Due to analytical limitation, only suitable samples aged for 24 hr were analyzed using the molybdic acid method. The results for PFSC, which are summarized in Fig. 2 for

comparison, showed that the Si/Fe ratio had an important effect on the type of silica species existing in PFSC. By increasing the Si/Fe ratio,  $Si_c$  increased while  $Si_a$  decreased. At a Si/Fe ratio of 3, the characteristic species distribution of samples remained similar to the mode of introduced silica, while the original silica species sample changed quickly after 24 hr aging. Obviously, complexation with Fe(III) inhibited further polymerization of silica. However, as the Si/Fe ratio increased, the species distribution of silica in PFSC changed markedly, depending on the Si/Fe ratio. By increasing the Si/Fe ratio, the amount of  $Si_b$  remained stable, indicating that the combination between silica and hydrolyzed Fe(III) species was reinforced with addition of alkalinity.

#### 2.1.3 Speciation by PCS

The lowest limit of particle size detection for the PCS instrument is 1–5 nm. However, only those with scattering intensity above 1 kcps were reliable.

The PCS diagrams (Fig. 3) show that the effective diameter of PFSC increased with increasing Si/Fe ratio. For example, when the Si/Fe ratio increased from 0.5 to 1 and 2, the diameter of PFSC changed from 243.8 nm to 273.6 nm and 339.6 nm, respectively. Along with the increase of Si/Fe ratio, more complicated polymers were formed and particle size distribution was broadened. It was evident that some co-polymerized species or aggregates between silica and Fe(III) polymers were formed. By decreasing the Si/Fe ratio, particle distribution was typical of PFSC, exhibiting a narrow particle diameter distribution. Thus, the Si/Fe ratio was a key factor in determining particle diameter.

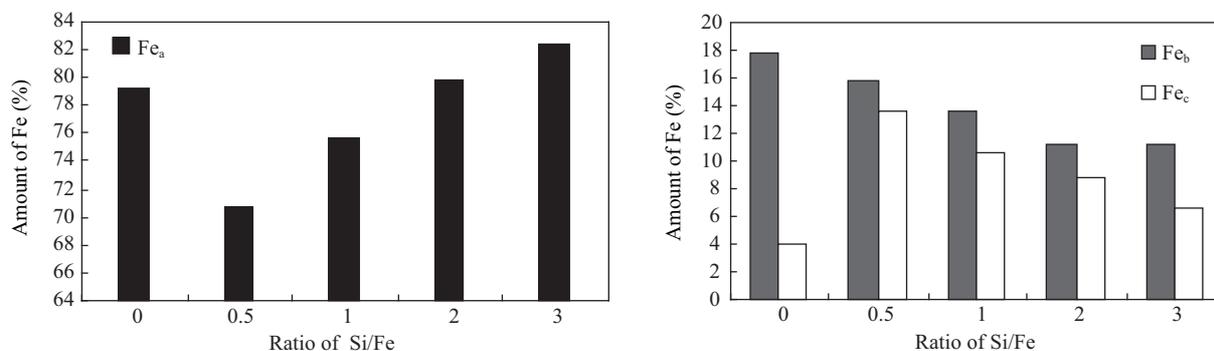


Fig. 1 Effect of Si/Fe ratio on hydrolyzed Fe(III) species distribution.

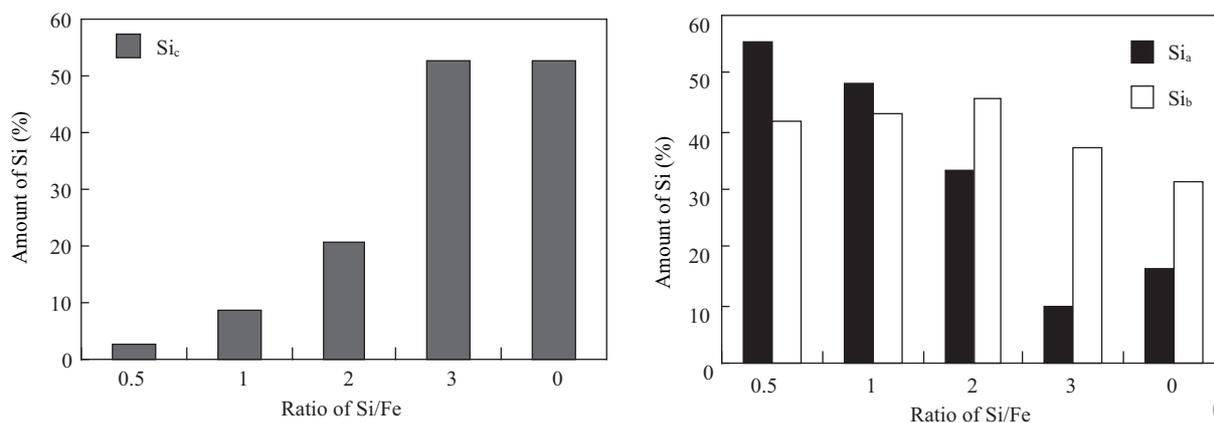


Fig. 2 Effect of Si/Fe ratio on silica species distribution.

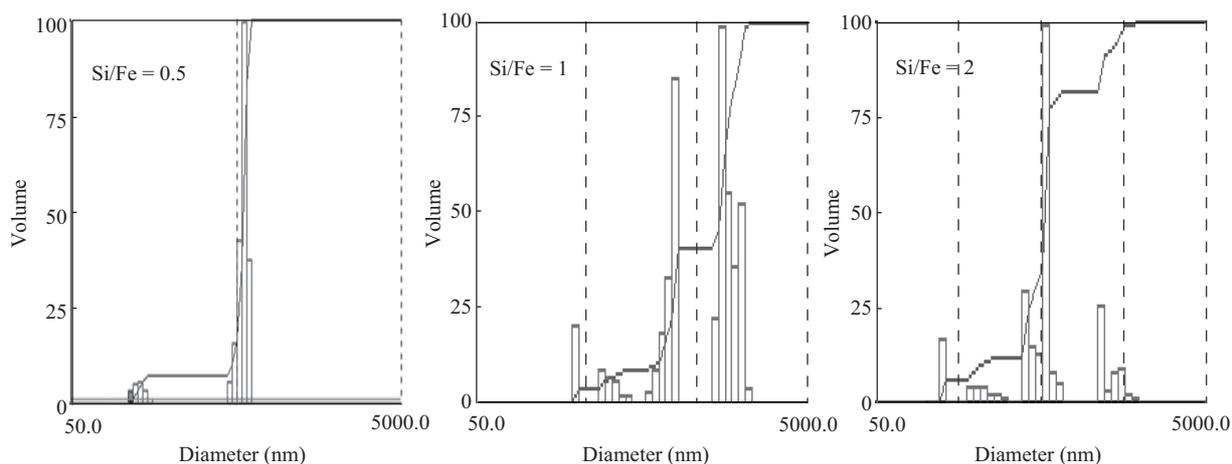


Fig. 3 Changes of particle size detection (PSD) with different Si/Fe ratios.

## 2.2 Coagulation efficiency and mechanism

### 2.2.1 Coagulation efficiency

The coagulation results and the change of particle charge with PFSC dosage (Fig. 4) show that zeta-potential was a controlling factor for double layer repulsion. Zeta-potentials determined by micro-electrophoresis can easily be used to interpret the trend of flotation parameters caused by the presence of chemical additives. When the dosage was increased, zeta-potentials of particles increased and became positive gradually. However, the trend decreased quickly with the increase in the Si/Fe ratio, indicating that charge neutralization capability of PFSC decreased significantly with the increase in the Si/Fe ratio. However, the zeta-potential decrease was only within a limited scale.

As shown in Fig. 4, when the dosage was increased, the zeta-potential gradually became positive. In terms of the effect of silica and the Si/Fe ratio on residual turbidity changes, results showed that turbidity removal was best for samples at high Si/Fe ratio, where flocs appeared fast, tight and large, and underwent rapid precipitation.

A similar trend existed for all kinds of PFSC when the Si/Fe ratio was 0 to 3 (Fig. 4). At low dosages such as 0.172 or 0.344 mg/L, the effect of turbidity removal was small. With dosage increases, the efficient was improved and the

maximum effect of turbidity removal was found at the dosage of 5.4 mg/L. The effect of the Si/Fe ratio on coagulation efficiency also became more obvious. By increasing the ratio, coagulation was enhanced with increased dosage even if particles remained negatively charged.

At the lower dosage, however, the effect of the Si/Fe ratio on turbidity removal was more remarkable (Fig. 4). In other words, when the Si/Fe ratio was high, coagulation efficiency became more obvious. While at the optimum dosage and Si/Fe ratio, the highest turbidity removal percentage was obtained. Thus, Si/Fe ratio increases resulted in efficient coagulation, which significantly lowered residual turbidity.

### 2.2.2 FI index

The coagulation of particulate matter can be reflected by a FI value. Although the detection of FI did not quantify the value of a true diameter of the floc, it was strongly correlated with suspended particle size and increased with particle growth. The FI value can offer a very useful indication of aggregates growth, breakage and re-growth, and allow comparisons to be made between different disturbing conditions. Koalin hanging liquid without coagulant in the initial FI value was set to be zero. Doses in different circumstances, by the line's ignition-coil monitoring, the

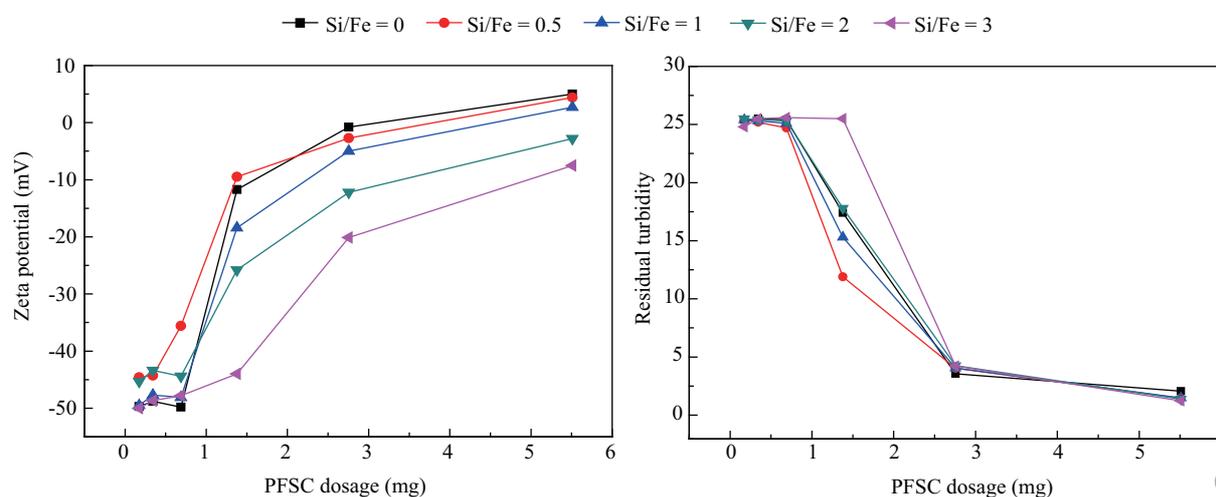


Fig. 4 Changes of zeta-potential and residual turbidity with different PFSC dosages.

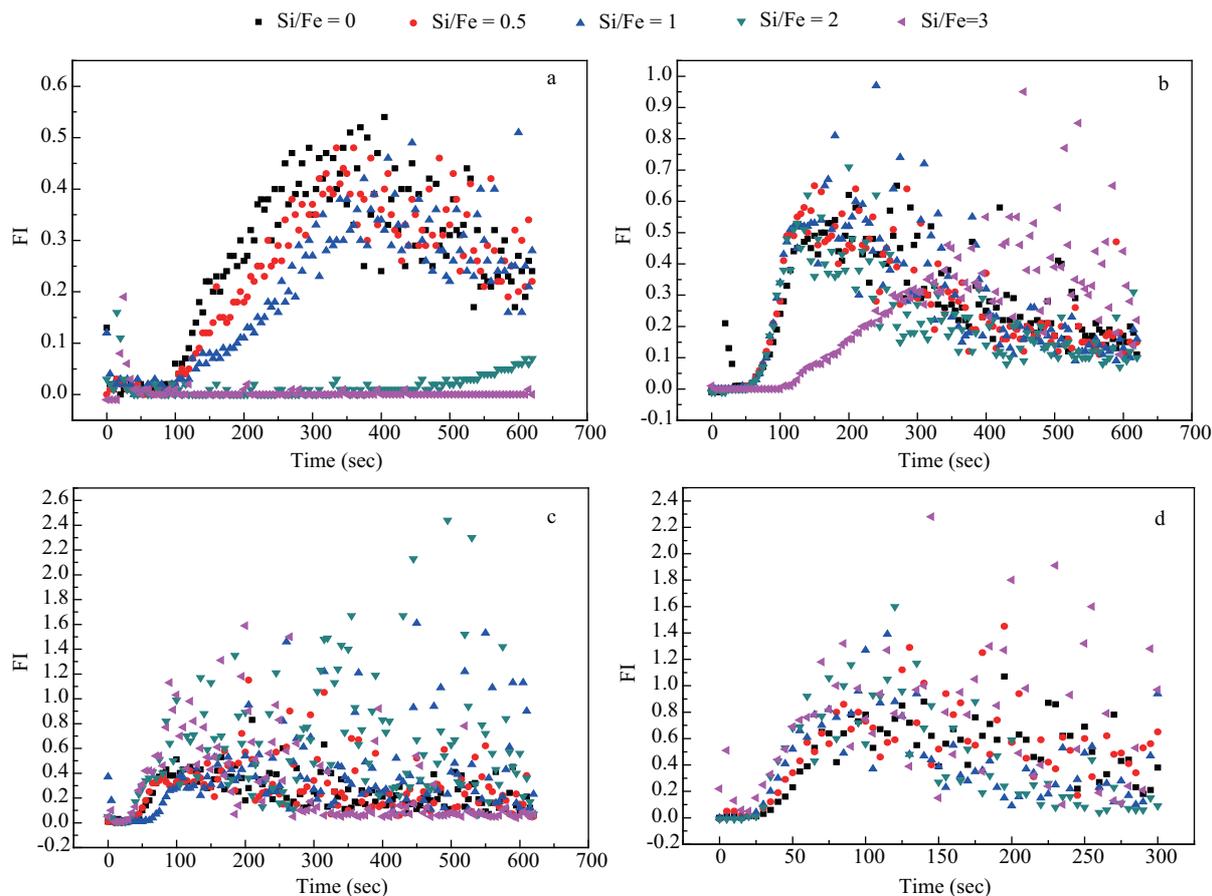


Fig. 5 Changes of FI index with different PFSC dosages. Dose: (a) 2.41 mg/L; (b) 2.76 mg/L; (c); 4.13 mg/L; (d) 5.51 mg/L.

process of PFSC coagulation in kaolin hanging liquid was detected with reaction time (Fig. 5).

As seen in Fig. 5, with the increase in reaction time, the FI value rapidly increased and reached a maximum value ( $FI_m$ ). The ratio (FI) then gradually reduced with floc aging and settling. The initial FI value of the kaolin hanging liquid without coagulant was around 0.08–0.09. After the addition of the coagulant to the system, the FI values increased as reaction time increased. This was mainly because suspended particles are off balance and subsequently form large flocs due to coagulate reactions. Although the Si/Fe ratio may affect the coagulation mechanism, general trends were found to be very similar.

When a low dose of coagulant was used, its contribution to the water's charge change was limited. As a result, when the Si/Fe ratio increased, the time required to reach the maximum FI value increased. That is, the higher the Si/Fe ratio, the longer the retard time. Introduced negative charge resulted in a decrease in the charge neutralization ability of PFSC. Thus, when the dosage was low, particle destabilization ability of PFSC's steadily declined, whereas when introduced activity silica was high, or the Si/Fe ratio was high, the charge neutralization ability became weak, which resulted in a longer time before the maximum FI value was reached.

With the increase in dosage, the time gap between the coagulants maximum FI values decreased. The FI value increased with the increase in Si/Fe ratio. Once the dosage

was large enough that the kaolin particles destabilized, the charge neutralization ability of ferric chloride decreased, together with the negatively charged silicon acid. The higher the Si/Fe ratio, the more significant this influence was. On the other hand, because the introduced polymerized silicon acted as the core hydrolysis product and functioned as the bridge between clay particles, the ability about entrapment in a precipitate and intraparticle bridging was enhanced. The particulate matter underwent a slower rate of destabilization at a high Si/Fe ratio. Such particles easily aggregated and formed larger ones for easy settling. As a result, the FI value achieved the maximum in a short period of time.

Figure 5 also shows that the response rate of reaction, the run time, and the formation of various particles with used dosage along with the change of Si/Fe ratios. With the increase in dosage,  $FI_m$  rapidly increased but residual turbidity decreased. When zeta potential was 0, the  $FI_m$  reached its maximum, as did residual turbidity (> 90%). With the increase in dosage, the zeta potentials of flocs from different coagulants also increased; however, their  $FI_m$  and residual turbidity values decreased significantly. These results suggest that the kinetics associated with the coagulation of PFSC, the destabilization reaction between particle formation with various coagulations and coagulation efficiencies were closely correlated. In such conditions, the largest particles were formed and the  $FI_m$  was obtained.

### 2.2.3 Residual hydrolyzed Fe(III) concentration

Even under the same experimental conditions, the residual hydrolyzed Fe(III) concentrations were different and varied markedly with the change in Si/Fe ratio.

As shown in Fig. 6, increases in dosage or Si/Fe ratio resulted in a decrease in residual hydrolyzed Fe(III) concentration. At low dosage a high residual hydrolyzed Fe(III) concentration was observed because the particles remained colloiddally stable due to highly negatively

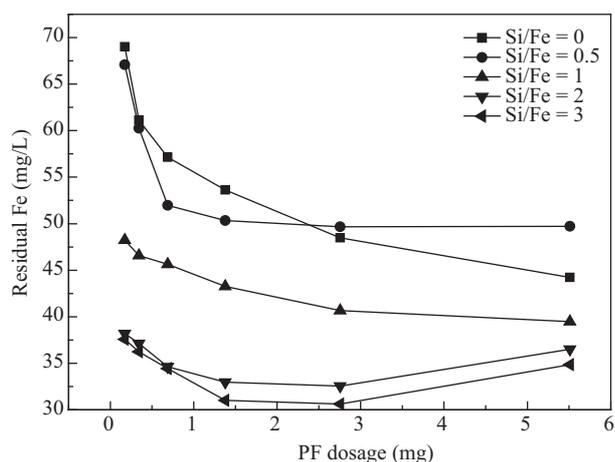


Fig. 6 Changes of residual hydrolyzed Fe(III) with different PFSC dosages.

charges. With the hydrolysis of polysilica acid, a large conglomeration was formed, which acted as the core and functioned as a bridge between clay particles. Therefore, an improved coagulation effect was obtained. On the other hand, however, the portion of polysilica that does not complex with the hydrolyzed Fe(III) was adsorbed the ferric hydroxide so that the residual hydrolyzed Fe(III) concentration in the solution decreased markedly. Obviously, the higher the Si/Fe ratio, the lower the residual hydrolyzed Fe(III) concentration in the solution.

### 2.2.4 DOC removal

Natural organic matter (NOM) in water exists in three forms: particle, colloidal, and dissolved organic matter (DOM). Small molecular organic particles usually less than 0.45  $\mu\text{m}$  in size and dissolved in water is known as DOM and can be characterization by dissolved organic carbon (DOC). The molecular weight, size, and distribution of DOC in water perform the internal structure of the organic matter, so we can determine the appropriate treatment method to remove DOM by DOC assay. In this article, jar tests were used to remove DOC by different Si/Fe ratios of PFSC.

As shown in Fig. 7, the coagulation performance of PFSC with various Si/Fe ratios was evaluated for DOC removal, and results indicated that maximum NOM removal occurs via two ways: acidifying the raw water or

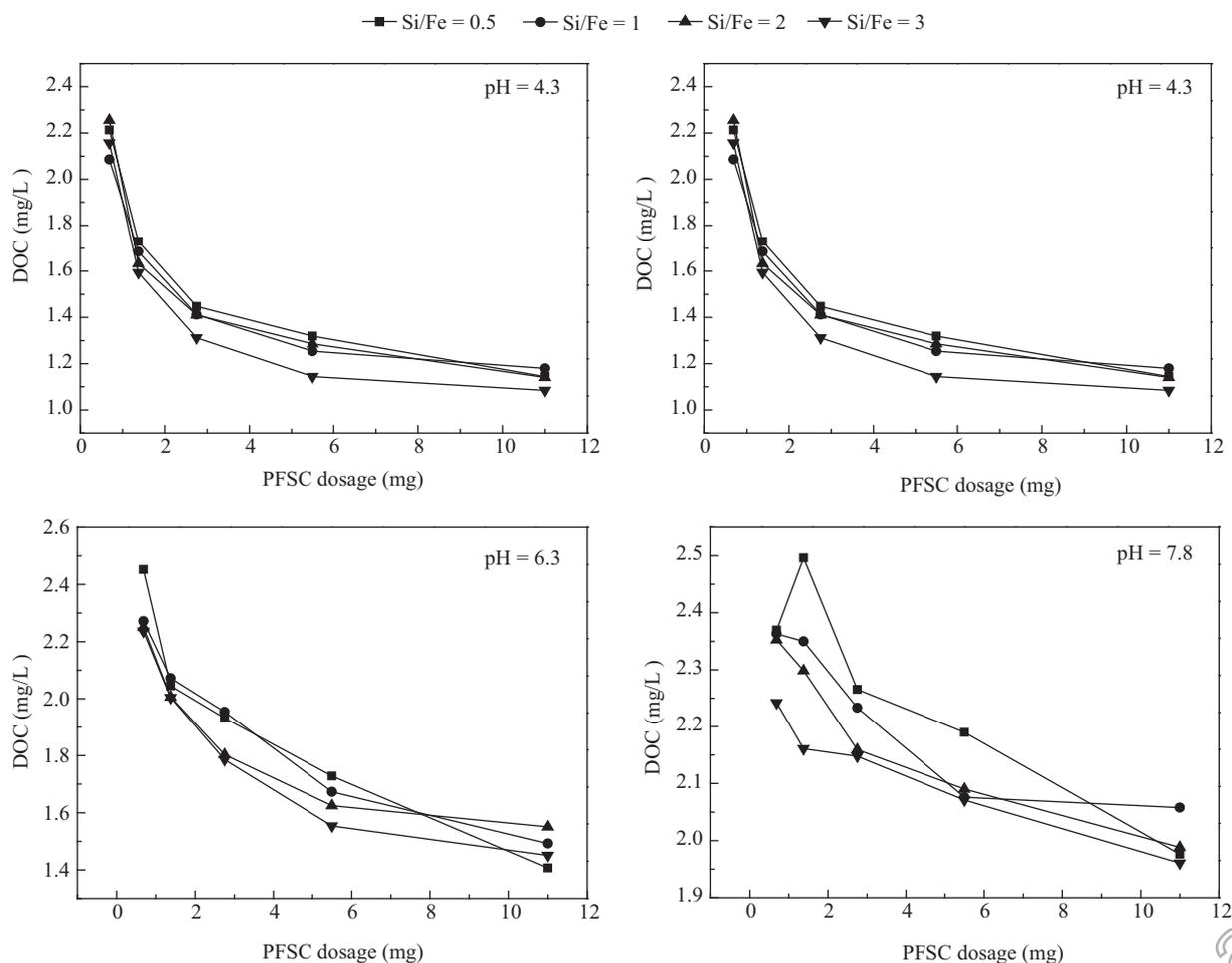


Fig. 7 Changes of DOC in different pH value with different PFSC dosages.

applying increased dosage of coagulants. Figure 7 shows that maximum NOM removal occurred under slightly acidic conditions ( $\text{pH} < 6.0$ ), and DOC can be removed easily through coagulation, with a maximum removal of 62.7 percent. The higher Si/Fe ratio PFSC coagulants were more effective than lower Si/Fe ratios in DOC removal, especially at lower pH values. We found that higher Si/Fe ratio PFSC coagulants had higher molecular weight than lower Si/Fe ratios coagulants, as well as better bridge-formation capability.

The introduction of activated silica into the PFSC weakened the charge neutralization ability. When the silica portion of the coagulant increased, it gave more negative streaming current and decreased the positive charge of PFSC. However, as the activated silica portion of the coagulant increased, the adsorption-precipitation mechanism became dominant, which meant that although the charge neutralization ability of PFSC was weakened when PF and activated silica combined together, the new PFSC adsorbed some portion of NOM or complex with NOM to form co-precipitates, and thus higher DOC removal was received. The activated silica improved bridging properties and absorbance of NOM ability of PFSC, which improved the efficiency of PFSC in NOM removal. Our results showed that when ratios were higher, so was DOC removal.

### 2.2.5 Mechanism of coagulation with PFSC

Chemical coagulants can destabilize colloidal particles or emulsions by four distinct mechanisms: double layer compression, charge neutralization, entrapment in a precipitate, and intraparticle bridging. With the chosen experimental conditions, the difference in coagulation results mainly depended on the composition of coagulants. Based on the ferron assay, the species in PFSC samples were classified similarly as  $\text{Fe}_a$ ,  $\text{Fe}_b$ , and  $\text{Fe}_c$ , which differed markedly with those in pure PFCl solutions. The main species in the PFCl solutions ( $\text{Fe}_a$  and  $\text{Fe}_b$ ) were highly positively charged monomers and oligomers such as dimers and trimers. When added to a suspension, they underwent rapid hydrolysis and adsorption. The hydrolysis formed species were still positively charged and caused efficient charge-neutralization with the negatively charged kaolin particles, since the solution was supersaturated with ferric hydroxide under the experimental conditions. However, the charge of the precipitation formed was largely dependent on the Si/Fe ratio. By decreasing the Si/Fe ratio, a charge reversal was observed. At higher coagulant dosage, the negatively charged clay particles were gradually neutralized. Particle destabilization was observed. The modifier  $\text{Si}_c$ , which was mainly composed of colloid particles, had little effect on the hydrolysis of Fe(III). The species in PFSC remained highly positively charged and the effect of charge-neutralization coagulation is likely explained by another mechanism, where the colloidal silica particles acted as the core of hydrolysis products and functioned as the bridge between clay particles. Therefore, improved turbidity removal was observed at high Si/Fe ratios for PFSC.

## 3 Conclusions

The polymer diameter and species distribution and transformation in PFSC solution were examined comprehensively by experimental methods and instrumental analysis techniques, including PCS, Ferron and Si-Mo timed complexation spectrophotometry. The property and speciation of modified-PFSC were highly dependent on the Si/Fe ratio. By increasing the Si/Fe ratio,  $\text{Fe}_a$  increased and  $\text{Fe}_b$  and  $\text{Fe}_c$  decreased, while  $\text{Si}_c$  increased,  $\text{Si}_a$  decreased,  $\text{Si}_b$  remained unchanged, and the polymer diameter increased markedly.

The coagulation efficiency of PFSC was markedly distinguished from traditional coagulation. The PFSC with appropriate polysilica acid provided better coagulation/flocculation efficiency in turbidity removal, enhanced the flocculation index and reduced residual ferric. The charge-neutralization ability decreased slightly, and coagulation was enhanced through a mechanism of electrostatic patch effect and the bridge effect.

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