Morphology and coagulation performance during preparation of poly-silicic-ferric (PSF) coagulant

Fu Ying [a,b], Yu Shuili [b,*], Han Chunwei [c]

[a] School of Civil and Architectural Engineering, University of Jinan, Jinan 250022, China
[b] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
[c] Liaoing Provincial College of Communication, Shenyang 11500, China

Abstract

A new inorganic polymer, liquid poly-silicic-ferric (PSF) coagulant with various Si/Fe ratios (PSF0.5, PSF1 and PSF3 represent Si/Fe molar ratio of 0.5, 1 and 3, respectively) was prepared using water glass, $FeSO_4 \cdot 7H_2O$ and $NaClO_3$ by co-polymerization. The pH value was measured during the preparation process, the influence of both Si/Fe ratio and reaction time (polymerization or aging time) on the morphology of PSF was explored by transmission electron microscopy (TEM) and turbidity removal by liquid PSF taken from different reaction time was studied by jar test in treating various waters. The solid PSF made from liquid PSF by two different solidification ways was investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Coagulation performance by solid PSF was studied compared to that by liquid PSF. The results show that the morphology of PSF by TEM is largely influenced by both reaction time and Si/Fe ratio. The reaction time for optimal species of PSF can be evaluated by measuring the pH value during the polymerization process. The pH value of PSF0.5, PSF1 or PSF3 tends to be stable at reaction time 10, 25 or 55 min, respectively, which is almost coincident with the time reaching the relative stable morphology that is just the optimal species of higher coagulation efficiency. Surface morphology of solid PSF by SEM is greatly influenced by both solidification method and Si/Fe ratio. PSF is found to be a complexation compound of Si, Fe and many other ions, instead of a simple mixture of raw materials. The influence of reaction time on performance efficiency by liquid PSF is more evident than that by solid PSF, and the reaction time needed in preparing solid PSF with excellent coagulation performance is shorter than that in liquid PSF. Solidification process may be not a simple dehydration from liquid coagulant, but a re-preparation process. When settling time with solid PSF as coagulant increases, the reduction of turbidity removal caused by solidification can be retarded, and the removal of dissolved organic matters can be improved.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Poly-silicic-ferric (PSF); Coagulant; Morphology; Liquid PSF; Solid PSF; Optimal species; Solidification

1. Introduction

The metal–polysilicate complexes mainly contain Al-polysilicate or Fe-polysilicate [1–4], but Fe-polysilicate coagulant has been attracting more and more attention in the field of water treatment [5–9] due to the possible biologic toxicity of residual Al in finished water [10,11]. As a new type of iron-based polymer, poly-silicic-ferric (PSF) coagulant has been studied since the late 20th century in Japan [12], and it is a complex compound of Fe-coagulant positively charged and polysilicic acid flocculant negatively charged.

Presently, the methods used in studying the characteristics of coagulant are as follows: chemical analysis (Ferron–Fe or Ferron–Al), potentiometric titration, ultra-filtration, transmission electron microscopy (TEM), infrared-spectrum (IR), nuclear magnetic resonance (NMR), laser light scattering, X-ray diffraction (XRD) and so on [13–16]. However, investigations related to the identification of the optimal coagulation species by measuring certain macroscopic parameters in the preparation process of coagulant are very rare.

On the other hand, inorganic coagulants produced by many technologies are often liquid products, so the transportation becomes the main problem which can be solved by solidification of liquid products. Generally, the coagulation efficiency by solid coagulant produced from liquid one will decrease to some extent, so how to retard the reduction of coagulation efficiency is worthy to be investigated,

* Corresponding author.
E-mail address: fuying8899@163.com (S. Yu).

while very few studies on this aspect have been done until now.

In this work, we produced PSF with different Si/Fe ratios by a special co-polymerization method, measured the pH value during the preparation process in which other preparation conditions are optimal and explored the influence of both Si/Fe ratio and reaction time on the morphology of PSF by TEM. We aimed at probing the species transformation law and finding the relationship among characteristics, characterization method and coagulation performance of PSF, thus, establishing the correlations between macroscopic behavior and species transformation, and providing a basic method to further understand the characteristics and to improve the effectiveness of coagulant in water treatment, and so on. At the same time, we investigated the surface morphology and component of solid PSF by scanning electron microscopy (SEM) and XRD, respectively, and studied the influence of both reaction time and Si/Fe ratio on the coagulation performance by solid PSF compared to that by liquid PSF. We tried to analyze the optimal solidification conditions or methods through surface morphology, species transformation and coagulation performance, thus, offering useful theoretical data for solidification or application of PSF.

2. Experimental

2.1. Instrumentation and reagents

S-570 Scanning Electron Microscope (SEM, Japan), D/max-rB X-ray Diffractionmeter (XRD, Japan), JEM-1200EX Transmission Electron Microscope (TEM, Japan), AQ2010 Turbidity Meter (America), DHSJ-3F pH Meter (China), MY3000-6K Stirring Meter (China), T6 New Century UV Spectrophotometer (China). Water glass (modulus = 3.1–3.4, $\rho = 1.36\,kg\,dm^{-3}$, $w(SiO_2) = 26\%$, Harbin Xinquan Water Purification Agent Factory) is of industrial grade, $FeSO_4 \cdot 7H_2O$ (Tianjin Yaohua Chemical Reagent Co., Inc.), $NaClO_3$ (Tianjin Bodi Chemistry Co. Ltd.) and H_2SO_4 (Harbin Chemical Reagent Factory) are of analytical grade, humic acid (Liaoning International Economic and Technical Cooperation Group Trading Corp. Ltd.) and kaolin (Tianjin Bodi Chemistry Co. Ltd.) are of chemical grade, water used is double-distilled.

2.2. Preparation of poly-silicic-ferric (PSF) coagulant

2.2.1. Preparation of liquid PSF

Polysilicic acid solution and PSF were all prepared under acidic condition.

Firstly, polysilicic acid solution was prepared. Water glass diluted with double-distilled water to the concentration of 7.5% ($w(SiO_2)$) was introduced slowly into H_2SO_4 solution (20%, 8 mL) at 20 °C and vigorous stirring, and was followed by 2 h of polymerization to obtain a polysilicic acid solution. The polysilicic acid solution shows the following properties: $1.07\,mol\,L^{-1}$ SiO_2 and pH value 3.

Secondly, PSF was prepared. First, according to different Si/Fe molar ratios, 35.21–10.52 g $FeSO_4 \cdot 7H_2O$ was dissolved

in H_2SO_4 solution (60%, 42 mL) to obtain a $FeSO_4$ solution. The second step is to mix $FeSO_4$ solution and the polysilicic acid solution at 40–60 °C and stirring, and then immediately add 0.9–0.32 g $NaClO_3$ according to different Si/Fe molar ratios and stir for 30 min, which is followed by an aging process. PSF samples were taken out at different aging time (reaction or polymerization time), and then were diluted with double-distilled water. Thus, liquid PSF with different Si/Fe ratios (PSF0.5, PSF1 and PSF3 represent Si/Fe molar ratio of 0.5, 1 and 3, respectively) was produced with Fe concentration $10\,g\,L^{-1}$, the products were transparent and brown-yellow liquid of pH 1.05–1.65 for Si/Fe molar ratio from 0.5 to 3.

Based on the results of many coagulation tests and on the consideration of industrialization, PSF produced using polysilicic acid with pH of 3 has better coagulation performance for various waters. Therefore, the investigation on PSF produced under this condition of polysilicic acid (pH 3) is of actual significance. In addition, the diluent of PSF is often used as storage coagulant due to the rapid gelation rate of un-diluted PSF (about 2–5 h), so the PSF diluent of Fe concentration of $10\,g\,L^{-1}$ was selected for the following investigation.

2.2.2. Preparation of solid PSF

Gelatinous PSF: un-diluted PSF with different Si/Fe ratios at final reaction stage (PSF0.5: 20 min; PSF1 and PSF3: 65 min) were stored at 20 °C for 30 days, thus, preparing a kind of gelatinous PSF.

Powder PSF: liquid PSF with Fe concentration $10\,g\,L^{-1}$ was dried at 50 °C in oven for 20–35 h for different Si/Fe ratios and was made powder samples with Fe weight ranging from 7.4 to 10.9%.

2.3. Characterization of liquid PSF

2.3.1. Measurement of pH value during the preparation process

In this preparation method, polysilicic acid solution was first added to $FeSO_4$ solution, and then $NaClO_3$ was added to the mixture at almost the same time (within 3 s). The pH value was measured with pH meter from $FeSO_4$ solution to the final reaction stage of the preparation process.

2.3.2. Morphology by TEM (magnified 10,000 diameters)

A little of PSF solution with Fe concentration $10\,g\,L^{-1}$ at different reaction time was adsorbed onto the copper net, followed by air-drying (at room temperature 21 °C) for more than 10 min, and then was observed and pictured by TEM under accelerating voltage 120 kV.

2.4. Characterization of solid PSF

2.4.1. Surface morphology by SEM

The surface morphology of the two solid PSF samples in Section 2.2.2 was observed by SEM under accelerating voltage 20 kV.

Table 1
Qualities of synthetic suspension

Water type	High turbid water	Low turbid water	High turbid color water	Low turbid color water
Temperature (°C)	25	23	22	22
pH	7.23	6.71	7.62	8.17
Turbidity (NTU)	258–300	6.2–8.8	230–242	6.2–9.5
UV_{254} (cm^{-1})[a]	–	–	0.133–0.163	0.113–0.148

[a] UV_{254} often represents total concentration of dissolved organic matters absorbing UV radiation at 254 nm, so it has been accepted extensively by water researchers. Here, UV_{254} in "High turbid water" and "Low turbid water" is very low, so it is negligible.

2.4.2. X-ray diffraction by XRD

The component of the powder samples was analyzed by XRD under the following conditions: graphite monochromatized Cu Kα radiation; voltage 45 kV; electric current 40 mA; slit: DS1°, SS1°, RS, 0.15 nm; scanning ratio: $2\theta = 5°$ min^{-1}.

2.5. Coagulation experiment

2.5.1. Coagulation performance by liquid PSF at different reaction time

The tested water was synthetic suspension made from kaolin particles. The synthetic suspension was made as follows: (1) Turbid water, 20 g dry kaolin was dispersed in 1 L tap water blended at high speed for 60 min. This dispersion was allowed to settle for 60 min, and then the upper 0.7 L was carefully decanted and added to 35 L of tap water to obtain high turbidity water. One gram kaolin was dispersed in 1 L tap water, and then low turbidity water was obtained according to the method mentioned-above. (2) Color water, a certain amount of humic acid stock solution was added to turbid water, and was followed by 20 min stirring. All synthetic suspension was settled for one night before tests.

The humic acid stock solution was made as follows: first, 5 g humic acid was dissolved into 0.1 mol L^{-1} NaOH solution and was stirred for 12 h, and then was added to 1 L deionization water with concentration 5 g L^{-1}. The qualities of synthetic suspension can be seen in Table 1.

The Fe concentration of working solution of coagulants was 1 g L^{-1}. All coagulation experiments were conducted by a six-beaker apparatus (Flocculator) equipped with a programmable mixer with variable speed and a timer. Each beaker contains 1 L of water samples. The fast mixing time was set to 1 min at a paddle speed of 200 rpm and a second rinsing was set at 30 s after coagulant was added. The slow mixing stage (2 min at 60 rpm followed by 3 min at 40 rpm, and followed by 5 min at 20 rpm) was followed to build up microflocs to large and dense flocs. A sedimentation stage was followed and the supernatant samples, after settling, were withdrawn from a position of 2 cm below the surface of the tested water samples for the analysis of residual turbidity with Turbidity Meter.

2.5.2. Comparison of coagulation performance between liquid PSF and solid PSF

The tested water was taken from Song Huajiang River polluted badly in Harbin city. Water qualities were as follows: turbidity = 65 NTU, temperature = 17.5 °C, $COD_{Mn} = 6.68$–

7.21 mg L^{-1}, $UV_{254} = 0.101$ cm^{-1}, pH 7.65. The coagulation procedure is the same as that in Section 2.5.1. After the measurement of residual turbidity, the remaining supernatant was filtered with 0.45 μm pore size membrane (China) for UV_{254} measurement (a surrogate parameter for dissolved organic matters).

3. Results

In this preparation method, the oxidation rate of NaClO$_3$ is very fast and the oxidation process can be finished within 5 min (according to transformation rate of Fe^{3+} from Fe^{2+}). 5, 10 and 20 min were selected as three reaction times (aging time) for PSF0.5 due to its rapid gelation rate, while for PSF1 and PSF3, 5, 35 and 65 min were selected as three reaction times, respectively.

3.1. Investigation on liquid PSF

3.1.1. Change of pH value during the preparation of PSF

Here, we evaluate the optimal reaction time of PSF according to the pH changes during its preparation process.

Fig. 1 shows the pH change during the mixing of raw materials (adding sequence in Section 2.3.1). The pH value of PSF0.5 or PSF1 increases first and then decreases, in comparison with a continuous increasing in PSF3. The pH value increases after addition of polysilicic acid solution, possibly because polysilicic acid solution has relative higher pH value resulting in a reduction of solution acidity. Generally, single Fe^{3+} only exists at pH < 1.1, hydrolyzes at pH 2.2, and evidently forms [Fe(H$_2$O)$_5$OH]$^{2+}$ at pH > 2 [17]. Fe^{3+} may be hydrolyzed instantly after the addition
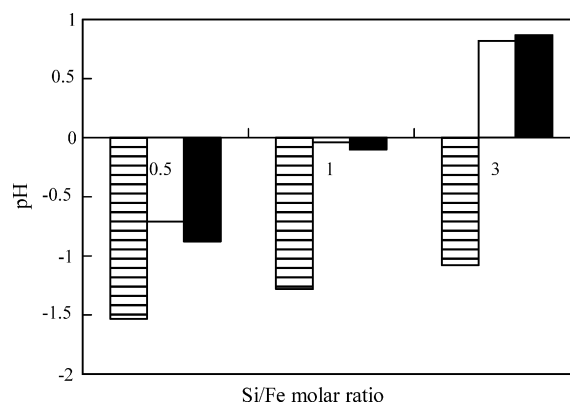

Fig. 1. pH value after addition of raw materials, FeSO$_4$ (▤), polysilicic acid solution (▢), NaClO$_3$ (■).

of polysilicic acid solution (pH 3), thus, leading to the simulta-
neous and complicated complexation of Fe^{3+} or its hydrolysis
products with polysilicic acid solution. But the pH value almost
decreases to lower than one within 5 s, so the further hydrolysis
of Fe^{3+} can be neglected due to the higher acidity of the reaction
system.

The pH change of PSF3 was different from that of PSF0.5 or
PSF1 after addition of $NaClO_3$, because pH may be affected by
the two following aspects: (1) as indicated in the following equa-
tion: $6Fe^{2+} + ClO_3^- + 6H^+ = 6Fe^{3+} + Cl^- + 3H_2O$, pH value will
increase, (2) pH value will decrease due to the de-polymerization
of polysilicic acid according to the previous studies [18] or due
to Fe^{3+} hydrolysis. For PSF0.5 and PSF1, the process (1) is the
main reaction due to the higher acidity and the large amount of
Fe^{3+}. While for PSF3, the relative higher pH value after addi-
tion of polysilicic acid solution leads to less de-polymerization
of polysilicic acid, so the pH value almost tends to be stable.

The different pH change in various Si/Fe ratios will greatly
influence both the polymerization process of Si–Fe and the for-
mation of optimal coagulation species in the subsequent process.
In addition, the pH change will play a significant role in the mor-
phology change of the prepared coagulants of same Si/F ratio.
For example, the morphology by TEM in Fig. 3 changes from
chain-like structures to multi-branched structures (for PSF0.5 or
PSF1) and further to net structures (for PSF3). The pH change
has also certain influence on the surface morphology by SEM,
shown in Fig. 6. In a word, the increase of pH value will result
in the size increase of morphology.

Fig. 2 displays the impact of reaction time on pH change in
different Si/Fe ratios. As shown in Fig. 2a, the pH value changes
a lot in PSF0.5, which corresponds to the rapid adjustment of

morphology (Fig. 3) or more evident change of surface morphol-
ogy (Fig. 6). The pH value has a sudden rise at 5 min or so, and
then decreases quickly. It could be believed that pH tends to be
stable at 10 min due to the wider change range of pH value. For
PSF3 (Fig. 2c), the extended increase of pH value indicates that
the species transforms smoothly. The pH reaches a stable value
of 1.02 at 55 min. PSF1 (Fig. 2b) is the mid-situation between
PSF0.5 and PSF3, and pH value first decreases a little (may be
due to the de-polymerization of polysilicic acid) and is followed
by an increase, and then achieves a stable value of 0.03 at 25 min.

The preparation of PSF is a very complicated process, con-
cerning the complexation between Si, Fe^{3+} or the hydrolysis
products of Fe^{3+} and so on, in which OH^- plays a signifi-
cant role in the formation, recombination and transformation of
bond. Therefore, the transformation of species can be reflected
through the amount of OH^- to some extent, thus, the optimal
reaction time for favorable species may be evaluated by testing
the pH change during the reaction process. On the other hand, it
can be concluded, from the comparison between pH value and
microstructure (Fig. 3), that the species may be relatively stable
when pH reaches a stable value, so that the reaction time reach-
ing the optimal species may be of a wider range, but not only a
time point.

3.1.2. Morphology of PSF by TEM (magnifies 10,000 diameters)

It is well-known that TEM can only observe the solid mor-
phology. The coagulant measured by TEM in this work is the
dilution sample which gives very thin and uniform dispersion on
the copper net, so TEM can be thought to be the most intuition-
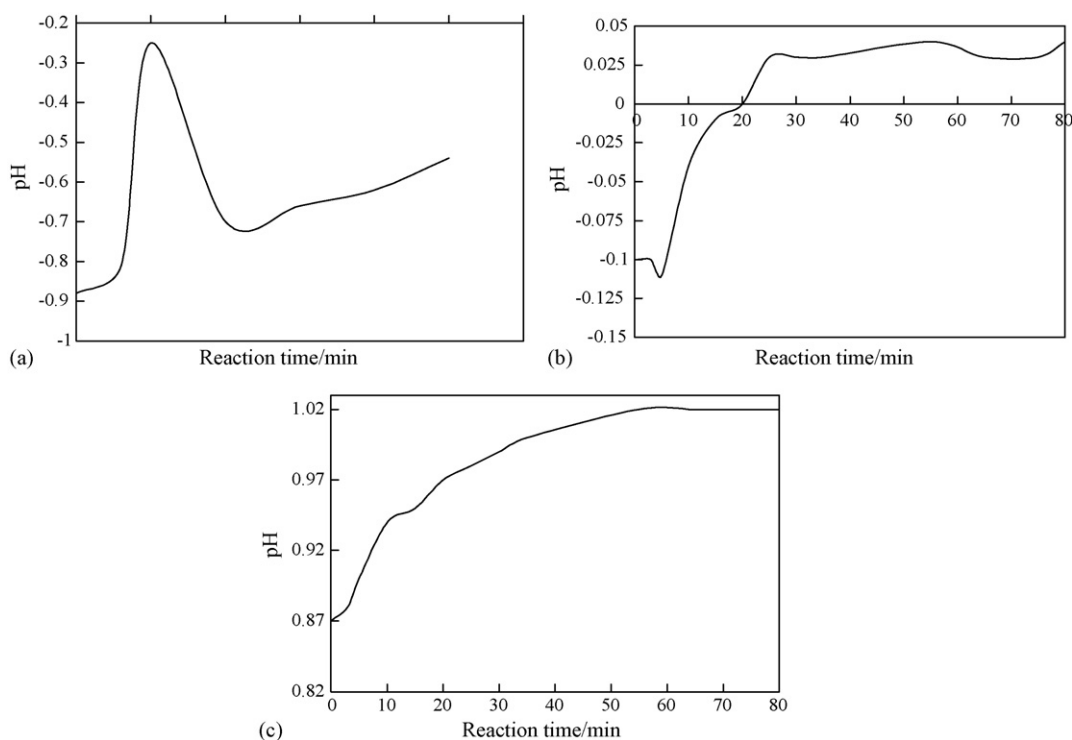istic way to observe the actual morphology of liquid coagulant

Fig. 2. Impact of reaction time and Si/Fe ratio on pH value of PSF: (a) reaction time in PSF0.5, (b) PSF1 and (c) PSF3.
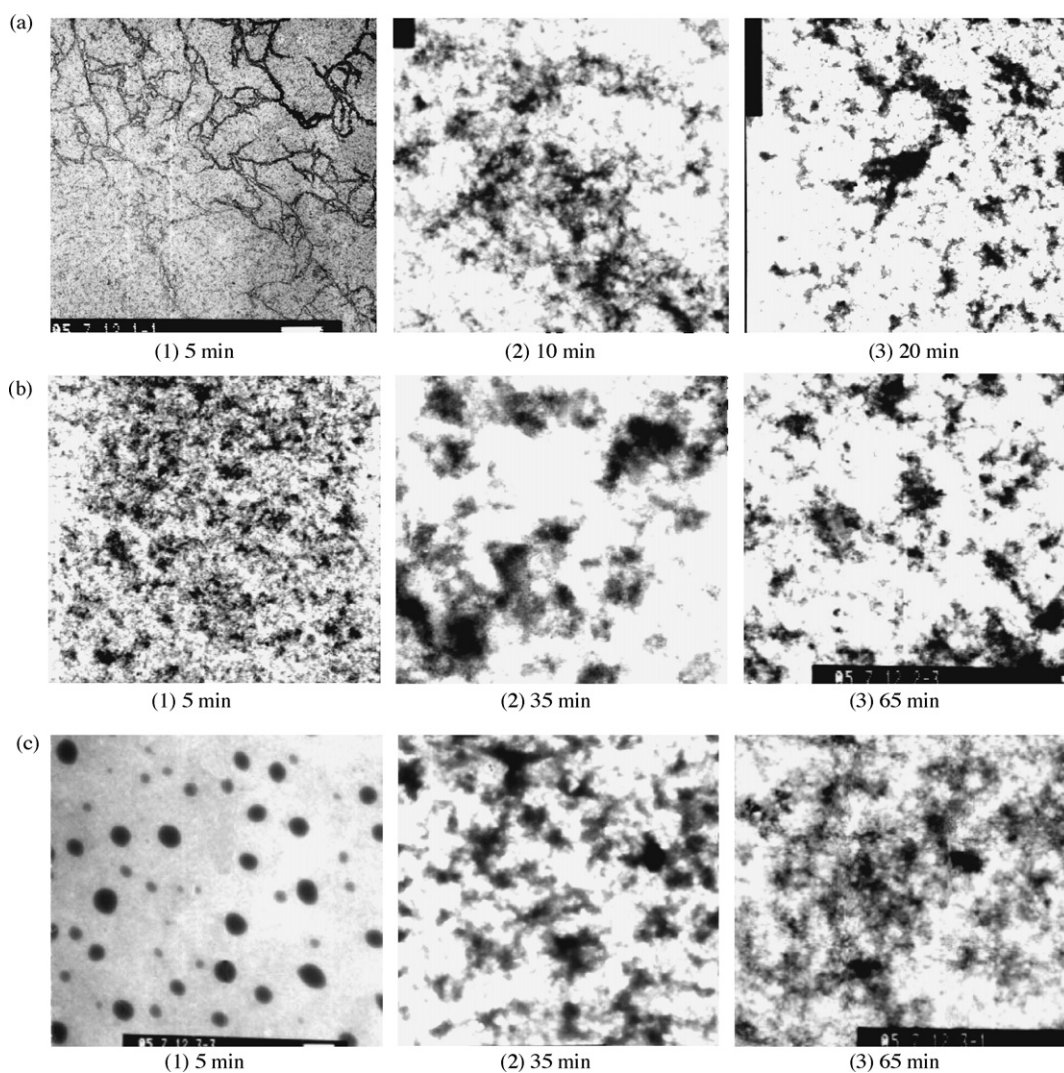
Fig. 3. Impact of reaction time and Si/Fe ratio on the electron micrographs of PSF: (a) PSF0.5, (b) PSF1 and (c) PSF3.

due to the similar shape of the solid coagulant to that of liquid one. The morphology of PSF with various Si/Fe ratios at different reaction time is shown in Fig. 3 and is the function of Si/Fe ratio and reaction time.

For PSF0.5 (Fig. 3a) and PSF1 (Fig. 3b), there appears a certain time range 5–10 min and 5–35 min, respectively, in which the morphology changes evidently. For PSF3, there appears two time ranges: 5–35 min and 35–65 min (Fig. 3c), in which the morphology has obvious change, while 35–65 min might be the change range when considering the actual preparation process.

As displayed in Fig. 3a, a thin multi-branched structure (wire-like) with larger size and bigger fractal dimension (a terminology in flocculation morphology) [19] is formed at 5 min. At 10 min, the wire-like morphology disappears, possibly because some change, such as bond breakage or bond recombination, occurs. At 20 min, more multi-branched structures are further formed with larger size and bigger fractal dimension. As shown in Fig. 3b, many short chain-like matters are formed dispersedly at 5 min, and is followed by the formation of much branched structure at 35 min. At 65 min, the morphology changes a little and

transforms into multi-branched structure by further coupling the chain-like matters. As illustrated in Fig. 3c, the morphology distributes spherically at 5 min, which can be speculated to be the morphology of polysilicic acid [20], thus, indicating that Fe^{3+} does not react with polysilicic acid. At 35 min, many chain-like structures with larger size than that of PSF0.5 and PSF1 distribute densely. At 65 min, a kind of closed-net structure coupled with branched structure is formed and is characterized by having larger size and bigger fractal dimension.

As revealed in Fig. 2, the pH value of PSF0.5, PSF1 or PSF3 tends to be stable at reaction time 10, 25 or 55 min, respectively, which is almost coincident with the time for relative stable morphology (or species, Fig. 3) that is just the optimal coagulation species (Fig. 4).

3.1.3. Turbidity removal with PSF in treating various waters (synthetic suspension)

In order to test the efficiency of turbidity removal by PSF samples at different reaction time in treating various waters, four kinds of waters are selected as samples (Table 1). Here, only two kinds of water samples (high turbid color water and low
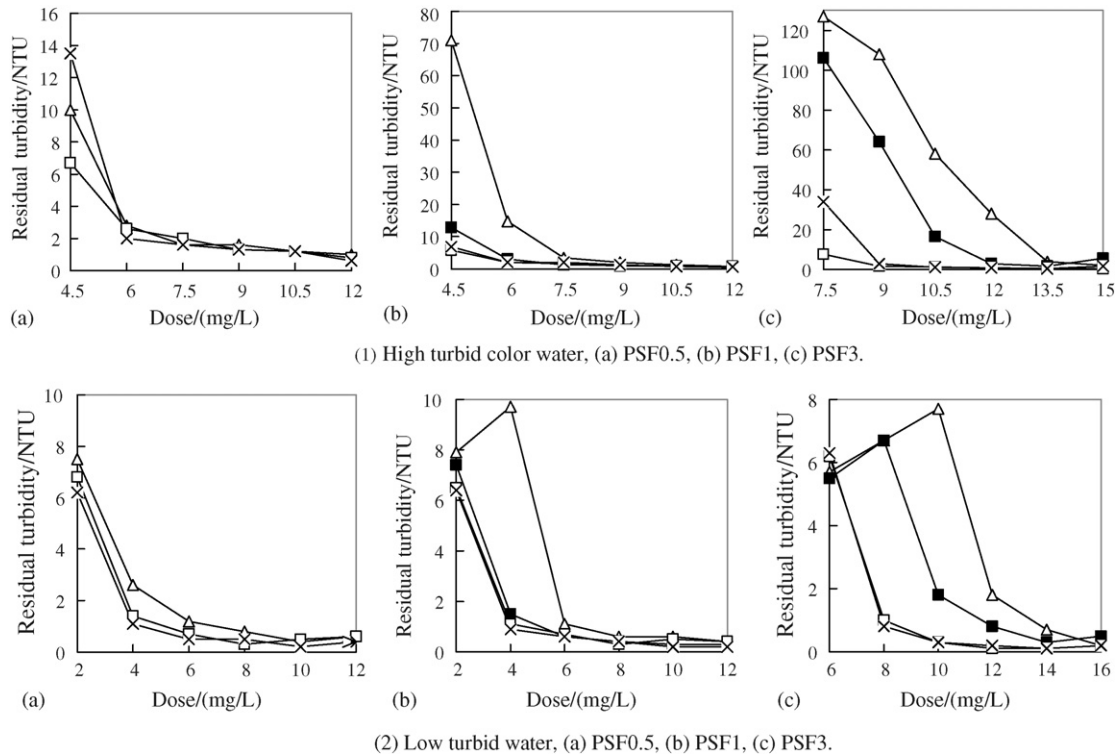
(1) High turbid color water, (a) PSF0.5, (b) PSF1, (c) PSF3.

(2) Low turbid water, (a) PSF0.5, (b) PSF1, (c) PSF3.

Fig. 4. Effect of reaction time and Si/Fe ratio on turbidity removal by PSF: 5 min (△), 10 min (□) and 20 min (×) for PSF0.5; 5 min (△), 35 min (■), 65 min (□) and 80 min (×) for PSE1 and PSF3.

turbid water) were used as examples due to the similar results, displayed in Fig. 4.

As shown in Fig. 4, PSF0.5 samples at different reaction time almost have similar coagulant efficiency, possibly because PSF0.5 gels rapidly during its preparation, resulting in no obvious difference. For PSF1, samples after reaction time of 35 min have similar and higher turbidity removal, in comparison with samples after reaction time of 65 min for PSF3.

As shown in Fig. 4(2), the residual turbidity by PSF3 (low turbid water) increases firstly at lower dose during the periods 5 and 35 min and not for 65 and 80 min. It can be explained as follows: (1) the coagulation performance by PSF3 samples at reaction 5 or 35 min is very lower due to the lower charge density at higher Si/Fe ratio ((2) in Section 3.2.1) and chain-like characteristics of morphology (Fig. 4); (2) the amount of particle impurities in tested water is lower, so the flocs formed by PSF3 will disperse in the supernatant if dose is not enough to destabilize and bridging the impurities, consequently increasing the residual turbidity.

As experimental results illustrated above, PSF samples of the same Si/Fe ratio at different reaction time have different coagulation performance, while the PSF samples having higher coagulation efficiency are characterized by having the same reaction time at which pH value tends to be stable (Fig. 2). On the other hand, according to the morphology (Fig. 3) and the coagulation efficiency (Fig. 4), short chain-like matters are not the favorable morphology for water treatment, while the multi-branched structure with larger size and bigger fractal dimension may be the desired morphology in coagulation process. More-

over, the desired morphology may not be one kind of changeless species but a combination of wider range species.

3.2. Investigation on solid PSF

3.2.1. Surface morphology of PSF by SEM
3.2.1.1. Influence of Si/Fe ratio on surface morphology of gelatinous PSF. As shown in Fig. 5, there are lots of protuberance morphology on the surface of PSF. The surface roughness of PSF0.5 is greater than that of PSF1. The morphology with great surface roughness in PSF3 differs completely from the two formers.

3.2.1.2. Influence of Si/Fe ratio and reaction time on surface morphology of powder PSF (magnifies 3000 diameters). As shown in Fig. 6(1), the surface in PSF0.5 consists of some sort of curl-slice morphology. The directionality of the morphology becomes evident and some curl-slice morphology connects with each other to form larger curl-slice ones with the increasing of reaction time. The curl-slice morphology changes from erected to tiled when reaction time ranges from 5 to 10 min. As shown in Fig. 6(2), the curl-slice morphology of PSF1 changes from erected to tiled when reaction time ranges from 5 to 35 min and is followed by an erection again with evident larger size of curl-slice morphology. Though PSF0.5 and PSF1 have the same surface morphology of curl-slice, the surface morphology in PSF1 is arranged compactly with smaller aperture diameter and size and without evident directionality compared to that in PSF0.5.
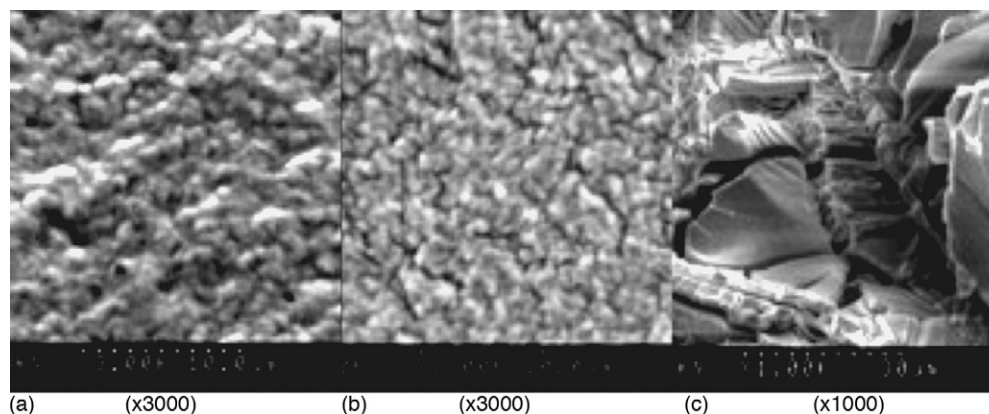
Fig. 5. Surface morphology of gelatinous PSF against Si/Fe molar ratios: (a) PSF0.5, (b) PSF1 and (c) PSF3.

As revealed in Fig. 6(3), the surface morphology in PSF3 differs from that in PSF0.5 or PSF1 and consists of lots of nano crystal-palpus with obvious directionality. The length of the crystal-palpus at 5 min is shorter, and increases with the increasing of reaction time, but changes little after reaction time of 35 min, indicating that reaction time has little influence on the species change at final reaction stage. As also seen in Fig. 6(3), the picture is a little darker and there are some lateral-cuts, suggesting that PSF3 gives weak electrical conductivity and brings discharge phenomena under condition of no gold-coating. This further shows that the charge density decreases with the increasing of Si/Fe ratio, which is consistent with the previous studies about Al [21].

From the comparison shown in Fig. 6, the surface morphology in PSF0.5 changes dramatically as reaction time varies. So it can be deduced that the inter species changes greatly, which is consistent with the experimental results and pH change: the lower the Si/Fe ratio, the faster the PSF sample gels and the more pH changes. There is a commonness in PSF0.5 and PSF1, namely that the curl-slice structure changes from erected to approximate tiled at certain reaction time (PSF0.5: 5–10 min; PSF1: 5–35 min), but the precise reason is expected to be further investigated by coupling with other analytical methods.

In this test, the powder PSF was stored for many days at room temperature, so the adherence of small particulate samples to larger ones is the result of the self-aggregation. The adherence may be shows the inherent adsorption ability of PSF. From the experiment, some small granule samples are attached to the surface of PSF1 or PSF3 (that can be observed by magnifying 1000 diameters), moreover, the amount of small granule samples attached to larger ones increases with the increasing of Si/Fe ratio. This indicates that the adsorption ability increases gradually with the increasing of Si/Fe ratio, which is also the result of the gradual increase of the amount of polysilicic acid solution in PSF.

As revealed by comparison between Figs. 5 and 6, the surface morphology of un-diluted gelatinous PSF differs greatly from that of powder samples produced from the diluent of PSF. The former is characterized by having compact structure without apertures, while the latter shows an incompact structure with many apertures. Therefore, the solid PSF may be dissolved again easily after its dilution first and then solidification. In fact, PSF can be diluted to different concentration before solidification according to different aims.

3.2.2. X-ray diffraction

Here, take the powder PSF as the analysis sample. Fig. 7 displays XRD patterns of the powder PSF samples with different Si/Fe molar ratios. Generally, a series of characteristic diffractive peaks of crystal materials can be observed at certain 2θ, instead of amorphous. As shown in Fig. 7, no standard crystals, such as $Fe_2(SO_4)_3$, Fe_2O_3, $Fe(OH)_3$, Fe_3O_4 and SiO_2 can be observed in PSF, which indicates that such materials as Fe^{3+}, SO_4^{2-} and polysilicic acid have been concerned with the polymerization, indicating that PSF may be a complexation compound of Si, Fe and many other ions, instead of a simple mixture of raw materials. Any certain matter cannot be determined in PSF0.5 or PSF1, suggesting that some new kind of compounds which are not included in the gallery or some new matter which does not give a standard formula may be have been formed. The matter measured in PSF3 is $Na_3Fe(SO_4)_3 \cdot 3H_2O$ which is a kind of hexagonal and some amorphous. Different chart of X-ray diffraction in different Si/Fe ratio indicates that the reaction mode between Si and Fe are different from various Si/Fe ratios.

3.3. Comparison of coagulation performance between powder solid PSF and liquid PSF

Here, L or S denotes liquid PSF or solid one, respectively, and L-5 or L-PSF0.5 represents the sample at reaction time of 5 min or the sample PSF0.5, respectively, and the same as others.

3.3.1. Influence of reaction time on coagulation performance

Here, take PSF1 as an example. Liquid PSF1 or solid one is diluted or dissolved to the same Fe concentration ($1\,g\,L^{-1}$), respectively. Dose is $8\,mg\,L^{-1}$, as Fe. The settling time is 10 min in the coagulation test.

As shown in Fig. 8a, the residual turbidity by liquid PSF1 decreases with the increasing of reaction time, in comparison with a little increase by solid PSF1, indicating that longer

(1)

(a)   5 min   (b)   10 min   (c)   20 min

(2)

(a)   5 min   (b)   35 min   (c)   65 min

(3)

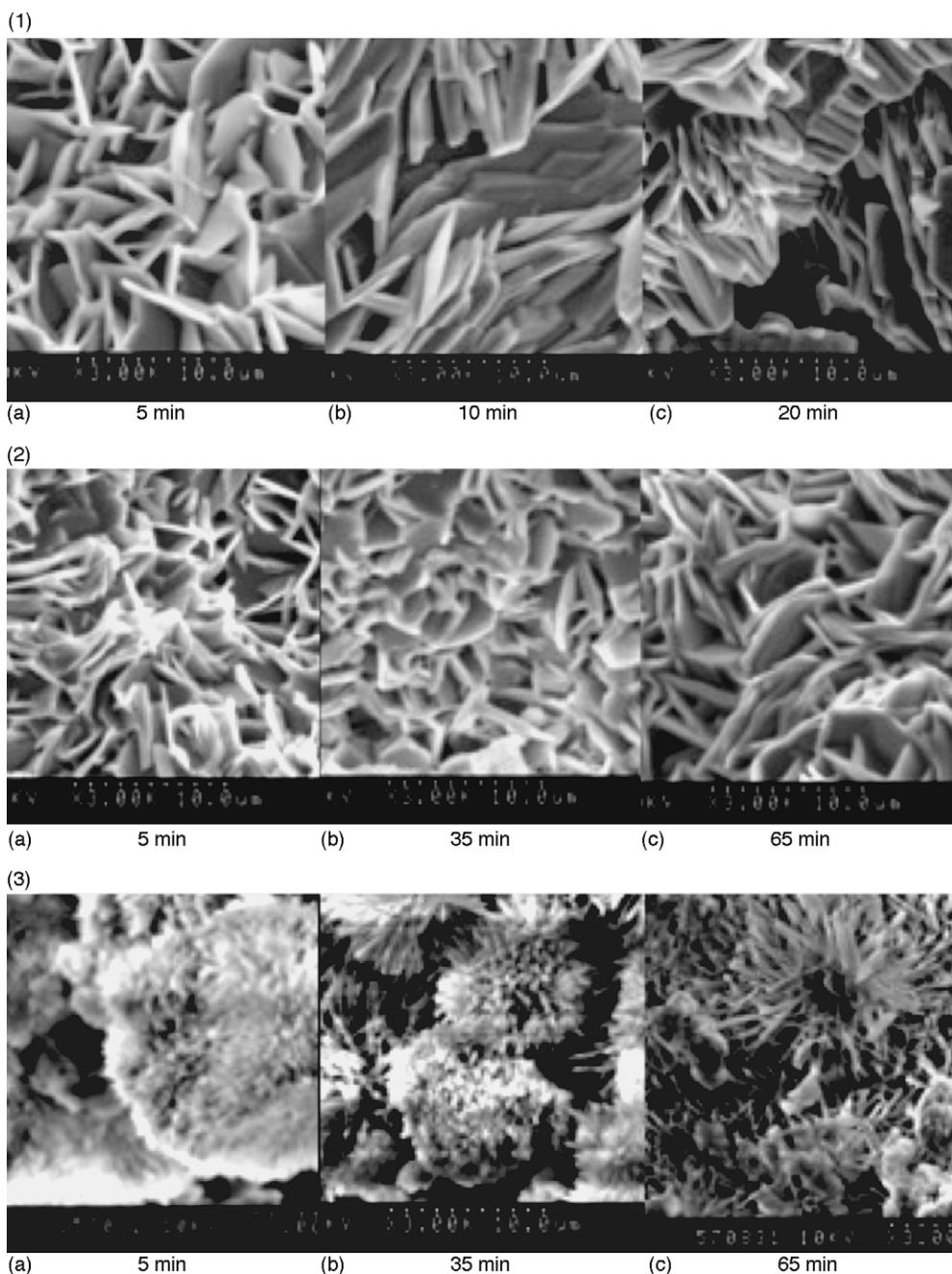(a)   5 min   (b)   35 min   (c)   65 min

Fig. 6. Surface morphology of powder PSF against reaction time and Si/Fe molar ratios: (1) PSF0.5, (2) PSF1 and (3) PSF3.
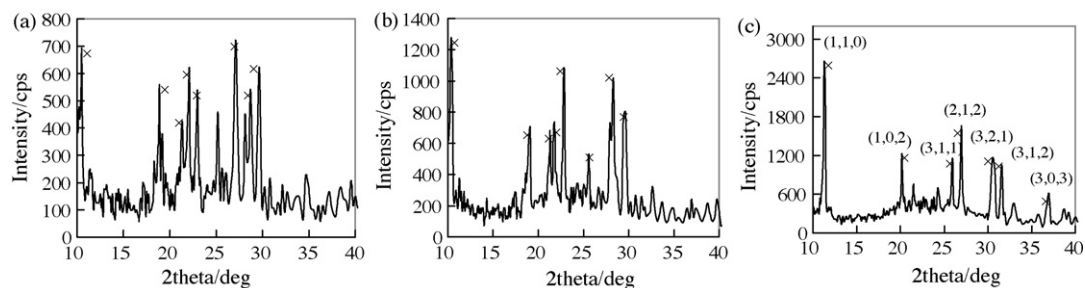

Fig. 7. XRD patterns of the powder PSF samples: (a) PSF0.5, (b) PSF1 and (c) PSF3.
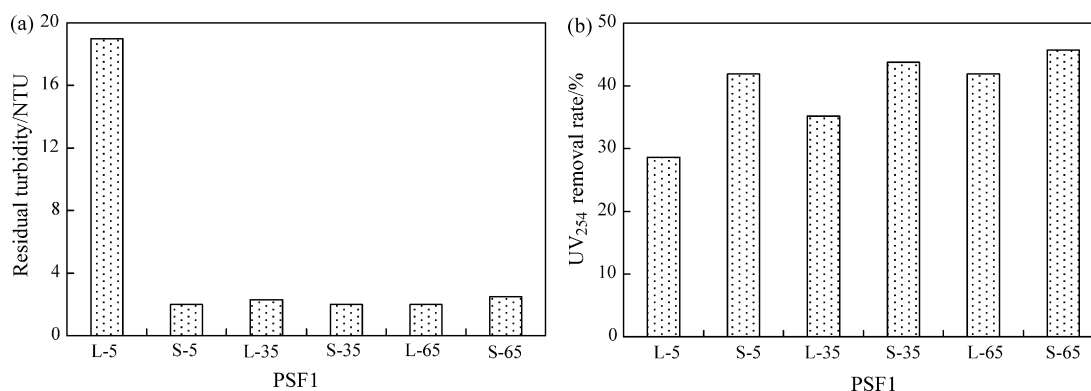
Fig. 8. Comparison of coagulation performance between powder solid PSF1 and liquid one.

reaction time (as 65 min) will slightly reduce the ability of removing turbidity by solid PSF1. As also seen in Fig. 8b, UV_{254} removal by solid PSF1 increases evidently compared to that by liquid one, with the increasing difference from 14.5 to 3.9% for reaction time from 5 to 65 min, but this increasing difference reduces gradually with the increasing of reaction time.

In a word, the influence of reaction time on the coagulation performance by solid PSF1 is smaller than that by liquid one. So we should seize the optimal reaction time (or polymerization degree) of liquid PSF1 when solidifying it, while this time differs greatly from the reaction time at which liquid PSF1 gives the optimal coagulation performance, namely, the reaction time needed for preparing solid PSF1 is shorter than that for liquid one. Controlling the optimal reaction time in preparing the solid coagulant has great significance for the actual manufacture process, which not only improves the production efficiency but also reduces the cost.

For PSF1 prepared in this work, the optimal reaction time can be ranged from 5 to 35 min.

3.3.2. Influence of Si/Fe ratio on coagulation performance

Here, take PSF0.5 at 20 min and PSF1, PSF3 at 65 min as examples. Dose is 7 mg L^{-1}, as Fe.

Compared to liquid PSF (Fig. 9), turbidity removal by solid PSF decreases gradually with the increasing of Si/Fe ratio compared to gradual increase of UV_{254} removal. So PSF with different Si/Fe ratios can be solidified according to different

aims of water treatment. Solid PSF and liquid one have the similar turbidity removal when increasing the settling time (for example, 18 min), in comparison with the larger difference in removing UV_{254}. When settling time with solid PSF as coagulant increases, the reduction of turbidity removal caused by solidification can be retarded, and the removal of dissolved organic matters can be improved.

The pH value of coagulation supernatant by liquid PSF is a little lower than that by other coagulants (neglected here due to the length of this paper), but its pH is still above 6.5 at the optimal dose, which can meet the requirement of drinking water. The pH value of coagulation supernatant by solid PSF is 0.3–1.2 higher than that by liquid one due to the reduction of the acidity during the solidification, and moreover, the higher the Si/Fe ratio, the larger this value increase.

From the comparison of the coagulation performance between solid PSF and liquid one (Figs. 8 and 9), it can be concluded that possibly the preparation conditions for solid PSF are very different from that for liquid PSF. Solidification is the successive aging process for liquid PSF, in which species changes greatly. So the time should be left for species transformation in the solidification of liquid coagulants in order to give solid coagulant the optimal coagulation species and to further improve the coagulation efficiency. Therefore, solidification is not a simple dehydration from liquid coagulants, but a re-preparation process. From the experimental phenomena, solid PSF gives smaller flocs with larger density and larger surface area having strong attrac-
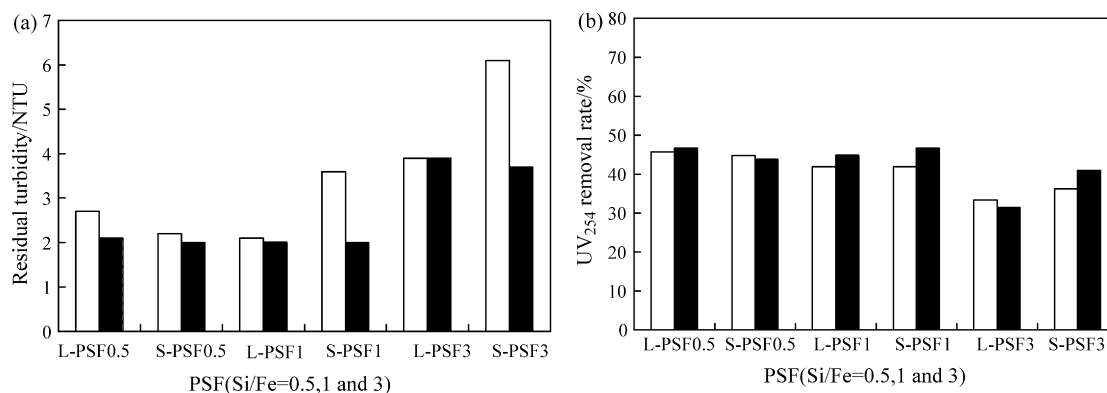

Fig. 9. Influence of Si/Fe molar ratio on coagulation performance by solid PSF and liquid one, settling 5 min (□) and settling 18 min (■).

tion than liquid one, so solid PSF gives great attraction force for dissolved organic matters, thus, resulting in the improvement of UV_{254} removal. In order to decrease the reduction of coagulation performance, to improve the coagulation effect and to decrease dose, we can select coagulant sample which has different reaction time, different concentration of diluent or different solidification method for solidification according to different aims in water treatment or to different qualities of raw waters. The solidification method taken in this paper only represents a method with lower cost, which differs greatly from spraying solidification process that is characterized by having fast solidification rate and little species change.

To sum up, according to the investigation into morphology and coagulation performance of both solid PSF and liquid PSF, we can almost identify the optimal reaction time reaching favorable species by measuring pH change during the reaction process. Next, we find the difference of the optimal reaction time needed to achieve the optimal species between preparing solid and liquid PSF. Last, we get some theoretical data for the solidification process, such as the optimal reaction time of PSF samples for solidification, solidification method or solidification conditions, of course, it is expected to have much work about these results.

4. Conclusions

The reaction time reaching the optimal coagulation species can be evaluated by measuring the pH change during the polymerization process. The pH value of PSF0.5, PSF1 or PSF3 tends to be stable at reaction time 10, 25 or 55 min, respectively, which is almost coincident with the time reaching relative stable morphology that is just the optimal species of higher coagulation efficiency.

PSF is found to be a complexation compound of Si, Fe and many other ions, instead of a simple mixture of raw materials. Reaction time needed in preparing solid PSF having excellent coagulation performance is shorter than that in liquid PSF. Solidification process may be not a simple dehydration from liquid coagulant, but a re-preparation process. In order to decrease the reduction of coagulation performance and to improve the application efficiency of coagulant, we can select coagulant sample which has different reaction time, different concentration of diluent or different solidification method for solidification according to the different aims in water treatment or to different qualities of raw waters.

The investigation on the surface morphology of solid PSF and on the coagulation performance will provide some theoretical data for the solidification process, and offer a cut-in point for the studies on the inherent species transformation of coagulant.

Acknowledgement

References

[1] T. Hasegawa, T. Hashimoto, T. Onitsuka, Characteristics of metal–polysilicate coagulants, Water Sci. Technol. 23 (1991) 1223–1713.
[2] B.-Y. Gao, H.H. Hahn, E. Hoffmann, Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment, Water Res. 36 (2002) 3573–3581.
[3] H.-Y. Yang, Z.-L. Chen, G.-B. Li, X.-L. Guan, Y.-Z. Zeng, Effects on residual aluminum by metal–polysilicate coagulants in low turbid water treatment, Harbin Gongye Daxue Xuebao 36 (2004) 313–316.
[4] Y.-Y. Dai, H.-Q. Qiu, Speciation analysis and coagulation behavior of PFSS., Tech. Equipment Environ. Pollut. Control 6 (2005) 61–64.
[5] K. Ohno, M. Uchiyama, T. Kamei, Y. Magara, Practical design of flocculator for new polymeric inorganic coagulant-PSI, Water Sci. Technol. 4 (2004) 67–75.
[6] Z.-B. Hu, X.-M. Wang, H.-L. Fu, A research on treatment of low-temperature low-turbidity water using ferric polysilicate, Ind. Water Wastewater 35 (2004) 21–22.
[7] Q.-Z. Jia, S.-Z. Yi, Studies on the preparation and preperties of polysilicic acid-polyferric chloride flocculant, Ind. Water Wastewater 24 (2004) 38–40, 49.
[8] Y. Fu, S.-L. Yu, S.-T. Fu, R.-P. Liu, Analysis of mechanism IN removing dissolved organic matters by poly-silicic-ferric sulfate (PSF), in: The Progress of Green Oxidation/Reduction Technologies, Jilin University Press; Air and Water Treatment by Green Oxidation/Reduction Technologies-Catalyst, Plasma and Hybrid Systems, Dalian, China, 2006, pp. 1–4.
[9] Y. Fu, S.-L. Yu, Fu, S.-T. Fu, Y.-J. Yang, Analysis of solid–liquid oxidizing poly-silicic-ferric sulfate (PSF1), Environ. Sci. 27 (2006) 2061–2066.
[10] C.R. Harrington, C.W. Wischik, F.K. McArrhur, Alzheimer' s-disease-like changes in tau protein processing: association with aluminum accumulation in brains of renal dialysis patients, The Lancet 343 (1984) 993–997.
[11] C. Exley, C. Schneider, J. Frédéric, Doucet, The reaction of aluminium with silicic acid in acidic solution: an important mechanism in controlling the biological availability of aluminium? Coordin. Chem. Rev. 228 (2002) 127–135.
[12] T. Hasegawa, T. Onotsuka, M. Ehara. Flocculation for water treatment and method for producing it, Eur. Pat. Appl., EP 479 219(CL.COZF 1/52), (1992-04-08), JP Appl. 90/260 591 (1990-10-01).
[13] E. Doelsch, A. Masion, J. Rose, W.E.E. Stone, J.Y. Bottero, P.M. Bertsch, Chemistry and structure of colloids obtained by hydrolysis of Fe(III) in the presence of SiO_4 ligands, Colloid Surf. A: Physicochem. Eng. Aspects 217 (2003) 121–128.
[14] X.-J. Liu, Y.-L. Tian, X.-O. Ma, Components interactions of coagulant polymeric ferric silicate-sulfate containing boron, J. East Univ. Sci. Technol. 27 (2001) 661–665.
[15] G.S. Pokrovski, J. Schott, F. Farges, J.L. Hazemann, Iron(III)-silica interactions in aqueous solution: insights from X-ray absorption fine structure spectroscopy, Geochim. Cosmochim. Acta 67 (2003) 3559–3573.
[16] D. Wang, H.-X. Tang, Modified inorganic polymer flocculant-PFSi: its preparation, characterization and coagulation behavior, Water Res. 35 (2001) 3418–3428.
[17] Wuhan University, Jilin University, Inorganic Chemistry, Higher Education Press, Beijing, 1994.
[18] D.-T. Wang, Research and application on aluminum polysilicate coagulant, Ph.D Thesis, Harbin University of Civil Engineering and Architecture, 1998.
[19] K.C. Rajat, H.G. Kevin, F.A. Joseph, E.V.B. John, Changes in fractal dimension during aggregation, Water Res. 37 (2003) 873–883.
[20] B.-Y. Gao, Q.-Y. Yue, Y.-H. Song, Electron microscope observation on the morphology of coagulant polymeric ferric silicate-sulfate, Environ. Chem. 17 (1998) 170–173.
[21] B.-Y. Gao, Q.-Y. Yue, Z.-D. Li, Y. Wang, H. Yu, S.-Y. Wang, Study on species and properties of electric charge of polyaluminum silicate chloride (PASiC) coagulant, Environ. Sci. 3 (1998) 46–49.