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Storage stability and oxidization of stable-oxidation-poly-Si-Fe (SOPSF) coagulant

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ABSTRACT

A new inorganic coagulant, stable-oxidation-poly-Si-Fe (SOPSF) was prepared by copolymerization and was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and redox potential meter. Storage stability and oxidation behavior of SOPSF in treating synthetic humic acid (HA) water samples were explored. The results showed that SOPSF appeared to be a crystal-like structure having a smooth appearance in SEM which prevented connection with each other, and was showed to be a fully extending tree-like structure in TEM. Like poly-Si-Fe (PSF), SOPSF gave stronger oxidization with redox potential (RP) value of 766 mV than Polyferric aluminum with RP of 285 mV, and the declines of their RP values were very small with the decreasing of concentration. SOPSF gave different longer storage time than PSF under different given Fe level ranges at 6 or 25°C, and compared to PSF; the lower the Fe concentration, the better was the SOPSF storage stability. SOPSF oxidization changed the molecular structure of some HA, thus modifying the surface nature of some HA and the interface nature between HA and water sample, which improved HA adsorption on Kaolin. SOPSF oxidization played a key role in removing organic matters, especially dissolved organic matters, during coagulation process.

Keywords: Stable-oxidation-poly-Si-Fe coagulant; Oxidization; Storage stability

1. Introduction

For many years, developing countries, including China, are undergoing lots of diseases caused by water [1]. World Health Organization estimated that more than 80% of the diseases were related to water sources [1], in which the increase of organic matters (OMs) in water body was the most serious pollution phenomena. Especially in recent years, OMs pollution of water bodies in China was successively caused by rapid development of industries and agricultures, which made most of the water samples more difficult to treat than before. Moreover, water scarcity has been a fact in life in arid and semi-arid regions (such as west or north regions in China) where agricultural, domestic, and industrial demands competed for limited water resources. In addition, the demands for water amount and water qualities have been increased significantly due to the population growth, rise in standards of living, industrialization, urbanization, and climate changes [2]. Therefore, low-cost technology has become more and more important in the field of water and wastewater treatment in China, in which

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a conventional unit process, chemical coagulation, is still a study focus [3,4].

Coagulation is a process of decreasing or neutralizing the electric charge on suspended particles or Zeta potential. Generally, most coagulation processes are primarily designed for particle and turbidity removal, so removal of OMs (especially dissolved organic matters (DOMs)) only by conventional coagulation was still lower until now. Moreover, turbidity removal would also be reduced due to the influence of DOMs on de-stabilization for colloids [5]. In addition, larger molecular weight of OMs was likely to be removed during coagulation, while DOMs not only decreased the removal rate of turbidity but also lowered the efficiency of the subsequent water treatment units (filtration or disinfection process). DOMs are a kind of complicated mixture of various molecules and are operationally defined as the OMs that can pass through a 0.45 μm filter. Therefore, removal of OMs (especially DOMs) has been attracting more and more attention in the field of water treatment in the recent 20 years [6,7]. Pretreatment, enhanced coagulation, advanced treatment, or hybrid processing have obtained many good results with some advantages [8–11] in treating water or wastewater samples containing lots of impurities including DOMs, in which the investigation on high-quality coagulants is still one of the emphases during enhanced coagulation [12–14].

Al-based and Fe-based salts are widely used inorganic coagulant in water treatments. However, the residual Al in finished water if accumulated is harmful to human body and animal tissues [15]. In addition, although Fe-based and Al-based coagulants have different effects in different applications (depending mainly on water sample natures and origins), it has been recognized that removal of OMs or DOMs by Fe-based coagulant was superior to that by Al-based salts [16–18]. Therefore, Fe-based salts attracted more and more attention [19–23], in which PSF coagulant was a relatively new type of agent [22,24]. PSF is an advanced polymer in inorganic composite Fe-based coagulants which is non-toxic, thus becoming the focus in coagulation research recently. PSF has been studied since the late twentieth century in Japan [25] and was a complex compound of Fe-coagulant positively charged and polysilicic acid (PSA) flocculant negatively charged. PSF was studied in China simultaneously with poly-aluminum silicate and some valuable results were obtained [26,27]. However, OMs removal by simple Fe-based salts was not as high as expected. In addition, growing complexity and non-timely predictability of water pollution will exist for a long period of time in China because increasing pollutants which are discharged randomly will interact with each other. Therefore, some researchers reported that synergy function of coagulant can improve the removal efficiency of OMs [28]. So the application of coagulant's synergy became a key research direction in the field of water treatment [29–31], in which multifunctional PSF was predicted to be very significant for Fe-based polymer. Oxidative PSF was first explored [32] a few years ago. However, the stability of PSF was not very satisfactory, thus retarding its application in real water treatment.

In addition, PFA is a widely used coagulant in drinking water treatment in China in recent years, so PFA was used as a comparing coagulant in some experiments in the following work.

In this work, a new kind of inorganic polymer coagulant—SOPSF was prepared using co-polymerization, and its characterization (using scanning electron microscope (SEM), transmission electron microscopy (TEM), and RPM) and storage stability were explored in comparison with those of PSF's. Some characteristics of PFA have been examined in another paper [33]. And then, the influence of SOPSF's oxidization on OMs (especially DOMs) removal using jar test was investigated. It was revealed, firstly, that oxidization of SOPSF played a significant role in removal of OMs, especially DOMs. This work will provide some information for treatment of surface water that was slightly polluted, sewage water and wastewater containing high OMs, and will provide some useful data for further development of this kind of coagulant.

2. Materials and methods

Polyferric aluminum (PFA, $w(\mathrm{Al_2O_3}) = 6.76\%$, $w(\mathrm{Fe}) = 0.6\%$) was sourced from a water plant in Hunan province in China. Double-deionized water was used to make all the following solutions.

2.1. Preparation of PSF and SOPSF

Preparation of PSA solution. Water glass (modulus = 3.1–3.4, $\rho = 1.36\ \mathrm{kg\ dm^{-1}}$, $w(\mathrm{SiO_2}) = 26\%$, industrial grade) diluted with distilled water to the concentration of 7.5% ($w(\mathrm{SiO_2})$) was added slowly to H_2SO_4 solution (20%, 8 mL) at 20℃ with vigorous stirring, and then was followed by 2 h of polymerization to obtain a PSA solution, in which SiO_2 and pH of PSA were $1.07\ \mathrm{mol\ L^{-1}}$ and 3, respectively.

2.1.1. Preparation of PSF [24]

35.21 g $FeSO_4{\cdot}7H_2O$ (analytical grade) was dissolved in H_2SO_4 solution (60%, 42 mL, analytical grade) to obtain a $FeSO_4$ solution. And the $FeSO_4$ solution and PSA solution were mixed at one step at 40–60℃ with stirring. Then 1.5 g $NaClO_3$ (analytical grade) was immediately added and the mixture was stirred for 30 min followed by aging for 65 min without stirring (polymerization process started after $NaClO_3$ was added, so polymerization time was from 0 to 95 min), and the product PSF (Si/Fe molar ratio equals to 1) was diluted to Fe concentration of 0.72, 0.54, 0.36, 0.18, and 0.09 mol L^{-1} with double-deionized water, respectively. The physico-chemical properties of the PSF product of 0.18 mol L^{-1} are shown in Table 1.

2.1.2. Preparation of SOPSF

The first part (from "35.21 g $FeSO_4 \cdot 7H_2O$ …" to "… so polymerization time was from 0 to 95 min") was the same to that of PSF. Finally, a little amount of H_2SO_4 solution (60%, 1–2 mL, analytical grade) and a few mL stabilizer M ($C_4H_4O_6Na_2 \cdot 2H_2O$:NaClO:HCl = 1:6:10) were added with stirring for 3 min at room temperature, and the product SOPSF (Si/Fe molar ratio equals to 1) was diluted to Fe concentration 0.72, 0.54, 0.36, 0.18, and 0.09 mol L^{-1} with double-deionized water, respectively. The physico-chemical properties of the SOPSF product of 0.18 mol L^{-1} are shown in Table 1.

Liquid SOPSF or PSF with Fe concentration of 0.18 mol L^{-1} was much more stable, in addition, this concentration is not much lower for storage, so SOPSF or PSF with this concentration is convenient for usage in water treatment.

2.1.3. Preparation of solid coagulants

Liquid SOPSF and PSF with Fe concentration 0.18 mol L^{-1} were dried at 50℃ in oven for more than 20 h and were made into powder samples for the analysis of characterization.

2.2. Characterization of coagulants

2.2.1. Surface nature by SEM

The surface nature of solid SOPSF and PSF was observed and analyzed by S-570 scanning electron microscope (SEM, Japan) at 3,000 times magnification under the following conditions: resolution 3.5 nm and accelerating voltage 10 kV.

2.2.2. Morphology by TEM

A little amount of liquidSOPSF and PSF of Fe concentration 0.18 mol L^{-1} were adsorbed onto the copper net, which was followed by air-drying for more than 10 min, and then was observed by JEM-1200EX transmission electron microscope (TEM, Japan) under accelerating voltage 120 kV to get the morphology of the coagulants.

2.2.3 Oxidization by RPM

Oxidization of SOPSF and PSF was characterized by RP value.

RP values of SOPSF and PSF diluted to Fe concentration 0.18 mol L^{-1} at different polymerization times (5, 35, 45, and 65 min) were measured by HANNA Microprocessor pH Meter (Italy) with working electrode 213 (platinum electrode) and reference electrode 232 (saturated calomel electrode) to study the influence of different polymerization times on the oxidization of coagulants.

RP values of SOPSF with different Fe concentrations of 0.18, 0.09, and 0.018 mol L^{-1} were measured, in comparison with those of PSF and PFA's (as Al concentration). Polymerization time was selected as 65 min for SOPSF and PSF.

Table 1
Characteristics of SOPSF, PSF, and PFA

Coagulant	Color	Concentration, as Fe or Al (mol L^{-1})	Density (kg.m^{-3})	Total solid as mass Percentage (%)	pH	State	Zeta potential (mV)
PSF	Brown-yellow	0.18	1.052	7.03	1.55	Transparent	1.75
SOPSF	Brown-yellow	0.18	1.016	7.09	1.50	Transparent	1.70
PFA	Brownish-red	0.18	1.011	6.04	1.62	Transparent	36.1

2.3. Storage stability of SOPSF

Storage stability was expressed as storage time. Liquid SOPSF and PSF with different Fe concentrations of 0.72, 0.54, 0.36, 0.18, and 0.09 mol L^{-1} were stored at 6 and 25°C under closed condition, respectively, and then their starting gelling time was defined as storage time. Polymerization time was selected as 65 min for SOPSF and PSF.

2.4. Oxidization behavior of SOPSF in removing organic pollutants

Oxidization behavior of SOPSF was examined using a series of bench-scale jar tests: influences of dose and coagulation time, and influence of oxidization on subsequent adsorption of DOMs.

Tested-water samples. As well known, HA is a large portion of DOMs present in natural water bodies. So tested water was selected as a synthetic water sample made from humic acid (HA, analytical grade, Shanxi Potachem Industrial Co., Ltd) stock solution, and double-deionized water; 13–19 mL HA stock solution was dispersed in 32 L double-deionized water with stirring for 10 min and was followed by settlement for 6 h. The qualities of this tested water are presented in Table 2. HA stock solution was made as follows: 5 g HA was dissolved in 0.1 mol L^{-1} NaOH solution with stirring for 6 h and then was followed by a filtration through 0.45 μm filters (FuZhou LanLo Filtration Equipment CO., ltd, China) to obtain a mixed solution. And then the mixed solution was added to 1,000 mL double-deionized water to obtain HA stock solution with concentration 5 g L^{-1}, which was stored below 4°C before usage. HA used here was extracted from the soil-containing rock formation in Shanxi province and was used as a surrogate matter for DOMs. The concentration of DOMs in HA was measured using UV absorbance at 254 nm (UV_{254}). UV_{254} absorbance often represents a surrogate measure of the concentration of DOMs and has been extensively used by water researchers [34]. It can be believed that HA existed in this tested water only due to the use of double-deionized water. This synthetic water sample did not represent any real water, but it will minimize the possibility of initial particle influence on test results due to the elimination of other substances, except for HA in this water sample and will allow the coagulant to perform its oxidization fully. As such, it is a better water sample to study the oxidization of SOPSF. To study pH influence, pH of some tested waters was adjusted to 4, 7, and 11, respectively, using 0.1 mol L^{-1} NaOH or HCl solution and then was allowed to settle for 1 h. It is known that pH 4 and 11 would be outside the levels experienced in most conventional water and wastewater treatment plants. However, the purpose of this work is to investigate the influence of pH (including very lower pH side and very higher pH side) on the oxidization nature of SOPSF in removing DOMs. Moreover, the adjustment of pH to a lower side or higher side is sometimes necessary during pretreatment processes in treating highly polluted water or wastewater samples.

Jar test. The working concentration of coagulant was 0.018 mol L^{-1}, SOPSF and PSF as Fe and PFA as Al. Experiments were performed using a jar test apparatus (JJ-4A flocculator, China). The standard jar test procedure consisted of a rapid mix at 200 $r.min^{-1}$ for 1 min after chemical's addition, and was followed by two five-min mixing periods at 50 and 20 $r.min^{-1}$, respectively. Then the flocs were allowed to settle for different times, and supernatant samples were withdrawn

Table 2
Qualities of tested water samples

Position of tested water sample in manuscript	[a]Section 2.4	[b]Section 2.4.1 pH 4	pH 7	pH 11	[c]Section 2.4.2
Temperature (°C)	17–17.5		17–17.5		17–17.5
DOC ($mg.L^{-1}$)	7.567–9.427	5.60	6.32	6.88	
UV_{254} (cm^{-1})	0.107–0.242	0.043	0.098	0.148	0.242
pH	5.24–5.84	4	7	11	5.6
Turbidity (NTU)	0.14–0.20				
[d]RP(mV)					150

[a]Section 2.4: *Oxidization behavior of SOPSF in removing organic pollutants.*

[b]Section 2.4.1: *Influence of dose and pH on residual HA.*

[c]Section 2.4.2: *Influence of coagulation time on residual RP and HA.*

[d]RP: Redox Potential value.

from a position of 2 cm below the surface for the following measurements. Turbidity and RP value were measured by SZD-2 Turbidity Meter (China) and HANNA Microprocessor pH Meter. Measurement of UV_{254} and dissolved organic carbon (DOC): part of supernatant was first filtered through 0.45 μm filters and then was measured by 752S UV Spectrophotometer (China) and 2000A TOC Analyzer (Japan) for measurement of UV_{254} and DOC, respectively.

Soluble and colloidal Fe may absorb UV_{254} slightly, so Fe concentration in dosing was constant in order to decrease the effect of Fe absorbance. The test conditions were all the same and the dosing was relatively low, therefore, the influence of ionic strength can be ignored here.

2.4.1. *Influence of dose and pH on residual HA*

SOPSF was used as a coagulant in this test (PSF has been tested in previous work [35]). UV_{254} and DOC at different pH values of this tested water are presented in Table 2. Settling time was 10 min, and UV_{254} and DOC were measured and SUV_{254} was calculated as UV_{254}/DOC.

2.4.2. *Influence of coagulation time on residual RP and HA*

Coagulation time here included jar testing time and quiescent settling time. SOPSF, PSF, and PFA were selected as coagulants, and dose was a constant 0.322 mmol L^{-1}. UV_{254}, pH, and RP of this tested water are shown in Table 2. The supernatant during coagulation (including quiescent settling time) was withdrawn at coagulation time from 0 to 101 min for the measurement of RP and UV_{254}, respectively, in comparison with that of the tested water sample.

2.4.3. *Influence of SOPSF oxidization on HA adsorption at different pH values*

SOPSF and PFA were selected as coagulants (PSF has been tested in previous work [35]), and dosage was selected as constant 0.107 mmol L^{-1}. UV_{254} and DOC of tested water were the same to those of Section 2.4.1. HA was selected as a kind of DOM and Kaolin (analytical grade) was selected as an absorbent. The surface of Kaolin contains hydroxyl or oxygen groups, and silicon surface is poorly hydrated in aqueous medium and the negative charge is slightly affected by pH [36]. The adsorption of HA on Kaolin was studied here to explore the influence of SOPSF oxidization on molecular or surface nature of DOMs.

Kaolin stock solution was made as follows. Thirty grams dry Kaolin was dispersed in 1,000 mL double-deionized water by a high-speed laboratory blender for 6 h, and was allowed to settle for 6 h. The upper 700 mL was decanted and used as a stock solution and was stirred for 5 min again just before use. The properties of Kaolin solution were as follows: turbidity = 356 NTU, pH 6.51, temperature = 17.5°C.

2.4.3.1. Coagulation supernatant (C). Zeta potential was measured by 3000HS Zeta sizer (Malvern Instruments Ltd, U.K.) after diluting five times the supernatant which was withdrawn after rapid mixing for 40 s during the standard jar test procedure stated first in Section 2.4. (Jar test). The 70 mL supernatant after settling stage was withdrawn from a position of 2 cm below the surface, and UV_{254} and DOC were measured, and SUV_{254} was calculated as UV_{254}/DOC.

2.4.3.2. Coagulation supernatant + kaolin stock solution (CK). Zeta potential was measured after diluting five times the mixture solution which was withdrawn after rapid mixing for 60 s during the standard jar test procedure stated first in Section 2.4 (Jar test), 5 ml of Kaolin stock solution was added to the 780 mL supernatant which was withdrawn from a position of 2 cm below the surface after settling stage and then was stirred for 18 h under a mixing speed of 100 $r.min^{-1}$ to obtain a mixed solution. This mixed solution was allowed to settle for 1 h, and UV_{254} and DOC of the supernatant was measured, and SUV_{254} was calculated as UV_{254}/DOC.

3. Results and discussion

In this paper, the word “oxidized” refers to a behavior or a result where OMs were oxidized by coagulants, and the word “oxidation” refers to a kind of capacity or ability to oxidize OMs that the coagulants owned.

3.1. *Characteristics of coagulants*

3.1.1. *Surface nature*

Fig. 1 presents the comparison of surface nature of powder samples between SOPSF and PSF. SOPSF gave a very different surface nature from PSF.

SEM is an important instrument to study the surface nature of solid materials, which not only gives a visual image, but also provides some quantitative data. For instance, a minimum size of 1 nm can be observed under voltage of 15 kV, and 3 nm under voltage of 1 kV [37].

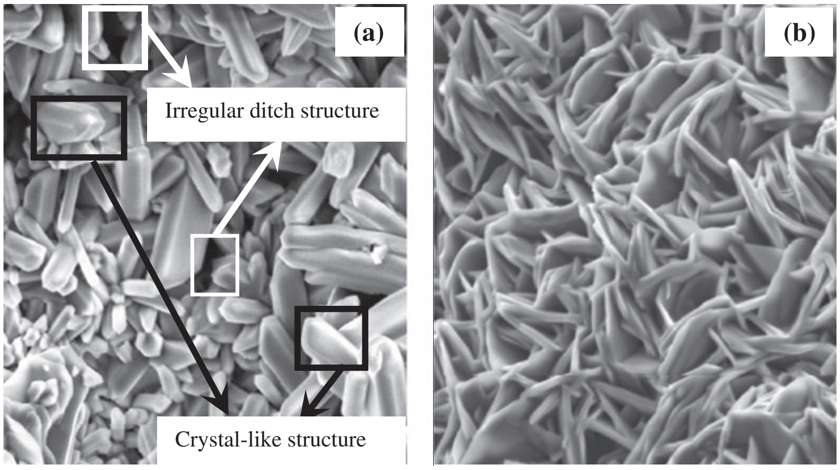

Fig. 1. Surface nature of SOPSF and PSF: (a) SOPSF(×3K), (b) PSF(×3K) [24].

As shown in Fig. 1, SOPSF (Fig. 1(a)) almost appeared to be a kind of crystal-like structure naturally grown with different sizes, in which some irregular ditches with different sizes were distributed among the crystal structures. These crystal-like structures showed a smooth appearance which could retard them in connecting with each other, which may be one of the reasons because of which SOPSF presented a better stability than PSF. The SOPSF having better stability than PSF will be demonstrated in the following Section 3.2. The surface morphology of PSF (Fig. 1(b)) consisted of some sort of curl-slice structures having evident directionality, in which there are some slit-type structures distributed among these curl-slice structures.

3.1.2. Morphology

Fig. 2 gives the comparison of TEM image between SOPSF and PSF.

TEM is an important technology to observe the morphology of solid coagulants [38,39]. The coagulant measured by TEM in this work was a dilution sample indicating very thin and uniform dispersion on the copper net, which made the shape of the solid coagulant similar to that of the liquid one. So TEM is thought to be an intuitionstic way to observe the actual morphology of liquid coagulant, which has a close relationship with the species having close relationship with the effectiveness of a coagulant. The morphology of SOPSF and PSF is shown in Fig. 2.

An evident tree-like structure having large size and lots of multi-branched structures having different size and fractal dimensions around it were observed in SOPSF (Fig. 2(a)), in which the tree-like structure was fully stretched out. This may be the other reason for which SOPSF gave a good stability. The morphology of PSF (Fig. 2(b)) was characterized by a multi-branched structure having relatively small size and fractal dimension.

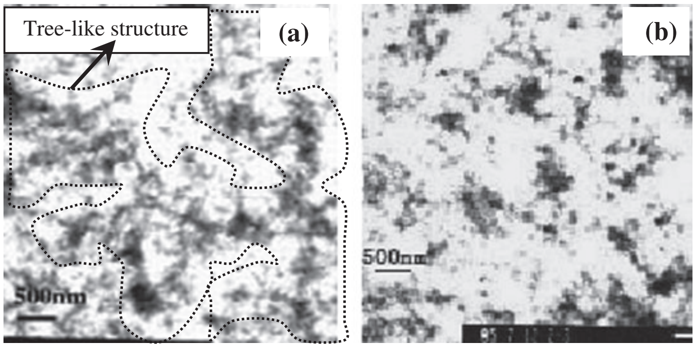

Fig. 2. Comparison of TEM image between SOPSF and PSF: (a) SOPSF, (b) PSF [33].

3.1.3. RP value

Fig. 3 displays the influence of polymerization time on RP value between SOPSF and PSF (Fig. 3(a)), and the influence of Fe level on RP value among SOPSF, PSF, and PFA (Fig. 3(b)).

As seen in Fig. 3(a), for SOPSF and PSF, RP values were almost unchanged when polymerization time ranged from 5 to 45 min. However, the RP value of SOPSF increased dramatically from 743 to 766 mV as polymerization time increased further up to 65 min, in comparison with little change in PSF. The rapid increasing of SOPSF's RP might have been caused by the addition of both H_2SO_4 and stabilizer to the SOPSF product at the final stage during its preparation process, which not only improved its storage stability, but also strengthened its oxidizing capacity to some extent.

As shown in Fig. 3(b), The RP values of the three coagulants decreased slowly with decreasing of the Fe concentrations, in which the RP value of PFA declined by 20 mV (from 285 to 265 mV) as Fe concentration varied from 10 to 1 mol L^{-1}, in comparison with those of SOPSF's and PSF's by 45 and 50 mV (from 766 to 721 mV and from 744 to 693 mV), respectively. The declines in RP values of SOPSF, PSF, and PFA were very small with the decreasing of Fe levels, thus indicating that the oxidizing capacity of these coagulants would remain relatively stable after they were dosed into water samples because coagulant concentrations were very low when they were dosed into the water needed to be treated.

Fig. 3(b) presented that SOPSF and PSF gave higher RP value than PFA at each Fe concentrations, thus suggesting that the former two coagulants have stronger oxidization which will be further explored and demonstrated in Section 3.3.

3.2. Storage time

Fig. 4 gives the influence of Fe concentration on storage time of SOPSF and PSF which was stored at 6℃ (Fig. 4(a)) and 25℃ (Fig. 4(b)), respectively. To further observe the influence of storage temperature on storage stability of different coagulants, ratios of SOPSF storage time to PSF storage time at different storage temperatures are drawn in Fig. 4(c).

As shown in Fig. 4, the storage time of SOPSF was longer than that of PSF over the whole Fe-level range at 6 and 25℃. Fig. 4(a) shows that SOPSF with Fe level 0.09 and 0.72 mol L^{-1} could be stored for 750 and 20 d without gelling at 6℃, in comparison with 520 and 2 d for PSF, respectively. While as seen in Fig. 4(b), the storage times of SOPSF at Fe concentration 0.09 and 0.72 mol L^{-1} were 250 and 1.2 d without gelling at 25℃, compared to that of 220 and 0.2 d for PSF, respectively.

As shown from Fig. 4(c), storage stability of SOPSF improved with decreasing of Fe concentration in comparison with that of PSF, that is, the lower the Fe concentration, the better the SOPSF's storage stability was. When Fe level was 0.18 mol L^{-1}, SOPSF's storage time was 220 d longer than PSF's at 6℃, which in comparison was 25 d at 25℃. As stated in Section 2.1.3, diluted SOPSF or PSF at Fe concentration 0.18 mol L^{-1} was often used as storage product, therefore, a proper reduction of temperature was very useful to improve SOPSF's stability.

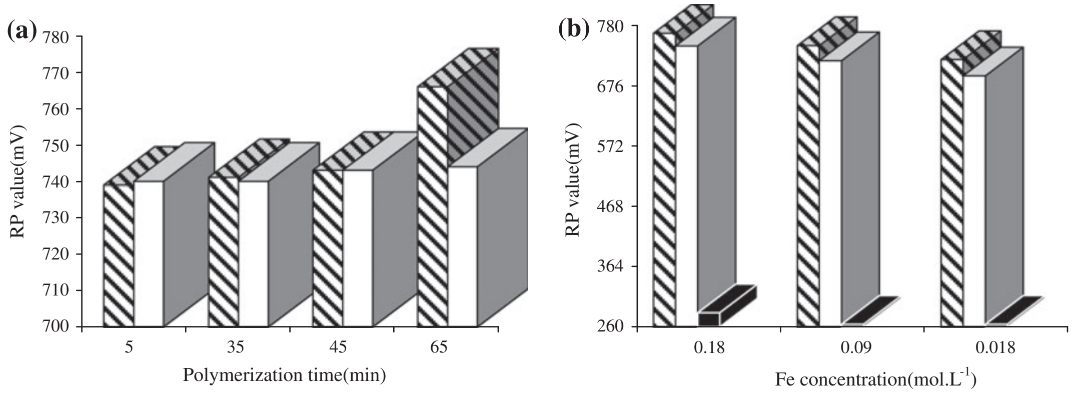

Fig. 3. Influences of polymerization time and Fe concentration on RP value of coagulant: (a) Influence of polymerization time on RP of SOPSF and PSF, (b) Influence of Fe concentration on RP of SOPSF, PSF, and PFA. SOPSF (▧), PSF (☐), and PFA (■). Fe concentration was 0.18 mol L^{-1} in (a). Polymerization time in (b) was 65 min for SOPSF and PSF.

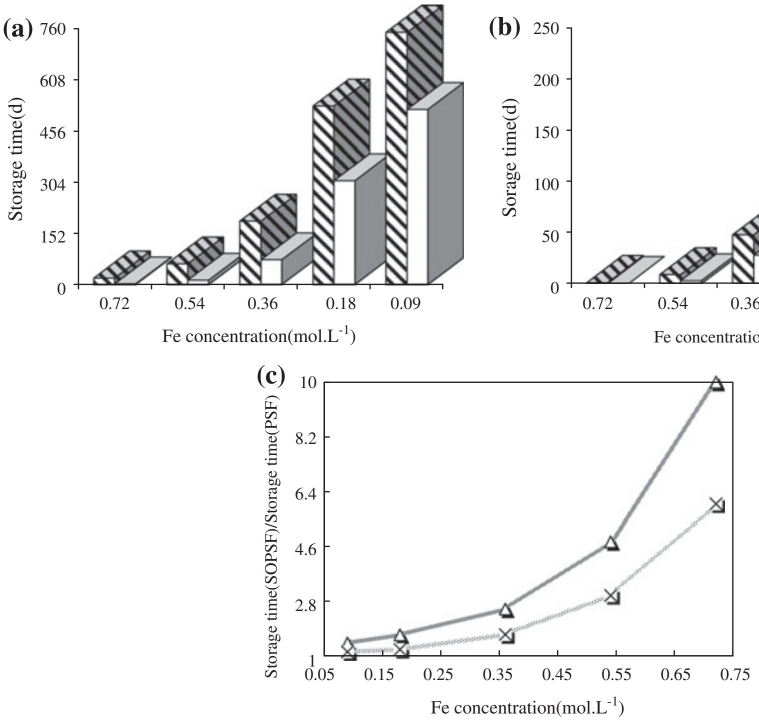

Fig. 4. Influence of Fe concentration on storage time of SOPSF and PSF: (a) At 6℃, (b) At 25℃, (c) Ratio of SOPSF storage time to PSF storage time with different Fe concentrations at storage temperature of 6℃ and 25℃. SOPSF (▨), PSF (☐), 6℃ (Δ) and 25℃ (×). Polymerization time was 65 min.

SOPSF having longer storage time than PSF was consistent with the difference of characteristics in Figs. 1 and 2 between them.

3.3. Oxidization behavior of SOPSF in removing organic pollutants

UV_{254} value is ultraviolet absorbance representing some OMs in water under 254 nm wavelength, reflecting the amount of natural humic type of macromolecular OMs and the amount of NOMs containing C=C double bond and some aromatic compounds. As an evaluation index of organic pollutants in water, UV_{254} was put forward in the 1970s and is an important control parameter to measure OMs in water. In Japan, UV_{254} has been officially listed as a water quality monitoring index in 1978, and Europe also has acted it as a monitoring indicator of removing effect of OMs in waterworks [40]. Generally, in water treatment field, UV_{254} was often a surrogate parameter for DOM's level. So in this work, we analyzed the oxidizing effect of coagulants through the increasing of UV_{254} or other parameters. The concept of $SUVA_{254}$ was first developed by Edzward and co-workers [41], and is an operational indicator of the nature of NOMs and the effectiveness of coagulation in removing NOMs, DOC, and disinfection by-product precursors. Edwards [42] and James [43] reported that larger $SUVA_{254}$ can be removed more easily than smaller $SUVA_{254}$. $SUVA_{254}$ was defined as UV_{254}/DOC, so we think $SUVA_{254}$ can represent dissolved organic pollutants to a large extent. Therefore, UV_{254} and $SUVA_{254}$ were used as main parameters in evaluating SOPSF oxidization on DOMs in this work. SOPSF4, SOPSF7, and SOPSF11 represented the pH value of the tested water as 4, 7, and 11 when using SOPSF as coagulant, respectively, the same to that of PFA.

3.3.1. Influence of dose and pH

Fig. 5 displays the influence of SOPSF dose on its oxidization behavior in removing HA with final Fe concentration in the tested water from 0.009 to 0.143 mmol L^{-1}.

From the experiment phenomena, no visible flocs was formed apart from SOPSF4 with dosages ranging from 0.009 to 0.0179 mmol L^{-1} and SOPSF7's from 0.0537 to 0.0716 mmol L^{-1} after chemical's addition. The flocs were very small (cannot precipitate) at the dosage of 0.0537 mmol L^{-1} for SOPSF7, thus leading to

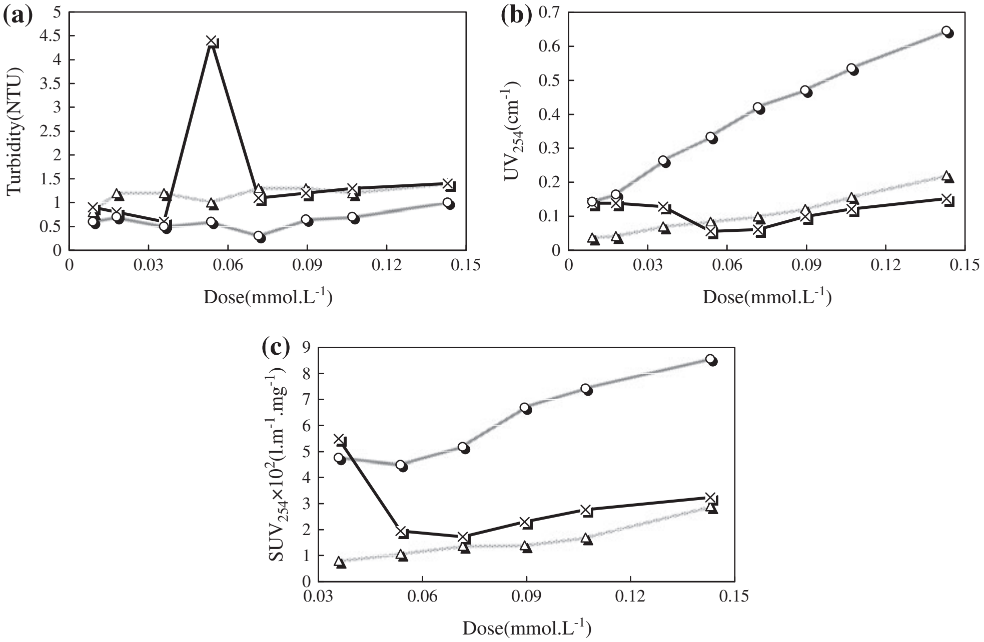

Fig. 5. Influence of dose and pH on residual HA: (a) Turbidity, (b) UV_{254}, (c) $SUVA_{254}$. SOPSF4 (Δ), SOPSF7 (×) and SOPSF11 (○). SOPSF4, SOPSF7, and SOPSF11 represented the pH values of the tested water as 4, 7, and 11, respectively, when using SOPSF as coagulant. UV_{254} and DOC of Tested water were 0.043, 0.098, and 0.148 cm^{-1}, 5.60, 6.32, and 6.88 mg L^{-1} at pH 4, 7, and 11, respectively. Temperature = 17℃.

a rapid increasing of turbidity and a decreasing of UV_{254} at this pH value. The amount of flocs formed at dosages ranging from 0.009 to 0.0179 mmol L^{-1} at pH 4 was much less than that at pH 7, therefore, there was not obvious increasing of turbidity and decreasing of UV_{254} at this pH value. In addition, turbidity change was very small for each pH values over the whole dose range, with fluctuation from 0.8 to 1.4 NTU, 0.6 to 1.4 NTU (apart from 4.4 NTU at a dosage of 0.0537 mmol L^{-1}) and 0.3 to 1.0 NTU at pH 4, 7, and 11, respectively, though turbidity increased slowly with increasing dosage.

Generally, residual UV_{254} of the supernatant after coagulation should be lower than that of the tested water, therefore, UV_{254} in Fig. 5(b) should be lower than 0.043, 0.098, and 0.148 cm^{-1} at pH 4, 7, and 11, respectively. However, the trend of the curve in Fig. 5(b) was very different from that in Fig. 5(a). And in most cases, UV_{254} of the supernatant was larger than that of the raw water sample. For instance, UV_{254} was greater than 0.043, 0.098, and 0.148 cm^{-1} with dosage ranging from 0.0358 to 0.143 mg L^{-1} at pH 4, 0.009 to 0.358 mg L^{-1}, and 0.0895 to 0.143 mg L^{-1} at pH 7, and 0.0170 to 0.143 mg L^{-1} at pH 11, respectively. Therefore, it can be inferred that SOPSF has an oxidization action, which probably led to an increasing of the amount of HA or a changing of molecular/surface structure of HA, further resulting in an increase in OMs' or DOMs' concentration after coagulation, which corresponded to its higher RP value (Fig. 3). Moreover, the greater the dose, the stronger the SOPSF oxidization was, thus resulting in the increasing of UV_{254} with the increasing amount of dosage (Fig. 5(b)). Of course, the oxidization action of SOPSF and its oxidization results were surely very complicated, so lots of works should be conducted about this aspect, for example, the surface properties of HA deserved to be studied in the future.

The trend of SUV_{254} curve (Fig. 1(c)) was almost consistent with that of $UV_{254,}$ which increased with increasing of dosage, demonstrating that SOPSF probably modified the molecular structure or surface nature of some HAs. So, it may be inferred that DOMs which could be originally affected by coagulation slightly would probably be changed into DOMs that would be likely to be effectively removed by SOPSF, which will be beneficial to the subsequent removal of HA if they could be adsorbed successively on the flocs that was formed during coagulation process.

3.3.2. Influence of coagulation time on residual RP and HA

To further demonstrate how SOPSF oxidization influenced HA's removal and whether SOPSF oxidization surely changed the surface or molecular structure

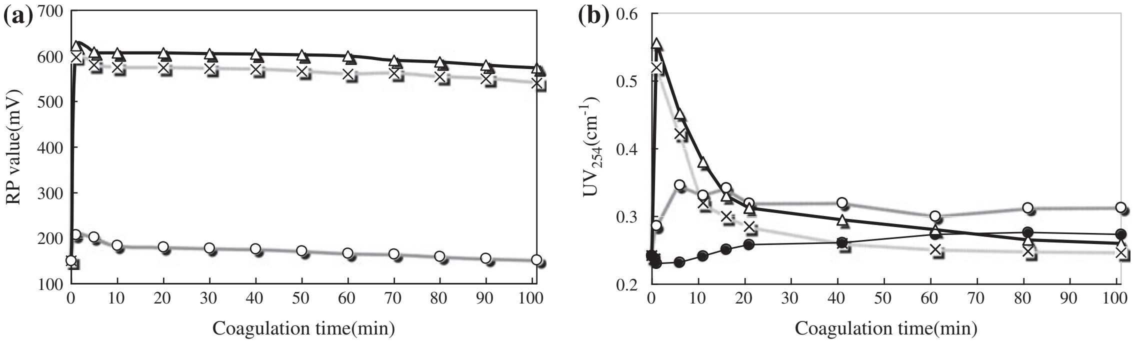

Fig. 6. Influence of coagulation time on coagulant oxidization and residual HA: (a) RP in the supernatant, (b) UV$_{254}$. SOPSF (Δ), PSF (×), PFA (○), and Tested water (●). UV$_{254}$, pH, and RP of the tested water were 0.242 cm^{-1}, 5.6, and 150 mV, respectively. Dose = 0.322 mmol L^{-1}. Temperature = 17.5℃.

of some HA, the coagulation supernatant was withdrawn at coagulation time from 0 to 101 min for RP and UV$_{254}$ evaluation, in which quiescent settling time was 90 min (as stated in Section 2.4), as shown in Fig. 6.

As seen from Fig. 6(a), RP value sharply reached the maximum value (up to 622, 598, and 207 mV for SOPSF, PSF, and PFA, respectively) within 1 min and decreased rather slowly with the increasing of coagulation time, down to 570, 540, and 150 mV for SOPSF, PSF, and PFA at 101 min, respectively. This demonstrated that the oxidization of SOPSF and PSF was very stable during the whole coagulation process, which will be beneficial to successive removal of organic pollutants. The RP value of PFA was very small, corresponding to the result in Fig. 3(b).

As shown in Fig. 6(b), UV$_{254}$ increased sharply first using SOPSF/PSF as coagulants and was followed by a quick decrease, and then successively declined slowly with the increasing of quiescent settling time. The former result stated in this sentence further confirmed that SOPSF/PSF has strong oxidation which modified the surface or molecular nature of some HAs and resulted in an enhancement of self-agglomeration. The latter result stated in this sentence suggested that SOPSF/PSF's oxidation played a key role during the whole coagulation process including quiescent settling stage. While for PFA, UV$_{254}$ increased first, and then almost tended to be a constant which was almost equivalent to the value of the tested water sample. This further confirmed that PFA almost gave no oxidization even at higher dosages (0.322 mmol L^{-1}).

In addition, $NaClO_3$ was used during the preparation process of SOPSF/PSF, in which Cl^{5+} has been reduced to Cl^{-1} before the use of SOPSF/PSF, so Cl^{-1} here has no oxidization ability. Of course, the oxidization process of SOPSF/PSF on DOMs may be very complicated, therefore, much work should be further conducted.

3.3.3. Influence of SOPSF oxidization on HA adsorption at different pH values

In order to more clearly investigate the adsorption of HA which had been oxidized by SOPSF on Kaolin, dosage was selected as 0.107 mmol L^{-1} that was overdosed for both SOPSF and PFA according to the results of Fig. 1. T, C, and CK represented Tested water, Supernatant of coagulation, and Coagulation supernatant and Kaolin stock solution, respectively. UV$_{254}$, SUV$_{254}$, and Zeta potentials of T are shown in Fig. 7 which represents the values after the adjustment of pH.

As well known, coagulant added into water samples would hydrolyze rapidly to generate various hydrolysis products which would migrate onto the surface of pollutants. Therefore, HA here was a mixed substance of HA and $\mathrm{SOPSF}_{\mathrm{OH}}^{n+}$ (or $\mathrm{PFA}_{\mathrm{OH}}^{n+}$), in which $\mathrm{SOPSF}_{\mathrm{OH}}^{n+}$ or $\mathrm{PFA}_{\mathrm{OH}}^{n+}$ represented various hydrolysis products of SOPSF or PFA.

As observed from the experimental phenomena, no visible flocs were formed in C by SOPSF and PFA at a dosage of 0.107 mmol L^{-1}, corresponding to the phenomena from the jar test in Section 3.3.1.

For SOPSF, flocs were formed by SOPSF4 and SOPSF7 in CK, thus resulting in the rapid decrease of UV$_{254}$ compared to that of C (Fig. 7(a)). UV$_{254}$ reduction of CK was definitely caused by the formation of flocs which, however, was formed by the improvement of adsorption of HA on Kaolin. Such improvement was caused by modification of some HA surface nature or interface nature between some HA and

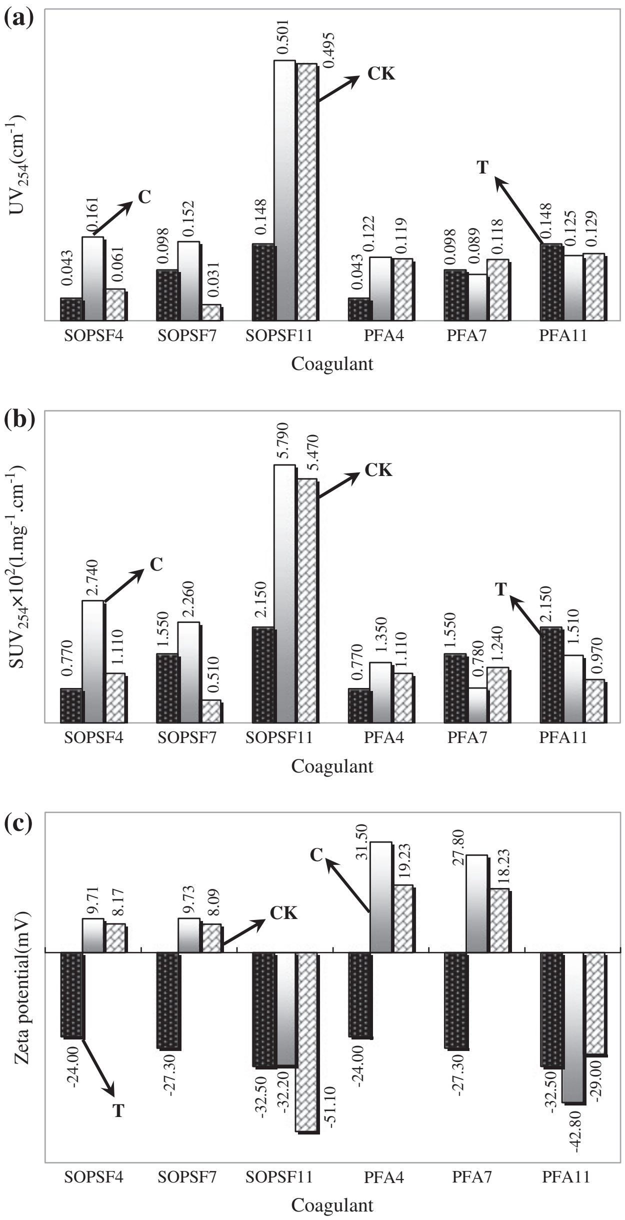

Fig. 7. Comparison of HA adsorption on Kaolin between SOPSF and PFA at different pH values: (a) UV_{254}, (b) SUV_{254}, (c) Zeta potential. SOPSF4, SOPSF7, and SOPSF11 represented the pH values of the tested water as 4, 7, and 11, respectively, using SOPSF as coagulant, the same to that of PFA. T = Tested water, C = Supernatant of coagulation, CK = Coagulation supernatant and Kaolin stock solution. UV_{254} and DOC of T were 0.043, 0.098, and 0.148 cm^{-1}, 5.60, 6.32, and 6.88 mg L^{-1} at pH 4, 7, and 11, respectively. Dose = 0.107 mmol L^{-1}. Temperature = 17.5℃.

water solution, which was caused by SOPSF oxidization. This modification can be confirmed by the results of Fig. 7(b). As shown from Fig. 7(b), SUV_{254} increased evidently in C, thus leading to its easy removal in CK due to its high values. In addition, UV_{254} (Fig. 7(a)) and SUV_{254} (Fig. 7(b)) in CK at pH 7 were lower than that at pH 4, revealing that the adsorption of HA which was oxidized by SOPSF under neutral condition was stronger than that at lower pH side. When pH was equivalent to 11, UV_{254} (Fig. 7(a)) and SUV_{254} (Fig. 7(b)) in C were far larger than those in T, further suggesting that HA in strong basic solution was easily oxidized, corresponding to the highest UV_{254} in Fig. 5(b). However, there was almost no difference of UV_{254} and SUV_{254} between CK and C at pH 11, indicating that most of the HA was not absorbed on Kaolin, which may be caused by larger repulsion among HA molecules having much lower Zeta potential (Fig. 7(c)).

For PFA, UV_{254} (Fig. 7(a)) and SUV_{254} (Fig. 7(b)) in C were larger than that in T at pH 4, but changed little in CK. It can be speculated that PFA oxidization was possibly different from SOPSF and could not modify the surface or molecular nature of HA even a little, which therefore will have no positive action for subsequent removal of HA still existing in re-stabilization. UV_{254} and SUV_{254} in C were almost equivalent to those in T at pH 7 or 11, indicating that PFA has no oxidization on HA at neutral or higher pH side.

As seen from Fig. 7(c), the Zeta potential of SOPSF or PFA in C at pH 4 or 7 was all higher than zero, in which PFA's Zeta potential was far higher than SOPSF's because PFA coagulant has higher Zeta potential of 36.1 mV than SOPSF of 1.70 mV (Table 1). This also further demonstrated that SOPSF or PFA had been overdosed in Fig. 7. However, the Zeta potential of SOPSF or PFA in C was lower than zero at pH 11, which was probably related to the hydrolysis process of coagulants or to the HA nature in strong alkaline-tested water sample. Zeta potential of SOPSF in CK at pH 4 or 7 was still much higher than zero (Fig. 7(c)) and SOPSF gave a large decrease of UV_{254} in CK compared to that in C (Fig. 7(a)), further demonstrating that SOPSF surely modified some HA surface nature, which made it easy for HA to aggregate with each other even if HA were all positively charged after chemical addition. Otherwise, no flocs would be formed due to the re-stabilization phenomena caused by overdosing.

From the analysis mentioned above, SOPSF gave oxidization on DOMs at each pH value, while PFA only gave oxidization at lower pH side, demonstrating that SOPSF was surely an oxidative coagulant. Oxidization of SOPSF played a key role in DOMs' removal during the entire coagulation process.

The real water samples in fact contained both colloid impurities carrying large amount of OMs and DOMs dispersed in solution. The migrating speed of the hydrolysis products of coagulants onto the surface of colloid impurities mainly depended on the rapid mixing time during the coagulation process. This rapid mixing time for inorganic coagulants was often selected as 60–90 s (60 s in this work), so destabilization of impurities almost occurred within 60 s. In fact, only 0.01–1 s was needed for destabilization of impurities [38] if the hydrolysis products of coagulant once were adsorbed onto the surface of impurities, in which the hydrolysis of coagulant occurred within 1 s [38]. As shown in Fig. 6(b), HA was almost oxidized within 120 s by SOPSF, demonstrating that the oxidization rate of SOPSF was slower than that of SOPSF's hydrolysis and destabilization process. Furthermore, the RP value of the water sample maintained a high value during the entire coagulation process (SOPSF/PSF in Fig. 6(a)), thus resulting in a continuous oxidization of SOPSF/PSF on DOMs dispersed in solution (uncombined with coagulant or colloid impurities), which improved the continuous adsorption of HA on the flocs formed. This may be one of the important reasons for which SOPSF gave successive UV_{254} removal during the settling process (Fig. 6(b)).

In short, coagulation mechanism of SOPSF in removing DOMs in real water samples may be the comprehensive results of alternating interactions of oxidization/adsorption–destabilization/oxidization, bridging, and sweeping.

4. Conclusions

SEM image showed that the surface morphology of SOPSF was composed of some crystal-like structures which presented a smooth appearance with different size, in comparison with some sort of curl-slice morphology connected with each other. TEM image showed that SOPSF was a kind of tree-like microstructure which was fully extended, in comparison with a multi-branched structure of PSF. These characteristics may be the important reasons that SOPSF have longer storage time than PSF.

SOPSF and PSF have stronger oxidization than PFA, with RP value 766, 744, and 285 mV, respectively, at Fe level 10 mol L^{-1} in which their RP values decreased a little with the decreasing of Fe concentration.

SOPSF has better storage stability than PSF over the whole Fe level range at given temperatures. SOPSF with Fe level 0.09 and of 0.72 mol L^{-1} could be stored for 750 and 20 d without gelling at 6℃, and 250 and 1.2 d without gelling at 25℃, in comparison with 520 and 2 d at 6℃, and 220 and 0.2 d at 25℃ for PSF, respectively. Moreover, compared to PSF, the lower the Fe concentration , the better the SOPSF's storage stability was. The better storage stability of SOPSF depended on its special micro-characteristics.

SOPSF oxidization changed the molecular structure of some HA, thus modifying some HA surface nature and interface nature between HA and water solution, which led to the improvement of adsorption of HA on Kaolin. Oxidization of SOPSF played a key role in DOMs' removal during the coagulation process.

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