Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.758060

51 (2013) 5674–5681
August

Taylor & Francis
Taylor & Francis Group

Study on structural characterization and algae-removing efficiency of polymeric aluminum ferric sulfate (PAFS)

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Received 11 October 2012; Accepted 2 December 2012

ABSTRACT

Polymeric aluminum ferric sulfate (PAFS), as a novel inorganic coagulant, was prepared through direct oxidation process using industrial by-product ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and industrial aluminum oxide (Al_2O_3 content of 16%) as the main materials. PAFS was characterized by Fourier transformed infrared spectrophotometer, scanning electron microscopy, and X-ray diffraction. The coagulation mechanism and molecular conformation of PAFS were analyzed and the different conditions of flocculation effect were investigated in the paper. In order to test the coagulating performances of PAFS, traditional coagulants such as polymeric ferric sulfate, polymeric aluminum chloride, and polymeric aluminum ferric chloride were used to carry out the comparison tests on algae removal efficiency. The results show the removal efficiency for turbidity and chlorophyll a using PAFS were 92.8 and 95.3%, respectively, which were higher than those of the traditional coagulants.

Keywords: Polymeric aluminum ferric sulfate; Direct oxidation process; Structural characterization; Algae removing

1. Introduction

In recent years, surface water has become the main source of water supplies in China. Eutrophication of major lakes and reservoirs in China has caused serious algae bloom. However, in surface water, algae bloom resulting from eutrophication may cause serious problems such as color, odor, and taste while at the same time produce toxins [1–3]. These problems may severely affect the function of the water bodies as the source for drinking water supply. As a result, the removal of algae and the algae toxins efficiently has become a focal point for researchers all over the world [4].

At present, there are many methods applied to remove algae from drinking water, which include physical process such as filtration and barriers, chemical process such as coagulation and chlorination, biological process such as slow sand filters for activated sludge, and the electromagnetic radiation such as ultrasonic irradiation [5–8]. Among these, chemical algae removal methods are considered to be cost-effective and user-friendly, while coagulation is also an effective method to remove algae. During coagulation, small particles are integrated with each other to form flocs large enough to be separated from solution in a reasonable period. The selection of flocculants with enhanced coagulation efficiency is a commonly used technology [9,10].

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Polymeric aluminum ferric sulfate (PAFS) is a new type of inorganic composite coagulant, which does not only have the advantages of fast sedimentation rate, low water treatment costs and good purification effect, but also abandons the disadvantages of high color and toxins. As a result, it has received more attention than poly aluminum ferric chloride (PAFC) [11,12]. But very limited work has been reported on the detailed research of the different morphologies of PAFS and PAFC, with few algae-removing efficiency tests being done to compare PAFS with some traditional coagulants such as PAFC, polyaluminum chloride (PAC), and polymeric ferric sulfate (PFS)[13].

In this study, the characterization of a novel coagulant PAFS was investigated. The main objective of this research was to investigate the following parameters: Firstly, the possible chemical bonds and morphologies of PAFS and PAFC were compared using Fourier transformed infrared (FTIR) spectrophotometer, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Secondly, research on the flocculation behavior of PAFS, including parameters affecting the coagulation of algae such as coagulant dosage, pH value of raw water, temperature, and mixing program. Finally, the effect of algae removing with different coagulants was investigated.

2. Experimental

2.1. Material and instruments

All the reagents used in this study were analytical grade. The reagents include concentrated nitric acid (HNO_3), concentrated sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH). All aqueous solutions and standard solutions were prepared with deionized water. PAFS was self-made, the traditional coagulants PAFC, PAC, and PFC were obtained from Chongqing Lanjie Co., Ltd. The equipments used in the experimental setup were as follows:

(1) FTIR spectrophotometer supplied by IR Prestiger-21 from Japan.
(2) XRD with Cu K radiation in the range of 5–75° (2θ) at a scan rate of 4°/min, supplied by D/Max-3C from Japan.
(3) ZR4-6 Jar Tester supplied by Zhongrun Water Industry Technology Development Co. Ltd, Shenzhen, China.
(4) DR/5000 UV spectrophotometer supplied by HACH, USA.
(5) Turbidimeter supplied by HACH 2100Q, USA.
(6) Desktop low speed centrifuge SF-TDL-4A supplied by Phicher analysis instruments Co. Ltd, Shanghai, China.

2.2. Preparation of PAFS

In this study, the inorganic coagulant PAFS was synthesized using HNO_3 as oxidant and H_2SO_4 as acidulent. Firstly, 55 g of $FeSO_4{\cdot}7H_2O$ was mixed with distilled water into a thin uniform paste by slow stirring in a beaker. Then, the mixture was acidulated using 4.0 mL of H_2SO_4 and 7.2 g industrial aluminum oxide (containing 16% Al_2O_3), followed by thorough stirring and dilution with a small amount of water. Lastly, the new liquid mixture was oxidized using 4.25 ml of HNO_3, and stirred slowly for 45 min in a thermostatic water bath at a temperature of 85℃. During the synthesis process, H_3PO_4 was added to improve the hydrolysis and polymerization reaction while $2\,\mathrm{mol\,L^{-1}}$ NaOH solution was added to adjust its alkalify degrees. Then, a thick liquid coagulant PAFS with reddish-brown color was produced after aging for more than 24 h at room temperature.

The physical–chemical parameters of the new coagulant were analyzed in accordance with Chinese standard method (GB/T 2153-91), which indicated the density, pH value (1% water solution), and the concentration of total iron were $1.38–1.63\,\mathrm{g\,cm^{-3}}$, 2.04–2.54, and 11–15%, respectively.

2.3. Characteristics of PAFS and PAFC

In order to obtain dried powder, samples of PAFS and PAFC were placed in beakers and dried in a vacuum at 50℃ for several days. FTIR was used to identify the structure of organic compounds of the copolymer powder. The IR samples were prepared with a KBr pellet before analysis using IR Prestige-21 infrared spectrometer (SHIMADZU, Japan). The possible chemical bonds in PAFS and PAFC were investigated by examining the FTIR characteristic peaks in the range of $4{,}000–500\,\mathrm{cm^{-1}}$ for matching the corresponding chemical bonds. The morphology of the copolymer was observed through SEM. The electron samples were prepared by shattering, planishing, and sputtering Au. The electron samples were dried and the SEM images were taken through scan electronic microscope. Finally, coagulants powder were characterized by XRD for the determination of crystalline phases using a D/Max-3C X-ray diffractometer with Cu K radiation in the range of 10°–80° (2θ) at a scan rate of $4^\circ\,\mathrm{min^{-1}}$.

2.4. Water sample

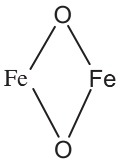
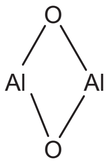
The water samples were collected from Democratic lake in Chongqing University. The water was characterized by measuring the turbidity and chlorophyll a. The chemical analysis of the water samples showed the concentrations of turbidity and chlorophyll a and pH values were 6.6–21.3 NTU, 18–78 μg L^{-1}, and 7.0–8.0, respectively.

2.5. Experimental procedure

In this experiment, algae removal effect was characterized by the removal rate of chlorophyll a, which was measured by a spectrophotometer. Different coagulation conditions including parameters affecting the coagulation of algae such as coagulant dosage, pH value of raw water, temperature, and mixing program were 100–300 μl L^{-1}, 4.5–10.5, 5–30˚C, and 1–5, respectively. The mixing conditions were as shown in Table 1. Coagulation–flocculation experiment was carried out using a program-controlled jar test apparatus at room temperature. The pH value of raw water was adjusted to desirable values using 0.1 M NaOH or 0.1 M HCl. The wastewater was stirred rapidly at the set agitation speed (rpm) for a predetermined rapid mixing time (min), followed by a slow mixing phase at a predetermined agitation speed for a certain slow mixing time, and then a 30 min settling. The supernatant sample was extracted from the depth of 2 cm below the water surface for measurement of turbidity, while 300 ml of the sample was taken for measurement of chlorophyll a.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 indicates a broad absorption peak in the range 3,750–3,000 cm^{-1} for both PAFS and PAFC (3,460 cm^{-1} for PAFS and 3,600 cm^{-1} for PAFC), which can be attributed to the stretching vibration of –OH groups and the corresponding aluminum and iron ion in the solid sample or from the water molecules and coordination water molecules which were adsorbed in the solid sample [14,15]. The peak in the range of 1,750–1,500 cm^{-1} was attributed to the bending vibration of –OH groups in the water molecule, namely the H–O–H angle distortion frequency, indicating that PAFS and PAFC may contain structural and adsorbed water [16]. In addition, there was a weak adsorption peak at 1,013 cm^{-1} for both PAFC and PAFS, which is the stretching vibration for P=O groups [17,18]. The sulfate exhibits symmetrical and antisymmetrical stretching vibration with IR activity because its structure is tetrahedral. The IR spectral studies indicate that the characteristic absorption peak for metal coordination SO_4^{2-} was evident in the range of 1,250–900 cm^{-1} [19]. There was a significant difference in the spectra of PAFS and PAFC at wave numbers of 2,357 and 1,231 cm^{-1}, which could be assigned to the HSO_4^- and SO_4^{2-} stretching vibration, respectively. Fig. 1 shows absorption peaks at 1,685 and 980 $cm^{-1}$for both PAFS and PAFC which were assigned to the Al–O–Al and Fe–O–Fe stretching and bending vibrations, respectively. But  and  bulk bending vibration bands at 680 and 625 cm^{-1}, respectively became an overlapped and broad band at 640 cm^{-1}, which were only present in PAFS [20,21].

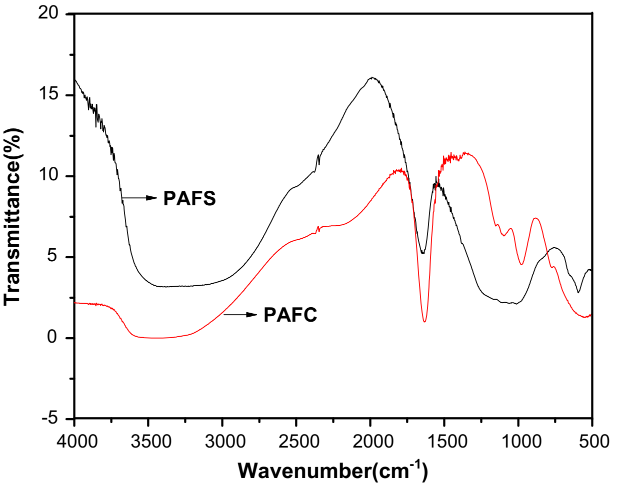


Fig. 1. FTIR spectra for PAFS and PAFC.

Table 1
Coagulation mixing procedure

Mixing procedure	Rapid mixing speed (rap/min)	Time (min)	Slow mixing speed (rap/min)	Time (min)
1	350	0.5	60	1
2	350	1	60	5
3	350	2	60	10
4	350	3	60	15
5	100	1	60	5

3.2. XRD and SEM analysis

The FTIR spectrum presented the possible chemical bonds of PAFS and PAFC. However, XRD and

SEM were used to identify the compounds and morphology, respectively. Figs. 2 and 3 illustrate the XRD patterns of solid PAFS and PAFC. The PAFS sample was largely amorphous structure with slight traces of crystallinity. Compared with the standard crystal peaks, some crystal peaks shifted along with the left–right axis, which might be attributed to the lattice expansion or contraction of the coagulant [11]. This observation was also supported by the examination of SEM. As displayed in Fig. 4, the PAFS and PAFC samples behave as an amorphous material in general, randomly forming aggregates of various sizes and shapes. In the size of 500 μm, PAFS was significantly larger than PAFC, while in the size of 20 μm, it presented a curl slice and compact network structure. Fig. 4(b) shows PAFC presented a branched and clump structure.

In general, the FTIR, XRD, and SEM analysis of PAFS samples indicate that the new inorganic composite coagulant PAFS had completely different structure and morphology from PAFC. The conclusions based on previous studies showed that curl slice and compact network were more favorable to coagulate colloidal particles, which were helpful to form bridge aggregation among flocs compared with the branched structure [22,23].

3.3. Coagulation experiment on algae removal effect by FAFS

In the coagulation process, there are many factors affecting the coagulation efficiency such as coagulant dosage, pH value of raw water, temperature, and mixing conditions.

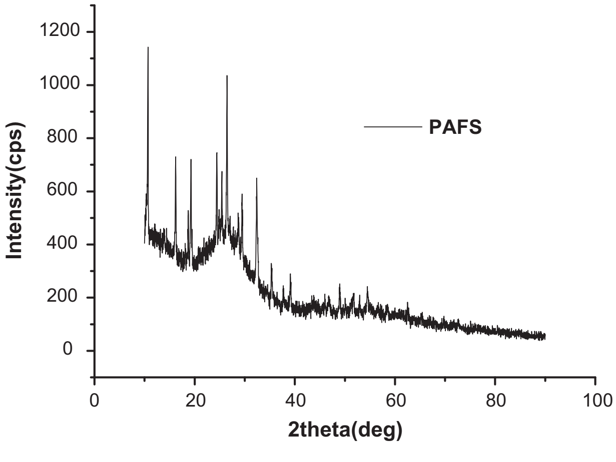


Fig. 2. XRD scan of PAFS sample.

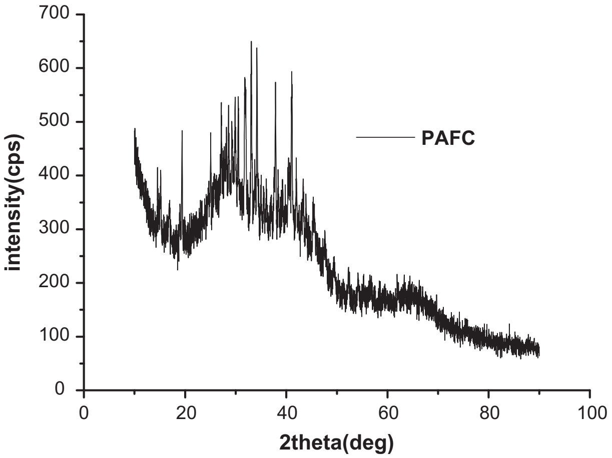


Fig. 3. XRD scan of PAFC sample.

3.3.1. Effect of coagulant dosage

The purpose of this experiment was to investigate the effect of the coagulant dosage on the surface charge of colloid, chlorophyll a, and turbidity removal efficiency while the raw water initial pH value and temperature were controlled at 7.48, 25℃, respectively.

Fig. 5 illustrates the effect of coagulant dosage on chlorophyll a and turbidity removal efficiency. It shows the removal of chlorophyll a and turbidity increased with the increase of coagulant dosage until 180 $\mu l L^{-1}$. However, for coagulant dosages above 180 $\mu l L^{-1}$, the removal of chlorophyll a and turbidity decreased. As shown in Fig. 5, there is a sharp decrease in the treatment efficiency as the coagulant dosage increased from180 to 300 $\mu l L^{-1}$. At low coagulant dosages, there were insufficient polymers to form adequate bridging links among particles, but with excess polymers, there was no longer enough bare particle surface available for attachment of segments and therefore particles became destabilized [24]. The main reason for the decrease was overdosing effect of the coagulant, which was based on the chain bridging mechanism [25,26]. Therefore, there should be an optimum polymer dosage for coagulation behavior, and the result shows the optimum treatment efficiency was achieved at the coagulant dosage of 180 μl L^{-1}, at which the chlorophyll a and turbidity removal efficiency were 95.2 and 92.8%, respectively.

3.3.2. Effect of initial pH value of raw water

The initial pH value of raw water is one important parameter influencing the algae and turbidity removal efficiency during the coagulation process. In this experiment, the effect of water initial pH value on the

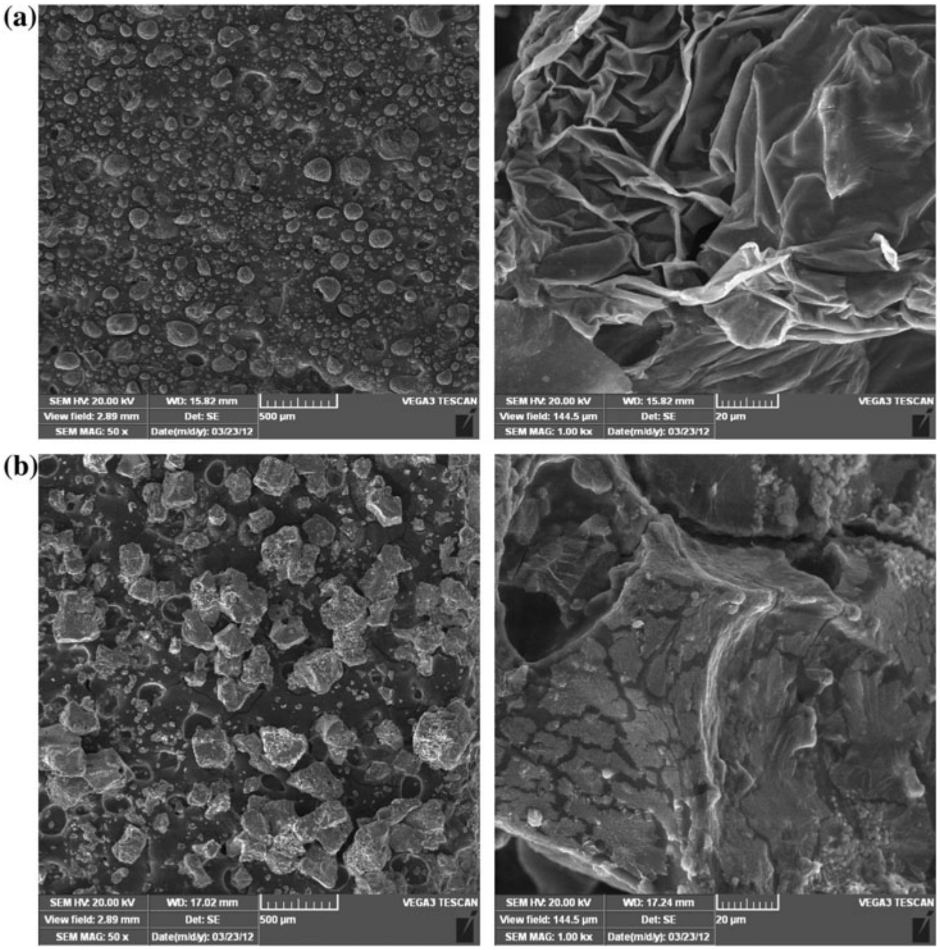


Fig. 4. SEM microphotographs: (a) PAFS and (b) PAFC.

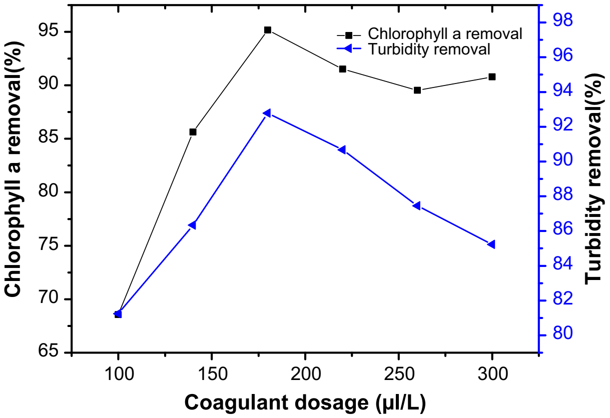


Fig. 5. Effect of coagulant dosage on chlorophyll a and turbidity removal.

coagulation process was investigated in the range 4.5–10.5 while the coagulant dosage and water temperature were fixed at 180 μl L^{-1} and 25℃, respectively. The results are as shown in Fig. 6.

Fig. 6 shows that the chlorophyll a and turbidity removal efficiency were stable and better in pH value of the raw water in the range of 6.5–8.5. In addition, Fig. 6 indicates the treatment efficiency increased as the pH increased from 4.5 to 7.5. However, there was a decrease in the chlorophyll a removal efficiency as the pH value increased above 7.5. The main reason for the increase in the removal efficiency could be attributed to more hydroxyl ions reacting with the $(Fe–Al)_a$ or Fe_a species to produce more high-ferrite polymers as the pH increased from 4.5 to 7.5, thus improving the bridging flocculation [11,12]. At the same time, the particle's charge was decreased by the charge neutralization mechanism, enhancing the destabilization of the colloidal particles in water [27]. However, previous research showed the ability of Fe(III) coagulants to neutralize the negative charge and to remove the pollutants was optimal in the middle pH range [28]. Therefore, there was a distinct decrease in the chlorophyll a and turbidity removal efficiency as the pH value increased above 7.5. At pH 7.5, the maximum

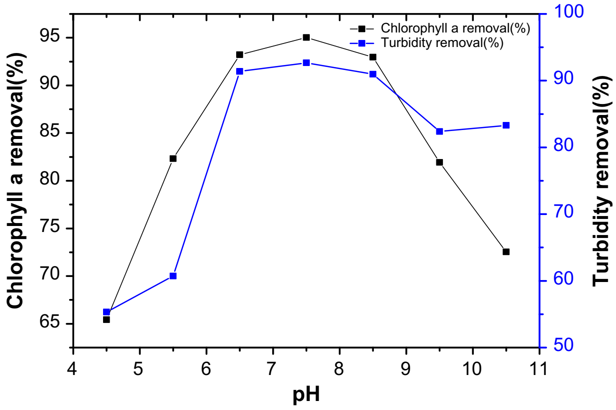


Fig. 6. Effect of pH value on chlorophyll a and turbidity removal.

chlorophyll a and turbidity removal efficiency were 95.0 and 92.7%, respectively. Because the initial pH value of water samples in this study was 7.48, therefore pH 7.48 was adopted as the optimum condition.

3.3.3. *Effect of water temperature*

In this experiment, the effect of water temperature on the coagulation process was investigated in the range 5–30˚C while the PAFS dosage was set at 180 µl L^{-1} and the water initial pH value at 7.48.

Fig. 7 illustrates the effect of water temperature on the chlorophyll a and turbidity removal efficiency. It shows an increase in the chlorophyll a and turbidity removal efficiency as the water temperature increased from 5 to 30˚C. The main reason for this trend could be attributed to role of water temperature as an important control factor on the growth, settlement and separation of flocs during coagulation process [29]. Usually, at high water temperature, flocculation is effective as the flocculent body is dense and easy to settle down. This is caused by the chemical reaction rate increasing with an increase in temperature. However, at low water temperature, the hydrolysis reaction is slow while the water is viscous. The hydration of a flocculation body increases with decreasing Brownian motions, and therefore the water content of sludge will be high resulting in a bigger volume. At the same time, low temperature affects the interaction between the impurity particles and particles, particles and colloid. The experimental results show the removal of chlorophyll a improved at higher water temperature. Therefore, at a water temperature of 30˚C, the achieved chlorophyll a and turbidity removal efficiency were 97.0 and 92.8%, respectively.

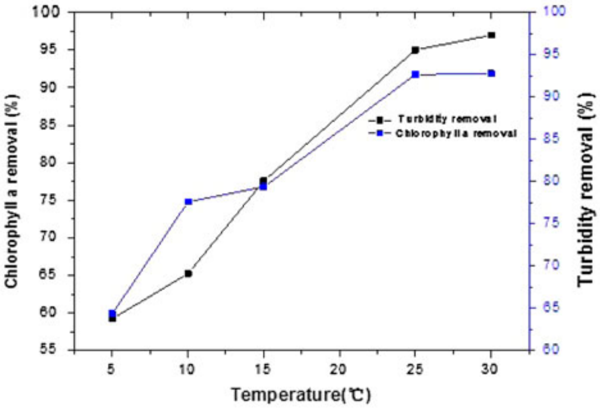


Fig. 7. Effect of water temperature on chlorophyll a and turbidity removal.

3.3.4. *Effect of mixing conditions*

In this experiment, the effect of mixing conditions on the coagulation process was investigated while the PAFS dosage, water initial pH value, and water temperature were fixed at 180 µl L^{-1}, 7.48, and 25˚C, respectively.

Fig. 8 shows the effect of mixing conditions on the chlorophyll a and turbidity removal efficiency. It indicates the maximum removal efficiency was achieved using mixing program 2, at which the chlorophyll a and turbidity removal efficiency were 94.8% and 92.3%, respectively. In addition, larger flocs were observed when using mixing program 2. The rapid mixing after addition of flocculating agent increases grain collision frequency and the chances of contact between particles and flocs. However, the appropriate mixing speed and time improves the effect of flocculation. Generally, the rapid mixing speed is applied during the coagulation–flocculant phase, while the slow mixing speed is used for the floc growth stage. But, with a controlled mixing speed, the effect of flocculation is decided by mixing time. Usually, as the time increases, the treatment efficiency increased. Short mixing time was not favorable for the flocculation agent to mix and react quickly with water, while with long reaction time, the efficiency of flocculation decreased because of breakage of flocs.

Fig. 8 shows using the mixing program 5 (Table 1), the treatment efficiency was the lowest while the flocs were the largest. The main reason could be the uneven dispersion of flocculants resulting in flocs settling down before particles are adsorbed to water. Therefore, the chlorophyll a and turbidity removal efficiency were very low.

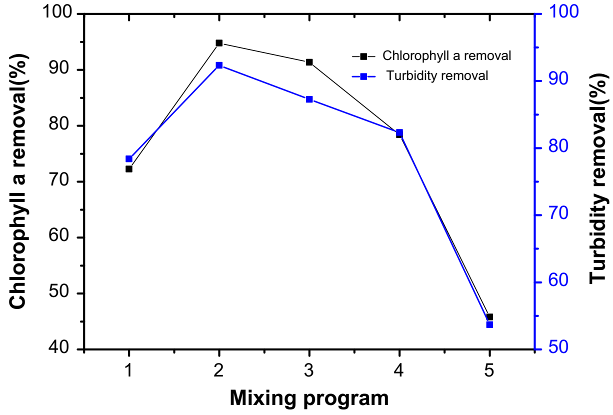
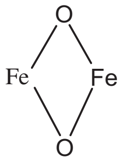
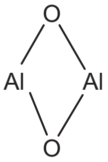


Fig. 8. Effect of mixing procedure on chlorophyll a and turbidity removal.

3.4. *Algae removal with different coagulants*

The purpose of this experiment was to further investigate the coagulating performances of PAFS. Removal of chlorophyll a and turbidity from raw water of Democratic lake was studied by using PAFS, PFS, PAC, and PAFC. The experiment was carried out using water temperature of 25℃, using mixing program 2, and raw water initial pH value of 7.48. The results are as shown in Figs. 9 and 10.

Fig. 9 shows the optimum dosages for turbidity removal using PAFS, PAFC, PAC, and PFS were 180, 220, 300, and 300 μl L^{-1}, respectively whereas the turbidity removal efficiencies at optimum dosages were 92.8, 87.6, 90.3, and 83.1%, respectively. Fig. 10 shows the optimum dosages for removal of chlorophyll a using PAFS, PAFC, PAC, and PFS were 180, 220, 140, and 300 μl L^{-1}, respectively. In addition, the chlorophyll a removal efficiencies at optimum dosages were 95.2, 86.3, 60.9, and 68.3%, respectively. The results show the coagulation efficiency of PAFS was better than other coagulations whereas its dosage was less. In addition, it was observed that PAFS flocs were bigger than PAFC, PAC, and PFS during coagulation process. Furthermore, the sedimentation rate of PAFS was faster than PAFC, PAC, and PFS. The main reason for these results was  and  structures were present in PAFS [20], and PAFS has better flocculating ability and lower dosage than PAFC, PAC, and PFS.

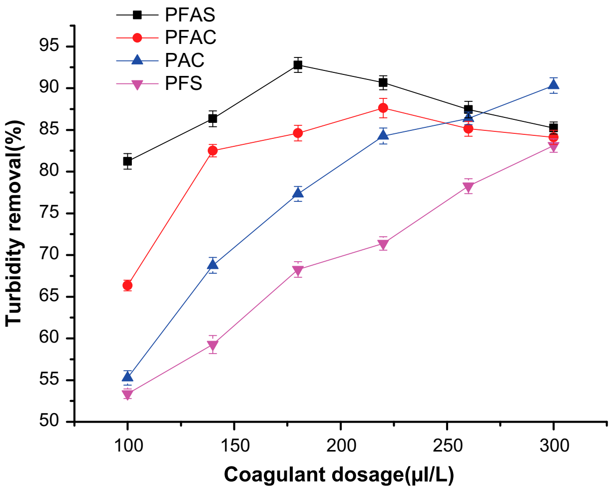


Fig. 9. Effect of typical coagulants dosages on turbidity removal rate.

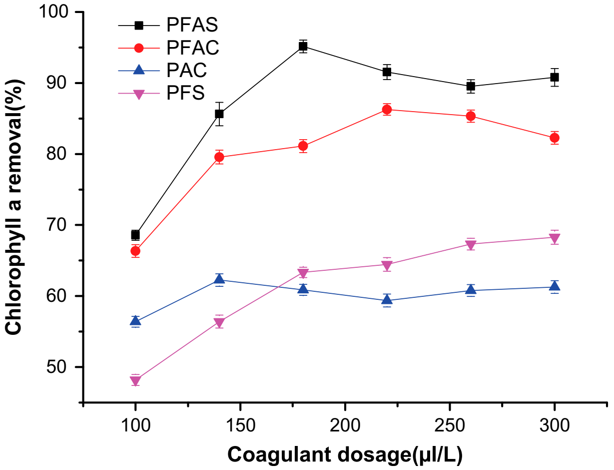


Fig. 10. Effect of typical coagulants' dosages on chlorophyll a removal rate.

4. Conclusions

In this paper, the structure and flocculation behaviors of the composite coagulant PAFS were investigated. From the above investigation, we came to the following conclusions: FTIR analysis indicates some possible chemical bonds such as H–O–H, –OH, P=O, Al–O–Al, Fe–O–Fe, HSO_4^-, and SO_4^{2-} bonds were introduced in PFS, resulting in a new composite coagulant with highly charged polynuclear polyhydroxy complexes. Characterization of PAFS by XRD shows it was a nonstoichiometric compound of basic iron sulfate salt. SEM images show PAFS presented a compact network structure, which was more favorable to coagulate colloidal particles and form bridge aggregation among flocs compared with the branched structure of PAFC. Coagulation experiments show the coagulation efficiency of PAFS was the best at a coagulant dosage of 180 μl/L, pH ranging from 6.5 to 8.5, water temperature at 15℃, and using mixing program 2. In contrast, the coagulation efficiency of PAFS was better than other coagulations whereas its dosage was less, and the removal efficiency for turbidity and chlorophyll a of PAFS was 92.8 and 95.3%, respectively, which were consistently superior to those of the traditional coagulants.

Acknowledgments

The authors are grateful for the financial support provided by the Scholarship Award for Excellent Doctoral Student granted by Ministry of Education; the National Natural Science Foundation of China (Project No. NSFC, 51078366); the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 708071); and Industrial Development Fund (production and research special projects) of Chongqing (No. 10-cxy-09).

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