Preparation, characterization and coagulation performance of a composite coagulant: Polymeric aluminum ferric sulfate

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Abstract. Polymeric aluminum ferric sulfate (PAFS) was a novel inorganic composite coagulant, prepared by direct oxidation process using aluminum oxide (Al₂O₃) and ferrous sulfate heptahydrate (FeSO₄·7H₂O) as typical materials. In order to obtain the optimal removal rate of the turbidity and humic acid, the optimum preparation conditions of PAFS was investigated as follows: SO₄²⁻/Fe, NO₃⁻/Fe, PO₄³⁻/Fe, Al/Fe molar ratio and reaction temperature. The resultant polymer was characterized by scanning electron microscopy (SEM). The results showed that the optimum preparation conditions were SO₄²⁻/Fe of 0.35, Al/Fe of 0.11, NO₃⁻/Fe of 0.45, PO₄³⁻/Fe of 0.09 and reaction temperature of 80°C, and the maximum turbidity and HA removal efficiency could reach 98.4%, 93.5%, respectively.

1. Introduction
In the past few decades, river water has become the main source of water supply in China[1], but river water are most vulnerable to suspended pollution from solids and organic matters[2]. Humic substances are one of the most ubiquitous forms of organic matters in water environmental systems. Humic acid (HA) is a main component of humic substances[3]. In order to access to clean drinking water, removing humic acid and turbidity from the river water have become a focal point for researchers around the world[4].

Coagulation as one of the most cost-efficient pretreatment processes in the water treatment plants is very efficient for removal of organic matters and suspended solids[5]. During the flocculation process, the small particles are combine to form flocs large enough to be separated from solution in a short time[6]. The selection of floculants with enhanced coagulation efficiency is a commonly used technology. According to the survey[7], the performance of the inorganic polymer flocculants are more cost-efficient to the organic polymer flocculants in coagulation process. The poly aluminum chloride (PAC), poly ferric sulfate (PFS) and poly ferric sulfate silicate (PFSS) were widely used as common inorganic flocculants in water treatment plants. Furthermore, Polymeric aluminum ferric sulfate (PAFS) as a novel inorganic composite coagulant can obviously speed up the sedimentation rate, decrease costs, color and toxins, which was superior to PAC, PFS and PFSS[8]. PAFS has received more attention than PAC, PFS and PFSS at present, however, very few studies has been reported on humic acid removal in water using PAFS[8]. Accordingly, it is interesting to study the preparation method for a new composite coagulant used in humic acid water.

In the study, preparation, characterization and coagulation performance of a novel coagulant (PAFS) was investigated. The main purposes of the research was to investigate as follows: research on the preparation of PAFS, including parameters affecting the coagulation performance such as SO₄²⁻/Fe,
NO$_3$/Fe, PO$_4^{3-}$/Fe, Al/Fe molar ratio and reaction temperature were examined. After that, the morphologies of PAFS was compared using scanning electron microscopy (SEM).

2. Experimental section

2.1. Chemicals and reagents
aluminum oxide (Al$_2$O$_3$) and ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O) were procured from Spartan. Nitric acid (HNO$_3$), sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were obtained from Aladdin.

2.2. Preparation of PAFS
PAFS was synthesized in aqueous solution by heating method. Firstly, FeSO$_4$·7H$_2$O was mixed with H$_2$SO$_4$ and Al$_2$O$_3$ into a thin uniform paste by slow stirring in a beaker. then the new liquid mixture was oxidized using HNO$_3$ by slow stirring in a thermostatic water bath at a certain temperature. Then H$_3$PO$_4$ was added to improve the hydrolysis and polymerization reaction. Further NaOH was added to adjust its alkalify degrees. Finally, the resultant polymer was ageing at room temperature for 24h[1].

2.3. Characteristics of PAFS
The copolymer was purified using acetone for three times in order to obtain the pure solid of PAFS. Then the copolymer was dried at 60℃ in an oven for several days. SEM images were taken through scan electronic microscope.

2.4. Water sample
The simulate water sample was prepared with deionized water. Mixed 1 g/L kaolin suspension and 10 mg/L HA were combined as synthetic water, which were simulated to high turbid river water containing high levels of aquatic humus. Before the flocculation experiments, the designed amount of matters was added into water, and the homogenized suspension was prepared by rapid stirring at 200 rpm for 3 min under the bath sonication.

2.5. Flocculation experiments
Flocculants were dosed under rapid stirring speed of 300 r·min$^{-1}$ for 1 min, then medium stirring speed of 160 r·min$^{-1}$ for 4 min, finally slow stirring speed of 40 r·min$^{-1}$ for 5 min using a program-controlled jar test apparatus in a beaker of 1L. The supernatant sample was obtained from the beaker for measurement of the turbidity and HA removal efficiency after settling for 2.0 h.

3. Results and discussion

3.1. Characterization of copolymer
The SEM image of PAFS is showed in Fig.1. It can be seen that PAFS sample is an amorphous material, which randomly forms aggregates of various sizes and shapes. While in the size of 20μm, the surface of PAFS presents a curl slice and compact network structure, which may produce more adsorption sites for adsorption and improve the bridging capacity. Fig. 1 also showed the linear correlation between the logarithm of perimeter (L) and area (A). The calculation result showed the average fractal dimensions of PAFS was 1.390 using image-pro Plus 6.0 Software.
3.2. Flocculate effect of $SO_4^{2-}$/Fe molar ratio
Fig.2 shows the flocculate effect of $SO_4^{2-}$/Fe molar ratio on turbidity and HA removal efficiency. It shows that the turbidity and HA removal efficiency increased as the increased of $SO_4^{2-}$/Fe molar ratio from 0.25 to 0.35. However, when the $SO_4^{2-}$/Fe molar ratio was from 0.35 to 0.50, there was a decrease in the turbidity and HA removal efficiency. That mainly because oxidation reaction of ferrous sulfate was conducted in acid condition, a certain dosage of sulfuric acid is advantageous to the reaction, which could improve the ability of flocculation. The optimum $SO_4^{2-}$/Fe molar ratio was 0.35, and the turbidity and HA removal efficiency reached 95.6%, 90.4%, respectively.

3.3. Flocculate effect of Al/Fe molar ratio
Fig.3 shows the flocculate effect of Al/Fe molar ratio on turbidity and HA removal efficiency. It shows that the turbidity removal efficiency increased as the increased of Al/Fe molar ration from 0.08 to 0.11. However, when the molar ration of Al/Fe molar ratio was from 0.11 to 0.13, there was a decrease in the turbidity removal efficiency. That mainly because Ferric ion and aluminium ion formed more stable complex in a certain Al/Fe molar ratio. The optimum Al/Fe molar ratio was 0.11, and the turbidity and HA removal efficiency reached 96.2%, 91.8%, respectively.
3.4. Flocculate effect of NO$_3^-$/Fe molar ratio

Fig.4 shows the flocculate effect of NO$_3^-$/Fe molar ratio on turbidity and HA removal efficiency. It shows that the turbidity and HA removal efficiency increased as the increased of NO$_3^-$/Fe molar ratio from 0.30 to 0.45. However, when the NO$_3^-$/Fe molar ratio was from 0.45 to 0.55, there was a decrease in the turbidity and HA removal efficiency. That mainly because nitric acid is strong oxidizer, Fe$^{2+}$ can be directly oxidized to Fe$^{3+}$ in the reaction system, but the nitric acid dosage is too much, by-products NO and unoxidized Fe$^{2+}$ will form relatively stable complex ion to hinder the further Fe$^{2+}$ oxidation. The optimum NO$_3^-$/Fe molar ratio was 0.45, and the turbidity and HA removal efficiency reached 97.4%, 92.2%, respectively.

Figure 4. Flocculate effect of NO$_3^-$/Fe molar ratio

3.5. Flocculate effect of PO$_4^{3-}$/Fe molar ratio

Fig.5 shows the flocculate effect of PO$_4^{3-}$/Fe molar ratio on turbidity and HA removal efficiency. It shows that the turbidity and HA removal efficiency increased as the increased of PO$_4^{3-}$/Fe molar ratio from 0.05 to 0.09. However, when the PO$_4^{3-}$/Fe molar ratio was from 0.09 to 0.10, there was a slight decrease in the turbidity and HA removal efficiency. That mainly because adding a certain amount of PO$_4^{3-}$ could strengthen the ability of bridging between Al-P-Fe, which could improve the ability of flocculation[9]. The optimum PO$_4^{3-}$/Fe molar ratio was 0.09, and the turbidity and HA removal efficiency reached 97.2%, 92.8%, respectively.
3.6. Flocculate effect of reaction temperature

Fig. 6 shows the flocculate effect of reaction temperature on turbidity and HA removal efficiency. It shows that the turbidity and HA removal efficiency increased as the increased of reaction temperature from 40°C to 80°C. However, when the reaction temperature was from 80°C to 90°C, there was a slight decrease in the turbidity and HA removal efficiency. That mainly because raising the reaction temperature not only could accelerate the polymerization rate, but also could improve the polymerization degree. When the higher temperature could lead the bond breaking, the effect has become worse[10]. The optimum reaction temperature was 80°C, and the turbidity and HA removal efficiency reached 98.4%, 93.5%, respectively.

4. Conclusions

In this study, the structure and coagulation performance of the novel composite coagulant PAFS were investigated. From investigations, we got the following conclusions: SEM images presented a curl slice and compact network structure, which suggested PAFS had a high adsorption-bridging ability in turbidity and HA removal from simulate water. The optimal synthetic conditions were SO₄²⁻/Fe of 0.35, Al/Fe of 0.11, NO₃⁻/Fe of 0.45, PO₄³⁻/Fe of 0.09 and reaction temperature of 80°C, and the maximum turbidity and HA removal efficiency could reach 98.4%, 93.5%, respectively.

Acknowledgments

Authors are grateful for the financial support provided by the Scientific and Science and Technology Research Program of Chongqing Municipal Education Commission (Grant No.KJQN202003306, No.KJQN201903408 and No.KJQN201803307), and Natural Science Foundation of Chongqing (Grant No.cstc2020jcyj-msxmX0949)
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