Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(5):801-807

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Preparation of polymeric phosphate aluminum-ferric chloride (PPAFC) and its application in humic acid removal

Peng Zhang*, Wei Zhang, Guocheng Zhu, Bozhi Ren, Xuemei Li and Hongpu Ma

College of Civil Engineering, Hunan University of Science and Technology, Xiangtan, Hunan, China

---

ABSTRACT

Polymeric phosphate aluminum-ferric chloride (PPAFC) in this study was prepared. In order to obtain the optimum conditions for preparation of PPAFC, resulting in a better turbidity removal efficiency, parameters such as the molar ratio of Al/Fe, P/(Al+Fe), OH/(Al+Fe) as well as the reaction temperature were examined. Results showed that the optimal synthetic conditions were Al/Fe of 6:4, P/(Al+ Fe) of 1:6, OH/(Al+Fe) of 0.6 and reaction temperature of 50 °C. Under this condition, the maximum removal efficiency of turbidity of 99.7% could be achieved. PPAFC was characterized by the infrared spectroscopy (IR spectroscopy) and scanning electron microscopy (SEM). The effects of PPAFC dosage, pH value, initial concentration of humic acid and anions SO42- on humic acid removal were studied, which indicated that the maximum removal efficiency of humic acid was 99.1% with the optimum flocculant dosage at pH 4.0, and that there was no anions coexisted.

Key words: Polymeric phosphate aluminum-ferric chloride, Humic acid, Flocculant, Turbidity, Water treatment

---

INTRODUCTION

In recent years, the water sources have suffered from serious contamination, which continue to deteriorate due to the economic development and ecological deterioration [1]. In the source water, the most common contaminants are the suspended solids and the organic matters [2-3]. Many have studied that the organic pollution was most likely caused by humic acid. In order to produce more fresh water for human use, research on removing turbidity and humic acid from water has attracted more attention [4-6]. Coagulation-flocculation as one of the most important pre-treatment processes in water and wastewater treatment plants has suggested to be effective for removal of the suspended solids and the organic pollutants [7]. In the coagulation-flocculation process, flocculant is a critical factor, which affects the coagulation-flocculation performance significantly [8-9]. It has long been found that the coagulation-flocculation performance of inorganic polymer flocculant is superior to that of organic polymer flocculant, especially in removing the turbidity and some organic pollutants. The commonly used inorganic flocculants at present are poly-ferric sulfate (PFS), poly-aluminum chloride (PAC), polymeric aluminum ferric sulfate (PAFS) and polymeric aluminum ferric sulfate (PAFS). Because the flocculation behaviors for these inorganic flocculants were closely correlated with their qualities and species [10-12], it is of importance to prepare some new flocculants, which contain many more effective species better suitable for flocculation. They have more advantageous over the existing in that they are more cost-effective.

PPAFC is a new type of inorganic composite flocculant with better flocculation performance [13-14], which was obtained by the copolymerization of the iron and aluminum and phosphate, and thus it had the combined effect of iron- and aluminum-based coagulants. The phosphate was added in order to increase the molecular bridging between the metals and PO_4^{3-}, which could improve the degree of polymerization of flocculant thus resulting in higher flocculation performance.

The purpose of this study was aimed to use a new method for preparation of PPAFC. Parameters affecting the coagulant performance such as the molar ratio of Al/Fe, P/(Fe+Al), OH/(Fe+Al) and reaction temperature were examined. The structure and morphology of PPAFC was characterized by IR spectroscopy and SEM. Finally, the effects of flocculant dosage and pH on the removal of humic acid were investigated using PPAFC. Another study on the influences of initial concentration of humic acid and anions (SO_4^{2-}) on humic acid removal was conducted.

EXPERIMENTAL SECTION

2.1 Material and instruments

All reagents used in this study were analytical grade or greater, which included disodium hydrogen phosphate (Na_2HPO_4), hydrochloric acid (HCl), sodiumhydroxide (NaOH), and hexahydrated ferric chloride($FeCl_3.6H_2O$). All aqueous solutions and standard solutions were prepared with deionized water. The traditional flocculant PAC was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The instruments used in this study were as follows:

- Fourier Transformed Infra Red (FT-IR) Spectrophotometer (Niclet 6700, Niclet instrument Company, USA)
- Jar Tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd. China)
- Portable Turbidimeter (HACH 2100Q, HACH Company, USA)
- The scanning electron microscope (SEM) (JSM-6380LV, JEOL Company, Japan)

2.2 Preparation of PPAFC

The inorganic flocculant PPAFC was prepared through a microwave radiation. Firstly, 7.0 g of PAC and 21.6 g $FeCl_3.6H_2O$ was mixed with deionized water into a thin uniform paste by slowly stirring in a beaker. Secondly, 3.6 g Na_2HPO_4 was added, followed by thorough stirring and dilution with a small amount of water. Thirdly, the mixture solution was stirred slowly for 10 min and then heated for 4 min microwave radiation with power at 20 W. Fourthly, 2 mol /L NaOH solution was used to adjust its alkalify degrees with a slowly stirring for 1 h in a thermostatic water bath at temperature of 50 ˚C. Then, a thick liquid flocculant PPAFC with a reddish-brown color was produced after aging for more than 12 h at room temperature.

2.3 Characteristics of PPAFC

In order to obtain dried powder, PPAFC was placed in a beaker and dried in a vacuum at 75˚C for several days. IR spectra of PPAFC was analyzed using a Magna-IR model spectrometer in the range of 4000–500 cm^{-1} with KBr as dispersant. The morphology of the copolymer was observed through SEM. The electron samples were prepared by shattering and planishing, and sputtering Au. The electron samples were dried and the morphology of PPAFC were obtained through SEM analyzer.

2.4 Water sample

The water samples were collected from a lake in campus of Hunan University of Science and Technology, which was characterized by the turbidity of 9.7-31.8 NTU.

1.0 g humic acid was dissolved in 250 mL beaker and 1.0 mol/L NaOH solution was used to improve the solubility of humic acid, and then the humic acid solution was transferred into a 1000 mL volumetric flask. The flask was filled with dilution water to the etched line. Finally, the humic acid solution of 1000 mL was stored in refrigerator at dark for later use.

2.5 Flocculation test

A ZR 4-6 stirring machine (Shenzhen Zhongran Water Industry Technology Development Co., Ltd., Shenzhen, China) with six stirrers was used in this experiment. 200 mL of water sample were transferred into a beaker. Flocculants were dosed at medium stirring speed of 350 r/min for 2 min, and then changed to the speed of 45 r/min for 8 min. After quiescent settling of 30 min, the samples were collected from 2 cm below the surface of suspension for measurement of turbidity and the specific absorbance at 254 nm (UV_{254}). The absorbance values was then translated into the concentration to calculate the removal efficiency with standard calibration curve for determination of humic acid.

RESULTS AND DISCUSSION

3.1 Preparation of PPAFC and effects on turbidity removal efficiency

In order to investigate the effects of Al/Fe, P/(Fe+Al), OH/(Al + Fe) and reaction temperature on the coagulant's performance, a series of coagulation–flocculation experiments were conducted at the pre-determined factor level. The experimental results are presented in Figure1.

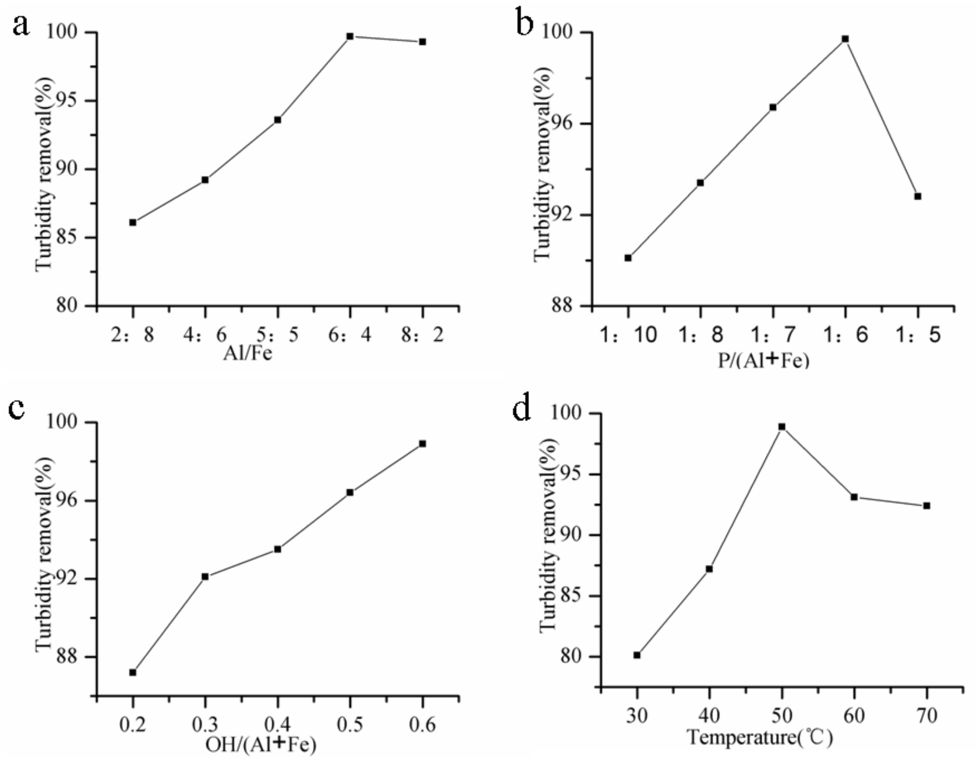

Figure 1. Effect of the operational parameters on removal of turbidity (a) Al/Fe molar ratio (b) P/ (Al+Fe) molar ratio (c) OH/(Al+Fe) ratio (d) temperature

Figure 1.(a) shows the effect of Al/Fe molar ratio on turbidity removal. It showed that the turbidity removal efficiency increased with increasing the Al/Fe molar ratio ranging from 2:8 to 6:4. However, there was a slight decrease in the turbidity removal efficiency as the molar ratio of Al/Fe increased to 8:2. Therefore, the optimum molar ratio of Al/Fe for turbidity removal in this study was 6:4.

Figure1.(b) shows the effect of P/(Al+Fe) molar ratio on turbidity removal. It showed that the turbidity removal efficiency increased sharply as the P/(Al+Fe) molar ratio increased from 1:10 to 1:6 but the further increase in the P/(Al+Fe) molar ratio resulted in a decrease. The results showed that the maximum turbidity removal efficiency of 99.7% was achieved at P/(Al+Fe) molar ratio of 1:6, whereas at the P/(Al+Fe) molar ratio of 1:5, the removal efficiency was decreased to 92.8%. Therefore, the optimum molar ratio of P/(Al+Fe) was 1:6. The main reason for the increase was that the approximate P was able to improve the ability of the bridging between the metals and P forming many more higher molecular complexes, which could improve the flocculaiton performance.

Figure1.(c) shows the effect of OH/(Al+Fe) molar ratio on turbidity removal. It showed that the turbidity removal efficiency increased as the OH/(Al+Fe) molar ratio increased from 0.2 to 0.6. The main reason for the increase was that with increasing the OH$^-$, the moderate polymeric species of hydrolytic polymerization of aluminum and iron were increased, most of the hydrolysis products of the polymer tended to flocculate the colloidal particles [15]. The optimum OH/(Al+Fe) molar ratio was 0.6 selected in this study.

Figure1.(d) shows the effect of temperature on turbidity removal. It showed that the turbidity removal efficiency increased with increasing the temperature from 30 to 50 ℃. However, there was a slight decrease in the turbidity removal efficiency from 50 ℃ to 70 ℃ as the temperature increased to greater than 50℃. Therefore, the optimum molar ratio of Al/Fe was 50℃. The main reason for the increase was that the reaction temperature not only accelerated the polymerization rate, but also improved the degree of polymerization. However, the temperature at higher level would be not conducive to the polymerization reaction possibly influencing the flocculation performance. In addition, it was not cost effective for preparation of PPAFC under higher temperature. Therefore, the optimum reaction temperature was 50℃.

3.2 Characterization of the product

3.2.1 IR spectroscopy

Figure2. indicates that the original strong absorption peak at 3422.79 cm^{-1} was attributed to the stretching vibration of -OH groups and the corresponding aluminum and iron ion in the solid sample. The peak at 1633.40 cm^{-1} was

attributed to the bending vibration of Fe-PO_4^{3-}-Fe. In addition, there was a weak adsorption peak at 1050 cm^{-1}, which is the stretching vibration for P-O groups [16].

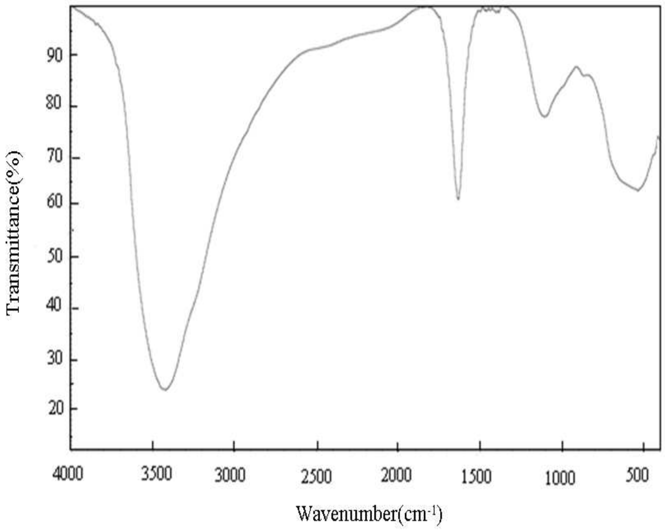

Figure 2. IR spectroscopy of PPAFC

3.2.2 SEM Analysis

The SEM images of PPAFC was depicted in Figure 3. It can be seen that the surface of PPAFC was a rough and microporous structure. It appears that on the surface of PPAFC the microporous structure was possible to increase the adsorption sites of surface of PPAFC, potentially improving its adsorption-bridging ability. The crystal structure of PPAFC was found to be amorphous.

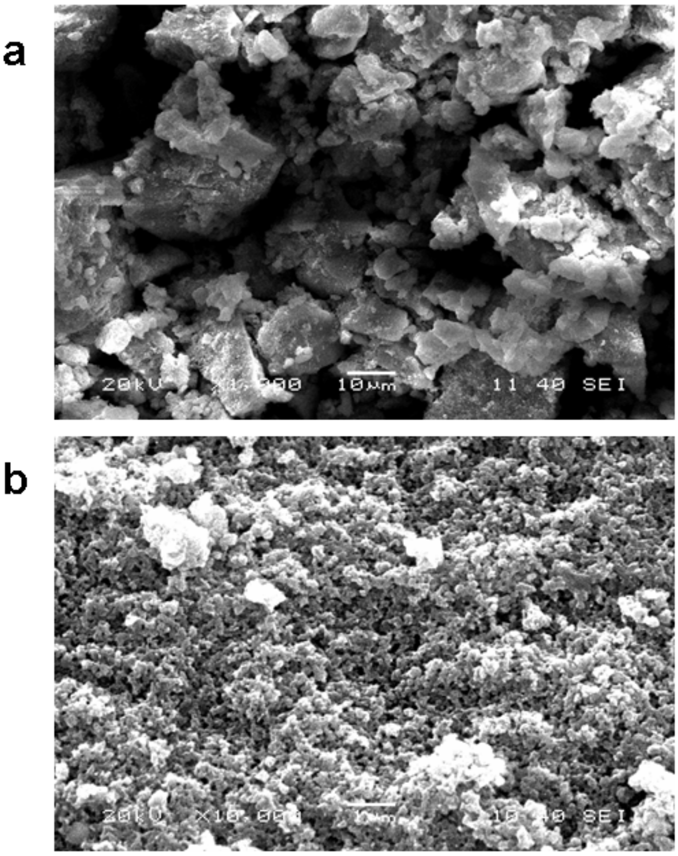

Figure 3. SEM images of PPAFC

3.3 Optimization of the coagulation–flocculation process

3.3.1 Effect of the dosage on humic acid removal efficiency

In this experiment, the effect of PPAFC and PAC dosage on the removal efficiency of humic acid was investigated with humic acid at an initial concentration of 10.0 mg/L, and the dosage of PPAFC ranging from 7.0 to 35.0 mg/L without adjustment of the pH at room temperature.

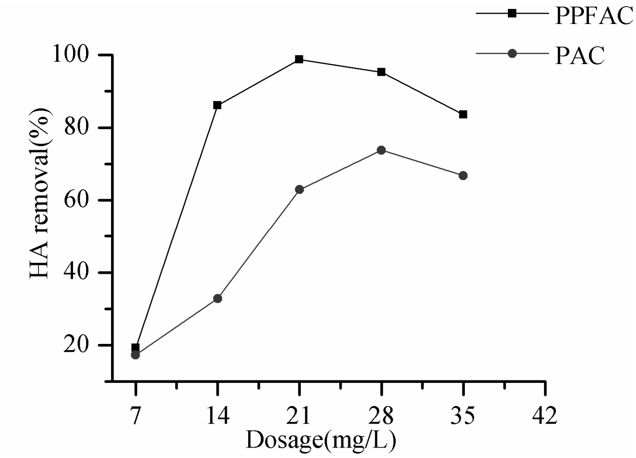

Figure 4. The effect of dosage on the removal efficiency of humic acid

Figure4. showed that the removal efficiency of humic acid by PPAFC had a better effect than that by PAC. The results showed that with PAC, the humic acid removal efficiency increased from 17.3% at 7.0 mg/L to the maximum of 73.8% at 28.0 mg/L but with further increasing the flocculant dosage the removal efficiency was decreased to 66.8% at the dosage of 35.0mg/L; with PPAFC the humic acid removal efficiency increased from 19.3% at 7.0 mg/L to the maximum of 98.8% at 21.0 mg/L but the removal efficiency was decreased to 83.6% as the flocculant dosage increased to the dosage of 35.0 mg/L. The main reason for the worsening performance was attributed to overdosing effect, which was based on the chain bridging mechanism. At lower dosage, there were insufficient polymers to form adequate bridging links among molecules, but when flocculant was over dosage, there was no longer enough bare molecules surface available for attachment of segments and therefore particles became destabilized. Compared with PAC, PPAFC showed better performance in removal of humic acid. The addition of Fe and PO_4^{3-} improved polymerization of flocculant as well as its coagulation behaviors [17].

3.3.2 Effect of pH value on humic acid removal efficiency

The pH of raw water is an important factor affecting flocculation efficiency. In this experiment, the effect of pH value on the humic acid removal efficiency was investigated with humic acid at an initial concentration of 10.0 mg/L, and the dosage of PPAFC of 21.0mg/L at room temperature. The pH was ranged from 4.0 to 10.0.

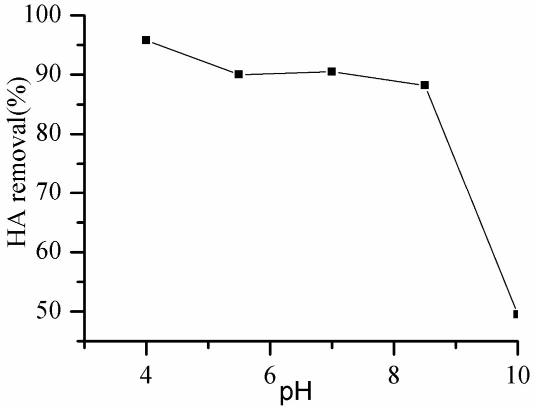

Figure 5. The effect of pH on removal efficiency of humic acid

Figure 5. showed that the effect of the pH of raw water on the removal efficiency of humic acid in the coagulation-flocculation process. It showed that the acid environment was able to enhance the coagulation-flocculation performance. In contrary, the performance would be inhibited at higher pH (e.g., pH=10). The result showed that the removal efficiency of humic acid increased with decreasing the pH value. The removal efficiency could reach the maximum of 95.8% at pH 4.0. In general, the humic acid was not better soluble in acid

condition thus having much more negative charges produced in water. Because the PPAFC was positively charged, the charge neutralization would make the humic acid molecules and the flocculant molecules attracted each other well under the acid environment. Therefore, an acid environment could enhance the flocculation performance in which the removal efficiency was decreased as the pH value decreased. On the contrary, under the alkaline environment, the solubility of humic acid was increased too much. Therefore, with the increase of the pH value, the hydrolysis products of PPAFC was largely affected. Thus the pH had a great influence on the removal of the humic acid in water.

3.3.3 Effect of initial concentration on humic acid removal efficiency

In this experiment, the effect of initial concentration of humic acid on the humic acid removal efficiency was investigated with the initial concentration ranging from 4.0 to 12.0 mg/L at PPAFC dosage of 21.0 mg/L without adjustment of pH at room temperature.

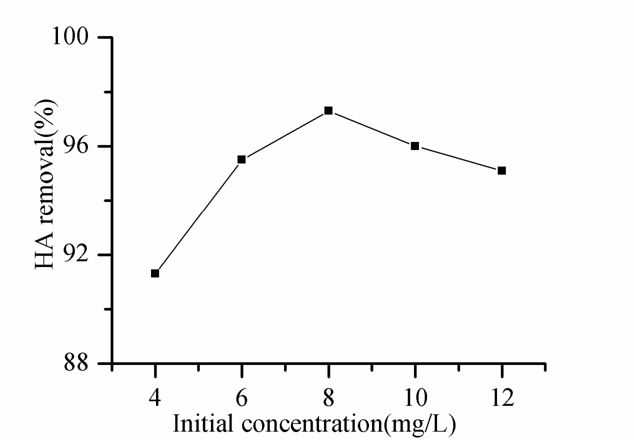

Figure 6. The effect of initial concentration on the HA removal efficiency

Figure 6. showed that the initial concentration of humic acid was an important parameter, which affected the removal efficiency of humic acid significantly. The removal efficiency of humic acid changed with varying humic acid initial concentration. At initial concentration of humic acid of 8.0 mg/L, the maximum removal efficiency of 97.3% was attained. At the initial concentration under 8.0 mg/L, 21.0 mg/L of PPAFC exceeded the optimum dosage, thus the redundant flocculant winded and covered with each other, which resulted in a decrease in the level of removal efficiency. When the initial concentration was greater than 12.0 mg/L, the 21.0mg/L of PPAFC dosage have not reached the optimum value.

3.3.4 Effect of anions SO_4^{2-} on humic acid removal efficiency

In this experiment, the effect of anions SO_4^{2-} on the humic acid removal efficiency was investigated with humic acid at an initial concentration of 10.0 mg/L and the concentration of SO_4^{2-} ranging from 20 mg/L to 100 mg/L, without adjustment of the pH at room temperature.

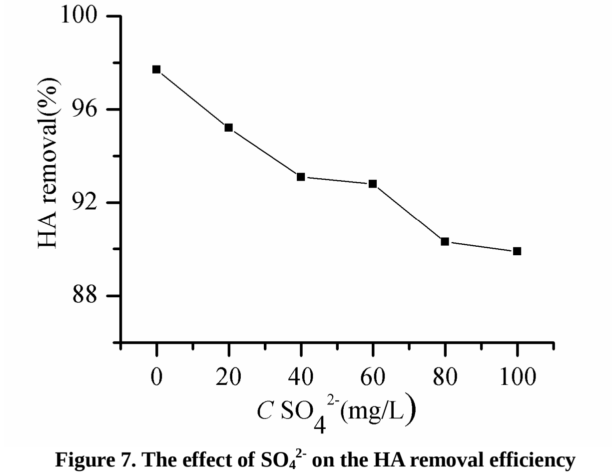

Figure 7. The effect of SO_4^{2-} on the HA removal efficiency

Figure 7. showed that the coexisted anions in raw water had a significant effect on the removal efficiency of humic acid in the coagulation-flocculation process. Because the SO_4^{2-} could accelerate the hydrolysis of Fe and Al, but it

was also a strong complexing agent, thus it could complex with the hydrolysates of Fe and Al, reducing the opportunities for contact of PPAFC with humic acid. Therefore, the presence of SO_4^{2-} would also cause an adverse effect on removing humic acid using PPAFC. The results showed that the removal efficiency was decreased with the increase of SO_4^{2-} concentration. When the concentration of SO_4^{2-} was 100 mg/L, the removal efficiency was 89.9%, which was reduced by 7.8% in comparison to that without SO_4^{2-} in raw water.

CONCLUSION

In this study, a new composite flocculant PPAFC was synthesized using microwave radiation in which parameters that affected the quality of flocculant was analyzed. Flocculation performance of humic acid was observed in detail. We came to the following conclusions:

The characteristics of the composite flocculant PPAFC by IR spectra and SEM indicated that the product was PPAFC, the surface of PPAFC was a rough and microporous structure, which could offer more adsorption sites for adsorption thus improving the bridging ability.

It was observed that Al/Fe (8:2-2:8), P/(Fe+Al) (1:10-1:5), OH/(Fe+Al)(0.2-0.3) and reaction temperature (30-70°C) were favorable to the synthesis of PPAFC. The optimal conditions for synthesizing PPAFC were Al/Fe of 6:4, P/(Fe+Al) of 1:6, OH/(Fe+Al) of 0.6 and reaction temperature of 50°C. With the PPAFC prepared under above condition, the maximum removal efficiency of turbidity could reach 99.7%.

The effects of the flocculation on the humic acid removal efficiency were studied and the experimental results showed that PPAFC had a better flocculation performance while the optimum PPAFC dosage was obtained for removing humic acid was 21 mg/L with the removal efficiency up to 99.1% at pH 4.0. The further study indicated that there was no anions coexisted.

Acknowledgments
This research is supported by the National Natural Science Foundation-funded Project of China (51174090) and Hunan Provincial Natural Science Foundation of China（12JJ8007）

REFERENCES

[1] LH Sun; WH Peng. *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(3), 1501-1505.
[2] DS Lloyd; JP Koenings; JD Laperriere. *N. AM. J. Fish. Manage.*, **1987**, 7(1), 18-33.
[3] DM Lawler; GE Petts; ID L Foster; S Harper. S. *Sci. Total Environ.*, **2006**, 360(1), 109-126.
[4] WS Wan Ngah; M Hanafiah; SS Yong. *Colloid. Surface. B.*, **2008**, 65(1), 18-24.
[5] L Zhao; F Luo; JM Wasikiewicz; H Mitomo; N Nagasawa; T Yagi; F Yoshii. *Bioresource Technol.*, **2008**, 99(6), 1911-1917.
[6] S Liu; LZ Yi; YZ Liang. *Sep. Purif. Technol.*, **2008**, 31(11), 2113-2137.
[7] Zeng Y; Park J. *Colloid. Surface. A.*, **2009**, 334(1), 147-154.
[8] DS Wang; W Sun, Y Xu , HX Tang; J Gregory. *Colloid. Surface. A.*, **2004**, 243(1), 1-10.
[9] C Satriano; M Manso; GL Gambino; F Rossi; G Marletta. *Bio-Med. Mater. Eng.*, **2005**, 15(1), 87-99.
[10] Y Zeng; J Park. *Colloid. Surface. A.*, **2009**, 334(1), 147-154.
[11] P Zhang; BZ Ren. *Asian J. Che.*, **2013**, 25(7), 3966-3970.
[12] P Zhang; BZ Ren; Y Zhou; KJ Liu. *Asian J. Che.*, **2013**, 25(8), 4431-4433.
[13] F Cao; Y Ling; JY Gu. *Environ. Sci. Tec.(Chinese)*, **2011**, 34(5), 69-72.
[14] F Cao; M Xiang; YB Tang. *Chinese J. Environ. Eng.*, **2010**, 11(4), 2547-2551.
[15] GC Zhu; HL Zheng; WY Chen; W Fan; P Zhang; T Tshukudu. *Desalination*, **2012**, 285, 315-323.
[16] J Gowsika; R Nanthini. *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(3), 1452-1461.
[17] HL Zheng; ZZ Jiang; JR Zhu; MZ Tan; L Feng; LW Liu; W Chen.*Desalin. Water Treat.*, **2013**, 25(8), 1-8.