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Preparation of a Novel Flocculant-Polyferric Magnesium Sulfate and its Application in Wastewater Treatment

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As a fundamental technique of environmental protection, coagulation has been used in the treatment of water and wastewater. In this work, a new type of coagulant, polyferric magnesium sulfate, was synthesized by co-polymerization. The effects of Mg/Fe molar ratio (n), temperature and the dosage of oxidant on coagulation performance were investigated systematically. The results showed that polyferric magnesium sulfate had an improved property of charge-neutralization in a kaolin (clay) suspension or municipal wastewater due to the magnesium ions. Additionally, polyferric magnesium sulfate exhibited a better coagulation performance than the conventional polymeric coagulants (*e.g.*, polyaluminum chloride and polyferric sulfate).

Key Words: Poly-ferric magnesian sulfate, Composite flocculant, Municipal wastewater.

INTRODUCTION

With the development in economy, industrial and urban sewage is becoming more complex in composition. One of the important steps in water and wastewater treatment is coagulation/flocculation, which is used for destabilization of colloidal suspensions and removal of suspended solids and organic substances[1]. In this field, multi-functional composite flocculants become the focus. Especially, a type of coagulants known as inorganic polymer coagulants (IPCs), such as polyferric sulfate (PFS), polyferric chloride (PFC) and polyaluminum chloride (PAC), have been developed[2-4]. Inorganic polymer coagulant has a high molar mass and carries a high density of positive charges, so it can disperse in water or wastewater due to electronic repulsion and remove the negatively charged colloidal particles[5]. Because of this charge-neutralization capacity, inorganic polymer coagulants are better than conventional coagulants.

However, the coagulation efficiency of an inorganic polymer coagulant is still lower than that of an organic one[6,7]. The basic criteria of an effective coagulant is large charge-neutralization and bridge-aggregation capabilities. The performance of inorganic polymer coagulants can be improved by two means: (1) increasing the proportion of polymeric species in the composition and (2) adding extra components to produce new composite coagulants.

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According to the literature[8], magnesium ions, as a water treatment agent, have the following advantages: fast generation of large-size and high-density flocs, large settling velocity of flocs, low water content of sludge and satisfactory removal of turbidity and decolorization.

In this research, an iron-based coagulant-polyferric magnesium sulfate (PFMS)-is prepared by adding magnesium(II) compounds. To examine the coagulation behaviour, PFMS will be used to treat kaolin (clay) suspensions and municipal wastewater. Furthermore, its capacity of removing turbidity and COD will be compared with other iron-based coagulants.

EXPERIMENTAL

Preparation of polyferric magnesium sulfate (PFMS): All reagents used were of analytical grade except those being pointed out. A solution of $FeSO_4$ was prepared by dissolving $FeSO_4 \cdot 7H_2O$ in 50 mL of distilled water. A calculated amount of H_2SO_4 solution was then added into the $FeSO_4$ solution under stirring. Under continuous stirring at a certain temperature in water bath, $MgSO_4$ and an oxidant were added into the solution by turn and the solution was then kept for 1 h. Finally, PFMS was obtained.

Coagulation experiments: The experiments were carried out in 500 mL beakers. The pH was adjusted by adding HCl or NaOH to the suspension. During the rapid mixing, the coagulant was added by a milli-injector. After 2 min rapid mixing and 4 min slow mixing, the suspension was left to settle for 10 min. Then, the sample was collected at 2 cm under the surface for determination of residual turbidity and COD.

The followings two laboratory water samples were used for coagulation experiments: (1) a suspension of clay particles prepared by dispersing kaolin powder in distilled water to a turbidity of 51.5 NTU and preserved in refrigerator (this suspension was mixed sufficiently prior to use) and (2) a municipal wastewater with a turbidity of 43 NTU, COD_{Cr} of 81.5 mg/L and pH of 7.

Analytical methods: Polyferric magnesium sulfate was analyzed according to the method of the national standard GB14159-93[9]. The results are shown in Table-1. Turbidity was measured using a turbidimeter (GDS-3C). Chemical oxygen demand (COD) was analyzed by the standard method[10].

TABLE-1
PERFORMANCES OF PFMS

Indexes	National standards of PFS	PFMSs
Density/g cm^{-1}	≥ 1.45	1.47
Total iron content (%)	≥ 11.00	10.16
The content of Fe^{2+} (%)	≥ 0.10	< 0.01
The content of Mg^{2+} (%)	–	1.19
B(OH^-/Fe) (%)	9.0-14.0	12.60
pH (1 % solution)	2.0-3.0	2.43
Appearance	Reddish-brown liquid	Orange liquid

RESULTS AND DISCUSSION

Effect of flocculating properties of PFMS at different temperatures: After the acidic solution of ferrous and magnesium salts was oxidized, hydrolysis of Fe^{3+} and Mg^{2+} occurred and then multi-core cross-copolymerized hydroxides were formed. At this time, Mg^{2+} was added into the PFS. Since the flocculating properties of PFMS are affected by the preparation temperature, three experiments at different temperatures were carried out. When treating the Kaolin (clay) suspension, PFMS was added and the residual turbidity was measured according to different settling time. The results are illustrated in Fig. 1. Obviously, the PFMS sample prepared at a temperature between 60-70 ºC exhibits the best coagulating performance in comparison with the other two coagulants. It is noted that throughout the experiments, the appearance of PFMS solution changed from transparent to turbid (precipitation and gelation) when the temperature was higher than 70 ºC. This can be attributed to the addition of magnesium ions into PFS, which causes iron-magnesium copolymer to hydrolyze and produce various polymeric and hydrolyzed species as temperature increases.

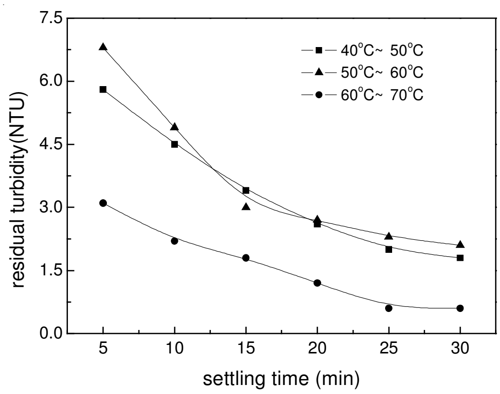

Fig. 1. Effect of temperature on the flocculating property of polyferric magnesium sulfate

Effect of Mg/Fe molar ratio (n) on the flocculating property of polyferric magnesium sulfate: Fig. 2 shows the effect of Mg/Fe molar ratio (n) on the flocculating property of PFMS in the Kaolin (clay) suspension. When n increases from 0.1-0.3, the residual turbidity decreases. This is because, at low n values, PEMS has short molecular chains and low positive charges. Polyferric magnesium sulfate (n = 0.5) also shows the higher removal turbidity than PFMS (n = 0.2) and PFMS (n = 0.4) due to the fact that high amount of magnesian in PFMS (n = 0.5) causes precipitation in solution. Therefore, controlling parameter (n) is very important to attain an optimum condition for both coagulation and stability. In general, PFMS can have high coagulation efficiency at the (n) range 0.2-0.4 since the long molecular chains in these PFMS samples not only carry high-density positive charges but also provide suitable substrates for adsorbing colloidal particles onto flocs[11].

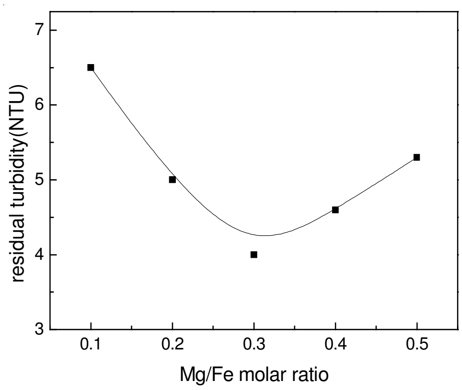

Fig. 2. Effect of Mg/Fe molar ratio on the flocculating property of polyferric magnesium sulfate

Effect of dosage of oxidant on the percentage of Fe^{2+} in PFMS: $MgSO_4$ was added to the $FeSO_4$ solution at a Mg/Fe molar ratio of 0.2-0.4 at temperature of 60-70 ºC and then the oxidant was mixed with the solution at different dosages. As shown in Table-2, the percentage of Fe^{2+} in PFMS reduces with an increase in the dosage of oxidant. When the dosage of oxidant is large, Fe^{2+} may be almost changed into Fe^{3+}, but the production cost increases and unnecessary waste is generated. Table-2 also shows that the percentage of Fe^{2+} in PFMS is much lower than the value of the national standards and can ensure the quality of the product when the dosage of oxidant is 6 %.

TABLE-2
PERCENTAGE OF Fe^{2+} AT DIFFERENT OXIDANT DOSAGES

Dosage of oxidant/%	5.00	5.50	6.00	6.50
Percentage of Fe^{2+}/%	1.37	0.47	< 0.01	Close to zero

Treatment of municipal wastewater

Effect of flocculant dosage on the removal of turbidity and COD: Different dosages of flocculants were added into municipal wastewater samples and then the residual turbidity and COD_{Cr} were determined. Figs. 3 and 4 show that PFMS samples exhibit better performance in comparison with PFS and PAC. The required dosage of PFMS, PFS and PAC are 4.8, 6.4 and 6.4 mg/L, respectively, when the residual turbidity decreases from 43-5NTU. In addition, PFMS is more efficient in COD removal than PAC and PFS and the removal rate of COD attains 93.4 % with PFMS. After addition of PFMS, the flocs and hydrolysate formed rapidly, grew fast into a large size and settled down easily. The flocs with chain-net or net structures could form a large entangled mass, resembling the cobwebs[12]. This can be explained by the bridging-aggregation mechanism.

Effect of pH on the removal of turbidity and COD: The pH values of seven municipal wastewater samples were adjusted to 5, 6, 7, 8, 9, 10 and 11, respectively.

The PFMS dosage was fixed at 8 mg/L for each wastewater sample. The results are shown in Table-3.

TABLE-3
EFFECT OF PH ON THE REMOVAL OF TURBIDITY AND COD

pH value	5	6	7	8	9	10	11
Residual turbidity/NTU	19.3	7.3	4.7	6.1	4.5	15.7	20.9
Removal rate of COD/%	77.5	85.3	93.4	92.0	92.9	79.3	76.8

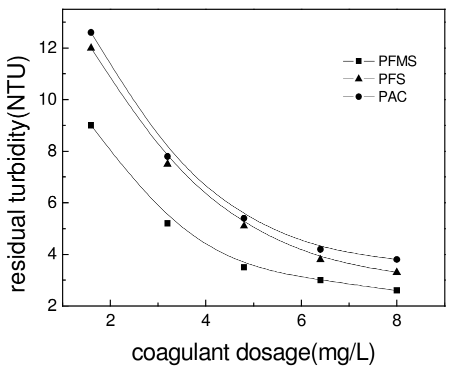

Fig. 3. Effect of flocculant dosage on the removal of turbidity

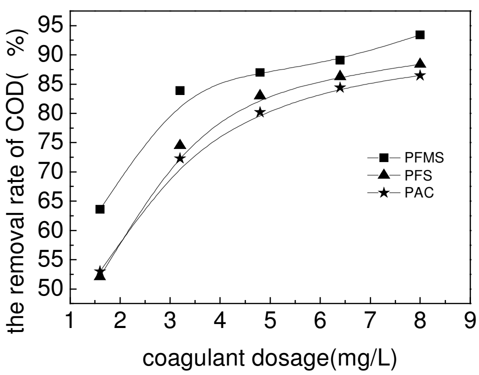

Fig. 4. Effect of flucculant dosage on the removal of COD

Table-3 shows that PFMS can have a high removal rate of turbidity and COD_{Cr} at pH 6-9.

Conclusion

A novel coagulant, polyferric magnesium sulfate, was synthesized by adding magnesium sulfate in PFS. The optimum conditions for preparation of PFMS are as follows: reaction temperature, 60-70 ºC; Mg/Fe molar ratio, 0.2-0.4; the dosage of oxidant, 6 %.

Polyferric magnesium sulfate can effectively compress double electrical layers and reduce potential. When used to treat municipal wastewater, PFMS has better performance in comparison with PFS and PAC. Moreover, since PFMS has the best flocculating properties at pH 6-9, it is not necessary to adjust pH when treating municipal wastewater and thus the treatment cost can be reduced.

It is noted that an industrial byproduct, $FeSO_4 \cdot 7H_2O$, was used to prepare PFMS in present research and this preparation route is a feasible means to simultaneously recycle byproducts and prepare coagulants at low cost. Hence, economic, social and environmental benefits can be achieved.

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REFERENCES

1. A.I. Zouboulis and G. Traskas, *J. Chem. Technol. Biotechnol*., **80**, 1136 (2005).
2. N. Parathasarathy and J. Buffle, *Water Res*., **19**, 25 (1985).
3. J.Q. Jiang and N.J.D. Graham, *J. Chem. Technol. Biotechnol*., **73**, 351 (1998).
4. W.P. Cheng, *Colloid Surf. A: Physicochem. Eng. Aspects*, **182**, 57 (2001).
5. J. Duan and J. Gregory, *Adv. Colloid. Interf. Sci*., **100**, 475 (2003).
6. D.F. Zeng, J.J.Wu and J.F. Kennedy, *Carbohydr. Polym*., **71**, 135 (2008).
7. J.P. Wang, Y.Z. Chen, S.J. Zhang and H.Q. Yu, *Bioresour. Technol*., **99**, 3397 (2008).
8. G. Baoyu and T. Suling, *J. Shandong Univ*., **28**, 327 (1993).
9. Standards Press of China, Chiness Compulsory National Standards Collection (Chemical Volumes) [M]. Beijing: Standards Press of China (1998).
10. APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, American Water Works Association and Water Environment Federation,Washington, DC, USA (1995).
11. W.P. Cheng, *Chemosphere*, **47**, 963 (2002).
12. Y.B. Zeng, C.Z. Yang, J.D. Zhang and W.H. Pu, *J. Hazard. Mater*., **147**, 991 (2007).

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