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Coagulation Performance of a Novel Inorganic Polymeric Coagulant-Polyferric-Magnesium Sulfate

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Coagulation processes are regarded as important environmental protection technology, finding wide applications in wastewater treatment facilities. The continuous need for more efficient coagulation processes have lead to the development of new modified coagulation reagents, such as polyferric magnesium sulphate (PFMS). The aim of the present study is to evaluate the coagulation performance of the reagents by treating a typical kaolin (clay) suspensions, printing and dyeing wastewater as well as wastewater from sauce plant, in comparison with the conventional polymer coagulants, *i.e.*, polyaluminum chloride (PAC) and polyferric sulfate (PFS). The effect of coagulation efficiency, such as pH, the dosage of coagulant and the settling time were discussed. The results indicate that PFMS has the best coagulation efficiency under the optimum conditions (including pH at 6-9, the dosage of coagulant at 4.8 mg/L and the settling time at 20 min, respectively). Additionally, PFMS exhibits a better coagulation performance than the conventional polymer coagulants, *i.e.*, polyaluminum chloride and polyferric sulfate in treatment of the wastewater.

Key Words: Poly-ferric magnesium sulfate, Coagulation performance, Printing and dyeing wastewater, Wastewater from sauce plant.

INTRODUCTION

With the development in economy, industrial sewage is becoming more complex in composition. Take the pulp and paper mill wastewater for example, common pollutants include suspended solid, colour compound, heavy metal, organic and inorganic substances and other soluble substances[1]. These wastewaters can cause serious environmental pollution if discarded untreated. Coagulation/flocculation processes are core environmental protection technology, which find wide range of applications in water or wastewater treatment facilities. In particular, coagulation is regarded as a viable option for destabilization of colloidal suspensions and removal of suspended solids and organic substances[2]. Research and practical applications have shown that coagulation will decrease the pollution load and could generate plenty of water recovery[3-7]. Because of the smaller load, the sewage treatment plant might be designed less energy at a smaller footprint and might be built at lower costs[8].

Coagulation is mainly caused by inorganic metal salts, such as aluminum and ferric sulphates and chlorides. Polyelectrolytes of various structures, *e.g.*, polyferric sulfate, polyferric chloride and polyaluminum chloride[9-11] and many more are usually used as coagulants help to enhance the formation of larger floc for the sake of improving the rate of sedimentation.

Inorganic polymer coagulant (IPC) 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[12]. So IPC[13-15] are widely employed as useful coagulants in wastewater treatment. However, limited information is available in literature about coagulation performance of the new coagulant (PFMS). In this paper, a novel inorganic coagulant (polyferric magnesium sulfate (PFMS)) based on PFS and $MgSO_4$ is introduced treatment of kaoling suspensions, printing and dyeing wastewater and wastewater from sauce plant. The main objectives are to investigate it's the coagulation efficiency. The effects of pH, coagulant dosage and settling time are studied. The removal of turbidity, decolorization and chemical oxygen demand (COD) are used as evaluating parameters.

EXPERIMENTAL

Water samples: A suspension of clay particles employed in this study was prepared by dispersing kaolin powder in distilled water and preserved in refrigerator (this suspension was mixed sufficiently prior to use). Its turbidity was 61.8

NTU. Wastewaters were obtained from printing and dyeing mill in Zhuzhou, China and from sauce plant in Zhongshan, China. Wastewater samples were characterized and the analyses were given in Tables 1 and 2.

TABLE-1
COMPARATIVE STUDY ON COAGULATION EFFICIENCY OF PFMS, PFS AND PAC APPLIED TO TREATMENT OF PRINTING AND DYEING WASTEWATER

Parameter	Untreated wastewater	Wastewater after treatment		
		PFMS	PFS	PAC
COD (mg/L)	478.8	121.6	163.4	200.2
Removal rate of COD (%)	–	74.6	65.9	58.2
Turbidity (NTU)	138.6	2.0	9.3	15.0
Removal rate of turbidity (%)	–	98.6	93.3	89.2
Colour depth (times)	80	6	15	24
Rate of decolourization	–	92.5	81.3	70.0

TABLE-2
COMPARATIVE STUDY ON COAGULATION EFFICIENCY OF PFMS, PFS AND PAC APPLIED TO TREATMENT OF WASTEWATER FROM SAUCE PLANT

Parameter	Untreated wastewater	Wastewater after treatment		
		PFMS	PFS	PAC
COD (mg/L)	14785	980.3	1937.9	2857.2
Removal rate of COD (%)	–	93.4	86.9	80.8
Turbidity (NTU)	173.8	3.5	12.1	17.3
Removal rate of turbidity (%)	–	97.9	93.0	90.0
Colour depth (times)	400	20	65	95
Rate of decolourization	–	95.0	83.8	76.3

PFMS preparation: 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 aged for 1 h. Finally, PFMS was obtained.

Experimental procedure: Coagulation experiments were carried out in 500 mL beaker in order to determine the optimum conditions. According to the procedure, PFMS was added to wastewater by a milli-injector and mixed for rapid agitation 2 min and then gentle agitation 4 min. The dosage of PFMS, pH and the settling time of coagulation process were all evaluated as independent variables to optimize the coagulation conditions. Residual turbidity, COD and colour were respectively measured as response parameters and their removal percentages were calculated by comparing the values for the wastewater after treatment to those for the original wastewater. After sedimentation, the samples were collected at 2 cm under the surface for determination of the relevant parameters.

Analytical methods: The manual standard methods for the examination of water and wastewater[16] was used to determine the parameters COD and colour. In addition, pH was measured by pH meter (PHS-3C, Shanghai REX Instrument Factory, China). Turbidity was measured using a turbidity meter (GDS-3C). The chemical reagents used here were all analytical grade.

RESULTS AND DISCUSSION

Effect of pH: To study the effect of pH on turbidity of kaoling suspensions. Experiments were conducted with pH adjusted from 4.0 to 11.0 and the coagulant dosage at 3.2 mg/L. The pH was adjusted by adding HCl or NaOH to the suspension. The results obtained are shown in Fig. 1. It can be observed that the turbidity is first on steep decrease and then on the sharply increase with the wastewater pH, with the minimum turbidity at pH 6.0-9.0. So the optimum pH is 6.0-9.0. The main reason are as follows: The pH in the wastewater to be treated may affect the pollutants form and the Zeta potential of colloid granule and furthermore affect the coagulation process. The colloid system in wastewater will be finally de-stabilized and settled only when the pH meets the certain value scope.

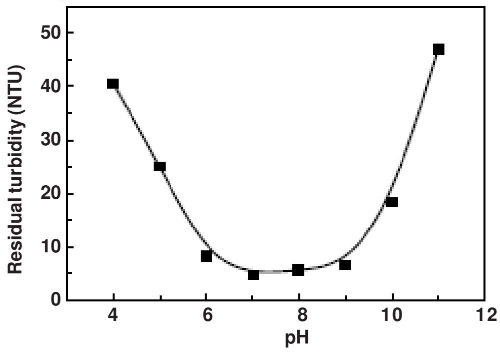

Fig. 1. Effect of pH on the residual turbidity

Effect of PFMS dosages: Fig. 2 shows the effect of PFMS, PFS and PAC dosages on the residual turbidity of the Kaolin (clay) suspension with pH at 7.0. The results show that the residual turbidity sharply decreases as coagulant dosage increase at the beginning but a trend level off afterwards. PFMS has better efficiency of removal turbidity than those of PFS and PAC. The main reasons are as follows: Different dosage of coagulants may bring a certain effect to the cooperation function of several de-stabilization mechanisms including charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate so-called sweep flocculation[12].

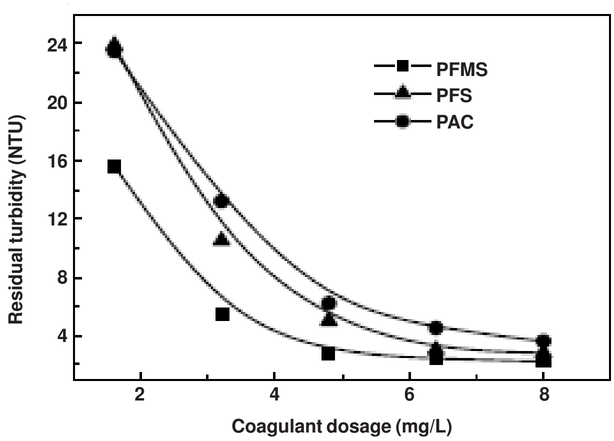

Fig. 2. Effect of coagulant dosage on the residual turbidity

When it comes to residual turbidity of PFMS is lower than PFS and PAC. This can be attributed to the addition of magnesium ions into PFS, which causes iron-magnesium copolymer to increase ability of sweep flocculation and bridging-aggregation. In a word, the optimum PFMS dosage is 4.8 mg/L. But much more coagulant dosages not only weaken the flocculation effect but also increase the cost.

Effect of settling time: In the coagulation-flocculation process, the settling time is important factor affecting the quality of treated supernatant. Even though excessive settling time may make the treated supernatant good quality, it will influence the overall cost and efficiency. To study the possible settling performance of the flocs obtained by dosing PFMS, PFS and PAC to the kaoling suspension, a series of experiments with different settling time are performed. With coagulant dosages 3.2 mg/L and pH 7.0, the residual turbidity as a function of settling time is shown in Fig. 3. It can be seen that the residual turbidity are on the sharp decrease trend with the settling time increasing to 20 min, while keeping gentle slope after that. These results indicate that the optimum settling time is about 20 min at the given conditions.

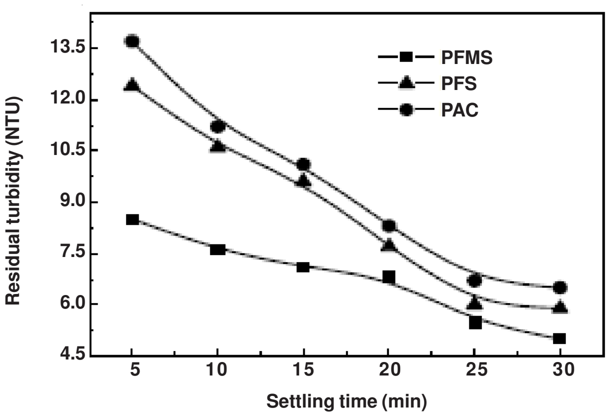

Fig. 3. Effect of settling time on the residual turbidity

Treatment of wastewater with the optimum conditions

Comparative study on coagulation efficiency of PFMS, PFS and PAC applied to treatment of printing and dyeing wastewater: The pH of wastewater was adjusted to 7.0. Coagulant was added to wastewater. And then the residual turbidity, COD and colour were detected after sedimentation 20 min. The results are shown in Table-1. Table-1 shows that PFMS samples exhibit better performance in comparison with PFS and PAC. The removal rate of COD is 74.6 %, removal rate of turbidity is 98.6 % and rate of decolorization is 92.5 %. 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[15]. This can be explained by the bridging-aggregation mechanism.

Comparative study on coagulation efficiency of PFMS, PFS and PAC applied to treatment of wastewater from sauce plant: The pH of wastewater was adjusted to 7.0. Coagulant was to wastewater. And then the residual turbidity, COD and colour were detected after sedimentation 20 min. The results are shown in Table-2. Table-2 shows that the removal rate of COD is 93.4 %, removal rate of turbidity is 97.9 % and rate of decolorization is 95.0 %. Tables 1 and 2 can be seen that rate of decolorization was high when PFMS was applied to treatment of the wastewater. The main reason was that magnesium ion had strong ability of decolorization.

Conclusion

A novel coagulant, polyferric magnesium sulfate, was synthesized by adding magnesium sulfate in PFS. So its coagulation rate and ability had been greatly improved and PFMS had the best coagulation efficiency under the optimum conditions including pH at 6-9, the dosage of coagulant at 4.8 mg/L and the settling time at 20 min, respectively. Additionally, PFMS exhibits a better coagulation performance than the conventional polymer coagulants, *i.e.*, polyaluminum chloride (PAC) and polyferric sulfate (PFS) in treatment of the wastewater.

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