Preparation of Amphoteric Polyacrylamide Flocculant and Its Application in the Treatment of Tannery Wastewater

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ABSTRACT: Through two-phase aqueous polymerization, amphoteric polyacrylamide (AmPAM) emulsion, as an environmental friendly flocculant for the tannery wastewater, was firstly synthesized using ammonium sulfate aqueous solution as the dispersion, using acrylamide, cationic monomer ethylene methyl propenoyl-trimethylammonium chloride (DMC), and anionic monomer acrylic acid (AA). The structure and properties of the synthesized AmPAM were characterized by means of FT-IR measurement, and the effects of various factors were studied, such as dispersing agent, dispersion medium concentration, initiator concentration, and AA/DMC feeding ratio on the intrinsic viscosity of the emulsion. The influences of pH, the AA/DMC feeding ratio, the intrinsic viscosity, and the dosage of polymer on the flocculating performance were also studied. When the weight percent of ammonium sulfate was 10.0% of emulsion total weight and dispersing agent polyvinylpyrrolidone was 1.2% and the weight percent of initiator was 4.0% of monomer total weight and m (acrylamide): m (DMC): m (AA) was 9: 5: 3, AmPAM achieved overall performance, good solubility, high stability, and application in a wide range of pH value between 4 and 10. The flocculating rate was more than 90.0%. AmPAM flocculant with both anionic group and cationic group provided a clear antipolyelectrolyte effect and a wide pH value range of the application, especially for tannery wastewater. It had not only charge neutralization and adsorption bridging role but also winding and enclosing effect among the molecules so as to flocculate and subside coarse particles of the sludge treated and dehydrate perfectly. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 518–523, 2011

Key words: amphoteric polyacrylamide; flocculant; tannery wastewater; flocculation mechanism

INTRODUCTION

Tannery pollution mainly refers that enterprises indiscriminately discharge the untreated pollutants that are from the production process. Tannery "three-wastes" treatment focuses on the waste water. So far, the most effective method of cleaning wastewater is to add ionic polymeric flocculants to improve the status of the wastewater to make impure particles and toxic ions susceptible to flocculate and to subside.[1–5] Amphoteric polyacrylamide (AmPAM) has good precipitation property. Furthermore, it also has the unique structure. So it is more suitable to deal with occasions that other flocculants can not treat.[6–8] It plays a significant role in tannery wastewater, and its overall performance is superior to the traditional cationic or anionic polyacrylamide.

The weaknesses of traditional polyacrylamide synthesis methods mainly include low solid content, high viscosity, poor solubility, and inconvenience.[9–11] Two-phase aqueous system polymerization is to dissolve water-soluble monomers in an aqueous solution of polymer or small molecules to form a homogeneous mixture system. Then, under certain conditions, it forms a polymerization system of dispersion solution where water-soluble polymers exist.[12–14] Its viscosity is relatively lower; the solid content is also higher in its reaction system; there is no organic solvent pollution during the polymerization process. So it has broad application prospects and environmental significance.

In this study, we aimed at fabricating an environmental friendly polymeric flocculant to deal with the leather sewage and sludge. We used two-phase aqueous polymerization method to synthesis AmPAM emulsion. Then, we characterized the structure of AmPAM and comprehensively discussed the influences on the system stability, viscosity, and molecular weight of the AmPAM emulsion. Besides, we

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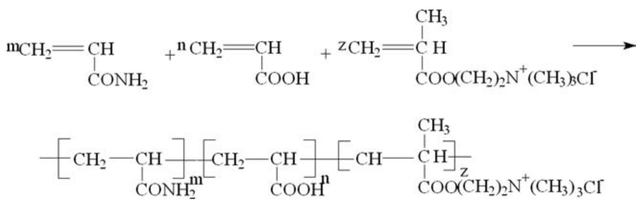

Figure 1 Scheme of the polymerization reaction.

studied AmPAM flocculation for the tannery wastewater.

EXPERIMENTAL

Materials

Acrylamide (AM), acrylic acid (AA), ammonium peroxydisulfate, sodium sulfite, ammonium sulfate, polyvinylpyrrolidone (PVP; molecular weight 10,000), and polyethylene glycol (PEG, molecular weight 6000-20,000) are AR; methyl acrylic acid ethyl trimethyl chloride Ammonium (DMC), polyethylene oxide (PEO, molecular weight 50,000) are GR; tannery wastewater was provided by College of Resources and Environment, Shaanxi University of Science and Technology.

Preparation of AmPAM flocculant

Appropriate amounts of distilled water, reaction monomers, such as AM, AA, and methyl acrylic acid ethyl trimethyl ammonium chloride, ammonium sulfate, and dispersing agent were placed in a 250-mL three-necked flask equipped with a reflux condenser. The reaction mixture was stirred and heated until 60°C in water bath. Then, initiators (ammonium peroxydisulfate and sodium sulfite) were added drop wise over a period of 2 to 3 h at 65°C to 70°C under stirred condition. Afterward, the reaction mixture was stirred at 65°C to 70°C for 3-5 h until a yellow emulsion was obtained. Finally, the emulsion was cooled to room temperature. The scheme of the reaction is described in the Figure 1.

Measurement

FT-IR analysis

Water dispersion polymer was repeatedly washed with acetone and then dried. Its spectra of polymer were obtained on a VECTOR-22 model FT-IR Spectrometer (Brucker, Ettlingen, Germany).

System stability test

Water dispersion emulsion was laid in constant temperature oven at 35°C, and the stability was determined by the time of phase separation.

Determination of molecular weight

According to GB12005.1-89 and G/T12005.10-92, the viscosity of polymer was measured by intrinsic viscosity meter. Then, the average molecular weight was determined using the following equation (2-1).

$$[\eta] = 3.74 \times 10^{-4} [M_V]^{0.66}$$

Where M_V is relative molecular mass and $[\eta]$ is intrinsic viscosity.

Measurement of the values of cationic and anionic groups

The values of cationic group and anionic group in the polymer were measured separately using precipitation titration method and hydrochloric acid titration method.

Determination of flocculation property

Flocculant was dropped in the 1000 mL beaker and mixed with a certain wastewater under stirred at a high speed (100-120 rpm). The mixture of liquids was stirred for 3 min so that the flocculant was dispersed in wastewater entirely. Then, the mixture was stirred at a low speed of 40 rpm for 5 min. After

TABLE I
The Influences Monomers Concentration and Mass Ratio on the Properties of AmPAM

Monomers concentration (%)	Mass ratio of monomer			η	Mv 10^4	I+ (%)	I− (%)
	AM	DMC	AA				
15	9	3	3	167.3	317	19.4	12.7
	9	4	2	203.4	426	27.6	17.8
	9	5	1	192.5	392	28.3	17.9
16	9	5	2	204.3	429	29.2	18.6
17	9	5	3	207.1	438	29.8	17.9
18	9	6	3	190.8	387	27.6	14.5

Initiator is 4% of monomers mass, $(NH_4)_2SO_4$, PVP is separately 10% and 1.2% of polymerization system

TABLE II
The Influence of $(NH_4)_2SO_4$ Content and PVP Content on Emulsion Appearance

$(NH_4)_2SO_4$/w%	gel content/w%	PVP/w%	Viscosity/mPa·s	Emulsion appearance
15	Gel	1.8	1500	Half transparent
13	13.6	1.5	1740	Half transparent
10	0.6	1.2	2360	Half transparent
8	Muddy	1.0	4200	White, opaque

The quality of initiator to monomer 4%, PVP was 2% of total weight of emulsion, $(NH_4)_2SO_4$ was 10% of polymerization system, monomer concentration was 17%.

that, it was left to stand for 15-20 min. Finally, after natural sedimentation through filtration, the values of COD_{Cr}, S^{2-}, Cr^{3+}, and chromaticity in the clear liquid were determined. COD_{Cr} value was measured by $K_2Cr_2O_7$ law with JH-12 type COD instrument. Chromaticity value was determined by dilution method. S^{2-} was determined by iodometry. Cr^{3+} was determined by 721-type spectrophotometry. The pH value was measured by PHS-3B pH instrument.

RESULTS AND DISCUSSION

The major influence of monomer concentration on polymerization system is the change of the viscosity in the polymerization process. If the monomer concentration was too high, the viscosity of polymeric system would be too high to stir, even form a dump. However, if the monomer concentration was too low, molecular weight of copolymer would be too difficult to improve. At the same time, the advantage of achieving high solid content could not be reflected. As could be seen from Table I, the partial viscosity of polymeric system was too high to stir and ultimately became a gelatinous when the monomer concentration arrived at 18%. So the optimum monomer concentration is 17%.

When the amount of anionic group and cationic group reached certain values and they continued increasing, the proliferation rate and reactivity of monomer would decrease, which resulted in the decline of the polymer molecular weight and monomer conversion rate. As shown in Table I, with the increasing amount of anionic monomer and cationic monomer, the copolymer molecular weight was also increasing. When m (AM): m (DMC): m (AA) was 9: 5: 3, the relative molecular weight reached maximum. If it continued to increase, the polymeric emulsion would become gel. At that time, the values of anionic group and cationic group were 29.8% and 17.9%, respectively. Moreover, the ratio of anionic value to cationic value was largest, which would be more beneficial to enhance flocculation performance of AmPAM. Therefore, the better mass ratio of the three polymer monomers is 9: 5: 3.

In this article, ammonium sulfate in aqueous solution was selected as the dispersion medium. Polyvinyl alcohol (1799), PEG (20,000), PEO (50,000), and PVP (10,000) were, respectively, chosen as dispersants. To keep low costs, the amount of dispersing agent was controlled at less than 3% of the total amount. At the same time, the ammonium sulfate content was adjusted. The result showed that polyvinyl alcohol, PEG, and PEO could not form a stable

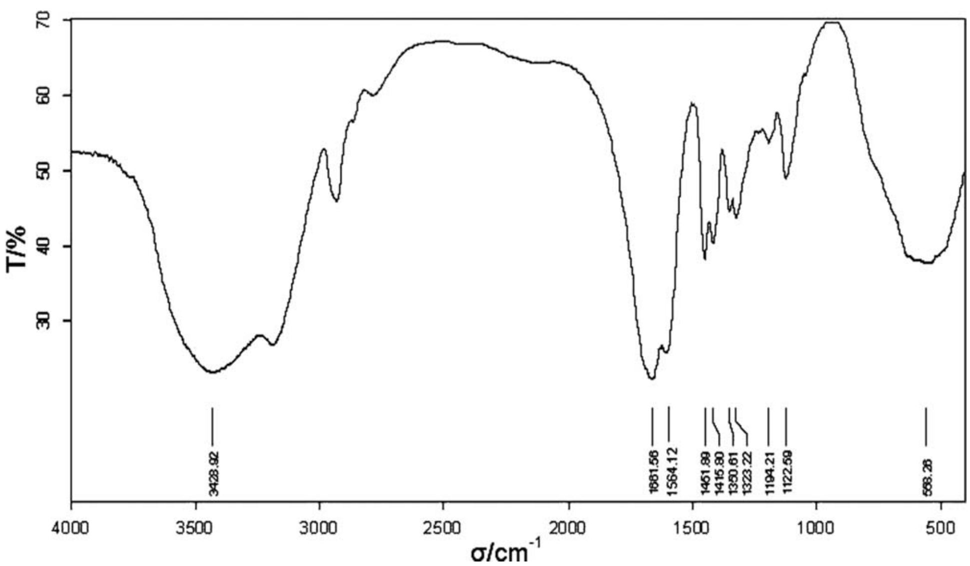

Figure 2 FT-IR spectrum of the AmPAM washed by acetone.

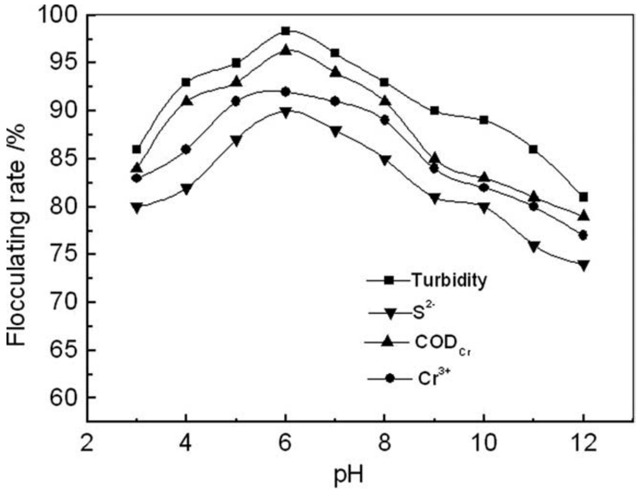

Figure 3 The influences of different pH values on flocculation performance of AmPAM.

emulsion. But, only PVP could form a stable aqueous emulsion.

It can be seen from Table II that the optimum amount of ammonium sulfate is 10% of the quality of the reaction solution. If ammonium sulfate was less, the emulsion would not be generated. But, if it was more, the emulsion would be prone to gel. PVP in a very wide range of concentration could form a stable emulsion. Because of the cost, dosage of PVP should be less and better. Thus, the optimum amount of PVP is 1.2% of the total reaction solution weight.

The spectrum of the modified PAM is shown in Figure 2. There spectra were characterized by the following bands: a O-H stretching vibration band at 3428 cm^{-1}, which peak was strong broad, showed there was primary amine of the symmetric stretching vibration peak; a C=O stretching vibration band characteristic the amide I and—$CONH_2$ bending vibration band characteristic the amide II respectively at 1564 cm^{-1} and 1661 cm^{-1}; the peaks —CO_2Na were at 1323 cm^{-1}; a methyl of—$N^+(CH_3)_3$ deformation vibration bond at 1451 cm^{-1}; a C—CH_3 stretching vibration bond at 1350 cm^{-1} showed that a product of the existence of quaternary ammonium-based group. The above analysis results that PAM molecules, modified with negative COO^- group and positive group—$N^+(CH_3)_3$, are the gender structure.

Under the condition of dropping the same dosage of flocculant AmPAM, pH value of wastewater was adjusted by alkali or acid to a certain pH value. The influences of different pH values on flocculation properties are shown in Figure 3. As can be seen in Figure 3, flocculation rate ascended with the increase of pH value. At the pH value of 6, flocculation rate got to the maximum. However, pH value was above 8, the flocculation performance started to decline rapidly. The solvent effect between the quaternary ammonium-based group of AmPAM and hydroxyl made the positive electricity of AmPAM weak. So the pH value had a great influence on the flocculant performance and surface charge of colloidal particles. Under different conditions of pH values, various groups of AmPAM molecular chain had different degrees of dissociation, so that the function of the electrical properties became different. And so did the adsorption bridge of macromolecular chain. On the condition of alkaline, the amide groups (-$CONH_2$) of polymer molecules started hydrolysis. In the meantime, with the viscosity of AmPAM reducing, the materials dissolved in water increased. And the role of adsorption bridging was weakened. At the same time, the quaternary ammonium structure was contained in AmPAM copolymer bind with H^+ in the acid medium and changed into the positively charged ammonium ion. Therefore, the AmPAM in acid medium was conducive to enhancing flocculation and subsidence. But, the pH value was too small to inhibit anionic group to dissociate, which weakened the collaboration efficiency of anion or cation in the flocculation process. Thus, the flocculation could not become better when the pH value was low. As can be seen from Figure 3, when the pH value ranged between 4 and 10, COD_{Cr}, Cr^{3+}, S^{2-}, and turbidity were flocculated observably. It is an evidence that AmPAM is suitable for practice in the application of wide pH value range.

The reaction temperature plays an important role in the flocculating performance of AmPAM. Under the condition of 1.2 $mg \cdot L^{-1}$ dosage and pH value of 6, the influences of different temperature on flocculation performance have been shown in Figure 4. As can be seen in Figure 4, with the increase of flocculation temperature, the flocculation rate ascended gradually and then arrived at the maximum at a temperature of 40°C. However, when the

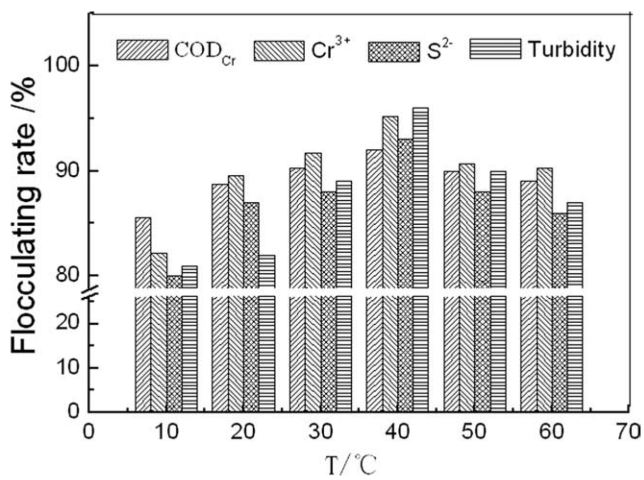

Figure 4 The influences of different temperatures on flocculation performance of AmPAM.

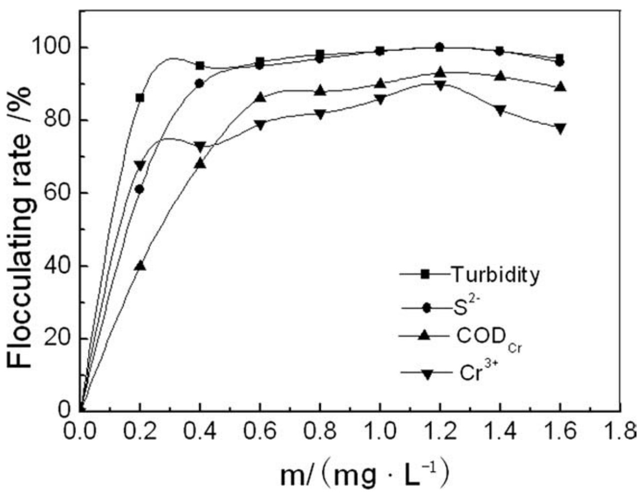

Figure 5 The influences of dosage of the flocculant on flocculation performance.

temperature continued to rise, the flocculation rate started to descend. Thus, 40°C is the optimum flocculation temperature. In the meantime, the reaction temperature, changing between 10°C and 60°C, took unremarkable effect on the AmPAM flocculation rate. There is an excellent evidence that AmPAM flocculant can be applied to a wider scope of temperature. Therefore, it can be used different in regions from the North to the South.

The dosage of flocculant plays an important part on the flocculation performance. Under the condition of pH value 6, temperature 40°C, the influences of different flocculant dosage on flocculation performance are observed in Figure 5. As can be seen in Figure 5, with the increase of AmPAM, the flocculation rates of COD_{Cr}, Cr^{3+}, $S^{2-}$and turbidity increased. When the dosage of AmPAM was 1.2 $mg \cdot L^{-1}$, flocculation rate reached the highest. However, flocculation rate would descend if AmPAM dosage continued to increase. Because of less flocculant dosage, its ability of electricity and adsorption bridging got to be enhanced. With the dosage increasing, the capacity of adsorption started to increase. Nevertheless, the adsorbed particles would be wrapped by the excessive polymer flocculant, so that they could not coagulate but dispersed when the dosage used was excessive. The results of experiments show that when the additional dosage of AmPAM is varying between 1.0 and 1.4 $mg \cdot L^{-1}$, floccules are coarse, and subsidence velocity is fast, and water quality is good.

The flocculation mechanism of AmPAM with the pollutions in the tannery wastewater can be seen in Figure 6. At first, through the electrostatic neutralization, the anionic group of AmPAM attracted the chromium salt particles with the positive electric charges in the tannery wastewater. At the same time, the cationic group of AmPAM neutralized with the organic particles with negative charges in the tannery wastewater. Then, the functional group of the AmPAM adsorbed on the surface of the pollutant particle bonded with another functional group of AmPAM, which was mainly the role of ionic bond. With the effective molecular weight of polymer increasing rapidly, the pollutant particles bridged and flocculated. Finally, when the anionic group and cationic group of AmPAM further cooperated with each other, the apparent molecular weight of the gender polymer increased. The pollutant particles that have been entangled by polymer chains formed larger floccules through the bridging role. In this changing process, the anionic part of the polymer molecule neutralized with the cationic part of the same molecule so that the size of the molecule reduced. And then, the pollutant particles that were bonded became dense and subside.

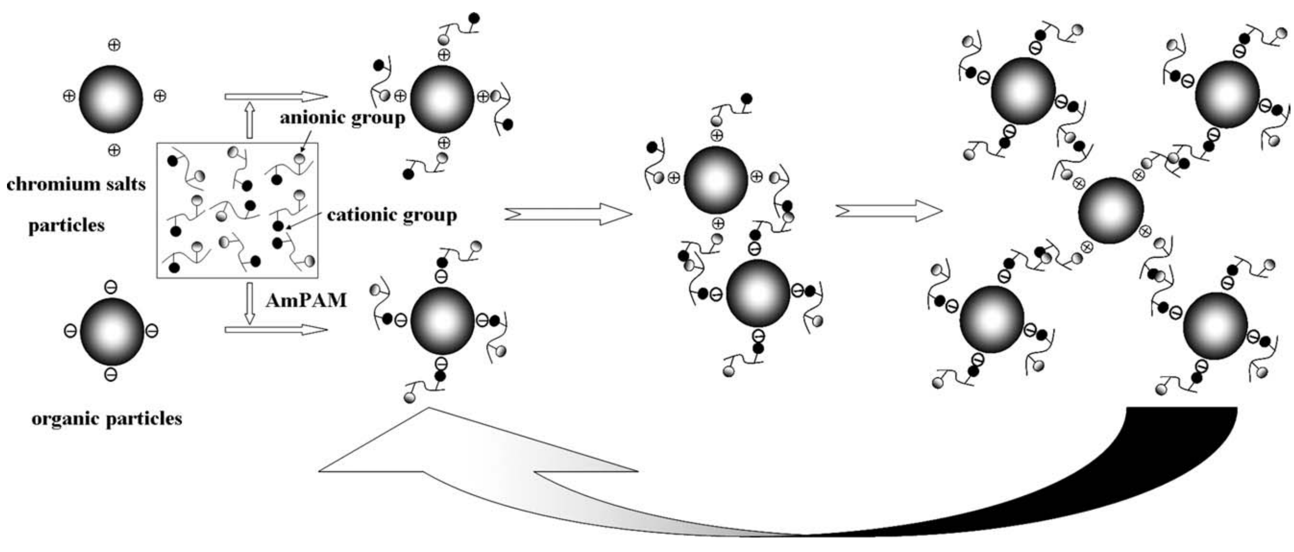

Figure 6 The flocculation mechanism of AmPAM with tannery wastewater.

CONCLUSIONS

Through two-phase aqueous polymerization, the environmental friendly flocculant has been prepared. The molecule of AmPAM weight is 4.38×10^4. The solid content of AmPAM flocculant is over 30%. The values of anionic group and cationic group are 29.8% and 17.9% respectively.

AmPAM flocculant has good flocculation performance. It can be applied in a wide range of the pH between 4 and 10 and is suitable for a wider temperature scope between 10°C and 60°C. Moreover, its flocculation is efficient. After treatment, the water becomes so clear and clean that the content of suspended substance conforms to the national emission standards. The optimum flocculation can be achieved according to the dosage of flocculant between 1.0 and 1.4 $mg \cdot L^{-1}$, pH value of 6, and temperature of 40°C.

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