Preparation and Application of Environmental Friendly AmPAM Flocculant 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 with acrylamide (AM), cationic monomer ethylene methyl propenoyl-trimethylammonium chloride (DMC) and anionic monomer acrylic acid (AA), using ammonium sulfate aqueous solution as the dispersion. The structures and properties of the synthesized amphoteric polyacrylamide were characterized by means of FT-IR measurement. Then effects of various factors such as dispersing agent, dispersion medium concentration, initiator concentration and AA/ DMC feeding ratio on the intrinsic viscosity of the emulsion were studied. The influences of pH, AA/ DMC feeding ratio, the intrinsic viscosity, and the dosage of polymer on the flocculating performance were also studied. When the mass percent of ammonium sulphate was 10.0% of emulsion total weight, dispersing agent PVP was 1.2%, the mass percent of initiator was 4.0% of monomer total weight, m(AM):m(DMC):m(AA) was 9:5:3, amphoteric polyacrylamide achieved the overall performance, good solubility, high stability and application in a wide range of pH value between 4-10. The flocculating rate was higher than 90.0%. Amphoteric polyacrylamide flocculant with both anionic and cationic groups provided a clear anti-polyelectrolyte effect and a wide pH value range of the application, especially for the tannery wastewater. It not only has charge-neutralization, adsorption bridging role, but also has a winding the parcel between the molecules so as to flocculate and subside coarse particles of the sludge treated and dehydrate perfectly.

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

1 Introduction

Tannery pollution mainly refer that enterprises indiscriminately discharge the pollutants not to treat which come from the production process. Tannery "three wastes" treatment focuses on the waster water, so far, the most effective methods of cleaning wastewater is to be added ionic polymer flocculants to improve the status of the wastewater to make impure particles and toxic ions susceptible to flocculate and subside.[1, 2] Amphoteric polyacrylamide has good precipitation property, furthermore, also has the unique structure, more suitable to deal with occasions which other flocculants couldn't treat. It plays a significant role in tannery wastewater, and its overall performance is superior to the traditional cation or anion polyacrylamide.[3]

The weakness of traditional polyacrylamide synthesis methods mainly includes production and utility issues such as low solid content, high viscosity, poor solubility and inconvenience[4, 5]. Two-phase aqueous system polymerization is to dissolve water-soluble monomers in an aqueous solution of polymer or small molecule to form a homogeneous mixture system, then, under certain conditions polymerize and form a polymerization system of dispersion solution where water-soluble polymers respectively exist. The

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viscosity is relative lower, the solid content is also higher in its reaction system, and there is no organic solvent pollution during the polymerization process, it has broad application prospects and environmental significance.

This article just echoes the request of leather enterprises, aiming at polymer flocculant which the leather sewage and sludge treatment needs, using two-phase aqueous polymerization method synthesizes environmental friendly AmPAM, then characterizes AmPAM structure, comprehensively discuses dispersion the factors of system stability, viscosity change and molecular weight, besides, studies AmPAM flocculation for the tannery wastewater.

2 Experimental

2.1 Materials

Acrylamide, acrylic acid, ammonium sulfate, potassium persulfate, sodium bisulfite, polyvinyl pyrrolidone, polyethylene glycol (PEG, molecular weight 6000-20000) and polyvinlpyrrolidone (PVP, 10000) are AR, methyl acrylic acid ethyl trimethyl chloride Ammonium (DMC), polyethylene oxide PEO (molecular weight 50000) are GR; tannery wastewater:provided by College of Resources and Environment, Shaanxi University of Science & Technology.

2.2 Preparation of AmPAM flocculant

Appropriate amount of distilled water, reaction monomer such as acrylamide, acrylic acid and methyl acrylic acid ethyl trimethyl ammonium chloride, ammonium sulfate and dispersing agent were added to a 250mL three-necked flask, equipped with a stirring device, until stirring evenly, heated to 60℃ in water bath, then initiator was dripped into the three-necked flask within 2-3h, heated to 65-70 ℃, constant temperature 3 to 5 hours, finally cooled to room temperature.

2.3 *Characterization*

2.3.1 *FT-IR Analysis*

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

2.3.2 System Stability Test

Water dispersion polymerization was laid inside constant temperature oven on the 35℃, the stability was determined by the time of phase separation.

2.3.3 Determination of molecular weight

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

$$[\eta]=3.74\times10^{-4}[M_V]^{0.66} \tag{2-1}$$

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

2.3.4 Measurement of action and anion values

Cation and anion value were separately measured using precipitation titration method and the hydrochloric acid titration method.

2.4 *Determination of flocculation property*

Flocculant was dropped in the 1000mL beaker with electric constant mixer for magnetic stirring in the limited time, under stirring at a high speed (100-120r/min), mixed 3min so that the flocculant was entirely dispersed in waste water, and then reducing speed to 40r/min, stirring 5min, standing 15-20min. Finally, COD_{Cr}, S^{2+}, Cr^{3+} and chromaticity values of the clear liquid after natural sedimentation through filtration were determined. COD_{Cr} values were measured by $K_2Cr_2O_7$ law with JH-12 type COD instrument , chromaticity values were determined by dilution method, S^{2+} was determined by iodometry, Cr^{3+} was determined by 721-type spectrophotometry, pH values measured by PHS-3B pH instrument.

3 Results and discussion

3.1 The influences of monomer concentration and mass ratio on the properties of AmPAM

The major influence of monomer concentration on polymerization system is the change of the viscosity in the polymerization process, when the monomer concentration is too high, the viscosity of polymerization system will be too high to stir, even form a dump. However, if the monomer concentration is too low, polymer molecular weight is too difficult to improve, at the same time, the advantage of high solid content will lost. As can be seen from Tab. 1, when the monomer concentration arrives at 18%, the partial viscosity of polymerization system is too high to stir, ultimately becomes a gelatinous, so the optimum monomer concentration is 17%.

Tab. 1 The influences monomers concentration and mass ratio on the properties of AmPAM [a]

monomers	mass ratio of monomer			η	Mv	I+	I-
%	AM	DMC	AA		104	%	%
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

[a] initiator is 4% of monomers mass, $(NH_4)_2SO_4$, PVP is separately 10% and 1.2% of polymerization system

When the amounts of anion and cation monomers reach certain values, they continue increase, the proliferation rate and reactivity of monomer will decrease, resulting that the polymer molecular weight and monomer conversion rate decline. As shown in Tab.1, with the increasing of the amounts of anion and cation monomers, the copolymer molecular weight is increasing, when m (AM):m (DMC):m (AA) is 9:5:3, the relative molecular weight reach maximum, if continue to increase, the polymerization becomes gel. At that time, the value of anion and cation monomers is respectively 29.8% and 17.9%, and the ratio of cation to anion value is largest, which will be more benefit to enhance flocculation performance of the polymer. Therefore, the better mass ratio of the three polymerization monomers is 9:5:3.

3.2 Selection of dispersant

In this paper, ammonium sulfate in aqueous solution was selected as the dispersion medium[6], polyvinyl alcohol (1799), polyethylene glycol (20000), polyethylene oxide (50000) and polyvinylpyrrolidone (10000) were chosen respectively as a dispersant. In order to keep low costs, the amount of dispersing agent was controlled at less than 3% of the total amount, in the same time the ammonium sulfate content was adjusted. The result shows that polyvinyl alcohol, polyethylene glycol and polyethylene oxide can not form a stable emulsion. Emulsion containing polyvinyl alcohol forms a little gel, polyethylene glycol all gel; polyethylene oxide forms a semi-transparent aqueous emulsion. Only polyvinyl pyrrolidone forms a stable aqueous emulsion.

It can been seen from Tab. 2 that the optimum amount of ammonium sulfate is 10% of the quality of the reaction solution, less not enough to generate emulsion, more incline to gel. PVP in a very wide range of concentration can form a stable emulsion, because of the cost, dosage of PVP should be less and better, thus, optimum amount of PVP is 1.2% of the total reaction solution weight.

Tab. 2 The influence of $(NH_4)_2SO_4$content and PVP content on Emulsion appearance [a]

$(NH_4)_2SO_4$/*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

[a] the quality of initiator to monomer 4%, PVP is 2% of total weight of emulsion, $(NH_4)_2SO_4$ is 10% of polymerization system, monomer concentration is 17%.

3.3 FT-IR Analysis of AmPAM

The spectrum of the modified PAM is given in Fig. 1. There spectra are characterized by the following bands: a O-H stretching vibration band at 3428cm^{-1}, which peak is strong broad, shows there is the 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 1661cm^{-1} and 1564cm^{-1}; a methyl of -$N^+(CH_3)_3$ deformation vibration bond at 1451cm^{-1}, a methane of -CH_2N^+ bond at 1415cm^{-1}; a C-CH_3 stretching vibration bond at 1350cm^{-1} 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.

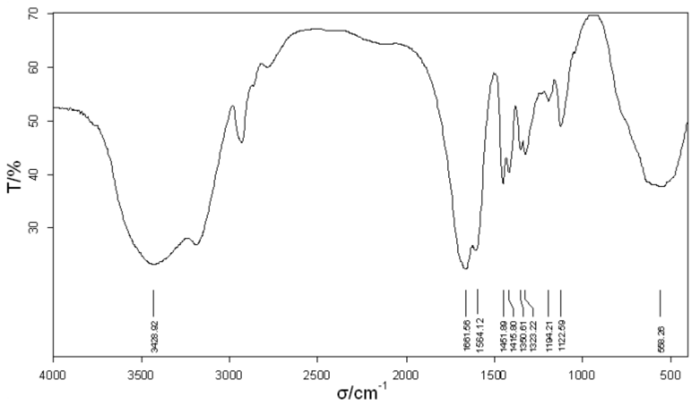

Fig. 1 FT-IR spectrum of the AmPAM washed by acetone

3.4 Influences of pH on flocculation performance of amphoteric polyacrylamide

Under the conditions of dropping the same dosage of flocculant AmPAM, pH value of wastewaters were adjusted by alkali or acid to a certain pH value, the influences of different pH values on flocculation properties were given in Fig. 2, as can be seen in Fig. 2, flocculation rate ascend with increase of pH value, in the pH value of 6, flocculation rate get to the maximum, after pH value of 8, the flocculation performance started to decline rapidly, the solvent effect between the quaternary ammonium-based of AmPAM and hydroxyl makes the positive electricity of AmPAM weaken. The pH value has a great influence on the flocculant performance and surface charge of colloidal particles, under different conditions of pH values, various groups of AmPAMmolecular chain have different degrees of dissociation, so that their function of the electrical properties become different ,and so does the adsorption bridge of macromolecular chain. In alkaline conditions, the amide groups (-$CONH_2$) of polymer molecules start hydrolysis, in the meantime, the viscosity of AmPAMreducing, the materials dissolved in water increasing, weakening the role of adsorption bridging. At the same time, the quaternary ammonium structures are contained in AmPAMcopolymer bind with H^+ in acidic medium, and change into the positively charged ammonium ion. Therefore, the AmPAM in acidic medium is conducive to enhance flocculation and subsidence. But the pH value is too small to inhibit anionic group dissociate, weakened the collaboration efficiency both anions and cations in the flocculation process. Thus, the flocculation may not become better as the pH value gets smaller. As can be seen from Fig. 2, pH value varies between 4-10, the flocculation of COD_{Cr}, Cr^{3+}, S^{2+} and turbidity all are better, it is an evidence that AmPAM is suitable to apply in practice because of its wide pH value range.

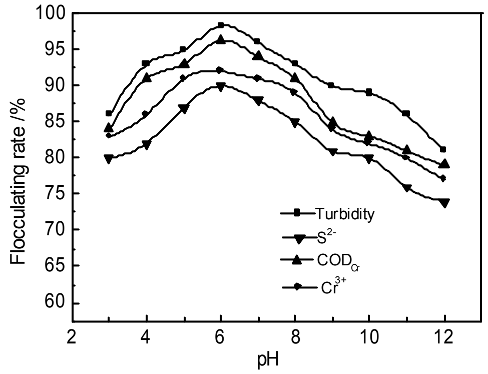

Fig. 2 The influences of different pH values on flocculation performance of AmPAM

3.5 Influences of temperature on flocculation performance of amphoteric polyacrylamide

The Reaction temperature plays an important role in the flocculating **performance** of amphoteric polyacrylamide. In the pH value of 6, under the condition of 1.2mL·L^{-1} dosage, the influences of different temperature on flocculation **performance** have been given in Fig. 3. As can be seen in Fig. 3, with the increase of flocculation temperature, the flocculation rate ascends gradually, the flocculation rate arrives at the maximum at a temperature of 40℃, however, continuing to raise the temperature, the flocculation rate started to descend. Thus, 40℃ is the optimum flocculation temperature. In the meantime, temperature changes between 10-60℃ take unremarkable effect on the AmPAM flocculation rate, there is excellent evidence that AmPAM flocculant can be applied to wider temperature scope, therefore, it can be used different regions from the North to the South.

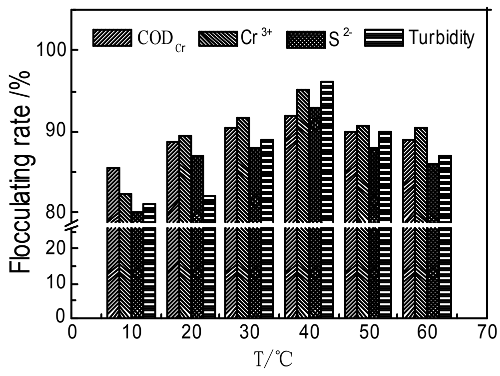

Fig. 3 The influences of different temperatures on flocculation performance of AmPAM

3.6 Influences of flocculant dosage on flocculation performance of amphoteric polyacrylamide

The amount of flocculant plays an important part on the flocculation **performance**. Under the conditions of pH value 6, temperature 40℃, the influences of different flocculant dosage on flocculation **performance** have been seen in Fig. 4. As can be seen in Fig. 4, with the increase of AmPAM, the flocculation rates of COD_{Cr}, Cr^{3+}, $S^{2-}$and turbidity increase, when dosage of AmPAM is 1.2mg • L^{-1}, flocculation rate reaches the highest, however, flocculation rate will descend if AmPAM dosage continues to increase. Because of less flocculant dosage, electricity and adsorption bridging role get to enhance. With the dosage increasing, the beginning of adsorption also increases which is in favor of electrical and building bridges with the adsorption, nevertheless, because of the dispersion of flocculant at the same time, if the dosage used is excessive, the adsorbed particles will be wrapped by the excessive polymer flocculant, so that they maintain dispersed not united. Experiments show that, when the addition dosage of AmPAM is varying between 1.0-1.4mg • L^{-1}, coarse floccules, fast subsidence velocity and good water quality are obtained.

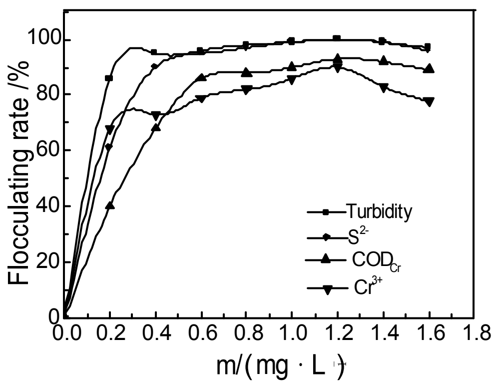

Fig. 4 The influences of dosage of the flocculant on flocculation performance

4 Conclusions

Through two-phase aqueous polymerization, the environmental friendly AmPAM flocculant has been prepared, whose molecular weight is 4.38×10^4, solid content is over 30%, cation and anion values is separately 29.8% and 17.9%.

AmPAM flocculant has good flocculation performance, can be applied in the wide range of the pH between 4 to 10, suitable for a wider temperature scope for 10-60℃, and its flocculation is efficient. The water after treatment is clear and clean, in which the content of suspended substance conform to the national emission standards. Under the dosage of flocculant between 1.0-1.4mg•L^{-1}, pH value 6, temperature of 40℃, the optimum flocculation can be achieved.

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