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Synthesis and application of amphoteric starch graft polymer

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ABSTRACT

An amphoteric starch-graft-polyacrylamide (S-g-PAM) was prepared by inverse emulsion polymerization, subsequent hydrolysis reaction and Mannich reaction. The copolymerization was carried out using ammonium persulfate and urea as redox initiator. The reaction conditions and application as flocculant were investigated. Experiments showed that in hydrolysis reaction, a stable emulsion of anionic S-g-PAM with high hydrolysis degree could be obtained in a shorter time when sodium carbonate and sodium hydroxide were used together as hydrolyzing agents. In Mannich reaction, after pre-formation of an aldehyde–amine adduct was added to the anionic emulsion product, the amination degree of amphoteric S-g-PAM could reach 43.6% and the highest solution viscosity was obtained. The application test showed that the results of treatment of several kinds of industrial waste water by amphoteric S-g-PAM were better than those treated with cationic polyacrylamide (PAM), hydrolytic PAM and amphoteric PAM.

1. Introduction

Starch is a naturally abundant polysaccharide and a low cost material. Many chemical modifications of starch have been carried out for its use, such as etherification, esterification, oxidization, cross-linking and graft copolymerization through hydroxyl groups. In recent years, particular attention has been attached to synthesis of starch graft copolymer due to an increasing interest in the synthesis of new cost-effective polymer. So the amount of active groups of the macromolecular chain largely increases, the polymers form the branch structure and contribute to catch and sedimentate the suspended substances in the waste water. Ma, Cao, and Cui (1998) reported synthesis of SCAM and application in petroliferous water treatment; Yasusato and Takahisa (2001) studied synthesis of starch-graft-polyacrylonitrile hydrolyzate and its characterization; Tai and Ma (2002) investigated synthesis of the graft copolymerization onto starch with acrylamide and diallydimethyl ammonium chloride as strong cationic flocculant; Tai and Liu (2004) studied synthesis and flocculation properties of starch-graft-acrylamide; Cao, Yang, and Liu (2004) investigated the graft copolymerization onto starch with acrylamide and acrylic acid in inverse emulsion. However most of these flocculants are only nonionic, cationic or anionic types. And many studies focus on polymerization in dilute solution. This technology is limited to special applications due to low solids content in the solution, poor solubility and high chance of cross-linking during polymerization. Synthesis of a latex amphoteric product may overcome the abovementioned weakness. This article discusses the preparation method of an inverse emulsion of the amphoteric starch graft polymer, the reaction conditions and the application of the amphoteric product as a flocculant.

2. Experimental

2.1. Materials and instruments

The materials used in this study were purchased from the following suppliers: acrylamide (AM) from Nanchang Changjiu Chemical Co., Ltd. (Nanchang, China); corn starch from Changchun Huanglong food Co., Ltd. (Changchun, China); liquid paraffin, ammonium persulfate, urea and formaldehyde (36 wt%) from Dandong Shengli Chemical Plant (Dandong, China); dimethylamine (33 wt%) from Shanghai Chemical Reagent Corporation (Shanghai, China); sodium carbonate from Shenyang Plant of Agents (Shenyang, China); sodium hydroxide from Shenyang Shenyi Fine Chemical Co., Ltd. (Shenyang, China); cationic polyacrylamide (PAM), hydrolytic PAM and amphoteric PAM from Dalian Guanghui Chemical Co., Ltd. (Dalian, China).

Infrared spectrum (IR) was carried out on a Spectrum One-B infrared spectrometer (Perkin-Elmer Company of USA); nuclear magnetic resonance spectrum (NMR) was tested by an INOVA400 nuclear magnetic resonance spectrometer (Varian Company of USA).

2.2. Preparation of amphoteric starch-graft-polyacrylamide

The reaction was carried out in a four-necked round-bottom flask with stirrer, thermometer, nitrogen gas inlet and condenser. About 70 mL of liquid paraffin and emulsifier (mixture of Span-20 and op-10) were added. The concentrations of Span-20 and

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op-10 were both 3% (w/w) for the continuous phase. The mixture was stirred until the emulsifiers were dissolved in the oil phase. AGU/L starch slurry (0.64 mol) and 2.12 mol/L acrylamide were added to the oil phase under stirring to give a final water/oil ratio of 1:1.4 (v/v). Nitrogen was allowed to bubble through the solution for 40 min. Then 0.15 g ammonium persulfate and 0.3 g urea were introduced into water-in-oil system. The pH value of the system was adjusted by adding aqueous ammonia. The stirring rate was 300 rpm and the temperature of the water bath was adjusted to 45 °C. After 4 h the reaction was complete.

Anionic starch-graft-polyacrylamide (S-g-PAM) was prepared by alkaline hydrolysis. The hydrolytic agent (mixture of sodium carbonate and sodium hydroxide) was added to starch-graft-polyacrylamide emulsion, the concentration of the hydrolytic agent was 2.12 mol/L, and the molar ratio of sodium carbonate to sodium hydroxide was 1:1. Then the temperature of the system was adjusted to 65 °C. The reaction lasted for 3 h.

Amphoteric starch-graft-polyacrylamide was prepared through Mannich reaction, which involved the preparation of an aldehyde–amine adduct as intermediate. The reaction was carried out in a three-necked round-bottom flask with a stirrer. First, a dimethylamine aqueous solution (33 wt%) was introduced into the flask at 25 °C, and then the formaldehyde solution (36 wt%) was added. The starting materials were allowed to react for 1 h at 25 °C. The formed formaldehyde–dimethylamine adduct was dropped into the anionic starch-graft-polyacrylamide emulsion. The temperature was adjusted to 50 °C, and the materials were allowed to react for 2.5 h. After the reaction, the product was washed, dried and analyzed.

2.3. Analysis of the sample

The prepared sample was precipitated in ethanol, and the precipitate was washed with acetone to remove oil phase and the unreacted reactants. Then it was dried at 40 °C. The homopolymer in uncharged graft copolymer was removed by extraction with a 60:40 (v/v) mixture of ethan-1,2-diol and acetic acid, then the polymer was washed with ethanol, and vacuum dried at 40 °C to constant weight. The amphoteric product was analyzed by IR (infrared) spectrometer as KBr pellet and by ^{1}H NMR (nuclear magnetic resonance) spectrometer using the deuteroxide as the solvent.

2.4. The hydrolysis degree of the product

The hydrolysis degree was measured according to GB 12005.6-89 (National Standard of China) and it was determined by conductometric titration using a conductometer DDS-11A (Shanghai, China). The measurement procedure was as follows: a dry sample (0.03–0.05 g) was dissolved in distilled water and titrated with a standardized solution of hydrochloric acid (0.02 mol/L). The endpoint of titration was determined conductometrically. The following formula was used to calculate the hydrolysis degree of the product:

$$\text{Hydrolysis degree } (\%, \text{w/w}) = (71 \times 100CV)/(1000W - 23CV) \times 100\%$$

where C (mol/L) is molar concentration of hydrochloric acid, and V (mL) is the volume of the consumed hydrochloric acid for the sample; W (g) is the weight of the sample. The difference between the molecular weights of sodium acrylate and acrylamide is 23. One milliliter of consumed standard hydrochloric acid (1 mol/L) is equivalent to 71 g of acrylamide.

2.5. The amination degree of the product

Since the Mannich reaction took place in an excess of HCl, quaternary ammonium chloride was formed as reaction product. The amination degree of the product could thus be calculated from the chlorine content of the sample.

To this end, a dry product sample (0.2 g) was dissolved in distilled water, and 1 mL of a potassium chromate solution was added. The mixture was back-titrated with silver nitrate solution (0.05 mol/L) until a brick red coloration was formed. The amination degree of the product was calculated as follows:

$$\text{Amination degree } (\%, \text{w/w}) = 128 \times 0.05 \times (V - V_0)/(1000W) \times 100\%$$

Where V (mL) and V_0 (mL) are the volumes of the consumed silver nitrate solution for titration of the sample and the blank, respectively, W (g) is the weight of the sample, and 128 is the molecular weight of dimethylaminomethylacrylamide.

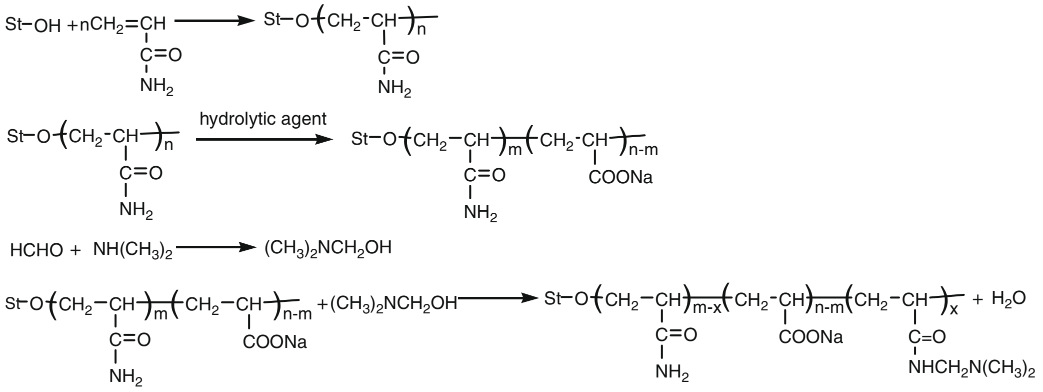
2.6. The intrinsic viscosity of the graft copolymer

The intrinsic viscosity of the polymer was determined with an Ubbelohde viscometer at 30 ± 1 °C in a 1 M aqueous $NaNO_3$ solution. A series of η_{sp} of the polymer with different concentration were measured. The data were processed and regression equation was established. The intrinsic viscosity [η] was calculated from the equation reported by Qian and Du (1988).

3. Results and discussion

3.1. Preparation routing

Copolymers of starch-graft-polyacrylamide (S-g-PAM) with anionic and cationic groups in the chains can be obtained by alkaline hydrolysis and Mannich reaction subsequently. The synthetic process of amphoteric S-g-PAM is as follows:



3.2. Proof of amphoteric S-g-PAM

The IR spectra of the products are shown in Fig. 1. Spectra A, B, C and D refer to starch, S-g-PAM, anionic S-g-PAM and amphoteric S-g-PAM, respectively. The ^{1}H NMR spectrum of amphoteric S-g-PAM is shown in Fig. 2.

Fig. 1 shows that the characteristic absorption peak of the sample at 1670 cm^{-1} results from C=O stretching vibration of the CONH$_2$ group in pattern B. The result proves that starch has grafted with polyacrylamide. In pattern C, intensity the characteristic peak at 1673 cm^{-1} is due to C=O stretching vibration in CONH$_2$ group. In comparison pattern C with B it can be seen that the intensity of C=O stretching vibration in CONH$_2$ group at 1673 cm^{-1} weakens and a new characteristic absorption peak has appeared at 1604 cm^{-1}. This peak is due to C=O stretching vibration in the carboxylate of the hydrolytic product. In pattern D, the characteristic absorption bands at 1662 cm^{-1} and 1594 cm^{-1} result from C=O stretching vibrations in CONH$_2$ group and in the carboxylate, respectively. Comparing patterns D and C, it can be seen that another new characteristic absorption peak appears at 1200 cm^{-1}. This peak is due to C—N stretching vibration of —CH$_2$N(CH$_3$)$_2$ in the amination product.

In Fig. 2, the resonances at 4.28 and 2.62 ppm are due to the protons of methylene and methyl groups in —CH$_2$N(CH$_3$)$_2$, respectively, which is an indication that the copolymer has been further modified.

3.3. Effect of the reaction conditions on hydrolysis reaction

3.3.1. Effect of the hydrolytic agent concentration on hydrolysis degree

We found that the method using NaOH and Na$_2$CO$_3$ together as hydrolytic agents was suitable. When NaOH was used alone, strong alkali easily led to cleavage of the starch backbone and graft chains. If hydrolytic agent was only Na$_2$CO$_3$, the hydrolytic process was slow. The hydrolytic degree increased with the rise of Na$_2$CO$_3$/NaOH molar ratio. However, after the ratio was larger than 1, the hydrolytic degree decreased. The reason might be that NaOH was not enough in that case and caused incomplete hydrolysis. The optimum molar ratio of Na$_2$CO$_3$ to NaOH was 1:1.

The effect of the hydrolytic agent concentration on hydrolysis degree was shown in Fig. 3. As illustrated, the hydrolysis degree increased with the increase of hydrolytic agent concentration from 1.27 to 2.12 mol/L. That was, the higher the content of the hydrolytic agent was, the more complete the hydrolysis and the higher the hydrolysis degree were. However, if the hydrolytic agent concentration was too high, the emulsion system was not stable. In our experiments, the hydrolysis degree reached a maximum when the hydrolytic agent concentration was 2.12 mol/L.

3.3.2. Effect of hydrolytic temperature and time on hydrolysis degree

The reaction temperature is another important parameter in hydrolytic reaction. The reaction was carried out at 55, 60 and 65 °C, and the other variables were kept constant. As illustrated

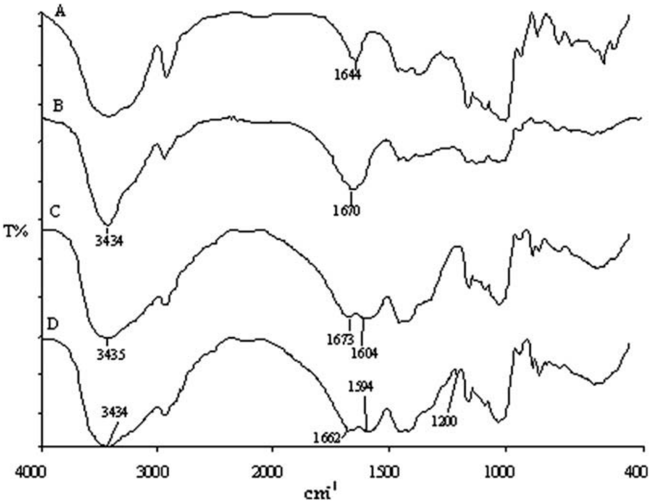


Fig. 1. IR spectra of the products (A, starch; B, S-g-PAM; C, anionic S-g-PAM; D, amphoteric S-g-PAM).

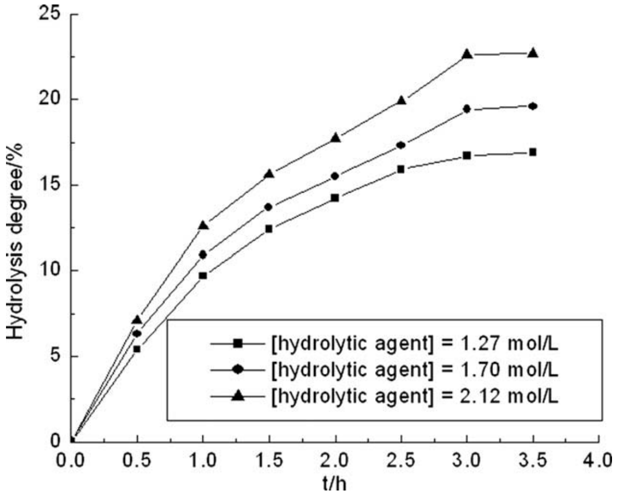


Fig. 3. Effect of the hydrolytic agent concentration on the hydrolysis degree ([AM] = 2.12 mol/L; Na$_2$CO$_3$/NaOH molar ratio = 1:1; reaction temperature = 65 °C).

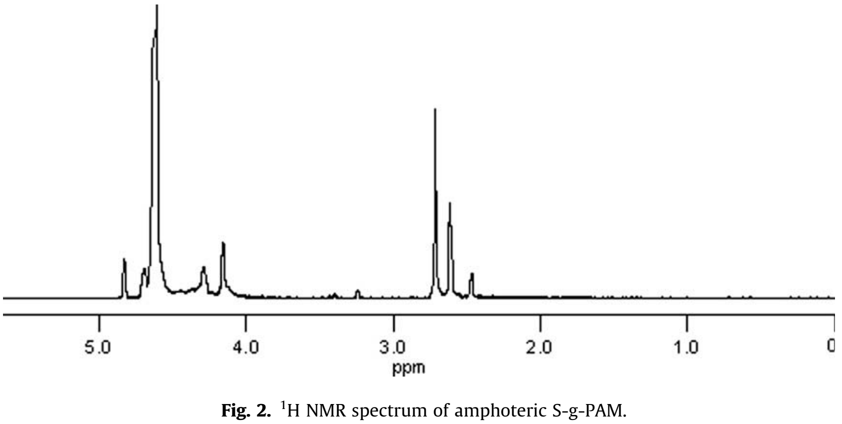


Fig. 2. ^{1}H NMR spectrum of amphoteric S-g-PAM.

in Fig. 4, hydrolysis degree increased with the rise of temperature at 55, 60 and 65 °C. The changes were explained as follows: at low temperature, polymer chains could not stretch well and the hydrolysis was insufficient. So increasing the temperature was favorable. However, the rise of hydrolysis degree was diminished after 65 °C and therefore there seemed to be a limit to increasing temperature. So the suitable reaction temperature is 65 °C.

The effect of the reaction time on hydrolysis was investigated. As shown in Fig. 4, the hydrolysis degree increased rapidly as the time prolonged. However, after 3 h the rise of the hydrolysis degree was diminished. This indicated that the hydrolysis basically reached equilibrium at 3 h.

3.4. Effect of the reaction conditions on Mannich reaction

In the reaction of anionic starch-graft-polyacrylamide with formaldehyde and dimethylamine, when formaldehyde and dimethylamine were added, respectively, amination degree was low and the maximum was only 35.8%. And the system usually led to cross-linking more easily. So we took the preformed aldehyde–amine adduct (hydroxymethyldimethylamine) instead. The obtained hydroxymethyldimethylamine was added to the inverse emulsion of anionic starch-graft-polyacrylamide with hydrolysis degree 22.6%. The amination degree of the product was higher and could reach 43.6%. The emulsion system was stable. Therefore, the latter method was chosen.

In the addition reaction of formaldehyde and dimethylamine, the effect of the molar ratio of dimethylamine to formaldehyde on the conversion ratio of formaldehyde is shown in Fig. 5. The conversion ratio of formaldehyde increased with increase of the content of dimethylamine. When the molar ratio of dimethylamine to formaldehyde reached 1.0:0.7, the conversion ratio was high. If the amount of dimethylamine still increased, excess dimethylamine caused the emulsion system to lose its stability. Therefore, the appropriate molar ratio of dimethylamine to formaldehyde was 1.0:0.7.

3.4.1. Effect of the materials molar ratio on amination degree and intrinsic viscosity

The effect of the molar ratio of hydroxymethyldimethylamine to acrylamide on amination degree and intrinsic viscosity of the product is shown in Fig. 6. As the molar ratio of hydroxymethyldimethylamine to acrylamide varied from 0.4 to 0.7, the amination degree and intrinsic viscosity increased with the increase of hydroxymethyldimethylamine. However, when the ratio was greater than 0.7, the reaction basically reached equilibrium and it was difficult to further increase the amination degree and the intrinsic viscosity. So it seemed that an appropriate ratio of hydroxymethyldimethylamine to acrylamide should be 0.7:1.0.

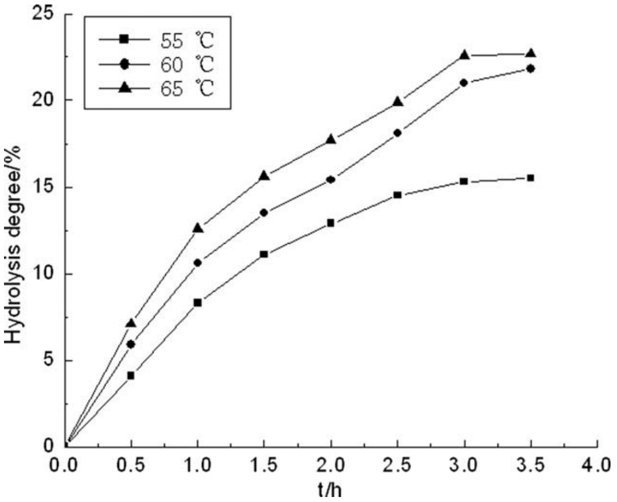


Fig. 4. Effect of temperature on the hydrolysis degree ([AM] = 2.12 mol/L; Na_2CO_3/NaOH molar ratio = 1:1; [hydrolytic agent] = 2.12 mol/L).

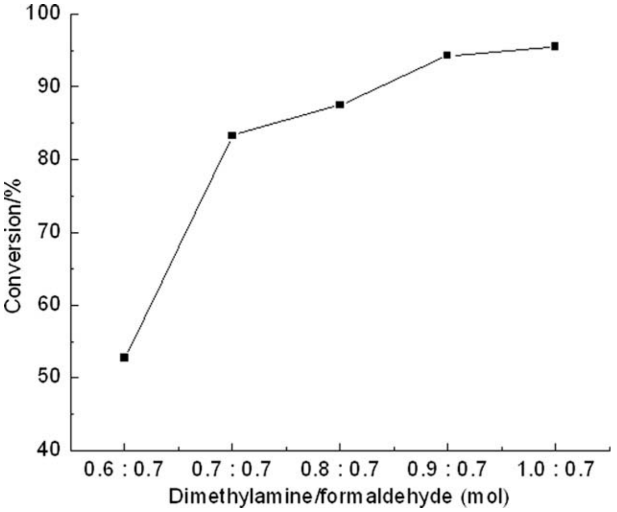


Fig. 5. Effect of the dimethylamine/formaldehyde molar ratio on the conversion ratio of formaldehyde (reaction temperature = 25 °C; reaction time = 1 h).

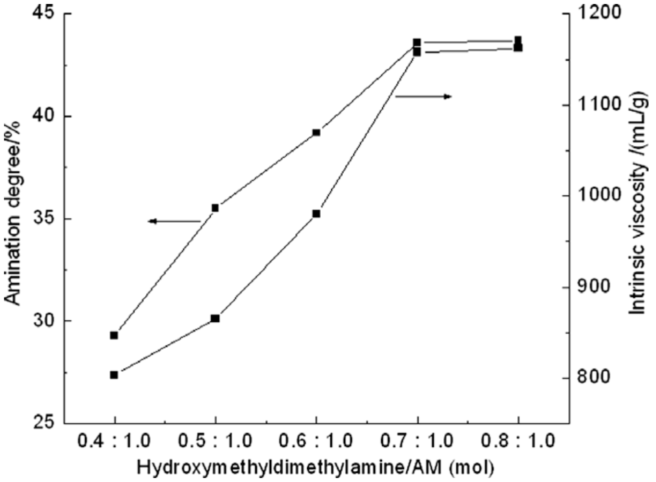


Fig. 6. Effect of the hydroxymethyldimethylamine/AM molar ratio on amination degree and intrinsic viscosity ([AM] = 2.12 mol/L; dimethylamine/formaldehyde molar ratio = 1.0:0.7; reaction temperature = 50 °C; reaction time = 2.5 h).

Table 1
Effect of the reaction temperature and time on the amination degree.

Reaction time (h)	Reaction temperature (°C)				
	30	40	50	60	70
	Animal degree (%)				
1.5	20.2	30.1	35.5	38.0	38.5
2	31.0	34.2	39.7	39.8	Gel
2.5	32.3	39.2	43.6	Gel	–
3	33.8	39.5	43.7	–	–

[AM] = 2.12 mol/L; dimethylamine/formaldehyde molar ratio = 1.0:0.7; hydroxymethyldimethylamine/AM molar ratio = 0.7:1.0.

Table 2
Comparison of flocculating effect of different agents.

Sample	Flocculant	Sedimentation ratio (cm/min)	SS removal ratio (%)	COD removal ratio (%)	Color removal ratio (%)
Dyeing waste water	Cationic PAM	3.1	68.2	75.1	85.3
	Hydrolytic PAM	2.6	63.0	72.7	83.7
	Amphoteric PAM	5.1	85.7	88.3	89.8
	Amphoteric S-g-PAM	6.5	95.2	90.1	97.4
Paper mill waste water	Cationic PAM	4.6	**72.2**	85.4	79.8
	Hydrolytic PAM	4.6	64.3	83.0	76.2
	Amphoteric PAM	5.1	77.9	90.2	86.6
	Amphoteric S-g-PAM	5.8	80.4	94.6	88.4
Refinery waste water	Cationic PAM	7.5	81.7	86.2	83.8
	Hydrolytic PAM	6.2	70.9	84.9	78.1
	Amphoteric PAM	8.1	87.9	88.7	89.1
	Amphoteric S-g-PAM	8.4	90.3	89.0	91.2

SS of the dyeing factory, paper mill and refinery waste water is 126, 2300 and 79 mg/L; COD of the dyeing factory, paper mill and refinery waste water is 464, 685 and 149 mg/L; absorbency of the dyeing factory, paper mill and refinery waste water is 0.35, 0.63 and 0.523. The dosage of these agents is 4 ppm.

3.4.2. Effect of reaction temperature and time on amination degree

The temperature is another important parameter in the reaction. Table 1 shows the changes of the amination degree is in dependence on the reaction temperature in the range of 30 °C to 70 °C. The amination degree initially increased with the rise of the temperature. Since increase in temperature contributed to the diffusion of the reactants, it accelerated the reaction and the conversion of dimethylamine was higher. However, there was always a limitation for the increase in temperature. When the temperature was higher than 50 °C, the system produced gel. Thus, 50 °C was selected as the reaction temperature.

The Mannich reaction time also affected the amination degree of the product. As illustrated in Table 1, the amination degree increased first, and after 2.5 h the increase became smaller. This can be explained as follows: Since the amount of the reactants was large initially, the reaction proceeded fast at this time. Reactants were consumed successively with the prolongation of the reaction time, the concentration of reactants became low and the reaction rate decreased. At 2.5 h the reaction equilibrium almost reached, therefore the appropriate reaction time was 2.5 h.

3.5. Application test

The amphoteric starch-graft-polyacrylamide (S-g-PAM) can be used as the flocculant and the results of disposing several kinds of waste water are shown in Table 2. It can be seen that suspended substance (SS), chemical oxygen demand (COD) and color removal ratio of the waste water treated with the amphoteric product were better than those of cationic PAM, hydrolytic PAM and amphoteric PAM. The reason was that starch provided rigid backbone as the main chain and modified polyacrylamide provided soft branch chains with anionic and cationic groups, so the obtained amphoteric product combined advantages of both starch and polyacrylamide. Therefore, the amphoteric S-g-PAM had high molecular weight and good flocculating effect.

4. Conclusions

A stable emulsion of amphoteric starch-graft-polyacrylamide as flocculant was obtained by inverse emulsion polymerization, hydrolysis reaction and Mannich reaction subsequently. In hydrolysis reaction, both NaOH and Na_2CO_3 were common hydrolyzing agents. A combined use of both hydrolyzing agents not only increased the hydrolyzing speed but also improved the effect of hydrolyzation. A synergistic effect of NaOH and Na_2CO_3 on the hydrolysis increased the hydrolysis degree and kept the emulsion system stable. In amination reaction, the amphoteric starch-graft-polyacrylamide with high amination degree and high viscosity was yielded through control of the material addition method and the reaction conditions. The stable emulsion of the amphoteric product could be used directly and there was no need for preparation of a powder. Compared with cationic PAM, hydrolytic PAM and amphoteric PAM, the amphoteric product had the better treatment effect when it was used as flocculant in industrial waste water treatment.

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