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Synthesis of polyamine flocculants and their potential use in treating dye wastewater

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Abstract

Polyamine flocculants were synthesized by the polycondensation of dimethylamine and epichlorohydrin, in which organic amines, e.g. 1,2-diaminoethane, were used as modifying agents. Different products were obtained by varying the reaction parameters, such as the molar ratio of epichlorohydrin to dimethylamine, the amount of 1,2-diaminoethane and reaction temperature. The polyamine flocculants were characterized by transmission electron microscope (TEM). Their flocculation performance was evaluated with simulated dye liquor and actual printing and dyeing wastewater. The behavior of the flocculants was compared with that of inorganic coagulant, polyaluminum chloride (PAC). The experimental results show that polyamine with the highest viscosity and cationicity could be prepared under following conditions: an epichlorohydrin to dimethylamine molar ratio of 1.5, a reaction temperature of 70 °C, a 3% content of 1,2-diaminoethane in the total reaction monomers and a reaction time of 7 h. Polyamine polymers can, as flocculants for treating simulated and actual dye wastewater, remove color and COD efficiently. The rate of color removal from reactive red liquor, reactive blue liquor and reductive yellow liquor reached as high as 96%, 97% and 96%, respectively. The highest efficiency of color removal and COD removal from polyamine for treating dye wastewater was 90% and 89%, respectively.

Keywords: Color removal; COD; Polycondensation; Polyamine flocculants; Wastewater treatment

1. Introduction

Due to rapid development of industries, the ingredients of printing and dyeing wastewater have become more and more intricate in recent years, which make color removal one of the most difficult tasks in dye wastewater treatment [1,2]. Physical and chemical treatment methods, including coagulation, adsorption, reverse osmosis, chemical oxidation and electrolysis, and biological treatment, have been extensively used in dye wastewater treatment [1,3–5]. Coagulation and flocculation processes were widely employed as pretreatment steps for the decolorization of dye wastewater [1,6].

Flocculating agents are classified into inorganic coagulants and polymeric flocculants. The use of inorganic coagulants in dye wastewater is quite limited because a large amount of coagulating agents is required and subsequently a large volume of sludge is produced. In contrast, a proper use of polymeric flocculants can successfully remove suspended particles and coloring matters in wastewater from dyeing industry. Because cationic polymeric flocculants destabilize the particles and coloring matters through the compression of electrical double layers, charge neutralization, and the adsorption and subsequent formation of particle-polymer-particle bridges [7,8], high removal efficiency can still be achieved even with a small amount of cationic polymeric flocculants, which generate a small volume of sludge output. Polyamines are quaternary cationic polymers and have been used as flocculants and charge neutralization agents in pulp and mining industries [9,14]. It was found that polyamines were effective in a wide range of pH, easy to handle, and immediately soluble in aqueous systems. Choi et al. synthesized polyamine by a two-step polycondensation of dimethylamine and epichlorohydrin, and found that color removal efficiency was improved when polyamine was used as flocculation aid [1]. However, very little information is available with respect to the application of polyamines as flocculant in dyeing wastewater treatment.

In this study, experiments were carried out to synthesize polyamine flocculants with different molecular structures, charge densities and molecular weights. First, viscosity and

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cationicity were measured to describe the characteristics of polymers. Then, transmission electron microscope (TEM) was used to characterize the structure of the polymers. Finally, the applicability of the synthesized polyamines for the treatment of dyes containing wastewater was investigated via a jar test.

2. Experimental

2.1. Materials

Epichlorohydrin (A.R.), dimethylamine (33%, C.P.) and 1,2-diaminoethane (A.R.) were obtained from Guang Mang Chemical Company of Jinan, China. Polyaluminum chloride (PAC) was prepared in our laboratory with an Al concentration of 1.0 M and a basicity ([OH]/[Al]) of 2.0. All the chemicals received were used without further purification.

2.2. Synthesis of polyamine

Epichlorohydrin (92.5 g) was first added to a 250 mL glass reactor equipped with a temperature controller at 30 °C initially and a mechanical stirrer. Then, dimethylamine at a selected dimethylamine-to-epichlorohydrin molar ratio (2:1, 1.5:1, 1:1, 1:1.5 and 1:2) was added by dropping into the reactor with constant stirring to form obligomers. After that, 1,2-diaminoethane at a chosen weight percentage in the mixture (0.5%, 1%, 3% and 4%) was added into the reactor with the stirrer on. And then, the reactive temperature was raised slowly to 60–75 °C. The polyamine polymers were finally obtained after 7 h reaction. The investigation of optimum experimental conditions was conducted by altering certain experimental parameters, such as the dimethylamine-to-epichlorohydrin molar ratio, the weight percentage of diaminoethane and the reactive temperature.

The viscosity measurement of the polymer solutions was carried out by using a NDJ-79 Rotary Viscometer. The greater the viscosity, the larger the molecular weight. The cationicity of the polymer solutions was measured by adding 10 mL sodium tetraphenylboron solution (0.1 mol L^{-1}) into 5 mL polyamine solution (1 g L^{-1}) firstly, then adjusting pH to 12 with titan yellow as the indicating agent, and finally using cetyltrimethyl ammonium bromide (CTAB) solution (0.1 mol L^{-1}) to titrate the sodium tetraphenylboron. Cationicity was calculated according to the following equation [10]:

$$\text{cationicity} = \frac{C(V_1 - V_2)}{V_0 S} \tag{1}$$

where C is the concentration of sodium tetraphenylboron solution and CTAB solution (mol/L), V_1 the volume of sodium tetraphenylboron solution (mL), V_2 the volume of CTAB solution (mL), V_0 the volume of polyamine solution (mL) and S is the concentration of polyamine solution (g L^{-1}).

2.3. TEM measurement

A JEM-100CXII TEM was used to carry out TEM analysis for the polyamines synthesized with and without 1,2-diaminoethane, respectively.

2.4. Flocculation behavior

All flocculation experiments were conducted in 1.0 L plexiglass beakers using a conventional Jar-test apparatus, the DC-506 Laboratory Stirrer. Wastewater (500 mL) were dosed with different flocculants. During coagulation addition, the solutions were first stirred rapidly at 200 rpm for 1 min and then at a slower pace of 40 rpm for 12 min, followed by sedimentation for 15 min. After sedimentation, supernatant samples were taken from a point of 3 cm below the surface of the test water sample for laboratory analysis.

Color was determined by a spectrophotometer (Shimadzu, UV-2450). COD was measured by following the standard methods [11]. The Malvern Zetasizer 3000 was used to measure Zeta potential of flocs. After 5 min of gentle stirring, the samples were analyzed and the data were recorded.

2.5. The simulated dye liquor and wastewater characteristics

The simulated dye water was studied in order to determine the effectiveness of coagulants in removing various types of dyes. Among the commercial textile dyes, reductive and reactive dyes are of great environmental concern because of their widespread applications. Therefore, reactive red and blue and reductive yellow waters, which were obtained from Jinan No. 2 Textile Dyeing Mill, China, were chosen for the investigation of polyamine effectiveness. The simulated dye water was prepared by adding 0.1 g of reactive red, reactive blue or reductive yellow to 1 L of distilled water. The characteristic wavelength of the simulated dye water was determined by running a scan of the dye on a spectrophotometer (UV-2450). The maximum absorbance wavelength (λ_{max}) was used for all absorbance readings. Percentage of color removal was calculated by comparing the absorbance values for the waste after treatment to the absorbance value for the original dye waste. Distilled water served as a reference. The maximum absorbencies for reactive red at $\lambda_{max} = 550$ nm, reactive blue at $\lambda_{max} = 598$ nm and reductive yellow at $\lambda_{max} = 408$ nm were 1.526, 1.475 and 1.342, respectively. And pH of reactive red liquor, reactive blue liquor reductive yellow liquor was 7.89, 7.32 and 6.63, respectively.

The actual textile wastewater to be tested was obtained from the Binzhou textile company in Shandong Province, China. The maximum adsorbance at $\lambda_{max} = 589$ nm, pH and COD of the wastewater were 1.480, 11.2 and 550 mg L^{-1}, respectively.

3. Results and discussions

3.1. Effect of dimethylamine-to-epichlorohydrin molar ratio on viscosity and cationicity of the polyamines

It is known that molecular weight and cationicity of organic flocculants are the main factors that affect their flocculating performance. It was found that during the process of synthesis, the viscosity of polyamine increased sharply in the first 3 h and varied very slightly after 7 h, Therefore, the reaction time was fixed at 7 h in the experiments presented next.

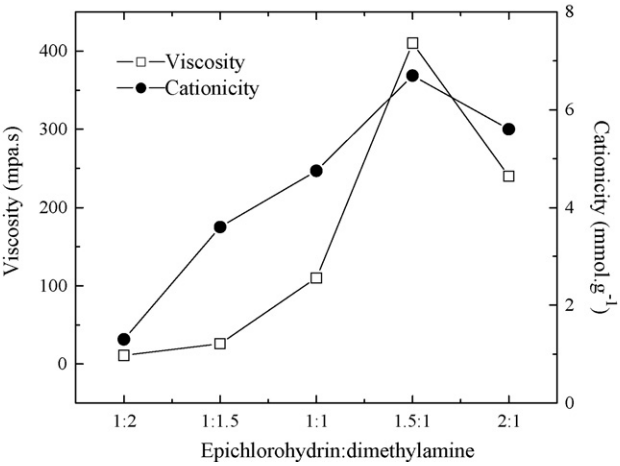


Fig. 1. Influence of dimethylamine-to-epichlorohydrin molar ratio on viscosity and cationicity.

Shown in Fig. 1 is the influence of dimethylamine-to-epichlorohydrin molar ratio on the viscosity and cationicity of the polyamines under the conditions of 65 °C reaction temperature, 3% content of 1,2-diaminoethane in the total reaction monomers and 7 h polymerization time, which were selected according the synthesized conditions of two-step polycondensation of dimethylamine and epichlorohydrin [1]. It can be seen that the changing trend of viscosity is in line with that of cationicity. When the ratio is below 1.5:1, the two parameters keep rising till the ratio reaches to 1.5:1, and then decrease with the increasing ratio of epichlorohydrin/dimethylamine. The ratio of 1.5:1 was selected to carry out following experiments.

3.2. Effect of the weight percentage of diaminoethane on the viscosity and cationic degree of the polyamines

In the experiments, the reaction temperature was set to 65 °C and the polymerization time to 7 h. The influence of the weight percentage of diaminoethane on the viscosity and cationicity of the polyamines is shown in Fig. 2. It is found that with the increasing content of 1,2-diaminoethane, viscosity goes up all the way, while cationicity first rises up and then drops starting at 3% content. This implies that 1,2-diaminoethane worked as a modifying agent in the polymerization reaction to increase the molecular weight of the polymers. Although 1,2-diaminoethane accelerates reaction rate and promote polymerization degree, excessive 1,2-diaminoethane causes gelatin due to fast reaction. The amount of 1,2-diaminoethane was set to 3% in the following experiments.

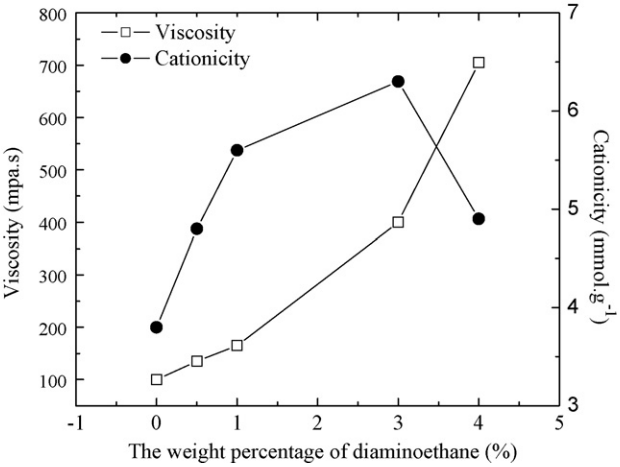


Fig. 2. Influence of the weight percentage of diaminoethane on viscosity and cationic degree.

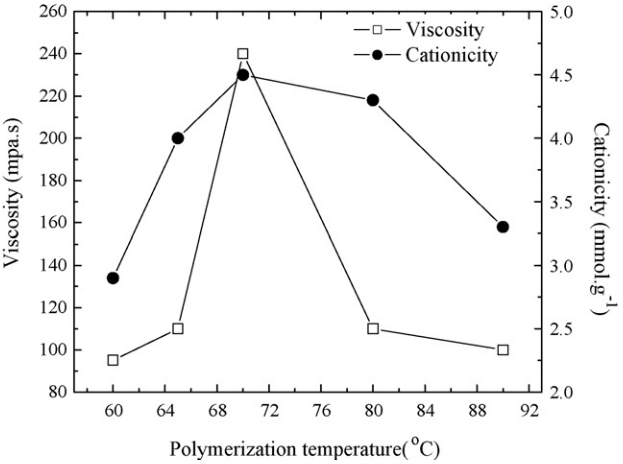


Fig. 3. Influence of reaction temperature on viscosity and cationicity.

3.3. Effect of reaction temperature on the viscosity and cationicity of the polyamines

Fig. 3 shows the influence of reaction temperature on the viscosity and cationicity of the polyamines (reaction time = 7 h). The changing trends of viscosity and cationicity are similar as both exhibit an increasing-and-dropping pattern and peaks at the polymerization temperature of 70 °C. It is clearly seen that the rising and falling of viscosity with polymerization temperature is sharper than that of cationicity.

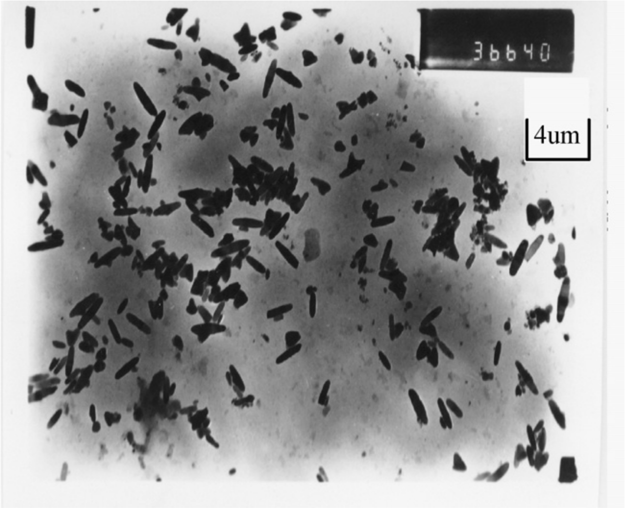
Based on the results obtained above, experimental conditions for preparing polyamine, used in the studies to be discussed below, were set to: the molar ratio of epichlorohydrin/dimethylamine = 1.5, the content of 1,2-diaminoethane in the total reaction monomers = 3%, reaction time = 7 h, and reaction temperature = 70 °C.

3.4. TEM analysis

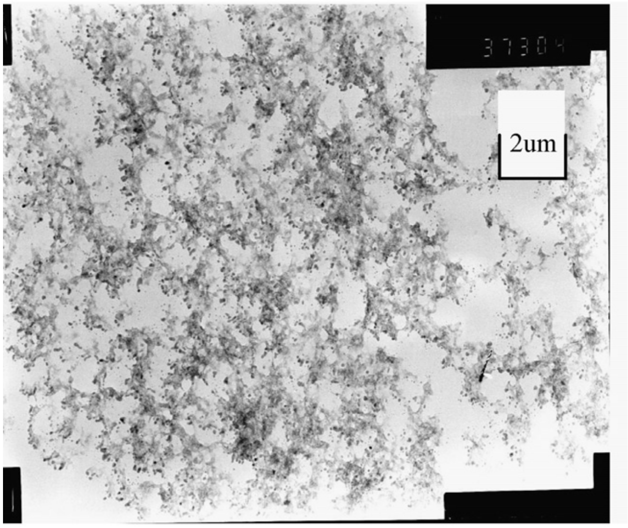
The results of TEM are presented in Fig. 4. When the product was synthesized without 1,2-diaminoethane, it dispersed in water; while the product was synthesized with the 1,2-diaminoethane as modifying agent, it became larger and assembled together, which can promote the absorption and bridging performance when used as a flocculant in water and wastewater treatment.

3.5. Flocculation study

The performance of polyamine flocculants was investigated by conducting tests using simulated dye liquor and printing and



Without diaminoethane



With diaminoethane

Fig. 4. TEM of polyamine.

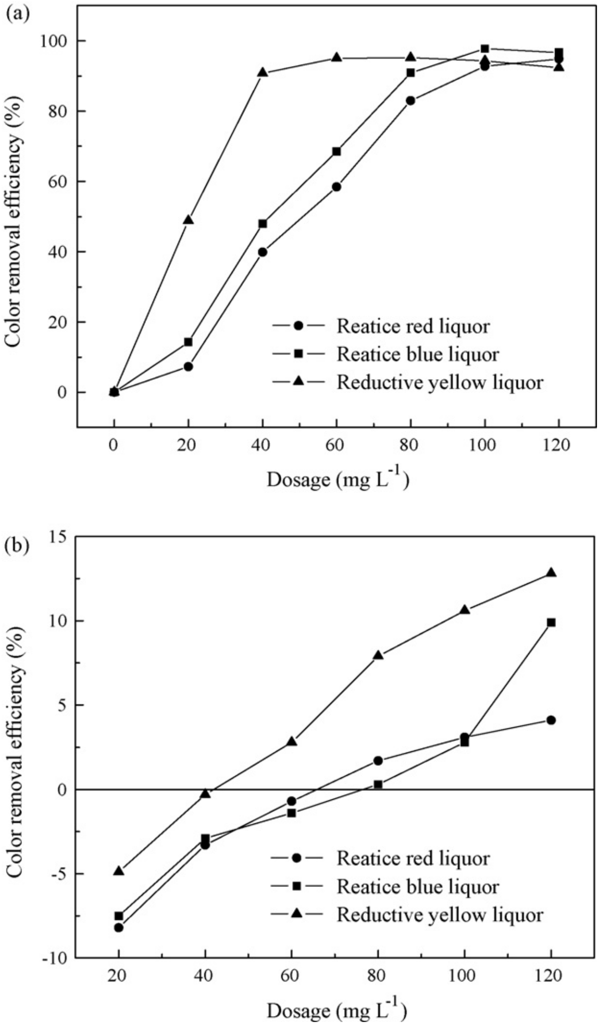


Fig. 5. Effect of polyamine dosage on color removal and zeta potential in the simulated dyes liquor.

dyeing wastewater. Results of the flocculation study are shown in Figs. 5–9. Plotted in Fig. 5 are the flocculation characteristic and zeta potential of polyamine in the simulated dye liquor. As shown in Fig. 5a the color removal efficiencies of the simulated dye liquor rise with increasing polyamine dosage, and the highest color removal rate of the reactive red liquor, reactive blue liquor and reductive yellow liquor is 96%, 97% and 96%, respectively. However, the optimal polyamine dosage is different for different dye. It is evident that for the quantitative removal of more than 90% of the reactive red liquor, reactive blue liquor and reductive yellow liquor, a minimum dosage of polyamine is 100 mg L^{-1}, 100 mg L^{-1} and 40 mg L^{-1}, respectively. This indicated that the dosage of polyamine needs to achieve the maximum removal efficiency was lower for the disperse dyes than for reactive dyes. This were mainly due to difference property between disperse dyes and reactive dyes. Kim et al. [12] have proved that the probability of successful chemical flocculation is lower for reactive dyes than that for disperse dyes, because that reactive dyes with high solubility are more strongly charged than disperse dye with low solubility.

Zeta potential is a controlling parameter of double layer repulsion for individual particles and can usually be used to inter-

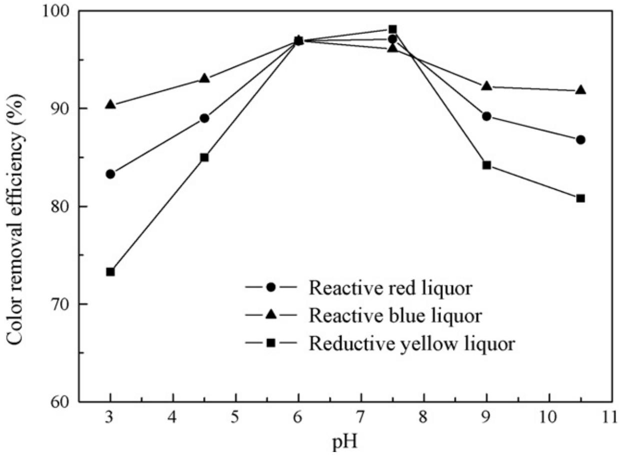


Fig. 6. Effect of pH on color removal of polyamine in the simulated dyes liquor.

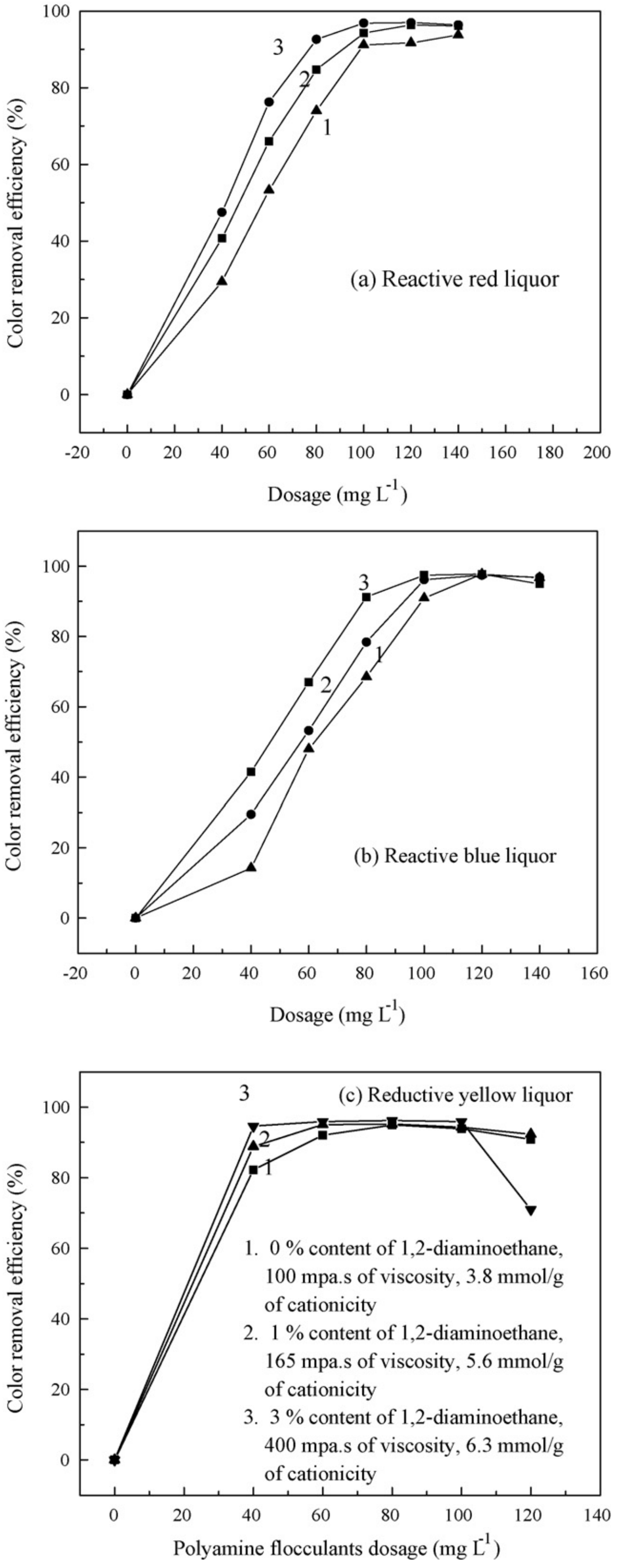


Fig. 7. Effect of different polyamines on color removal in the simulated dyes liquor.

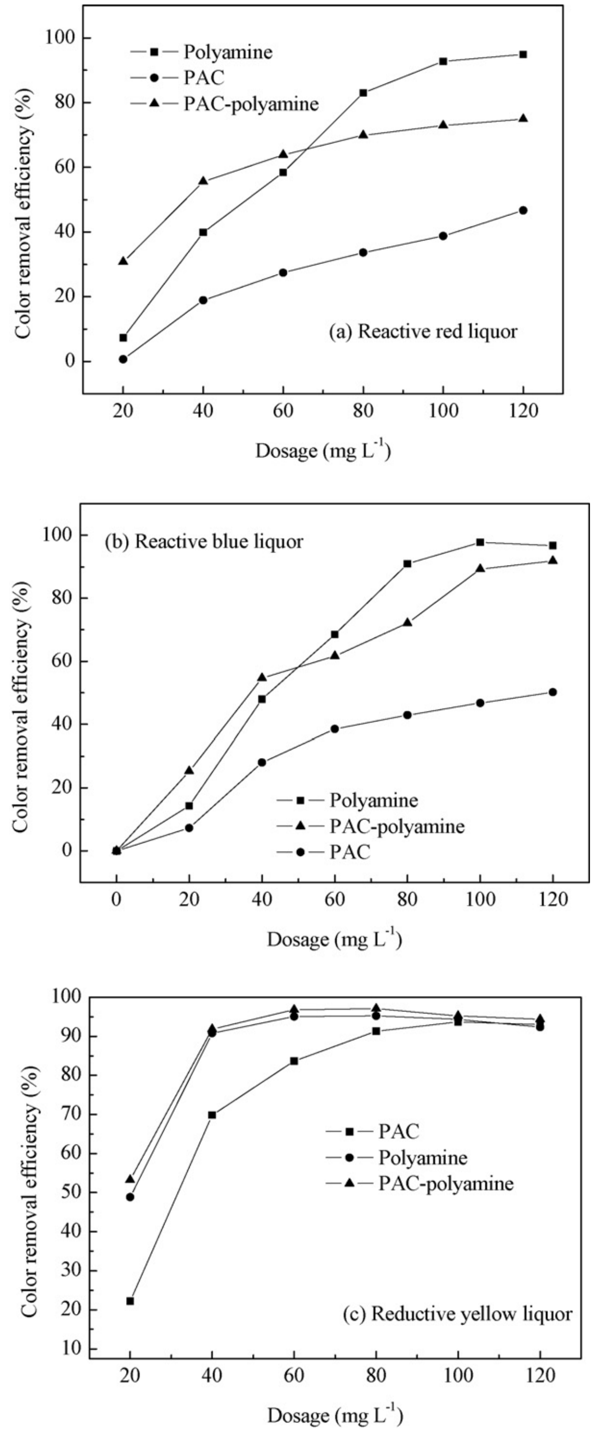


Fig. 8. Comparison of effect of polyamine and PAC in the simulated dyes liquor.

pret the mechanism of flocculation. An increase in polyamine dosage results in an increase of the zeta potential value (Fig. 5b). When the zeta potential reversal is observed, the maximum color removal efficiency is achieved. Generally, if charge neutralization is the only path for flocculation, the maximum removal efficiency is achieved when zeta potential is mostly close to zero [13]. Therefore, the results in Fig. 5b indicated that the removal of dye was mainly due to charge neutralization.

Fig. 6 shows the effect of pH of the simulated dye liquors on color removal efficiency by polyamine. Destabilizations of the simulated dye liquors were examined at various pH conditions (3, 4.5, 6, 7.5, 9, 10.5), respectively. The dosage of polyamine for reactive red, reactive blue and reductive yellow liquor was

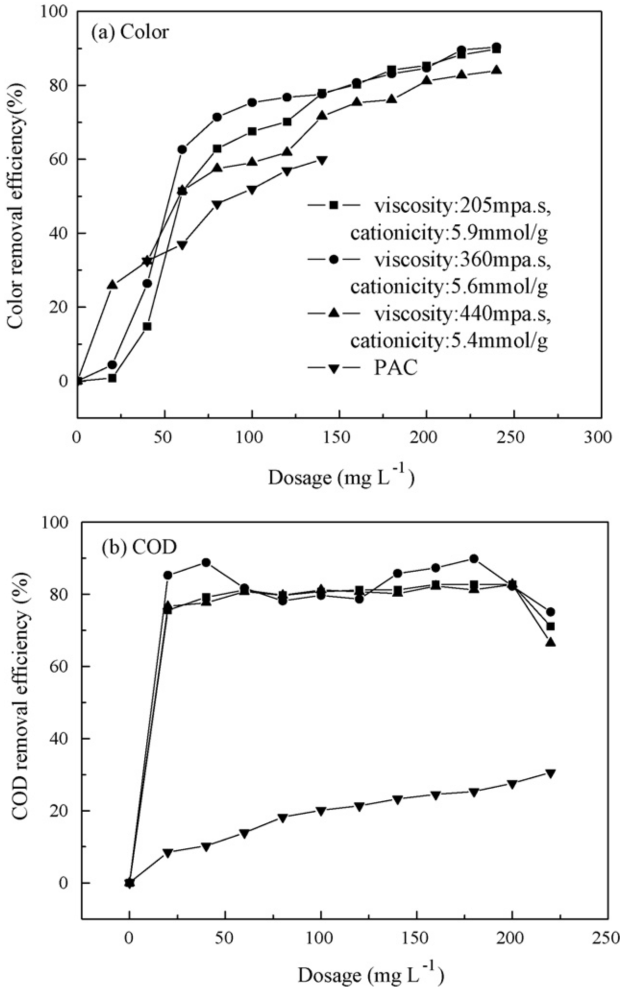


Fig. 9. Effect of different polyamines and PAC on color and COD removal in actual textile wastewater.

100 mg L^{-1}, 100 mg L^{-1} and 40 mg L^{-1}, respectively. For reactive red liquor, the color removal efficiency increases from 83% to 97% as the pH value increases from 3.0 to 7.5, and the efficiency decreases as the pH is higher than 7.5. Small changes in the color removal efficiency of polyamine for reactive blue liquor are observed in all pH range. All of the color removal efficiency for reactive blue liquor is in the range of 90–96%. The maximum removals of polyamine for reductive yellow liquor is 98%. And the difference of color removal efficiencies of polyamine is significant at different pH. For example, the color removal efficiencies for reductive yellow liquor is 73% at pH 3.

Fig. 7 presents a comparison of the flocculation performance of polyamines under different contents of 1,2-diaminoethane, viscosity and cationicity in the simulated dye liquor. It can be seen that the higher the content of 1,2-diaminoethane, viscosity of the polyamine and the cationicity, the better the color removal performance. The reason is that the charge neutralization of polyamine increases with increasing cationicity of polyamine. The results mentioned above clearly indicate that both viscosity and cationicity play an important part in treating dye-contained wastewaters. In general, the polyamine with higher viscosity and cationicity gives greater color removal results.

The effects of polyamine on color removal of reactive red solution was investigated by comparing treatments using PAC alone and PAC/20 mg L^{-1} polyamine in combination (PAC–polyamine). The results were shown in Fig. 8. PAC can remove reductive yellow dye effectively, but it was not effective in decolorizing reactive dye solution. The maximum removal efficiency of PAC for reductive yellow dye is 93%, while the maximum removal efficiency for reactive red dye and reactive blue dye is 46% and 50%, respectively. However, both polyamine and PAC–polyamine are effective in removing reactive and disperse dyes. The color removal of PAC–polyamine for reactive dye is highest at lower dosage, while when dosage is more than 80 mg L^{-1}, polyamine can achieve the highest color removal efficiency. However, the color removal of PAC–polyamine for reductive yellow dye is highest in our study.

A flocculation test has been carried out on the treatment of actual textile wastewater from the Binzhou Textile Company, Shandong, China. Fig. 9 shows the relationship of color removal efficiency with coagulants dosage of PAC and the polyamine flocculants with different viscosity and cationicity values. When the dosage of coagulant was lower than 40 mg L^{-1}, the efficiency of PAC was the highest among all coagulation. However, the color removal efficiency of PAC was only 32% at the dosage of 40 mg L^{-1}. When the dosage was higher than 40 mg L^{-1}, the efficiency of polyamine was the highest and it can reach 90%. It can be seen that in Fig. 9b that polyamine was more efficient in removing COD than PAC. The removal efficiency of polyamine at the dosage of 180 mg L^{-1} was 89%. While at the same dosage, the color removal efficiencies of PAC approached 25%. Generally, coagulants remove contamination from water and wastewater by charge neutralization and bridging action. Polyamine with the high positive surface charge and large molecular weight can remove COD effectively by strong charge neutralization and bridging action.

It can be seen that viscosity and cationicity has significant impact on the flocculation efficiency of polyamine. Polyamine with medial viscosity and cationicity value gave a better color and COD removal rate when treating real wastewater. This is different from the results of treating the simulated dye liquor mentioned above. The reason is that the ingredient of actual wastewater is more complex than that of simulated dye liquor.

4. Conclusion

Polyamine with the highest viscosity and cationicity could be prepared under the conditions of 1.5 molar ratio of epichlorohydrin/dimethylamine, 70 °C reaction temperature, 3% content of 1,2-diaminoethane in the total reaction monomers and 7-h reaction time.

Polyamine polymers can remove color and COD efficiently as flocculants for treating simulated and actual dye wastewater. The highest color removal rate of the reactive red liquor, reactive blue liquor and reductive yellow liquor is 96%, 97% and 96%, respectively. The maximum color removal efficiency and COD efficiency of polyamine for treating actual dye wastewater can reach 90% and 89%, respectively. The viscosity and cationicity of polyamine polymers have great effects on flocculation performance. The polyamine with higher viscosity and cationicity achieves a better flocculation result for the simulated dyes liquors, while polyamine with medial viscosity and cationicity value gave a better color and COD removal rate when treating real wastewater.

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