Synthesis of Complex Polymeric Flocculant and Its Application in Purifying Water

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Received 29 June 1999; accepted 6 October 1999

ABSTRACT: A novel flocculant was synthesized, a method consisting of a poly(acrylamide-*co*-acrylic acid) complexed with an inorganic coagulant through the chemical bond between metal ions and carboxyl acid groups or amide ligands within the polymer. This complex polymeric flocculant is more readily available for purifying water than any single or mechanical mixture. The mechanism of flocculating is discussed and a practical use performed for wastewater from paper mill. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 2093–2097, 2000

Key words: polyacrylamide; complex; flocculant

INTRODUCTION

Water is absolutely necessary to human life, industry, and agriculture. Most of the natural water for public and industrial use must be purified with a water-treating agent. The wastewater from a factory cannot be drained off before treatment. According to the water-treating agent's structure, we can divide the coagulants into two catalogs: inorganic and organic compounds. For example, alum floc is a typical inorganic coagulant and polyacrylamide is a widely used organic coagulant. The dosage of organic coagulants for wastewater treatment is 1/10 to 1/100 that of inorganic ones. The advantages of organic coagulants are far from inorganic coagulants, such as small sludge produced, fast precipitation rate, easy dewatering, small ash after burning, and high stability.

Natural materials were recently employed in the treatment of wastewater, such as immobilized biopolymers[1] for removing metal ions from wastewater, chitosan[2] for treating wastewater in papermaking, and polysaccharide[3] for treatment of wastewater from swine farms, but more of the organic polymer flocculants are those containing polyelectrolytes. Polyelectrolytes may be polyanions such as poly(methacrylic acid)[4] or polycations such as quaternary polyallylamine,[5] or their mixture.[6] Three-dimensional polyelectrolytes that deviate from the conventional linear polymers show distinct availability for demulsification as well as for flocculation.[7]

Here we suggest a method to prepare a complex polymeric flocculant (CPF) through a chemical bond between inorganic and organic coagulants. Such a flocculant is more available for clarifying water than any single or mechanical mixture.

EXPERIMENTAL

Inorganic Flocculant

Aluminum sulfate [chemically pure (CP), Zong He Chemical Plant, Shanghai, China], ferric sulfate (CP, Chang Nan Chemical Plant, Shanghai, China), and calcium oxide (CP, Shanghai Chemical Reagent Stocking and Providing Station, Shanghai, China) were selected as inorganic flocculants (IF). They were all dried at 200°C for 8 h and well levigated through 50 sieve before use.

Poly(acrylic acid-*co*-acrylamide) Flocculant (PF)

A mixture of 1.6 g of acrylic acid (CP, Shanghai Wu Lian Chemical Plant, Shanghai, China), 3.8 g

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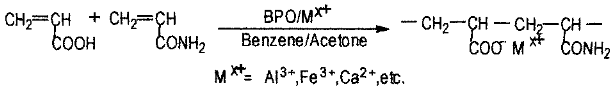
Journal of Applied Polymer Science, Vol. 76, 2093–2097 (2000)



Scheme 1

of acrylamide (CP, Medicine Company of China, Beijing, China), and 0.2 g of benzoyl peroxide (BPO; CP, Shanghai Chemical Reagent Factory No. 1, Shanghai, China) was dissolved in a mixed solvent containing 76 mL benzene and 70 mL acetone. The reaction was performed in a three-neck flask equipped with a mechanical stirrer and a reflux condenser. Copolymerization was carried out at 70°C in nitrogen atmosphere for 4 h under stirring. Poly(acrylic acid-*co*-acrylamide) precipitated from the system was then filtrated, washed by the mixed solvent, and dried at 60°C for 24 h in a vacuum drier.

Complex Polymeric Flocculant

Inorganic agent containing 41.6 g aluminum sulfate was dispersed in the benzene/acetone mixture under strong stirring. The mixture of acrylic acid and acrylamide with the same amount as above was instilled into the system. Suspension copolymerization of acrylic acid with acrylamide was initiated by 0.2 g of BPO at 70°C in nitrogen for 4 h under stirring. Because the inorganic agent contains metal ions on its surface and the organic one contains acid groups and amide ligands, the polymer would cover the surface of the inorganic powder through chemical bonds and other strong interactions. The formed complex flocculant was filtrated and washed with benzene and acetone mixture and then dried at 60°C for 24 h in a vacuum. The reaction in the presence of metal ions is shown in Scheme 1.

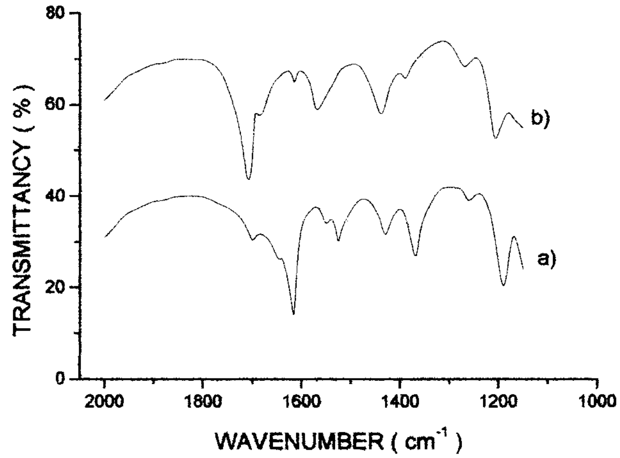


Figure 1 IR spectrum of (a) CPF compared with (b) poly(acrylamide-*co*-acrylic acid.

Mechanical Mixed Flocculant

A mixture of 41.6 g of inorganic powder of aluminum sulfate and 5.4 g of poly(acrylic acid-*co*-acrylamide) powder as triturated by muller, forming a

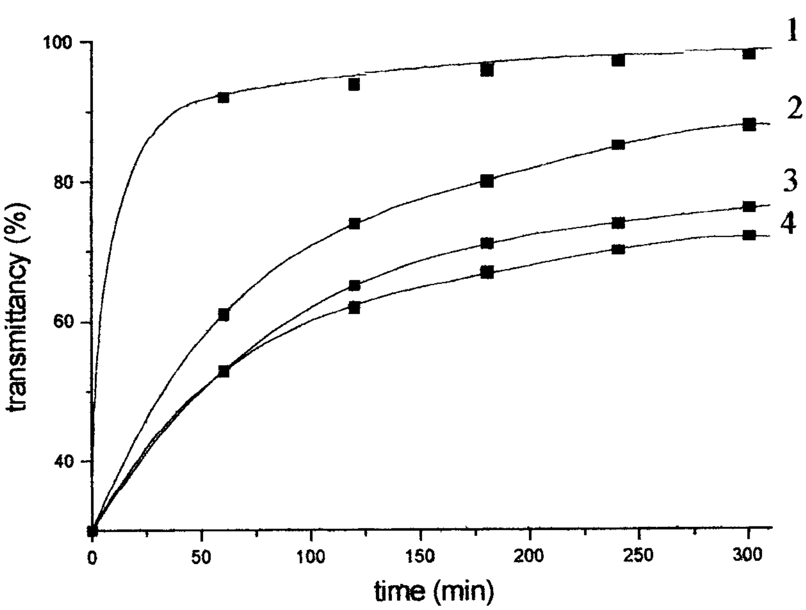


Figure 2 Flocculation effect of different flocculants. (1) complex polymeric flocculant; (2) mechanical mixture; (3) inorganic coagulant; (4) polymeric flocculant.

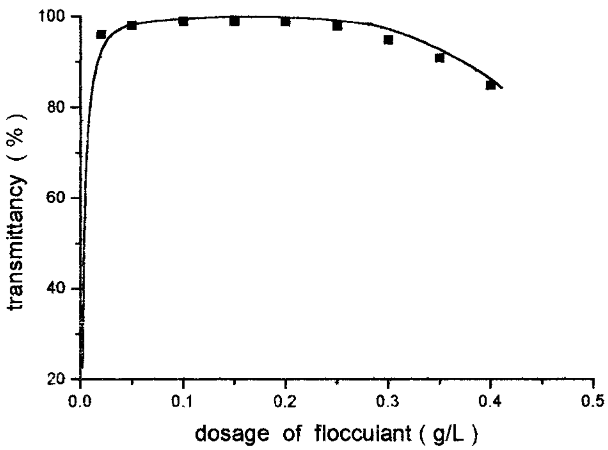


Figure 3 The flocculation effect of dosage of the complex polymeric flocculant.

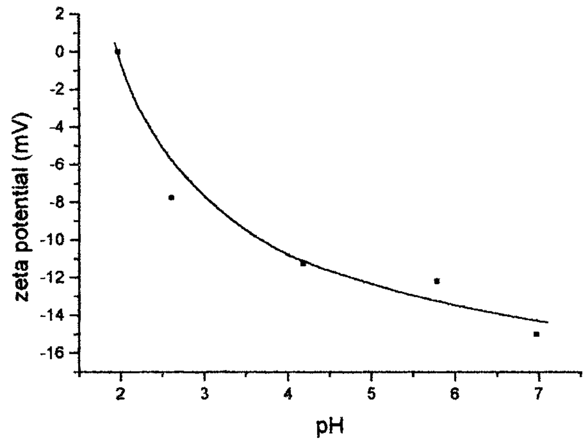


Figure 5 Zeta of colloid varying with pH.

mechanical mixture consisting of inorganic coagulant and organic polymeric flocculant. This mechanical mixed flocculant (MMF) was dried at 60°C for 24 h in a vacuum before use.

The samples of PF, CPF, and MMF were characterized by infrared spectrum (Perkin–Elmer FTIR-1600 system).

Efficiency of Wastewater Treatment

Under stirring, a certain amount of IF, PF, CPF, or MMF was added into wastewater taken from the moat at Jiading in Shanghai. The transmittance of the upper liquid in the container was measured at different times by a 751G spectrophotometer (Shanghai Analytical Instrument Factory, Shanghai, China) at 600-nm wavelength. The effect of flocculant dosage was examined.

Wastewater of Wuxi Paper Mill (Jiangsu Province, China) was treated by CPF. The zeta electrical potential was measured with the water, the flocculant, and the precipitate before and after treatment. The effect of CPF dosage on removal of chemical of oxygen depletion (COD) and transmittance of the water was also detected.

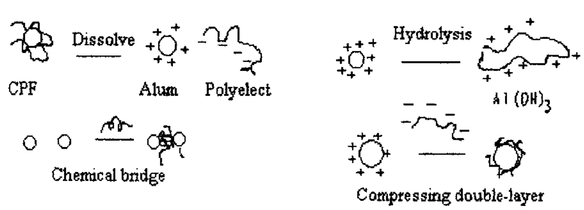


Figure 4 The mechanism of flocculation of CPF.

RESULTS AND DISCUSSION

The Structure of CPF

The CPF contains poly(acrylic acid-*co*-acrylamide) and inorganic flocculant. The IR spectrum of CPF was compared with the pure polymer (PF) shown in Figure 1. It can be seen that the vibration absorption of the functional groups within the complex polymers differs from that of the pure polymer, that is, the CPF was not a simple mixture of organic polymer and inorganic coagulant. The stretch–shrink vibration of C═O of carboxyl group in the polymer was extremely weak in the complex, but the asymmetric and symmetric vibrations of O—C—O at 1610 and 1525 cm^{-1} appeared, which implied that the carboxyl group had been ionized to the carboxyl root ion. From the spectra, it could also be found that the vibrations of C═O, C—N in amide units shifted from 1645 and 1367 cm^{-1} to 1690 and 1390 cm^{-1}, which represented that the coordination between the amide group and the metal ion had formed.

Effect of Structure and Dosage on Coagulation

The process of four kinds of flocculants for dreggy water cleansing was shown in Figure 2. It can be seen that the complex polymeric flocculant was more efficient than any other flocculant, which was reflected in the high transmittancy of the treated wastewater and fast deposition rate.

The dosage of flocculant was another factor affecting the treatment program (Fig. 3). By increasing the amount of the flocculant, the transmittancy of the treated water reached the maximum value rapidly. If excessive flocculant was used, the transmittancy decreased, implying that

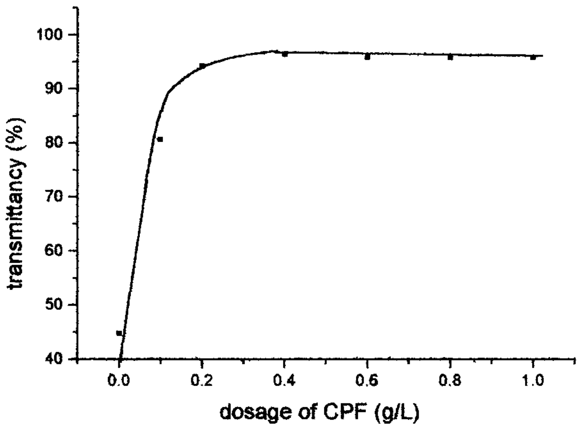


Figure 6 Transmittancy of the water during treatment.

the effect went down. This was because the excessive polymeric flocculant could restabilize the feculence in the water. Only the dosages from 0.020 to 0.200 g/L (wastewater) of the complex polymeric flocculant were often effective.

Mechanism of Flocculation of CPF

The behavior of the complex flocculation can be concluded by the following characteristics. It is well known that colloidal particles stabilize by double electric-layer repulsion force. To induce the particles to aggregate, two distinct steps may occur: the repulsion forces-reducing step and the particles-contacting step. CPF contains an ion bond between inorganic and organic components that the polyions may be hydrolyzed in water solution at once and may remain oppositely charged along the polymer chain. When certain CPF is added to wastewater in sufficient amounts, it can be dispersed rapidly because of the soluble polymer chain with same charge. Meanwhile, the inorganic-parts hydrolyze so that precipitates occur momentarily. Colloids may serve as condensation nuclei for these precipitates or may become enmeshed as the precipitates settle. Removal of colloids in this manner is frequently referred to as sweep–floc coagulation. The charged precipitates can also compress the double layer of colloids and decrease their surface charge by the interaction of the opposite charge, adsorption, and charge neutralization. So an optimum pH may exist for each coagulant to reduce the colloids' zeta potential. Neutralization of surface charge also depends on adsorption of colloids on precipitates, which will promote precipitate formation. Polymeric flocculant can become attached to a colloidal particle at one or more sites to form polymer bridges. This bridging action results in the formation of a floc particle having a favorable settling characteristic.[8] Such a process is shown in Figure 4.

The complex polymeric flocculant consists of inorganic and organic components that combine together because of the ion bond of metal ions with the oppositely charged poly(acrylic acid) root, and the coordination bond of transition metal ion with the polymeric ligands. In an aqueous solution, the organic-component polymeric acid can be ionized to cause the polymer chain to extend, which can be assumed as a rod because of the electrical repulsion

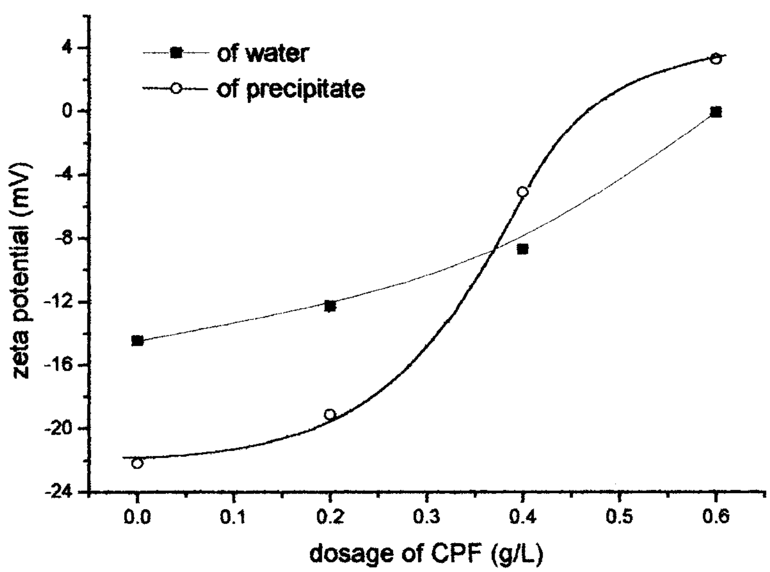


Figure 7 Removal of COD and its remainder varying with the dosage of CPF.

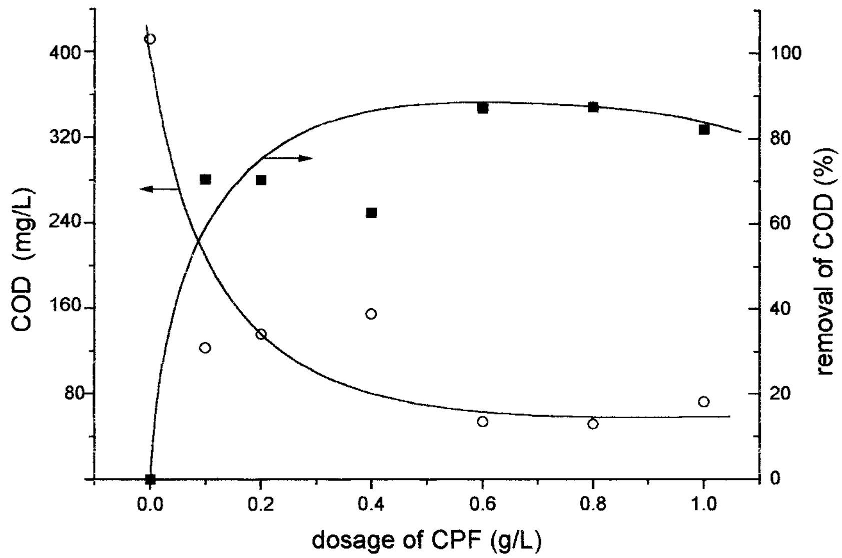


Figure 8 Effect of CPF dosage on zeta potentials of wastewater and the precipitate.

within the polymer chain. For the mechanical mixture, the organic-component polymeric acid cannot be ionized immediately from the polyacid so that most of the polymers remain a helical structure, which cannot offer a chemical bridge effect. Except for the complex flocculant, the polyacid was ionized in bulk state, so that the polymer chain can unwind rapidly in the solution. Besides, the advantages of this complex polymeric flocculant over common polymeric flocculants included fast precipitation, easy dosage control, and more satisfactory performance.

Practical Application

A practical application of CPF was actualized for Wuxi Paper Mill (Jiangsu Province, China). The wastewater treatment was carried out and the results are shown in Figures 5–8. The relationships between various parameters of the wastewater and the dosage of CPF and pH of the solution indicated that CPF could reduce the surface potential by compressing the double layer, thus enhancing aggregation between particles.

Negative zeta potential of the colloidal in wastewater at neutral state, shown in Figure 5, accounted for an acid waste mass. The basic component of CPF, aluminum sulfate, and calcium oxide could contribute to aggregation rather than the organic component. The efficient dosage of CPF was 0.2 g/L for cleansing water (Fig. 6) and for COD removal (Fig. 7), but was 0.5–0.6 g/L for reducing the zeta potential (Fig. 8).

CONCLUSION

CPF containing inorganic and polymeric components was not a simple mixture of them but a complex combined by chemical bond. Because of the poly(acrylic acid) ionized in the bulk state, the polymer chain of CPF could extend extremely in the wastewater. The rate of treatment process was faster and the transmittancy of the wastewater after treatment was higher than those treated by inorganic or polymeric flocculant alone.

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