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Synthesis of Poly(vinyl pyrrolidon-co-acrylamide) Flocculants by Radical Polymerization

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The copolymerization of acrylamide (AAm) and 1-vinyl-2-pyrrolidon (VP) using disodium salt of 4,4'-azo-bis(4-cyanopentanoic acid) (ACPA-Na) as water-soluble catalyst was carried out to yield poly(acrylamide-co-1-vinyl-2-pyrrolidon) in aqueous solution at 70°C. The cross-linking of the polymer formation of water-insoluble polymer could be avoided by the addition of K_2CO_3 to raise the pH of the reaction mixture above 7.0. The copolymers were used as flocculants in the flocculation of suspension of tincal concentrate and showed good flocculating properties.

Key Words: Synthesis, Radical polymerization, Copolymerization, Poly(vinyl pyrrolidon-co-acrylamide), Flocculants.

INTRODUCTION

Polyacrylamide (PAAm) and acrylamide copolymers have been used as effective flocculants for various types of solid-liquid separations[1–3]. In these applications, polymeric flocculants based on PAAm operate by a variety of mechanisms including bridging, charge neutralization and complex formation. In flocculation, the most important factors are the molecular weight, adsorption, structure and charge density of the polymer[4]. When considering the bridging mechanism of flocculation, it is essential to consider the particle concentration as well as the charge type of the high molecular weight polymer. Cationic polymers are electrostatically attracted to the negatively charged particle surface. Anionic polymers must penetrate the repulsive electrical double layer before adsorption can occur. But nonionic polymers do not see the electrical double layer. They are neither strongly attracted like cationic polymers or repelled like anionic polymers. Adsorption is through weaker forces such as hydrogen bonding and molecular weight appears to play an important role[5]. There are several processes suitable for the production of high-molecular weight water-soluble polymers. Some redox catalyst which can initiate the polymerization at relatively low temperature has been used industrially to produce high molecular weight polymers[6]. We have recently obtained water-soluble PAAm with high molecular

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weight using some redox initiator[7, 8]. Additionally, we have also synthesized high molecular weight poly(acrylamide-b-ethyleneglycol-b-acrytamide) triblock copolymer by photopolymerization[9].

EXPERIMENTAL

Acrylamide (AAm) (Merck) and 1-vinyl-2-pyrrolidon (VP) (Merck) were purified by conventional methods. 4,4′-Azo-bis(4-cyanopentanoic acid) (ACPA) (Fluka) was used as purchased. Disodium salt of ACPA was prepered by reaction of aqueous NaOH with ACPA. PAAm based, commercial polymeric flocculants called Magnofloc 351 and Superfloc N100 were supplied by Cyanamid Company and Allied Colloids Limited. These commercial flocculants have nonionic character and their structures are not defined by the producers. Tincal ore was supplied from Kirka borax plant (Turkey) which is the largest borax deposit of the world.

Copolymerization of Acrylamide and 1-vinyl-2-pyrrolidone

Monomers (AAm and VP) containing a known amount of disodium salt of ACPA, K_2CO_3 and water were outgassed in the usual manner and placed in a thermostat at 70°C. At the end of the polymerization, the reaction mixtures were poured into a ten-fold excess of acetone and the precipitated polymers filtered and dried under reduced pressure at 40°C. Viscosity measurements of aqueous solutions of the polymers were made in an Ubbelohbe viscosimeter at 30°C.

Flocculation Test:

Polymers obtained above were studied in jar-test experiments by using a simple laboratory method[7–9]. PAAm based conventional polymeric flocculants were used for comparison. These flocculants were chosen because they are recommended for the flocculation of tincal concentrate. Full description of polymers used in jar-tests is given in Table 1. In flocculation experiments, used tincal concentrate (enriched tincal ore) contains 27% water-insoluble material. Appropriate amount of tincal concentrate, determined from the solubility in water at 15°C, was dissolved in distilled water and stirred for 30 min at 130 rpm. Different volumes of polymer solution (0.05% w/w) were added to the suspension while stirring at 60 rpm. The suspension was then mixed for 2 min at 130 rpm after which the suspension was allowed lo settle for 30 min. Supernatant samples were filtered and the turbidity was measured on a Hach turbidimeter. The effect of polymer concentration on flocculation was determined as 14.7 mg/L by jar test results and all experiments were carried out at this concentration.

RESULTS AND DISCUSSION

Copolymerization of acrylamide and 1-vinyl-2-pyrrolidone

The copolymerization of AAm and VP was carried out by free radical mechanism using a water-soluble azo-initiator. Low molar concentration of ACPA-Na was used to yield high molecular weight copolymers in all experiments. The cross-linking caused by the imidation of the two amide groups of acrylamide was prevented by the addition of K_2CO_3. The copolymerization results are shown in Table-1.

Flocculation

Polymers obtained in this study and some commercial polymers were used as flocculants to clear an aqueous solution of colloidal tincal solids. The results are presented in Table-1.

TABLE-1
SYNTHESIS OF PAAm-PVP COPOLYMERS AND JAR-TEST RESULTS FOR SUSPENSION OF TINCAL CONCENTRATE

VP: 2.5 mol/L, AAm 2.5 mol/L, P_8 and P_9 are commercial polymers,.

Code	ACPA-Na (mol/L)	K_2CO_3 (mol/L)	Time (h)	Yield (g)	η (mL/g)	Supernatant turbidity (NTU)
P_1	4.28×10^{-3}	0.23	1	15.46	98	10^a
P_2	2.14×10^{-3}	0.23	1	12.40	89	12^a
P_3	1.03×10^{-3}	0.23	1	9.63	79	13^a
P_4	2.61×10^{-4}	0.23	1	2.28	33	18^a
P_5	7.83×10^{-5}	0.54	4	4.44	61	12^b
P_8	—	—	—	—	89	27^b
P_9	—	—	—	—	147	30^b

a: optimum polymer dosage 14.7 mg/L, b: optimum polymer dosage 9.8 mg/L

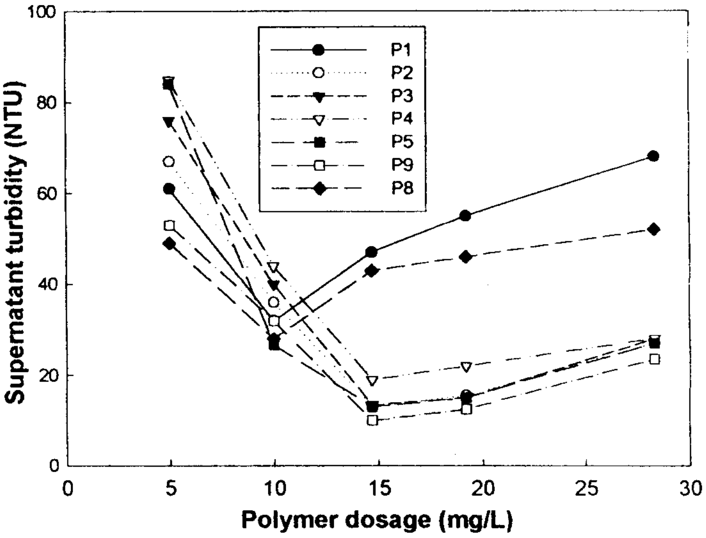

Fig. 1. The effect of polymer dosage on flocculation (the initial turbidity of all of the suspensions is higher than 200 NTU)

The turbidities of flocculated samples as a function of flocculant content were also shown in Fig. 1. As can be seen from Table-1 and Fig. 1, there are some differences in flocculation activity between commercial polymers and copolymers obtained in this study. This might be related to differences in molecular weight distribution or unknown structural variations of the commercial polymers such as branching. Therefore, each flocculant should be considered separately. On the other hand, on considering all of the polymers used in jar-tests are nonionic, molecular weight distribution appears to play an important role in flocculation. Polymers obtained in this study have higher optimum polymer dosage than commercial polymers.

In flocculation tests, after the optimum polymer dosage is obtained, the supernatant turbidity increases. It is well known that, if excess polymer is adsorbed, the particles can become restabilized because of surface saturation or by steric stabilization. It is also interesting to note that these copolymers have lower turbidity value at the same polymer dosage. It is known that the copolymers of acrylamide have better flocculating properties than homopolyacrylamides[9]. Therefore, it can be said that the structure of polymer as well as molecular weight plays an important role in flocculation. According to these results, polymers obtained in this study can be used as flocculants instead of commercial polymers for flocculation of tincal concentrate.

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