Separation and Purification Technology 106 (2013) 90–96

Contents lists available at SciVerse ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Consolidation of suspended particles by using dual ionic thermosensitive polymers with incorporated a hydrophobic component

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ARTICLE INFO

Article history:
Received 29 September 2012
Received in revised form 18 December 2012
Accepted 19 December 2012
Available online 8 January 2013

Keywords:
Thermosensitive polymer
Hydrophobic interaction
Consolidation
Dual ionic polymers
Hydrophobic component

ABSTRACT

The flocculation/consolidation of suspended particles using the hydrophobic transition of a thermosensitive polymer is a promising method for sludge dewatering. However, flocculation/consolidation using thermosensitive polymers requires heating of the suspension. Furthermore, although ionic thermosensitive polymers are usually effective for flocculation/consolidation of charged suspended particles, the transition temperature increases when the ionic component is incorporated into the thermosensitive polymer. To alleviate this problem, we proposed the use of dual ionic (i.e. cationic and anionic) thermosensitive polymers. The use of an anionic thermosensitive polymer in combination with a cationic thermosensitive polymer resulted in the formation of a polymer complex. As a result, the transition temperature of the polymer molecules adsorbed on the suspended particles decreased. However, heating of the sludge was still required. In this work, a hydrophobic component was incorporated into the ionic thermosensitive polymers to decrease the transition temperature, and the consolidation of suspended particles using these dual ionic thermosensitive polymers was examined. *N*-isopropylacrylamide, *N*,*N*-dimethylaminopropyl acrylamide, acrylic acid, and *N*-*tert*-butylacrylamide (BAAM) were used as the thermosensitive, cationic, anionic, and hydrophobic components, respectively. By incorporating BAAM into either cationic or anionic thermosensitive polymers, the transition temperature of these ionic thermosensitive polymers decreased. The consolidation of kaolin suspension was observed near room temperature by adding the anionic polymer with the incorporated BAAM in combination with the cationic polymer.

1. Introduction

Polymeric flocculants have been widely used in the flocculation and dewatering of sludge. It is well known that the flocculation of suspended particles using hydrophilic polymeric flocculants occurs by the bridging of the suspended particles through the polymer molecules [1,2]. However, the flocs formed by conventional polymeric flocculants are usually bulky and contain a large amount of water. This is attributed to the hydrophilicity of the solid surface and the polymer molecules. It is difficult to remove this large amount of water effectively by the conventional mechanical dewatering method. Recently, thermosensitive polymers have attracted considerable interest as flocculants to alleviate this problem [2–7]. Thermosensitive polymers are soluble in water at low temperatures. However, they are insoluble above the intrinsic transition temperature of the polymer because of a transition to hydrophobicity. This intrinsic temperature is referred to as the lower critical solution temperature (LCST) or the transition temperature. Poly(*N*-isopropylacrylamide) (poly(NIPAM)) is a representative nonionic thermosensitive polymer with a transition temperature of about 32 °C [8,9].

The use of thermosensitive polymers as flocculants was reported in the 1980s. Guillet and Heskins [10] reported that below the transition temperature, cationic thermosensitive polymers were effective flocculants that exhibited behaviors similar to cationic polyacrylamide, whereas above the transition temperature, the copolymers were not effective flocculants. In contrast, Deng and Pelton [11] found that the cationic thermosensitive polymer (poly(NIPAM-*co*-diallyldimethylammonium chloride)) induced the flocculation of a TiO_2 suspension even at temperatures above the transition temperature. These findings were explained by the fact that the cationic copolymer consisted of cationic colloidal particles above the transition temperature. On the other hand, recent studies have been based on the hydrophilic/hydrophobic transition or the conformational change of polymer molecules adsorbed on suspended particles.

Authors of this article also proposed the flocculation/consolidation mechanism based on the hydrophilic/hydrophobic transition of thermosensitive polymers more than 10 years ago [12,13]. The flocculation/consolidation procedures are as follows. First, by mixing the suspended particles with the thermosensitive polymer below its transition temperature, the surface of the particles is

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http://dx.doi.org/10.1016/j.seppur.2012.12.030

sufficiently covered by adsorbed polymer molecules. Similar to the excess dosage condition in the conventional flocculation process using polymeric flocculants, these particles are stably dispersed. When this suspension is heated above the transition temperature, the polymer molecules adsorbed on the particles become hydrophobic. As a result, the surface of the suspended particles also becomes hydrophobic, and flocs are formed because of these hydrophobic interactions [5,14]. The subsequent application of an adequate mechanical force to the flocs causes the particles in the flocs to rearrange, thereby discharging the water molecules and leading to consolidation.

Franks and coworkers proposed a procedure to achieve enhanced consolidation of the sediment bed [3,4]. The mechanism of floc formation by the hydrophobic interaction of thermosensitive polymers adsorbed on the suspended particles was basically the same as that proposed by the authors of this article, but the procedure to achieve consolidation was different. In their approach, after the sediment bed was obtained, the temperature was decreased below the transition temperature of the polymer to re-solubilize the polymer. This reduced the inter-particle attractive force and allowed enhanced consolidation. In contrast, in the mechanism proposed by the authors, the application of an adequate mechanical force to the flocs causes the particles in the flocs to rearrange, thereby discharging the water molecules and leading to consolidation.

The mechanism proposed by the authors was confirmed using kaolin-poly(NIPAM); compacted kaolin sludge could be easily obtained on the basis of the hydrophobic transition of poly(NIPAM) [12,13]. Furthermore, this method was applied to the dewatering of the activated sludge, and a lower water content in the dewatered cake was achieved compared with that from commercial flocculants [15]. However, the authors found that the use of nonionic poly(NIPAM) had limitations, and the ionic thermosensitive polymers were effective for the consolidation of suspended particles with a high surface charge. In addition, there was a serious problem in the use of ionic thermosensitive polymers: the transition temperature increased remarkably, compared with that of nonionic poly(NIPAM), when the copolymerization ratio of the ionic component increased [16].

To alleviate this problem, the authors proposed the use of dual ionic thermosensitive polymers, i.e., cationic and anionic thermosensitive polymers [17,18]. The use of an anionic thermosensitive polymer in combination with a cationic thermosensitive polymer results in the formation of a polymer complex. As a result, the transition temperature of the polymer molecules adsorbed on the suspended particles decreases [19]. However, heating of the sludge is still required. In this work, a hydrophobic component was incorporated into the ionic thermosensitive polymers to decrease the transition temperature, and the consolidation of the suspended particles using these dual ionic thermosensitive polymers was examined.

2. Experimental

2.1. Preparation of cationic and anionic thermosensitive polymers with incorporated hydrophobic component

The cationic thermosensitive polymer was prepared by copolymerizing the cationic component, *N,N*-dimethylaminopropyl acrylamide (DMAPAA, Kohjin Co., Ltd., Japan), with NIPAM (Kohjin Co., Ltd., Japan). The incorporation of a hydrophobic component into the cationic thermosensitive polymer was performed by copolymerizing *N-tert*-butylacrylamide (BAAM, Sigma–Aldrich Inc., USA) with NIPAM and DMAPAA. The anionic thermosensitive polymer was prepared by copolymerizing acrylic acid (AAC, Katayama Chem. Ind. Co. Ltd., Japan) with NIPAM; and BAAM was copolymerized to incorporate the hydrophobic component. The chemical structures of these monomers are shown in Fig. 1. The compositions of these polymers are listed in Table 1. Previously reported polymerization procedures were used to prepare the polymers [12]. These polymers were prepared by radical polymerization using *N,N,N′,N′*-tetramethylethylenediamine (Kishida Chem. Co., Ltd., Japan) and ammonium peroxodisulfate (Kanto Chem. Co., Inc., Japan) as the polymerization accelerator and initiator, respectively. A mixture of water and acetonitrile (Sigma–Aldrich Inc., USA) in a volume ratio of 5:1 was used as the solvent in the copolymerization of the hydrophobic component (BAAM) [20].

2.2. Measurement of transition temperatures of polymers

An aqueous solution of a thermosensitive polymer is transparent below the polymer's transition temperature, because the polymer molecules are hydrophilic and soluble in water. However, when the solution is heated above the transition temperature, the solution becomes milky white because the polymer molecules become hydrophobic, and thus, insoluble in water. Therefore, the transition temperature is usually estimated on the basis of the changes in the transmittance through the polymer solution, with temperature. The transition temperatures of the cationic and anionic thermosensitive polymers that were not copolymerized with BAAM were measured by this method. The transmittance was measured at 600 nm using a spectrophotometer equipped with a temperature control system (V-530, Japan Spectroscopy Co., Ltd.). The polymer concentration was 0.5 wt.%.

However, by incorporating BAAM, a long period was required for the polymer solution to change from transparent to opaque near the transition temperature, and gelation was observed. Considering this phenomenon, in this study, the transition temperatures of the polymers with incorporated BAAM were estimated by measuring the temperature dependence of the shear stress using a rotating viscometer (RE80, Toki Sangyo Co., Ltd., Japan).

2.3. Consolidation experiments

Consolidation experiments were performed with a plunger test using a highly concentrated kaolin suspension (250 kg/m^3, Sigma–Aldrich Japan K.K.) to clearly visualize the consolidation. Sodium hydroxide (NaOH) was used as a dispersant, and the kaolin suspension was prepared in 1 mM NaOH aqueous solution. The pH of the suspension was about 4.3. It was reported that the isoelectric point or point of zero charge of kaolin particles produced by Sigma–Aldrich was observed at pH ≈ 2.3, and that kaolin particles were negatively charged above that pH [21]. The procedure for the consolidation experiment shown in Fig. 2 was the same as that previously reported [12,16]. First, 60 ml of kaolin suspension was stirred in a beaker using a magnetic stirrer at room temperature. Then, 20 ml of cationic thermosensitive polymer solution of the desired concentration was added to the suspension, and the mixture was stirred vigorously for 5 min. Subsequently, 20 ml of anionic thermosensi-

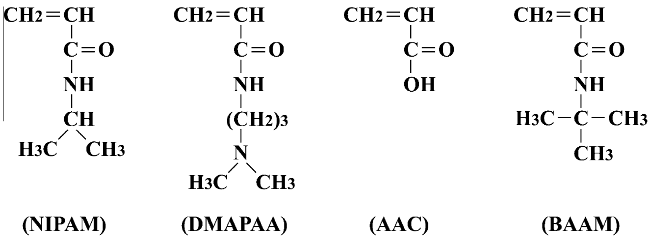

Fig. 1. Chemical structures of NIPAM, DMAPAA, AAC, and BAAM.