Sludge Dewatering Utilizing Hydrophilic/Hydrophobic Transition of Thermosensitive Polymers
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ABSTRACT

Thermosensitive polymers are soluble in water at low temperature, but are insoluble above the intrinsic temperature of the polymer because of the transition to the hydrophobicity. Poly(N-isopropylacrylamide) (poly(NIPAM)) is a representative nonionic thermosensitive polymer, with a transition temperature of about 32°C. In this work, a novel dewatering method of activated sludge utilizing the hydrophilic/hydrophobic transition of thermosensitive polymers was examined. Cationic thermosensitive copolymers of NIPAM and N,N-dimethylaminopropylacrylamide (DMAPAA) synthesized with various DMAPAA contents were used. The activated sludge and the polymer solution were mixed well at room temperature. The mixture was heated to the desired temperature, and then the constant pressure filtration and expression were carried out. The temperature of the filtration/expression apparatus was kept at the desired one during the dewatering, i.e., the filtration and expression processes. When the dewatering was carried out at the room temperature, the moisture content of the dewatered cake increased with increasing the polymer dosage, because the sludge covered sufficiently with the adsorbed hydrophilic polymer molecules is dispersed stably. On the other hand, by dewatering above the transition temperature of the polymer, which depended on the content of DMAPAA in the polymer, the moisture content of the dewatered cake decreased remarkably with increasing the polymer dosage. The dewatering performance depended on the temperature and the content of DMAPAA in the copolymer. Such a high dewatering performance with thermosensitive polymers are attributed to the hydrophobic interaction of thermosensitive polymer molecules adsorbed on the sludge.

KEYWORDS
thermosensitive polymer, dewatering, activated sludge, hydrophobic interaction

INTRODUCTION

In the field of water treatment, high molecular weight polymeric flocculants have been widely used in the flocculation of suspended particles and sludge dewatering. It is well known that flocculation of suspended particles using these polymeric flocculants occurs by bridging the suspended particles
through polymer molecules (Sakohara et al., 1981). However, the formed flocs are usually bulky and contain large amount of water. The high water content of the flocs is attributed to the hydrophilicity of the solid surface and the polymer molecules. So, it is difficult to remove sufficiently this large amount of water by conventional mechanical dewatering methods.

In an effort to alleviate this problem, the authors proposed a novel flocculation/compaction method using thermosensitive polymers (Sakohara and Nishikawa, 2000; Sakohara et al., 2002). Thermosensitive polymers are soluble in water at low temperature, but are insoluble above the intrinsic transition temperature of the polymer. A hydrophilic/hydrophobic transition in a thermosensitive polymer is reversible. Poly(N-isopropylacrylamide) (poly(NIPAM)) is a representative nonionic thermosensitive polymer, with a transition temperature of about 32°C (Ito, 1989).

Flocculation of suspended particles with thermosensitive polymers was described in a patent by Guillet et al. (1985). This method employed cationic thermosensitive polymers prepared by copolymerizing NIPAM with cationic monomers. The main claim of their patent was that below the transition temperature, the cationic thermosensitive polymers were effective flocculants exhibiting behavior similar to that of cationic polyacrylamide, whereas above the transition temperature, the copolymers were not effective flocculants. In contrast, Deng et al. (1996) found that the cationic thermosensitive polymer (poly(NIPAM-co-diallyldimethylammonium chloride)) induced the flocculation of TiO₂ suspension, even at temperatures above the transition temperature. These findings were explained due to the fact that the cationic copolymer consisted of cationic colloidal particles above the transition temperature. On the other hand, we previously reported (Sakohara and Nishikawa, 2000) that with a highly concentrated kaolin suspension, the compacted kaolin sludge was easily obtained upon the hydrophilic/hydrophobic transition of poly(NIPAM). The concept describing the compaction mechanism involves the hydrophobic interaction, which is described in the following section (Sakohara et al., 2002).

In this work, the compaction method of suspended particles utilizing the hydrophilic/hydrophobic transition of thermosensitive polymers mentioned above was applied to the dewatering of activated sludge. For such a application, ionic thermosensitive polymers might be effective. Thus, cationic thermosensitive polymers were synthesized.

**COMPACTION MECHANISM OF SUSPENDED PARTICLES BY THERMOSENSITIVE POLYMER**

Figure 1 shows a schematic representation of the compaction mechanism of suspended particles involving the hydrophobic interaction of thermosensitive polymers proposed by the authors (Sakohara et al., 2002). First, by mixing the suspended particles with the thermosensitive polymer molecules below the transition temperature of the polymer, the surface of the suspended particles is sufficiently covered with the adsorbed polymer molecules. Similar to the excess dosage condition in the conventional flocculation operation with polymeric flocculants, these particles were considered to be stably dispersed. By heating
this suspension above the transition temperature, the polymer molecules adsorbed on the surface of particles become hydrophobic. As a result, the surface of the suspended particles becomes hydrophobic. The particles aggregate and the flocs are formed due to these hydrophobic interactions. Subsequent application of an adequate mechanical force to the flocs induces the particles in the flocs to re-arranged, discharging water molecules from the flocs and leading to compaction. The flocs disorganize and return to the stable suspended particles upon cooling below the transition temperature of the polymer, because the hydrophilic/hydrophobic transition of thermosensitive polymer is reversible. The compaction mechanism shown here was confirmed using poly(NIPAM) and kaolin suspension (Sakohara and Nishikawa, 2000; Sakohara et al., 2002).

**MATERIALS AND METHODS**

\(N,N\)-dimethylaminopropylacrylamide (DMAPAA, Kohjin Co. Ltd.) was used as the cationic component, in addition to NIPAM of the thermosensitive component. The chemical structures of these monomers are shown in Figure 2. NIPAM (Kohjin Co. Ltd) was purified by re-crystallization from hexane, and DMAPAA was used without further purification. \(N,N,N',N'\)-teteramethyl-ethylenediamine and ammonium peroxodisulfate were used as the polymerization accelerator and the initiator, respectively. These chemicals were reagent grade.

![Figure 1. Schematic diagram of the compaction mechanism for suspended particles using a thermosensitive polymer.](image)

![Figure 2. Chemical structures of NIPAM and DMAPAA.](image)
Preparation of cationic thermosensitive polymers

Four kinds of cationic thermosensitive polymers with different DMAPAA contents were prepared. The mole ratios of DMAPAA monomer in preparing these cationic copolymers were 0.05, 0.1, 0.2 and 0.3, for CP-5, -10, -20 and -30, respectively. Nonionic poly(NIPAM) was also prepared for use as a control. These polymers were synthesized by free radical polymerization. The procedures previously reported were used to prepare the polymers (Sakohara and Nishikawa, 2000). The conditions for synthesis are shown in Table 1.

<table>
<thead>
<tr>
<th>Monomer:</th>
<th>N-isopropylacrylamide (NIPAM)</th>
<th>750</th>
<th>750</th>
<th>500</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-monomer:</td>
<td>N,N-dimethylaminopropylacrylamide (DMAPAA)</td>
<td>40</td>
<td>82</td>
<td>125</td>
<td>214</td>
</tr>
<tr>
<td>(Mole ratio: NIPAM/DMAPAA)</td>
<td>(95/5) (90/10) (80/20) (70/30)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accelerator:</td>
<td>N,N,N',N'-tetramethylethylenediamine</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Initiator:</td>
<td>Ammonium peroxodisulfate</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Synthesis temperature : 25°C
Solvent : water

Measurement of transition temperature of poly(NIPAM-co-DMAPAA)

The aqueous solution of thermosensitive polymer was transparent below the transition temperature of the polymer, because the polymer molecules are hydrophilic and water-soluble. However, upon heating the solution above the transition temperature, the solution becomes milky white because the polymer molecules become hydrophobic and thus water-insoluble. Therefore, the transition temperature can be estimated by the changes in the transmittance through the polymer solution with temperature. The transmittance of a 5 kg/m³ aqueous polymer solution was measured at 600 nm using a spectrophotometer equipped with a temperature control system (V-530, Japan Spectroscopy Co., Ltd.). The measurements were performed under various pH conditions, because it is well known that the transition temperatures of cationic thermosensitive polymers are pH dependent.

Sludge dewatering method

Activated sludge samples were supplied from the wastewater treatment plant in Higashi-Hiroshima city. The sludge concentration was around 2.5 kg/m³ in the experimental period. The dewatering test was performed with the constant pressure filtration/expression apparatus, in which a piston pressed the sludge at the constant pressure and the dewatering was done through a filter paper on
the sintered metal plate. First, the activated sludge of 450 ml and the polymer solution of 50 ml with the desired polymer concentration were mixed well at room temperature in a stainless steel agitation tank with six baffle plates. The agitation was done at 400 rpm with a paddle blade for 5 min. Then the tank was transferred to a water bath controlled at the desired temperature, and the agitation was continued for 30 minutes at 200 rpm. The mixture was transferred to the filtration/ expression apparatus, and the constant pressure of 0.22 MPa was applied for 1 hour. The displacement of a piston was measured by a CCD laser displacement sensor and recorded (Keyence Co.). The temperature was kept constant at the desired one during the filtration and expression processes. Finally, the dewatered cake was taken out, and the moisture content was measured by drying the cake at 105°C for one night. In this paper, the dewatering performance is estimated by the moisture content.

RESULTS AND DISCUSSION

Transition temperature of poly(NIPAM-co-DMAPAA)

Figure 3 shows the change in the transmittance with temperature through the aqueous solutions of nonionic poly(NIPAM) and four kinds of cationic copolymers, poly(NIPAM-co-DMA-PAA), CP-5, -10, -20 and -30. The pH of these aqueous solutions was adjusted to about 9. The transmittance of polyNIPAM solution changed drastically around 32°C, the transition temperature of poly(NIPAM). On the other hand, the temperature, at which the transmittance of poly(NIPAM-co-DMAPAA) solution changes drastically, shifted to higher temperature as the DMAPAA content in the copolymer increased. In other words, the transition temperature increased. The change in the transmittance with temperature was reversible.

In addition, the transition temperature of cationic copolymer depended on pH of the solution. The transition temperatures of these cationic copolymers were quite high in the neutral pH region and were observed to decrease with increasing pH.

Figure 3. Temperature dependence of transmittance through aqueous solutions of poly(NIPAM) and cationic copolymers, poly(NIPAM-co-DMAPAA) prepared with various DMAPAA contents.
Effects of polymer dosage and heating of sludge on moisture content in cake

Figure 4 shows the effect of the polymer dosage on the moisture content in the dewatered cake. The experiments were performed at 25°C and 50°C using CP-5 polymer. At 25°C, CP-5 polymer works as a hydrophilic polymer, and the moisture content increased as the polymer dosage increased. This phenomenon indicates that in the same manner as common polymeric flocculants the sludge disperses stably by adding CP-5 polymer excessively. On the other hand, at 50°C the moisture content decreased with increasing the dosage of CP-5 polymer. This finding suggests that the compaction of sludge occurs by the hydrophobic interaction of CP-5 adsorbed on the sludge as expected.

Effect of DMAPAA content in copolymer on moisture content in dewatered cake

Figure 5 shows the effect of the DMAPAA content in poly(NIPAM-co-DMAPAA) thermosensitive polymers on the moisture content in the dewatered cake. CP-5, -10, -20 and -30 polymers were used. The polymer dosage was 0.05 kg/kg-sludge, and the dewatering temperature was 50°C. The moisture content decreased as the DMAPAA content in the copolymer increased in the experimental range. This result suggests that the neutralization of the surface charge of sludge by the adsorption of the ionic groups in the copolymer is important for the compaction of sludge by the hydrophobic interaction.
Temperature dependence on moisture content in dewatered cake

Figure 6 shows the temperature dependence of the moisture content in the dewatered cake obtained by using CP-5 and -30 polymers. In case of CP-5 polymer, the moisture content decreased as the temperature increased, and increased a little at 70°C. The optimum temperature was observed. This finding is considered as the followings: High temperature might be more effective for the hydrophobic interaction of thermosensitive polymers. But the higher temperature damages the activated sludge. It can be guessed from the fact that the color of the solution released from the dewatering apparatus changed to be yellow. Therefore, it can be said that the dewaterability rather decreases at the higher temperature. On the other hand, in case of CP-30 polymer, the moisture content decreased as the temperature increased in the experimental range. Furthermore, the moisture content decreased largely above 50°C, though the transition temperature of CP-30 polymer is quite high as shown in Figure 2. This result suggests that the transition temperature of thermosensitive polymer absorbed on the sludge is differ from that measured in aqueous solution.

CONCLUSIONS

Activated sludge dewatering utilizing the hydrophilic/hydrophobic transition of cationic thermosensitive polymer was developed. The moisture content in the dewatered cake decreased with increasing the temperature and the DMAPAA content in the copolymer in the experimental range (the maximum DMAPAA content: 30 mol%), though the extremely high temperature damages the sludge and makes the dewaterability decrease. The decrease in the moisture content was observed at relatively low temperature compared with the transition temperature measured in aqueous solution. This result suggests that the transition temperature of the copolymer adsorbed on the sludge differs from that measured in aqueous solution.
REFERENCES