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Synthesis and characterization of a novel cationic chitosan-based flocculant with a high water-solubility for pulp mill wastewater treatment

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ABSTRACT

In this work, pulp mill wastewater was treated using a novel copolymer flocculant with a high water-solubility, which was synthesized through grafting (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) onto chitosan initiated by potassium persulphate. The experimental results demonstrate that the two main problems associated with the utilization of chitosan as a flocculant, i.e., low molecular weight and low water-solubility, were concurrently sorted out. The physicochemical properties of this flocculant were characterized with Fourier-transform infrared spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy, X-ray powder diffraction and field emission scanning electron microscopy. Reaction parameters influencing the grafting percentage, such as temperature, reaction time, initiator concentration and monomer concentration, were optimized using an orthogonal array design matrix. With an increase in grafting percentage, the water-solubility of the flocculant was improved, and it became thoroughly soluble in water when the grafting percentage reached 236.4% or higher. Its application for the treatment of pulp mill wastewater indicates that it had an excellent flocculation capacity and that its flocculation efficiency was much better than that of polyacrylamide. The optimal conditions for the flocculation treatment of pulp mill wastewater were also obtained.

1. Introduction

There are more than 10,000 papermaking mills in China, and more than 63% of the mills are using the straw slurry as the feedstock. It is estimated that for each ton of paper produced, about 10–15 m^3 wastewater is generated. The large amount of base (such as alkali lignin and sodium salts of organic acids) in the wastewater increases the difficulty of treatment. In general, there are two methods for the treatment of pulp mill wastewater. One method is to be concentrated and then used as fuels to recover the energy and base. Another method is to be acidized at about 70–80 °C firstly to precipitate the lignin, followed by flocculation and biological treatment. However, these two methods will expand a great deal of additional energy and are expensive. On the other hand, the abundant lignin existing in the wastewater could not be reclaimed efficiently and thus increases the burden of the biological treatment. Therefore, a convenient and cost-effective method, e.g., flocculation, for the pretreatment of pulp mill wastewater prior to biological treatment is necessary. In this case, an

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efficient and environmentally friendly flocculant that could be used under basic conditions is highly desirable for the pretreatment of pulp mill wastewater.

Utilization of natural or modified natural polymers as flocculants for wastewater treatment has recently attracted increasing interests (Xiao et al., 1995; Yang et al., 2004; Franks, 2005). Chitosan, the second most abundant natural organic resource next to cellulose on the earth, has been extensively used as a flocculant for wastewater treatment and sludge dewatering, as it is nontoxic, biodegradable and environmentally friendly (Bratskaya et al., 2004). When chitosan is used as a flocculant, its molecular weight and water-solubility are both most concerned factors (Divakaran and Pillai, 2004). Its high molecular weight is favorable for improving the aggregation of colloids, thus promoting the separation of aggregates with water, but because of the inter-molecular and intra-molecular hydrogen bonding, chitosan can only be dissolved in an acidic solution through the interaction between H^+ and $–NH_2$. However, at pH lower than 5, the acidic condition could accelerate the degradation of chitosan and consequently reduce its flocculation efficiency (Divakaran and Pillai, 2004). On the other hand, so far, all the modifications of chitosan could only improve one of the two factors, either molecular weight or water-solubility, but not both (Sashiwa et al., 2001; Li et al., 2004; Bratskaya et al., 2004). In our previous studies, two types of flocculants based on chitosan were prepared using the grafting method, which were initiated by gamma-ray radiation (Wang et al., 2007a, 2008). However, such a modification resulted in only an improvement of molecular weights, rather than water-solubility.

Grafting has been proven to be an effective modification technique for chitosan, as there are abundant amino groups and hydroxyl groups in chitosan backbone, which could react with vinyl monomers under mild conditions (Lazaridis et al., 2007). A large amount of work has been carried out to perform grafting copolymerization of chitosan and vinyl monomers (Jenkins and Hudson, 2002; Neira-Carrillo et al., 2005; Lazaridis et al., 2007; Zhou et al., 2007). The graft copolymers could be biodegradable to some extent because of the presence of polysaccharide backbone, and also be stable against shearing because of the attachment of flexible synthetic polymers onto rigid or semi-rigid polysaccharide backbones (Rath and Singh, 1997). In addition, the flexible grafting chain would increase the possibility for the flocculant to approach to particles in wastewater, and thus improve the flocculation ability (Singh, 1995). Because colloids in the pulp mill wastewater are negatively charged, the cationic flocculant is suitable for charge neutralization, and thus favorable for the flocculation of the wastewater. However, synthetic cationic polymers, e.g., PDMC [poly (2-methacryloyloxyethyl) trimethyl ammonium chloride], are expensive and hydrophilic, which makes them difficult for transportation and storage, and thus holdbacks their application. Moreover, their molecular weights are not sufficiently high for a flocculant. Therefore, synthesis of a cationic flocculant without these disadvantages of the synthetic cationic monomer is highly desirable for the pretreatment of pulp mill wastewater.

Taking into account all the factors above, a cationic monomer, (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC), was selected as the monomer grafted onto chitosan initiated by potassium persulphate to prepare a flocculant for the pretreatment of pulp mill wastewater in this work. The introduction of DMC onto chitosan backbone was expected to increase the molecular weight and cationic content, and to improve its water-solubility. The synthetic flocculant, chitosan-*g*-PDMC [chitosan-*graft*-poly (DMC)] was characterized, its flocculation ability was evaluated by jar tests with kaolin suspensions, and it was used for the treatment of the pulp mill wastewater.

2. Materials and methods

2.1. Synthesis of the chitosan-based flocculant

The grafting reaction was initiated by a radical initiator, potassium persulphate. Since the deprotonated C-2 amino group in chitosan is a powerful nucleophile ($pK_a \approx 6.5$) (Ashmore and Hearn, 2000), it could react with electrophilic reagents readily. Such a reaction process is illustrated in Fig. 1.

The chitosan with a molecular weight of 520 kDa and a deacetylation degree of 95% concentration was kept at 0.115 mol/L throughout the experiment. First, chitosan and DMC solution were prepared with 1.0% acetic acid in a three-necked flask with constant stirring and bubbling of a slow stream of nitrogen at ambient temperatures. Then, the flask was placed in a preset water bath and a given amount of potassium persulphate was added into the solution as an initiator. After that, the mixture was continuously stirred with a mechanical stirrer under nitrogen atmosphere. At the end of reaction, the sample solutions were precipitated in acetone and separated through filtration. Thereafter, the homopolymer formed in the reaction was removed using ethanol in Soxhlet apparatus. The extracted products were dried in a vacuum oven at 50 °C until a constant weight was obtained. The grafting percentage was calculated according to the following equation:

$$\%\ \text{grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of original and grafted samples, respectively.

2.2. Characterization of the chitosan-based flocculant

Infrared spectra of chitosan and the flocculant were recorded with a Fourier-transform infrared spectroscopy (FTIR) spectrometer (Magna-IR 750, Nicolet Instrument Co., USA) using a potassium bromide disc technique (Lim et al., 2008). The ^1H nuclear magnetic resonance spectroscopy (^1H NMR) spectra were measured on a 300-MHz spectrometer (AVANCE) with standard pulse programs in D_2O (Chang et al., 2002). X-ray powder diffraction (XRD) patterns of the polymers were obtained with an X-ray diffractometer (D/Max-rA, Japan) with graphite monochromatized Cu Kα radiation ($\lambda = 1.54056$ Å). Field emission scanning electron microscopy (FESEM) images of chitosan and chitosan-*g*-PDMC particles were obtained using a JSM-6700F electron microscope (JEOL CO., Japan). All samples were metalized with gold prior to the analysis.

Flocculation ability of chitosan and chitosan-*g*-PDMC with different grafting percentages was evaluated using the same