Evaluation of structural effects on the flocculation performance of a co-graft starch-based flocculant

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A B S T R A C T

The molecular structure of a material substantially determines its final application performance. In this work, a series of starch-based flocculants with different charge densities and average graft chain lengths were prepared by the co-graft polymerization of acrylamide and [(2-methacryloyloxyethyl) trimethyl ammonium chloride] (St-g-PAM-co-PDMC). The flocculation performance of St-g-PAM-co-PDMC was studied systematically at neutral pH using kaolin suspension and sodium humate (NaHA) aqueous solution as synthetic wastewaters. The effects of the two structural factors on the flocculation efficiency of the starch-based flocculants have been investigated. The experimental results showed that the charge density and average graft chain length contributed distinctly to flocculation performance during the removal of both kaolin particles and NaHA under insufficient and excessive flocculant dose conditions. The flocculation mechanisms of this starch-based flocculant were discussed in detail on the basis of the structure-activity relationship, which are significant to optimize the flocculation conditions and guide the development of novel high-performance flocculants.

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1. Introduction

Coagulation/flocculation removes the suspended colloidal particles and various dissolved contaminants from water bodies to achieve efficient solid-liquid separation and water purification (da Silva et al., 2016; Jiang, 2015; Yang et al., 2016). Thus, coagulation/flocculation is considered as a highly important technique in water treatment and plays an indispensable role in many environmental strategies. Obviously, the final coagulation/flocculation performance is largely dependent on the coagulants/flocculants used.

Traditional coagulants/flocculants mainly include inorganic coagulants, such as polyaluminium chloride and polyferric sulfate, as well as synthetic organic polymeric flocculants (Jiang, 2015; Lee et al., 2014; Matilainen et al., 2010), such as polyacrylamide (PAM) and its derivatives. These conventional compounds are widely applied in water treatment plants because of their high water purification efficiencies and reasonable costs (Joo et al., 2007; Li et al., 2005; Renault et al., 2009). However, the residual metal ions of inorganic coagulants and the released noxious monomers from synthetic organic polymeric flocculants in water bodies bring serious health risks (Bolto and Gregory, 2007; Okuda et al., 2014; Renault et al., 2009; Stechemesser and Dobiáš, 2005).

Natural polymer-based flocculants, such as starch (St), chitosan, and cellulose, have recently received increased research attention because of their environmental friendliness, biodegradability, and variety of sources (Bolto and Gregory, 2007; Crini, 2005; Guibal et al., 2006; Laue and Hunkeler, 2006; Sharma et al., 2006; Vijayaraghavan and Yun, 2008; Yang et al., 2016). To improve the flocculation performance of these natural polymers, scholars have used many chemical modification methods, including graft, etherification, and esterification, and obtained various types of natural polymer-based flocculants to generate different applications (Bratskaya et al., 2004; Huang et al., 2016; Laue and Hunkeler, 2006; Liu et al., 2014; Lu et al., 2011, 2014; Rani et al., 2012; Sen et al., 2009; Song et al., 2009; Sonmez et al., 2002; Wang et al., 2011, 2013; Wu et al., 2016). The methods were realized because of the existence of numerous active groups, such as hydroxyl and amino groups, which can be easily modified (Bolto and Gregory, 2007; Crini, 2005; Guibal et al., 2006; Laue and Hunkeler, 2006; Sharma et al., 2006; Vijayaraghavan and Yun, 2008; Yang et al., 2016). As a result, different functional groups can be introduced onto the polysaccharide backbone (Bratskaya et al., 2004; Huang et al., 2016; Laue and Hunkeler, 2006; Liu et al., 2014; Lu et al., 2011, 2014; Rani et al., 2012; Sen et al., 2009; Song et al., 2009;

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The performance of a material is highly dependent on its molecular structure (Elias, 1984; Flory, 1953; Yang et al., 2016). A material's quantitative structure-activity relationship is greatly significant to successfully facilitate the precise control of the molecular structure and thus improve the final application performance. For natural polymer-based flocculants, various structural factors are involved, such as charge density (CD), grafting ratio, degree of functional group substitution, and distributions. However, previous investigations on the structural effects of polymeric flocculants, including natural polymers, on flocculation performance were quite limited and unsystematic (Bratskaya et al., 2004; Huang et al., 2016; Liu et al., 2014; Lu et al., 2011, 2014; Rani et al., 2012; Sen et al., 2009; Song et al., 2009; Sonmez et al., 2002; Wang et al., 2011, 2013; Wu et al., 2016; Yang et al., 2016).

Starch is a low-cost and highly popular natural polymer material (BeMiller and Whistler, 2009; Bolto and Gregory, 2007; Huang et al., 2016; Wu et al., 2016). In the present study, a series of different CDs and average graft chain lengths (Ls) of the co-graft St-based flocculant, starch-*graft*-polyacrylamide-co-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] (St-*g*-PAM-co-PDMC), was prepared. The procedure involved adjusting the mass feeding ratio of two co-graft monomers, namely, acrylamide (AM) and [(2-methacryloyloxyethyl) trimethyl ammonium chloride] (DMC), which are neutral and strongly cationic monomers respectively. A kaolin suspension and a sodium humate (NaHA) aqueous solution were selected as synthetic wastewaters representative of natural water mainly containing inorganic suspended colloids and water-soluble organic contaminants respectively. The flocculation efficiencies of the various St-*g*-PAM-co-PDMC flocculants were then studied systematically at neutral pH. The effects of both CD and L of this St-based flocculant on flocculation behavior have been investigated and discussed in detail. The two aforementioned structural factors were simultaneously considered to reveal their individual relationships with flocculation performance. The flocculation mechanisms are discussed in detail on the basis of the structure-activity relationship.

2. Materials and methods

2.1. Materials

Starch (St, approximately 1.5×10^5 g/mol weight-average molecular weight) was obtained from Binzhou Jinhui Corn Development Co., Ltd. Kaolin (average particle diameter ~4.18 μm), AM, and toluidine blue O (TBO) were purchased from Sinopharm Chemical Reagent Co., Ltd. Poly(vinyl sulfate) potassium salt (PVSK) and NaHA were obtained from Aladdin Industrial Corporation. DMC (Shanghai Bangcheng Bilogical Technological Co., Ltd.), ammonium persulfate (APS; Shanghai Lingfeng Chemical Reagent Co., Ltd.), and other chemicals were used as received without further purification. Distilled water was used in all the experiments.

2.2. Preparation of St-g-PAM-co-PDMC

A desired amount of solid St was dispersed in 100 mL water with continuous stirring under N_2 atmosphere at 80 °C for 1.0 h. After full gelatinization, the St aqueous mixture was cooled down to 55 °C. A known amount of APS aqueous solution as the initiator was then added rapidly to the mixture, and a St-to-APS mass ratio of 1:0.1 was achieved. The system was maintained for 10 min for St pretreatment by the initiator to suppress the self-polymerization of the two monomers (Sonmez et al., 2002). Next, the mixed aqueous solution of AM and DMC monomers was added to the St mixture dropwise. The amounts of St and APS were both kept constant, but

the masses of the two monomers were varied for each synthesis experiment to obtain a series of co-graft St-based samples with different CDs and Ls. The detailed mass ratios of St to each of the two monomers are listed in Table 1. After a 3-h reaction under N_2 atmosphere, the copolymerization was stopped by pouring the sample solution into acetone, and the obtained white precipitates were St-*g*-PAM-co-PDMC. The obtained crude co-graft product was then purified three times by a repeated dissolving-precipitating treatment, followed by Soxhlet extraction using ethanol as solvent for 72 h. Finally, the product was vacuum-dried at room temperature for 48 h. Six final co-graft samples were named from St-1 to St-6, with each containing increasing feeding masses of AM (Table 1).

2.3. Characterization

2.3.1. Spectral characterization

The molecular structures of St-*g*-PAM-co-PDMC were basically characterized by Fourier transform infrared (FTIR; Bruker Model IFS 66/S) spectroscopy and ^1H nuclear magnetic resonance (^1H NMR; Bruker Ascend 400) spectroscopy. The wave numbers measured by FTIR ranged from 500 cm^{-1}–4000 cm^{-1}. ^1H NMR was operated at 400 MHz using D_2O as the solvent.

2.3.2. Charge density

The CD of St-*g*-PAM-co-PDMC was determined by colloidal titration (Zhang et al., 2012). A St-*g*-PAM-co-PDMC aqueous solution with a known concentration was titrated using a PVSK standard solution, an anionic polyelectrolyte. TBO was used as indicator. The calculated CDs of the various co-graft St-based samples are all listed in Table 1.

2.3.3. Average graft chain length

Here, L was defined as the average number of the grafted monomers per branched chain, which is far different from the hydrodynamic size of polymer in a solution (Elias, 1984; Flory, 1953). The actual L of a graft copolymer is highly difficult to determine precisely using current characterization methods, because the initiator's initiation efficiency and graft copolymerization efficiency are affected by various environmental factors (Fanta, 1973). Herein, L was roughly estimated in theory on the basis of some assumptions. First, all initiated free radicals would efficiently propagate graft chains for the initiator in each synthesis experiment. Besides, APS can dissociate into two free radicals after initiation. Thus, the number of graft chains was positively correlated to the twice of the mole number of the initiated initiator. Given that the reaction time was 3 h in this case and the half-life of ammonium persulfate was about 60 h (FMC Corporation, 2001), the percentage of the actual disassociated APS (η) here was about 3.4%. As aforementioned, the mass feeding ratio of St to APS was kept constant at about 1:0.1. Accordingly, the number of graft chains (N) was estimated by Eq. (1) as 0.005, i.e., 5 per 1000 saccharide rings, as follows:

$$N = \frac{2 \cdot \eta \cdot m_{(APS)} \cdot M_{(St)}}{M_{(APS)} \cdot m_{(St)}} \tag{1}$$

where $m_{(APS)}$ and $m_{(St)}$ are the mass amounts of APS and St respectively, and $M_{(APS)}$ and $M_{(St)}$ are the molar masses of APS and the saccharide ring of St respectively.

Second, in the graft copolymerization, the two monomers were all grafted onto the St backbone, since the yields of products were all quite high more than 90%. The graft copolymerization efficiency was assumed as 1.0. The last one involved the two monomers AM and DMC fully randomly entering the graft chains. Therefore, the Ls