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Research article

Dual functionality of a graft starch flocculant: Flocculation and antibacterial performance

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ABSTRACT

In this work, a series of quaternary ammonium salt grafted starch flocculant, starch-*graft*-poly(2-methacryloyloxyethyl) trimethyl ammonium chloride (St-*g*-PDMC), with different grafting ratios was prepared by a simple method. Various characterization techniques were employed to investigate the structure and charge property of the starch-based flocculants. The efficiencies of St-*g*-PDMC for flocculation of kaolin and *Escherichia coli* suspensions as well as their mixtures were systematically examined in laboratory scale. In addition to environmental factors, such as flocculant dose and pH, the effects of grafting ratio were also evaluated. Results indicated that St-*g*-PDMCs exhibited dual functionality of high flocculation effects and antibacterial properties. Moreover, the flocculation and antibacterial mechanisms were investigated in detail based on apparent flocculation performance, charge properties, floc structures (floc size and its two-dimensional fractal dimension), and cell surface morphology, respectively.

1. Introduction

Water treatment agents, including coagulants/flocculants, bacteriostatic/bactericidal agents, scale inhibitors, etc., play very important roles in the field of water treatment (Li, 2005). However, traditional water treatment agents usually possess single functionality only, causing a wide variety of agents with high doses, complicated devices, and fussy operations in actual applications (Li, 2005). Therefore, it is of great significance to develop multi-function water treatment agents containing coagulation/flocculation, bacteriostasis/sterilization, and scale inhibition in both scientific researches and practical applications (Huang et al., 2016a, 2016b; Xiao, 2008). After combination of various functionalities into one agent, the multi-functional materials may have the potentials of more cost efficiency and wider application ranges (Derek, 1971; Huang et al., 2016a; Xiao, 2008; Zhang et al., 2014).

Flocculation and disinfection are two necessarily steps in drinking water treatment (DeZuane, 1997; Goncharuk, 2014). However, rapid industrial development and population growth lead to continued contamination of surface water and groundwater, contributing to serious deterioration of water qualities (Schwarzenbach et al., 2006; Shannon et al., 2008). As a result, required doses of flocculants and disinfectants have increased to meet the national drinking water health standards. Accordingly, the treatment costs have increased remarkably, as well as the secondary pollution risk of disinfection byproducts (DBPs) produced in disinfection processes using chlorine (Bond et al., 2011; Fang et al., 2010; Sadiq and Rodriguez, 2004; Strand et al., 2001). Therefore, a dual-function agent for water treatment with high-efficiency flocculation and antibacterial properties is needed. In fact, bacteria flocculation for biomass harvesting using existing coagulants/flocculants has been employed for biotechnological purposes (Chang, 2011), but their antibacterial activity was rarely found and reported in water treatment.

Recently, considerable attention has been given to natural polymers owing to their wide availability, environmental friendliness, and biodegradability (Guibal et al., 2006; Hebeish et al., 2010; Renault et al., 2009; Szygula et al., 2009; Verma et al., 2012; Yang et al., 2011b, 2016). Among them, starch is considered one of the high-performance, low-cost natural polymeric materials (Sen et al., 2009; Huang et al., 2016a; Wu et al., 2016). Many kinds of efficient starch-based flocculants have been developed for water treatment because they are inexpensive, biodegradable, shear stable, and effective (Hansel et al., 2014; Pal et al., 2005; Vandamme et al., 2009; Wang et al., 2013; Wu et al., 2016). However, little work has been reported regarding dual-function starch-based flocculants

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(Huang et al., 2016a, 2016b), and their widespread use need experimental validation in field operation. In particular, in-depth study of the synergistic mechanisms would further provide a theoretical basis for research and development of dual-function water treatment agents based on structure–activity relationships.

Grafted quaternary ammonium salt groups onto polymers are mostly beneficial to both flocculation and antimicrobial activity for the enhancement of positively charge characteristics, given that most inorganic suspended colloidal particles and microbes in water possess negative surface charges (Jiang et al., 2010; Mishra et al., 2011; Song et al., 2009). Moreover, the dangling branches on the polymeric flocculants' backbone cause easier accessibility to and adsorption of contaminants in water (Wu et al., 2016; Yang et al., 2016). Starch-*graft*-poly(2-methacryloyloxyethyl) trimethyl ammonium chloride (St-*g*-PDMC) is a kind of quaternary ammonium salt grafted starch flocculants, which showed good performance in both turbidity removal and sludge dewatering (Wang et al., 2013). However, its dual-functional performance has not been investigated yet. In the present work, a series of St-*g*-PDMC with different grafting ratios was prepared by graft copolymerization. The flocculation and antibacterial properties of St-*g*-PDMC were investigated in detail. Kaolin and *Escherichia coli* suspensions, as well as their mixtures, were employed as synthetic wastewaters in laboratory experiments. Besides two environmental factors, i.e., flocculant dose and pH, the effects of grafting ratio were also evaluated systematically. The flocculation mechanism of St-*g*-PDMC was further investigated on the basis of apparent flocculation performance, zeta potential (ZP) of supernatants after flocculation, and floc properties (i.e., floc size and two-dimensional fractal structure), respectively. The antibacterial mechanism was studied from the three-dimensional excitation-emission matrix (3D EEM) spectra and direct cell morphological observation by scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

Starch (St), of which weight-average molecular weight is approximate 1.5×10^5 g/mol, was purchased from Sinopharm Chemical Reagent Co., Ltd. (2-Methacryloyloxyethyl) trimethyl ammonium chloride (DMC, Shanghai Bangcheng Biological Technol. Co., Ltd.) and ammonium persulfate (APS, Shanghai Lingfeng Chemical Reagent Co., Ltd.) were used without further purification. Luria broth (LB) powder from Beijing Aoboxing Bio-tech Co., Ltd. was composed of 20 wt% yeast extract, 40 wt% tryptone, and 40 wt% sodium chloride. Agar powder was obtained from Sigma-Aldrich Co., Ltd. All other chemicals were purchased from Nanjing Chemical Reagent Co. Ltd. Distilled water was used in all experiments.

2.2. Preparation of St-g-PDMC

5.0 g of starch was dispersed in 100 mL of water and then stirred under N_2 for 60 min at 80 °C. After gelatinization, the mixture was cooled to 55 °C. 0.5 g of APS as the initiator was added and kept for 10 min for pretreatment of starch by the initiator to suppress the formation of PDMC homopolymer (Sonmez et al., 2002). Then, the aqueous solution of DMC monomer was added dropwise for 20 min. The reaction was allowed to proceed for 3.0 h under N_2, and then stopped by precipitating the sample solution in acetone. The obtained solid product was filtered, washed with ethanol, extracted using ethanol as solvent in a Soxhlet apparatus for 72.0 h to remove all the impurities, and then vacuum-dried at room temperature. For further comparison, four different St-*g*-PDMCs with various grafting ratios, i.e., St-*g*-PDMC1, St-*g*-PDMC2, St-*g*-PDMC3, and St-*g*-PDMC4, were prepared only by changing the feeding weight ratios of the raw materials (starch to DMC) at 1:0.5, 1:1, 1:1.5, and 1:3, respectively, during preparation. St-*g*-PDMCs were finally stored as solid powders to achieve long-term shelf stability.

2.3. Characterization

The molecular structures of St-*g*-PDMCs were characterized by Fourier transform infrared (FTIR, Bruker Model IFS 66/S) spectroscopy with the measured wavenumber from 400 to 4000 cm^{-1} and ^1H nuclear magnetic resonance (^1H NMR, Bruker AVANCE Model DRX-500) spectroscopy using D_2O as solvent. The ZP of different sample solutions were recorded by a Malvern Model Nano-Z Zetasizer in a wide pH range from 2.0 to 10.0, which was adjusted by 0.01 mol/L HCl or 0.01 mol/L NaOH aqueous solutions. A Hitachi F-7000 fluorescence spectrophotometer was employed to record the 3D EEM spectra of the supernatants before and after flocculation using St-*g*-PDMC2. The excitation wavelength is 200–450 nm, and the emission spectra are in the range of 280–550 nm. The width of the excitation and emission slit is 10 nm with the scanning speed of ~2400 nm/min. The SEM (FEI Quanta 250 FEG, USA) images of *Escherichia coli* (*E. coli*) before and after flocculation by St-*g*-PDMC2 were obtained at an acceleration voltage of 25.0 kV.

2.4. Bacterial culture

Escherichia coli (CMCC 44102) was cultured in the liquid LB medium (LLB) at 37 °C in 500 mL of presterilized glass flasks for 24.0 h before tests. LLB was prepared by dissolving 25.0 g of LB powder into 1.0 L of water, adjusting the pH to 7 using dilute NaOH aqueous solution, and then sterilizing in an autoclave at 121 °C for 15 min beforehand. Cells were separated by centrifugation at 3000 rpm for 5 min, and then diluted and dispersed in deionized water to obtain a stable *E. coli* suspension, which was used as synthetic bacteria effluent.

2.5. Flocculation experiments

A six-place paddle flocculator was used to carry out the standard jar tests in 1.0 L jars. Stock solution of St-*g*-PDMC was prepared freshly by dissolving 0.1 g of the flocculant into 100 mL of distilled water before each test. Three kinds of synthetic wastewater were prepared: (1) 0.1 wt% of kaolin suspension; (2) freshly dispersed *E. coli* with initial cell density of approximately 1.0×10^8 CFU/mL; and (3) mixed suspension of kaolin (0.1 wt%) and *E. coli* (1.0×10^8 CFU/mL). After the pH of synthetic wastewater was adjusted to the designed value with 0.1 mol/L HCl or 0.1 mol/L NaOH aqueous solutions, a known amount of flocculant stock solution was fed into each jar under rapid mixing at 200 rpm for 5 min, then a slow mixing step at 50 rpm for 15 min. Finally, the mixture was kept still to settle without stirring for 60 min for ensuring the flocculation equilibrium. Samples were then collected at a depth of 2.0 cm in the supernatant for further ZP analysis. Each measurement was repeated three times, and the final results were the average of three runs. The relative errors of experimental results were all less than 5.0%.

The flocculation performance of St-*g*-PDMC for purification of various synthetic suspensions was determined by measuring the transmittance of the treated water during the flocculation experiments by a 722s model spectrophotometer (Shanghai Lengguang Tech. Co.) at a wavelength of 600 nm. The removal rate was defined in Eqs. (1) and (2):