Colloids and Surfaces A: Physicochem. Eng. Aspects 455 (2014) 28–35

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Amphoteric starch-based flocculants can flocculate different contaminants with even opposite surface charges from water through molecular structure control

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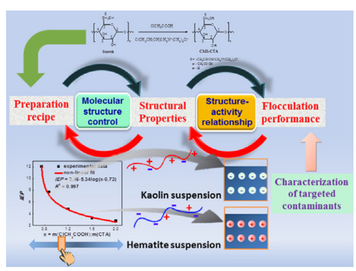
HIGHLIGHTS

- A starch-based flocculant (CMS-CTA) was prepared by molecular structure control.
- The ratio of anion/cation moieties on the starch was changed.
- CMS-CTA can flocculate different contaminants with even opposite surface charges.
- The structure–activity relationship of CMS-CTA was built.
- Quantitative correlation between preparation recipe and structural feature was built.

GRAPHICAL ABSTRACT

Through molecular structure control, i.e. controlling mass feed ratio of anion/cation modifiers, amphoteric starch-based flocculants can flocculate different contaminants with even opposite surface charges from water.



ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form 11 April 2014
Accepted 15 April 2014
Available online 24 April 2014

Keywords:
Molecular structure control
Structure–activity relationship
Amphoteric starch-based flocculants
Flocculation performance
Isoelectric point

ABSTRACT

Flocculation is one of the most widely applied techniques in water treatment. Polysaccharide-based flocculants have been paid much attention for their eco-friendliness recently. However, precise molecular structure control is greatly important in improving their flocculation performance. In this work, a series of amphoteric starch-based flocculants with different substitution degrees of functional groups (3-chloro-2-hydroxypropyl trimethyl ammonium chloride modified carboxymethyl starch, denoted as CMS-CTA) was synthesized. The flocculation experiments confirmed that the well-designed CMS-CTA flocculants exhibited improved performance in both optimal dosage and pH sensitivity, for not only kaolin, but also hematite suspensions, which have opposite surface charges. Further quantitative mathematical correlations among the preparation recipe, structural features, and flocculation properties were built, providing operational feasibility in the precise molecular control of the flocculants to achieve their desired flocculation performance. Additional experimental results demonstrated that a suitable flocculant could be designed successfully according to the characteristics of the targeted contaminants and structure–activity relationship, proving the effectiveness of molecular structure control for optimization of the flocculation process.

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http://dx.doi.org/10.1016/j.colsurfa.2014.04.043
0927-7757/

1. Introduction

Flocculation is an important technique for solid–liquid separation in water treatment works because of its facile operation and high efficiency [1–4]. Traditional inorganic-based and synthetic polymeric flocculants cause potential secondary pollution [5,6]; thus, natural bioresource-based flocculants have recently emerged as promising environment-friendly alternatives that address the public concerns [7–16]. Among these bioresource-based flocculants, starch, one of the most abundant polysaccharides with relatively low cost, has attracted considerable attention [2,17–19]. Since most suspended colloidal particles carry some charges in aqueous media [20], the attraction and approachability to these particles can be greatly enhanced when the flocculants have opposite charges because of the significant effects of charge interaction in flocculation [2,14]. Thus, several studies [2,21,22] have focused on introducing certain ionic groups onto the starch backbone through chemical modification.

Nevertheless, the contaminants in real water are normally complicated. The surface charges of suspended colloidal particles can either be negative or positive. Single ionic-type flocculants in previous studies [2,21,22] are incapable of interacting with a wide variety of contaminants. Instead, amphoteric ones [14,17,23], containing both cations and anions, are necessitated. Furthermore, the property of surface charge is diversified at different pH conditions even for the same contaminant. The imprecise design or the current selection of flocculants is insufficient in exerting desirable flocculation performance.

The performances of materials fully depend on their structure, and can be greatly improved by precise molecular structure control according to their structure–activity relationship [24–26]. Thus, designing or selecting appropriate flocculants based on the relationship between structural characteristics and flocculation performance is expected to be an effective solution for the efficient flocculation of contaminants with diverse features in water. However, little work concerning this strategy has been reported in the field of flocculation.

In view of the aforementioned aspects, a kind of amphoteric starch-based flocculants, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride modified carboxymethyl starch (CMS-CTA), was synthesized through a cost-effective one-pot process in the present study. The molecular structure of CMS-CTA was controlled by adjusting the mass feed ratio of the raw materials. The activities of the starch-based flocculants were examined at various pHs against different contaminants, even those with opposite surface charges in water, including kaolin, which is commonly present in natural turbid water [14], and hematite, which commonly exist in mineral processing operations [27]. More importantly, the relationship among the preparation recipe, structural feature of the flocculants, and flocculation property were quantitatively determined to guide the precise structure control of the flocculants for better flocculation performance. Finally, an additional experiment was carried out to demonstrate the effectiveness of the molecular structure control in the preparation of proper flocculants.

2. Materials and methods

2.1. Raw materials

Natural corn starch was obtained from Binzhou Jinhui Corn Development Co., Ltd., which weight-average molecular weight is approximate 1.5×10^5 g/mol. Monochloroacetic acid (Zibo Lushuo Economic Trade Co., Ltd.) and CTA (Wuhan Yuancheng Technology Development Co., Ltd.) were both used without further purification. Kaolin, with an average particle diameter of 4.18 μm, was purchased from Sinopharm Chemical Reagent Co., Ltd., whereas hematite, with an average particle diameter of 0.18 μm, was purchased from Strem Chemicals Inc. The rest of the chemicals were purchased from Nanjing Chemical Reagent Co., Ltd.

2.2. Synthesis of CMS-CTA

A series of CMS-CTA was prepared according to the process shown in Fig. 1(a).

The detailed synthesis method is described as follows. A desired amount of previously dried starch was added into a three-necked flask with 100 mL of 5 wt% NaOH solution to facilitate swelling and alkalization at 70 °C in a water bath for 1 h. An aqueous mixture with known amounts of monochloroacetic acid and CTA was then added dropwise into the flask. The reaction was carried out for 2 h at 70 °C, followed by the adjustment of the pH value of the solution to 7.0 with a dilute HCl aqueous solution. Afterward, the sample was precipitated in ethanol. The obtained solid product was filtered and washed by ethanol for three times. Finally, the product was extracted in a Soxhlet apparatus for 72 h, using ethanol as solvent, to remove all the impurities [14], and then vacuum dried at 45 °C, thereby obtaining CMS-CTA. Six different CMS-CTA samples with various substitution degrees of functional groups were prepared in this work. The detailed preparation recipe is listed in Table 1.

2.3. Structural characterization

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Model IFS 66/S FTIR spectrometer, within the wave number range of 3800 cm^{-1} to 600 cm^{-1}. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded with a Bruker AVANCE Model DRX-500 spectrometer operating at 500 MHz, with standard pulse programs in D_2O. Zeta potential (ZP) was measured on a Malvern Model Nano-Z zetasizer. Water solubility of CMS-CTA samples was tested according to the reported method [28], which was estimated from measurement of transmittance of the solution using a spectrophotometer. All characterization experiments were performed at room temperature.

2.4. Flocculation performance

Jar tests were conducted using 1 L jars and a six-place programmed paddle flocculator model of TA6 (Wuhan Hengling Tech. Co., Ltd.) at room temperature to evaluate the flocculation performance of the starch-based flocculants. After adding 1 g of kaolin or hematite into 1 L of distilled water, the suspension underwent ultrasonic stirring at 200 rpm for 3 min. The suspension was designated as synthetic wastewater. pH was adjusted by dilute HCl or NaOH aqueous solutions. Stock solutions of various CMS-CTA flocculants were always freshly prepared with distilled water. All flocculants were fully dissolved with magnetic stirring in 5 min.

After adding a known amount of stock solution of flocculants into the synthetic wastewater, the jar tests consisted of an initial period of rapid mixing at 200 rpm for 5 min for the primary floc formation, a period of slow mixing at 50 rpm for 15 min for floc growth, and finally, a period without stirring for 40 min for floc sedimentation. After these three steps, the supernatant was immediately collected and analyzed for both ZP and transmittance by a Malvern Model Nano-Z zetasizer and a UNIC Model UV2100 UV–vis spectrophotometer at the wavelength of 550 nm, respectively.