Colloids and Surfaces A: Physicochem. Eng. Aspects 520 (2017) 841–849

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Fabrication of a cationic polysaccharide for high performance flocculation

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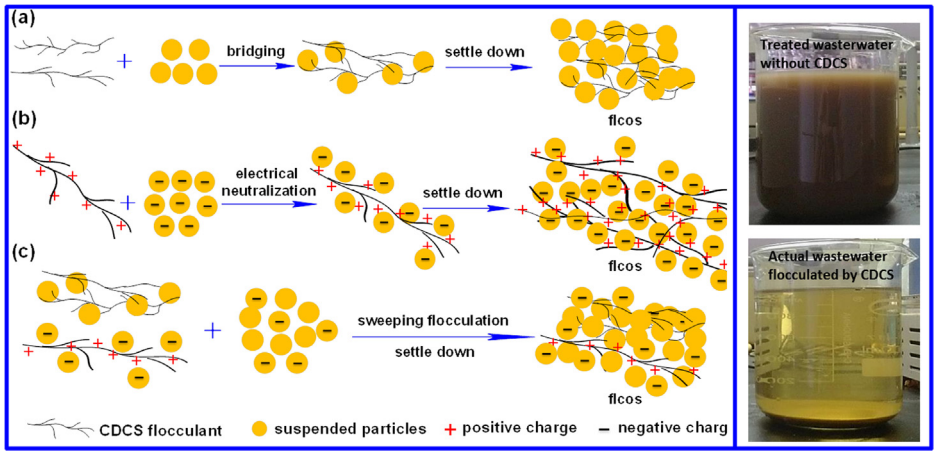
HIGHLIGHTS

- The CDCS flocculant was fabricated by crosslinking method.
- The CDCS overcame the shortcomings of chitosan and dextran in flocculation.
- The CDCS presented enhanced high flocculation performances in a wide pH range.
- The flocculation mechanism included charge neutralization, bridging and sweeping.
- The CDCS performed much better than commercial polyacrylamide and ferric sulfate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 December 2016
Received in revised form 9 February 2017
Accepted 24 February 2017

Keywords:
Polymer
Flocculation
Chitosan
Dextran
Water treatment

ABSTRACT

A cationic polysaccharide (CDCS) derived from dextran and chitosan was fabricated by crosslinking method as an eco-friendly flocculant. The flocculant was characterized by thermogravimetric analysis and Fourier transform infrared spectroscopy. Influences of temperature, pH and flocculant dosage on flocculation efficiency were examined. The CDCS presented enhanced high flocculation properties in a wide pH range conditions. In kaolin suspension, when pH was in the rang of 3–7, the flocculation efficiency was over 96.9% with dosage below 5 mg/L. In alkaline condition, it also presented a high flocculation efficiency of 98.2% (pH = 9) and 93.7% (pH = 11) with a low dosage of 7 and 17 mg/L, respectively. The flocculation efficiency decreased as the temperature rose from 10 to 40°C. For actual wastewater treatment, the CDCS flocculant performed much better than commercial polyacrylamide and ferric sulfate. It removed 97.7% of the solid suspended particles in the wastewater. The flocculant mechanism study suggested charge neutralization, adsorption bridging and sweeping flocculant mechanisms were included in the flocculation process. The flocculant CDCS exhibited a broad prospects for wastewater treatment.

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http://dx.doi.org/10.1016/j.colsurfa.2017.02.078
0927-7757/

1. Introduction

Flocculation is an efficient and widely applied technology for wastewater treatment [1–4]. Flocculants are the core materials for flocculation, which are used in solid-liquid separations by an aggregation process of colloidal particles [5]. There are a lot of inorganic and organic flocculants reported in literatures [6–8]. Inorganic flocculants such as aluminium chloride, ferric sulfate and polyaluminum chloride generally require a high dosage to be efficient or contaminate the biomass with metal salts [9–11]. The use of alum may lead to the hazard potential derived from residual aluminum and the excess use of iron flocculant may cause unpleasant metallic taste, odor, corrosion or stainin, which make their application limited [12]. Thus, organic flocculants have been developed as an alternative. The synthetic organic flocculants are most frequently used in industrial applications because of their low cost. However, they are not biodegradable and some of their degraded monomers such as acrylamides are neurotoxic and even show strong carcinogenic potential [13]. For the purpose of environmental friendliness and sustainability, organic flocculants with biodegradable properties have been investigated as replacements [14,15]. Natural polysaccharides based flocculants such as chitosan, cationic starch, cellulose and tannins are considered as promising because they are biodegradable and their degradation intermediates are harmless to human and the environment [16,17].

Chitosan is an attractive alternative as a flocculant since it is the second most abundant and unique positively charged natural polysaccharide [18]. It contains a lot of free amino groups and is excellent in flocculation for various wastewater from pulp mills, printing and dyeing, mineral processing, and oil industry [19]. Nevertheless, owing to the inter- and intra-molecular hydrogen bonding, chitosan is water insoluble providing high moisture barrier and water resistance [20]. It can be only dissolved in acidic solution through the interaction between H^+ and-NH_2, which limits its application as a flocculant [21]. In order to sort out this problem, lots of efforts have been focused on the modification of chitosan by methods including grafting, crosslinking, polyelectrolyte complexation, carboxymethylation and etherification [22]. Among various modification techniques for chitosan, covalent crosslinking is recognized as most promising, because the abundant amino groups and hydroxyl groups in chitosan backbone can react with other activate function groups [5]. Dextran, a hydrosoluble polysaccharide, has good biocompatibility, hydrophilicity, and nonfouling properties, and can provide enhanced colloidal stability of water-insoluble polymers such as polylactide when conjugated with [23,24]. However, its application as flocculant is limited due to its high water affinity and brittleness, which cause loss of physical structure [23]. To improve these drawbacks, it is usually modified with other natural biopolymers [24], among which chitosan is a good candidate. Therefore, we assumed that fabrication of flocculant through modification of dextran and chitosan by cross-linking could provide great complementary and produce an efficient, stable and biocompatible flucculant. As far as we known, there are few work reported flocculant derived from chitosan and dextran.

Herein, a cationic polysaccharide (CDCS) based on dextran and chitosan was investigated and used as an eco-friendly flocculant for wastewater treatment. Dextran was cationic modified and crosslinked onto the chitosan macromolecular chain as a complementary component to get enhanced flocculation properties. This flocculant was first synthesized in our laboratory. Cationic dextran crosslinked onto the chitosan macromolecular chain improved the positive zeta potential and increased the polymer-pollutants-polymer adsorption bridging function of the flucculant, but also made it effective in a wide pH range. The obtained product was characterized by thermogravimetic analysis and Fourier transform infrared spectroscopy. The flocculant was used to treat kaolin suspension and actual wastewater. Effects of initial pH, CDCS dosage, and temperature on flocculation properties were studied. The flocculation performance of CDCS was compared with those of commercial flocculants, polyacrylamide (PAM) and ferric sulfate (FS).

2. Materials and methods

2.1. Materials

Chitosan (molecular weight 5.0×10^5, deacetylation over 95%) was purchased from Jinan Tianben Biological Technology Co. Ltd, China. Sodium hydroxide, ethanol, and acetic acid were purchased from Shanghai Chemical Reagent Co. Ltd, China. Dextran, (3-Chloro-2- hydroxypropyl) trimethylammonium Chloride (60% in H_2O) and epichlorohydrin 98% were bought from Aladdin. Polyacrylamide (PAM, mean molecular weight 5×10^6) was obtained from Shanghai Chemical Reagent Co. Ltd, China. Ferric sulfate (FS), was obtained from Tianjin Chemical Regent Co. Ltd, China.

2.2. Synthesis of cationic dextran

Cationic dextran (CDT) was prepared by reacting dextran with (3-Chloro-2- hydroxypropyl) trimethylammonium chloride under the condition of pH = 11. The pH of the solution was adjusted to the desired value with 0.1 mol/L HCl and 0.1 mol/L NaOH. Typically, 3.24 g dextran was dissolved in 10 mL deionized water, and then the pH value of the mixture was adjusted to 11. After that, 3-Chloro-2- hydroxypropyl-trimethylammonium chloride was injected in gradually. At last, the mixture was heated to 70 °C and reacted for 6 h. The obtained CDT was washed with 85% ethanol aqueous solution, separated by centrifugation, and then dried in a vacuum oven at 50 °C for 4 h. The nitrogen content of CDT was estimated using a vario El cube elemental analyzer and the degree of substitution (*DS*) was calculated from nitrogen content [26]:

$$DS = \frac{162N}{1400 - 151.5N} \quad (1)$$

N is the mass percentage of nitrogen element in the sample. The *DS* of CDT synthesized in this experiment was 0.22.

2.3. Preparation of the flocculant CDCS

The flucculant CDCS was fabricated by crosslinking CDT with Chitosan (CS) in the present of epichlorohydrin as a crosslinker. Specifically, 0.7 g CDT was dispersed in 5 mL distilled water and 1 g chitosan was dissolved in 45 mL 1% acetic acid solution. They both were mixed together in a three mouth flask and stirred for 15 min using a YuHua DS-2 multi-functional stirrer. After that, the pH value was adjusted to 10, followed which 2 mL epichlorohydrin was added gradually. At last, the mixture was reacted at 70 °C for 4 h. After the reaction, the mixture was cooled down to room temperature and the pH value was adjusted to 7. The obtained flocculant CDCS was separated by centrifugation and dried in a vacuum oven at 50 °C for 4 h.

2.4. Characterization

Fourier transform infrared spectra (FT-IR) were obtained on a NICOLET, AVATAR 360 FT-IR spectrometer (USA). The spectrum widths were typically in the range of 4000–400 cm^{-1}. All the dried samples were mixed with KBr and then compressed into thin pellets. Thermogravimetric analysis (TGA) measurements were performed on a thermal analyzer (STA449C, Germany) and taken under a constant flow of nitrogen of 40 mL/min. Zeta potential was conducted with a zetasizer nano potential analyzer (Malvern Nano ZS, England) using He-Ne laser at a wavelength of 633 nm.