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An efficiently sustainable dextran-based flocculant: Synthesis, characterization and flocculation

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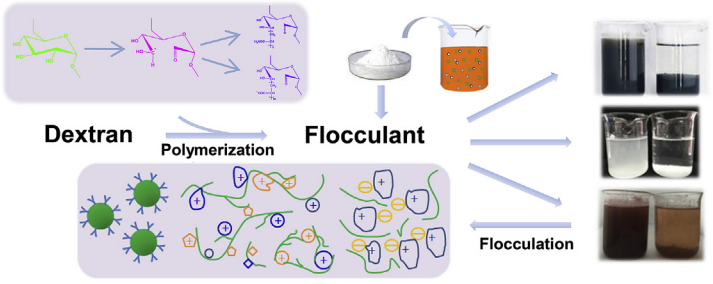
HIGHLIGHTS

- A new bio-polysaccharide polymer to separate cationic pollutants was synthesized.
- Dextran optimized by our lab has controlled high molecular weight (10,000 kDa).
- The viscosity of polymer is extremely high.
- This polymer is efficient, heat-resistant and biodegradable to water treatment.
- RSM was applied to optimize the flocculation conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Polysaccharide-modified flocculant is a notable material in the field of wastewater treatment. Synthesis of biopolysaccharide derivatives as eco-friendly flocculants is remarkably desired for environmental protection. This work presents an efficient flocculant synthesized through copolymerization of acrylamide, sodium acrylate (AS), and dextran. Physicochemical properties of the flocculant were evaluated. Process parameters of coal-washing wastewater flocculation were tested using Response Surface Method. The application of graft polymers exhibited efficient flocculation performance at low level of flocculant dosage in alkalescent environment. The improved dextran contributes to handle industrial effluent and sanitary sewage.

1. Introduction

Social development always depends on industries at the expense of resource consumption and damage to the environment. Thereby, efficient and environmentally friendly wastewater treating methods, including coagulation-flocculation, sedimentation and filtration (Poerschmann et al., 2008), have been grabbing our attention. Flocculation is of vital significance in treating industrial wastewater and can reduce the hazards caused by discharged contaminated liquids from industrial factories (Jarvis et al., 2006). Flocculants can separate solid impurities from wastewater with convenience and maneuverability (Yu et al., 2010). Various chemical flocculants, such as natural polymer products (Xing et al., 2010; Wang et al., 2007), anionic/cationic polyacrylamides (PAMs), polyferric chloride, and polyaluminum chloride (Yan et al., 2008), are widely utilized for sewage separation (Jirapraserkul et al., 2006; Zheng et al., 2013). Inorganic flocculants are widely utilized in

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different areas for their evident flocculation effect, however, they need high dosage and limited applicable scope that hardly meet the growing demand of wastewater treatment (Aguilar et al., 2005).

At present, with the emphasis on environmental protection and efficiency technology, particular attention has been focused on natural polymer materials. Many modification methods, e. g. esterification, oxidization, crosslinking and grafting, have been widely used and grafting is considered as an effective and maneuverable method (Wang et al., 2013). Hence, grafted flocculants are needed for the continuous increase of wastewater treatment market. Dextran is a natural high-molecular weight compound that is synthesized by dextransucrase with sucrose as the substrate. During the process of enzyme catalysis, alpha-D-glucose base units are sent to glucan chains to form polymers along with fructose generation. Dextran is mainly composed of alpha (1–6) links. However, alpha (1–3) and alpha (1–4) links also exist in the dextran molecular structure (Robyt et al., 2008). The unit of dextran molecular is shown in figure below:

Dextran is depolymerized mildly under vacuum heating at 100 °C, loses bound water and is discolored during heating at 150 °C, and is completely decomposed after 3 h–4 h heating at 210 °C. It is well known that stronger aggregates can be attained from polymer bridging rather than other flocculating modes (Bolto and Gregory, 2007). At this moment, flocculation effect mainly depends on high molecular weight of flocculant and very strong flocs. The molecular weight of dextran can be controlled and optimized in enzyme-catalyzed reactions. The ultra high molecular weight (HMW) dextran that is prepared in our laboratory can be modified to achieve 10,000 kDa of viscosity-average molecular weight, which is rather higher than many kinds of organic flocculants and can meet the growing requirement of HMW polymer flocculants for wastewater treatment. In addition, enzymatic method of dextran preparation yields a considerably purer product than the traditional fermentation method. Therefore, biodegradable polysaccharide flocculants that are safe, desirably efficient, and sustainable show wide applications and market prospects (Ren et al., 2016).

In the present study, a novel polysaccharide graft copolymer for environmentally friendly wastewater treatment was synthesized by a free radical polymerization method. The acrylamino and carboxyl groups grafted onto the dextran backbone enhanced the anionic properties of dextran and increased its molecular weight, viscosity, solubility and hydrophilicity, thereby promoting capture and settling. Through the determination of the optimal experiments for flocculation, we suggested an optimal flocculating window, furthermore, dextran graft copolymer was finally confirmed that it can be degraded conveniently.

2. Materials and methods

2.1. Materials

Dextransucrase was extracted from an engineered strain *E. coli* BL21 (DE3)/pET28-dexYG (Zhang et al., 2008) that was constructed based on *Leuconostoc mensenteroides* 0326 in our own laboratory. Sucrose, acrylamide (AM), anionic polyacrylamide (APAM), sodium hydroxide and kaolin were from Xilong Chemical Reagent Limited Company. The molecular weight of APAM was 20,000 kDa. Acrylic acid (Xilong Chemical Reagent Co., Ltd.) was distilled under reduced pressure for purification before use. Hematite was from Tedia Company, Inc. and coal washing sewage was from Hefei Coal Washery that initial pH, suspended solids content are 7.99 and 74,300 mg/L, respectively.

2.2. Graft polymerization

Dextransucrase synthesized dextran with sucrose as initiator primer (Robyt et al., 2008). The molecular weight of dextran changed under different reaction conditions (Gan et al., 2014). To the sucrose substrate solution (5–20%, 200 mL) prepared with 5 mM acetic acid-calcium acetate buffer solution of pH 5.4 was added dextransucrase crude enzyme (220 U/mL, 5–15 mL). The reaction solution was stirred continuously to promote the enzymatic reaction at 25 °C. After 24–28 h' reaction, HMW dextran was precipitated from ethyl alcohol.

5–15% of dextran was added to distilled water to prepare a solution with a certain concentration. Then, the dextran solution was stirred under nitrogen atmosphere until clear, and during the process nitrogen can be observed bubbling from dextran solution. 1–4 mM of the initiator primer was added into dextran solution. After 15 min of reaction with continuous stirring, the grafting monomer was added to the dextran solution. Then, the water bath was rose to around 30–50 °C and the mixture was continuously stirred for 4 h, filling with nitrogen to the container. After aggregation was finished, grafted polymer was precipitated in ethyl alcohol and placed into a mixed solution of ethylene glycol and glacial acetic acid (3:2) to dissolve unreacted dextran and monomer homopolymers. Final graft products were obtained after filtration and drying.

$$\text{Grafting ratio} = \frac{(m_2 - m_1)}{m_1} \times 100\% \quad (1)$$

where m_1 and m_2 are the mass weights of the original dextran and the graft copolymer, respectively.

2.3. Characterization methods

The Fourier-transform infrared spectra (FTIR) of dextran and the graft copolymer were recorded by a FTIR spectrometer (Nicolet-IR 6700, Thermo Nicolet Co., USA) in solid state, that utilizes a potassium bromide disc. The scope of the detection wave ranged from 500 cm^{-1}–4000 cm^{-1}.

X-ray powder diffraction (XRD) patterns of the samples were recorded by an X-ray diffractometer (X'Pert PRO MPD, PANalytical B.V., Holland) with graphite-monochromatized Cu Kα radiation at 4°/min. The relative crystallinity degrees of dextran and graft copolymers were calculated by MDI-Jade 6.0 software.

Thermal analysis (TG) of the copolymer was detected by using a thermal analyzer (STA-449F3, Netzsch Co., Germany). Approximately 3 mg of dried samples were dissolved in 6 μL of deionized water, and then the mixtures were sealed in an aluminum pan, treated at a heating rate of 10 °C/min from 20 °C to 650 °C under nitrogen atmosphere.

Zeta potential and particle size measurements were recorded by a Malvern Model Nano-Z Zetasizer (Nano-ZS90, Malvern Instruments Ltd., England).

The comparison of solubility between dextran and the graft product was measured by conductometer (DDSJ-308F, Inesa Scientific Instrument Co., Ltd). A given amount of grafting sample and dextran powder was respectively added into 100 mL of deionized water. And the total dissolved solids (TDS) values of samples were listed in Table 2a.

2.4. Flocculation performance

2.4.1. Jar test

Jar tests were conducted by using the suspension solution of 0.5 g of kaolin (or hematite) in 200 mL of water, which was