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Synthesis of a terpolymer based on chitosan and lignin as an effective flocculant for dye removal

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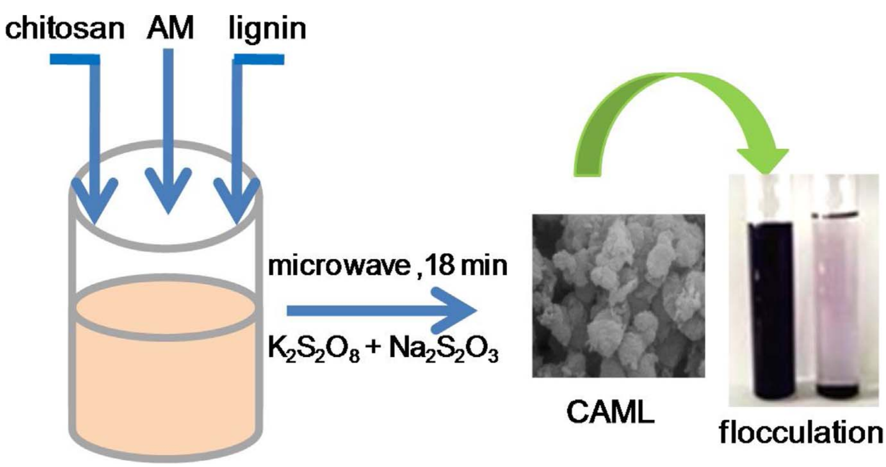
GRAPHICAL ABSTRACT



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ABSTRACT

Flocculant based on natural polymer has attracted more attention duo to its rich source, low cost and eco-friendliness. In this paper, we adopted a synthetic monomer of acrylamide to graft chitosan and lignin together by microwave assisted method. Flocculation studies showed that chitosan-acrylamide-lignin (CAML, 2 g:2 g:2 g) terpolymer exhibited maximum percentage removal of 99.3% and 67.0% for reactive orange C-3R and methyl orange, respectively. The soluble CAML flocculant had a wide flocculation window and pH effective range, although the flocculation efficiencies were enhanced slightly under acid condition. The flocculation mechanism was combined charge neutralization and bridging effects. The cost-effective, eco-friendly and high efficient terpolymer has great potential to serve as an excellent flocculant for dye removal.

1. Introduction

Currently, method of wastewater treatment mainly includes flocculation [1], adsorption [2], redox process [3], biological degradation [4] and membrane separation [5]. Among all these methods, the flocculation is used extensively because of its high efficiency, low cost and simplicity [6,7].

Flocculation efficiency primarily depends on the choice of flocculant. In the present researches and available industrial products, flocculant is chiefly divided into two classes: inorganic and organic

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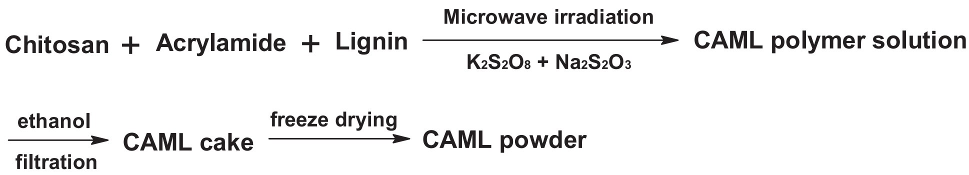

Fig. 1. Synthetic process of CAML.

(including synthetic and natural polymers) flocculant [8]. Traditional inorganic flocculants have been used for decades due to the advantage of low cost. However, their weaknesses include large dosage, highly sensitive to pH, inefficient towards very fine particles and applicable only to a few disperse systems have severely limited their applications in wastewater treatment [9]. Organic synthetic polymer flocculants, dominated by poly-acrylamide and its derivatives in the current market, have potential health threat due to their toxic residual monomers [10–12]. In recent years, flocculants based on natural polymers have been attracted more attention. Natural polymers are formed by biochemical or photosynthetic process in the nature, which widely exist in animals, plants or minerals. They can be purified, processed or modified by chemical and physical methods. Natural polymers have an enormous market potential due to their advantages of low cost, rich source, non-toxicity, biodegradability, and excellent flocculation performance compared with traditional flocculants [9,13,14]. For example, cellulose, as the most abundant organic matter and renewable energy on the earth, not only is widely used in papermaking industry, but also is the raw material of flocculant [15,16]. Lignin, the byproduct of the papermaking wastewater, causes serious environmental problems and resource waste unless it is utilized after recovery [17]. What is more, lignin molecule contains a high content of functional groups (such as hydroxyl, carboxyl, and carbonyl), which is useable as the raw material of flocculant [18]. Run et al. prepared lignin-based cationic flocculant and used it to remove anionic azo dyes effectively [19]. Chitosan, a natural amino polysaccharide, has been applied extensively in the graft modification of natural polymer based flocculants [9,20,21]. Dharani and Balasubramanian synthesized a binary flocculant of chitosan-g-N-methyl piperazinium chloride, the flocculation performance was excellent against bentonite suspension [22]. Nair et al. prepared a range of chitosan-alkali lignin composites as absorbent to remove dyes [23]. Previous researches suggested that natural polymers could be ideal candidates of flocculant, we hypothesis that ternary copolymer of chitosan and lignin grafted by a synthetic monomer would own higher molecular weight and multiple functional groups from their respective components. Therefore, it could improve the flocculation performance and universality of flocculant.

Dyes wastewater grows rapidly in recent years due to the consumer demand for printing and dyeing products [24,25]. The contaminants in the dyes wastewater are toxic, carcinogenic and difficult to be treated. Treatment of dye wastewater becomes an important issue in environmental governance. In the present printing and dyeing industry, the reactive dyes are used extensively due to its vivid luster, wild chromatogram, good color fastness, simplicity and low cost [26]. Azo dye, the most important class of synthetic organic dyes, is also widely used in printing and dying industry [27]. In this study, reactive orange C-3R and methyl orange were selected as the representative reactive and azo dyes, respectively.

The objective of this paper is to prepare a terpolymer based on chitosan, acrylamide and lignin by microwave assisted method as an effective flocculant. Different from previous researches, two natural polymers were adopted. By introducing multiple functional groups from various components, it might enhance the flocculation performance significantly. Moreover, the eco-friendliness could also be improved by more natural polymer contents in the final products. The flocculation performance was studied by two representative reactive and azo dyes on various conditions, and the flocculation mechanism was also discussed.

2. Materials and method

2.1. Materials

Unless otherwise stated, all materials were obtained from commercial sources and used as supplied. Sodium lignosulphonate was collected from Qingzhou Dongyang Chemical Co., Ltd., it derives from the sodium sulfite process of softwood in papermaking industry. Chitosan was supplied by Qingdao Haisheng Biological Co., Ltd. The degree of deacetylation and molecular weight of chitosan was 85% and 2.0 × 105 g/mol, respectively. The analytical grade of sodium thiosulfate ($Na_2S_2O_3$), potassium persulfate ($K_2S_2O_8$), acrylamide ($CH_2CHCONH_2$, AM), acetic acid (CH_3COOH), and ethanol (C_2H_5OH) were purchased from Tianjin Bodi Chemical Co., Ltd. Reactive orange C-3R (RO, $C_{20}H_{17}N_3Na_2O_{11}S_3$) and methyl orange (MO, $C_{14}H_{14}N_3NaSO_3$) were purchased from Huntsman Textile Effects (Qingdao) Co., Ltd.

2.2. Microwave assisted synthesis of chitosan-acrylamide-lignin terpolymer

The synthesis reaction was carried out in microwave oven with the microwave power of 280W. The synthesis process is shown in Fig. 1. Firstly, a certain quality of lignin and acrylamide were dissolved in distilled water. Then, a certain amount of chitosan was dissolved in the mass fraction of 1% acetic acid solution. Afterwards, a chemical initiator solution (same amount of $Na_2S_2O_3$ and $K_2S_2O_8$) with mass fraction of 1.0% was prepared. The three solutions were mixed thoroughly in a 250 ml glass flask. Finally, the flask was located in microwave oven and irradiated for 18 min. After reaction finished, the mixture was cooled down to room temperature and added with 200 ml anhydrous ethanol to precipitate out the product. The product was obtained by freeze drying for 12 h after purification by ethanol for three times. The detailed chitosan-acrylamide-lignin (CAML) samples prepared are shown in Table 1.

2.3. Characterization of CAML

CAML powder microstructure was determined by scanning electron microscopy (JSM-6390LV, JEOL). The powder was sputter-coated with gold for 150 s with a current of 18–20 mA prior to the observation. FTIR spectra were recorded on a Thermo Fisher FTIR spectrometer (Model: Nicolet 6700) in range of 400 and 4000 cm^{-1} by potassium bromide (KBr) pellet technique.

2.4. Flocculation experiment

Flocculation experiment was carried out in a 30 ml glass tube at

Table 1
Experimental condition for preparing the CAML terpolymer.

Sample	chitosan: AM: lignin (g)	$K_2S_2O_8$ + $Na_2S_3O_8$ (%)	Reaction time (min)	Yield (%)
CAML123	1:2:3	1.0	18	46.5
CAML222	2:2:2	1.0	18	61.2
CAML312	3:1:2	1.0	18	77.0
CAML212	2:1:2	1.0	18	57.3