Separation and Purification Technology 210 (2019) 10–19

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Efficient cationic flocculant MHCS-g-P(AM-DAC) synthesized by UV-induced polymerization for algae removal

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ARTICLE INFO

Keywords:
Algae removal
Flocculant
Chitosan
UV initiation
Graft copolymerization

ABSTRACT

The graft copolymer flocculant of chitosan namely, maleoyl chitosan-graft-poly(acrylamide–acryloxyethyl trimethyl ammonium chloride) [MHCS-g-P(AM-DAC)], was prepared by UV initiation to improve the solubility and flocculation efficiency of chitosan. Flocculating properties for algae removal were studied systematically. The effects of parameters such as monomer concentration, MHCS content, illumination time, photoinitiator concentration, cationic degree, pH and grafting efficiency over synthesis process of MHCS-g-P(AM-DAC) were studied. The characterization of obtained MHCS-g-P(AM-DAC) were carried out through different analytic techniques. The influences of dosage, pH, and G value on the flocculating properties were also investigated to support that MHCS-g-P(AM-DAC) was more effective than organic flocculant (CPAM) and inorganic coagulant (PFS and PAC) on algae removal. The flocculation mechanisms of MHCS-g-P(AM-DAC) were determinate by obtained zeta values.

1. Introduction

With agricultural and industrial developments, large amounts of nitrogen, phosphorus, and organic matter are discharged into rivers and lakes, resulting in water eutrophication and algae overgrowth [1]. Harmful algal bloom has caused many environmental problems worldwide. Algal toxins released by algae can cause animal poisoning and pose health hazard to humans through water used for drinking and recreation [2]. In China, eutrophication has widely occurred in many lakes and reservoirs and has received great concern in the past decades. In 2007, the water supply in Wuxi City was even cut off due to the algal bloom in Taihu Lake [3]. Algal cells and toxins not only adversely affect water quality after water treatment [4] but also increase the levels of dissolved organic carbon and promote the formation of disinfection byproducts [5].

Algal cells in water possess low specific gravity, high negative charge, and high stability [6]. Algae cannot be effectively removed from the coagulant-flocculation process by using conventional coagulants and flocculants to increase the algae concentration and turbidity in settling tank, resulting in poor sedimentation efficiency [7]. Meanwhile, aluminum and ferric-based salts have been commonly used as coagulants to agglomerate the microalgae through precipitation. A low flocculation efficiency for algae is obtained in spite of the high efficiency during the treatment of algae-containing water flocculants to remove turbidity [8]. In this regard, scholars must determine effective, economical, and environment-friendly flocculants for controlling algal growth in drinking water treatment and river water quality control [9].

Moreover, natural flocculants has been widely used as water treatment chemicals due to their efficient, economic, biodegradable and environment friendly nature compared to traditional aluminum-ferric-based salts and polyacrylamide flocculants [10]. Among natural polymers, chitosan with having low toxicity and good biodegradability properties, has received increasing attention as a promising natural macromolecule material used for preparing flocculants [11]. The chain of chitosan contains abundant free amino groups, which are easily transformed into cations in acidic media due to the protonation of amine groups [12]. Chitosan has become a potential flocculent in water treatment due to macromolecular structure [13]. However, native chitosan suffers from poor water solubility and low molecular weight, leading to limited application in water treatment [14]. Thus, substantial methodology has been developed to overcome solubility related problems in chitosan [15]. Among the developed techniques, graft

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https://doi.org/10.1016/j.seppur.2018.07.090
Received 29 March 2018; Received in revised form 21 July 2018; Accepted 31 July 2018
Available online 01 August 2018

copolymerization techniques has been widely accepted techniques for modification of chitosan to synthesize the flocculants; in this method, some functional monomers are introduced into the backbone of chitosan [16]. In addition, the soluble derivatives of chitosan are used for performing modification reaction; of these derivatives, maleoyl chitosan has been proven to have improved solubility.

Poly(acrylamide- acryloxyethyl trimethyl ammonium chloride), denoted as P(AM-DAC), is a water-soluble polymer that exhibits high flocculating efficiency in water treatment [17]. In ordered to increase the solubility of chitosan, chemical combination of chitosan with P(AM-DAC) has been carried out, which may provide potential applications of chitosan through enhancing the properties [18]. In our previous work, maleyl chitosan-graft-polyacrylamide flocculants was found to possess remarkable solubility and excellent flocculation efficiency because of the introduction of a water-soluble group. Furthermore, the flocculating performance of the graft polymer was significantly improved by enhancing charge neutralization and adsorption bridging [19,20]. Still, maleyl chitosan-graft- P(AM-DAC) copolymer used as flocculants is a unique direction, where no report has been found yet.

In this study, the modification method of chitosan was improved, and a novel chitosan derivative was designed as a copolymerization monomer for synthesis of a chitosan-based flocculant. Maleification reaction was used to prepare maleyl chitosan (MHCS) to introduce the water-soluble group and double bond. The graft copolymerization of MHCS, DAC, and AM was initiated by UV. The effects of concentration of monomer, pH values, cationic degree, MHCS counts, illumination time and photo initiator concentration on the features of MHCS-g-P(AM-DAC) were systematically investigated. While, for the assessment of structural characteristics of MHCS-g-P(AM-DAC), the samples were analyze by XRD, TG-DSC, FTIR, ^{1}H NMR, and SEM. Finally, the flocculation performance of MHCS-g-P(AM-DAC) was tested in low-turbidity algal water, and the dominant mechanisms involved were proposed accordingly.

2. Materials and methods

2.1. Materials

AM, CS with 95% deacetylation degree, maleic anhydride, and DAC were obtained from Hefei Bomei Biotechnology. Co., LTD, and all other reagents including cationic polyacrylamide (CPAM), polyferric sulfate (PFS), and polymeric aluminum (PAC) were obtained from NanJing WanQing Chemical Classware Istrument Co., LTD., and used as received.

2.2. Preparation of MHCS-g-P(AM-DAC)

The possible grafting polymerization schemes of MHCS and MHCS-g-P(AM-DAC) are illustrated in Fig. 1. During the synthesis of MHCS, maleic anhydride (2% CH_3COOH solution) and chitosan were weighted as per their mass ration (2:1) and transferred to round bottom flask to stirred at 30 °C in a water bath for 5 h, followed by purification through dialysis membrane and vacuum drying. Finally, the obtained liquid product was purified using a dialysis membrane and dried in vacuum to obtain MHCS powder [21]. The certain mass of AM, DAC, and MHCS with mass ratio of 3.0:3.5:3.5 was dissolve in deionized water with 35% monomer concentration and continuous stirring until complete dissolution in ordered to obtain a homogeneous solution. 0.6 wt% photoinitiator was also added after the homogeneous solution was completely deoxygenated by bubbling with pure N_2 for 30 min. The homogeneous solution was irradiated in a UV light reaction device at room temperature for 120–180 min. After UV irradiation, the obtained gels were

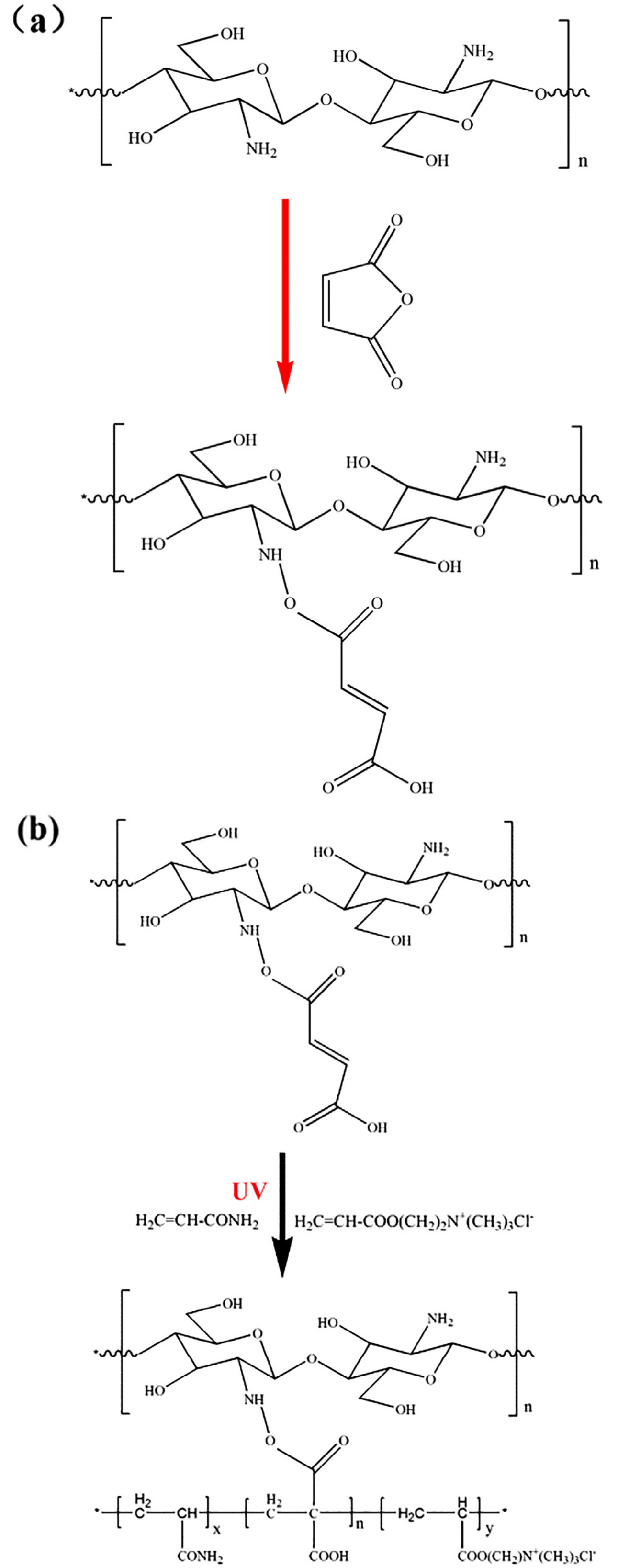

Fig. 1. Possible grafting polymerization schemes of (a) MHCS and (b) MHCS-g-P(AM-DAC).