



A novel carboxyl-rich chitosan-based polymer and its application for clay flocculation and cationic dye removal

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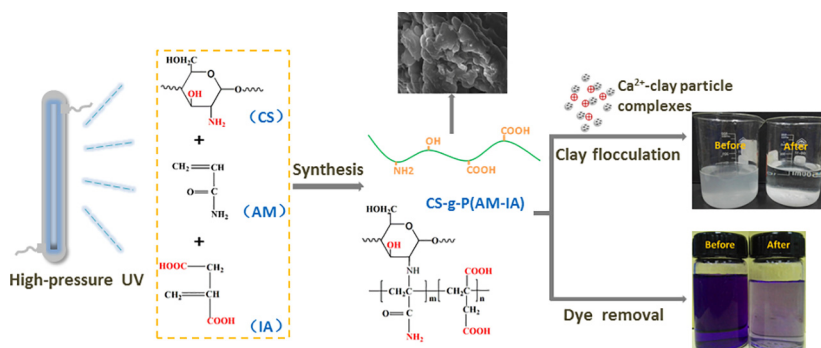
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HIGHLIGHTS

- A carboxyl-rich chitosan-based flocculant was prepared via UV-initiated graft copolymerization reaction.
- Solubility was greatly improved.
- Crystal form and surface morphology have changed dramatically.
- The surface ionic groups play a significant role in clay flocculation and decolorization.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to the complexity of contaminants, the effectiveness of traditional flocculants toward water purification is insufficient. To break the limitation, a novel polymer flocculant [chitosan grafted poly (acrylamide-itaconic acid), CS-g-P(AM-IA)] was synthesized via ultraviolet-initiated graft copolymerization reaction. Characterization results revealed that the graft copolymers were successfully synthesized and with rougher surface structure. The solubility of CS-g-P(AM-IA) and chitosan grafted polyacrylamide (CS-g-PAM) were greatly improved and they can dissolve in the wide pH range of 2.0–12.0. CaCl_2 was used as a source of cation bridge to enhance the flocculation of kaolin particles, and its optimum dosage was $150 \text{ mg} \cdot \text{L}^{-1}$. At dosage of $30 \text{ mg} \cdot \text{L}^{-1}$ and pH of 5.0, the turbidity removal efficiency of CS-g-P(AM-IA) reached the maximum of 93.8%, whereas those of CS-g-PAM and CS were 96.7% and 76.9%, respectively. The patchwise adsorption of ionic groups embedded in the molecular chain on Ca^{2+} -clay complexes took effect to generate flocs with larger particle size. Besides, the decolorization ability of cationic dyes by CS-g-P(AM-IA) was greatly enhanced due to the role of abundant carboxyl groups. In the crystal violet (CV) adsorption experiment, the maximum CV dye removal efficiency for CS-g-P(AM-IA) reached the maximum of 81.6% at dosage of $0.7 \text{ mg} \cdot \text{mL}^{-1}$ and pH of 9.0, while those for CS-g-PAM and CS were 51.7% and 36.5%, respectively.

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1. Introduction

Fine suspended particles with the average lateral size range of $0.001\text{--}10 \mu\text{m}$ which commonly exist in industrial wastewater, are

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difficult to agglomerate into heavier mass for setting. If left untreated, the suspended particles with surface charges can be suspended in water for years due to the adverse electrostatic interactions (Bolto and Gregory, 2007; Nasser and James, 2006). Nowadays, water contamination triggered by the chemicals such as heavy metals, aromatic molecules, dyes and so on, has caused some serious environmental problems and posed a great threat to aquatic organisms and human health. In view of the pressure on water supply and water pollution control, it is imperative to develop effective technologies for removing colloidal particles and toxic pollutants in wastewater.

Among various wastewater treatment methods, flocculation is widely used in wastewater purification and sludge chemical treatment on account of its effectiveness, operation simplicity and economy (Jiang et al., 2011; Li et al., 2017a). Generally, flocculants are divided into two categories: i) inorganic flocculants, such as aluminum and iron salts; ii) organic polymer flocculants, such as polyacrylamide, chitosan derivatives, etc. (Tang et al., 2016; Zhu et al., 2016). In addition, polymer flocculants can be further divided into synthetic flocculants and natural flocculants. Compared with natural flocculants, the synthetic flocculants can achieve ideal flocculation efficiency under less dosing (Mittal et al., 2015; Xie et al., 2007). Nevertheless, synthetic flocculants are usually non-degradable, and the petroleum raw materials contained in them are expensive and highly toxic. To obviate the drawbacks of polymeric flocculants, biodegradable polysaccharides based flocculants have aroused considerable attention in the field of water treatment (Du et al., 2018; Salehizadeh et al., 2018). In recent years, the graft copolymers combined natural polysaccharides with synthetic monomers are particularly attractive (Mittal et al., 2015; Sarkar et al., 2013; Sarkar et al., 2015). Such polysaccharide derivative flocculants can be also more functionalized to effectively remove multifarious water pollutants (Lin et al., 2012; Xie et al., 2011; Zhu et al., 2015). In general, functional groups such as amino, carboxyl and hydroxyl functional groups are incorporated into natural polymer chains, so as to obtain good binding properties to various types of organic matters and inorganic substances in water (Liu et al., 2018a; McFarlane et al., 2008).

Chitosan is a linear polysaccharide rich in primary amino groups, which is one of the most potential natural alternatives for commercial synthetic polymer flocculants (Crini and Badot, 2008; Pal et al., 2011; Reddy and Lee, 2013; Yang et al., 2016; Yang et al., 2014). To the best of our knowledge, chitosan can also be used as an adsorbent to remove heavy metals and dissolved dyes from aqueous solutions due to the presence of amino and hydroxyl groups, which can serve as the active sites (Wu et al., 2001; Wan Ngah et al., 2011). However, the adsorption capacity of chitosan is not broad-spectrum, for the reason that the amine and hydroxyl groups of chitosan for trapping cationic dyes is rather inefficient (Salzano de Luna et al., 2017). Moreover, the poor solubility limits the application of chitosan in water treatment. It is well known that polyacrylamide (PAM) is widely used in water treatment due to its high molecular weight (Liu et al., 2017). Grafting polyacrylamide onto chitosan chains is expected to improve the solubility of chitosan derivatives and fully combine the merits of natural polymers and synthetic polymers (Lu et al., 2017; Sanaeishoar et al., 2018; Yang et al., 2012). Some studies have tried to insert some specific functional groups that act as active binding sites to the chitosan skeleton chains to improve the adsorption capacity (Liu et al., 2018a; Boddu et al., 2003).

The carboxylic acid polymers is a type of water-soluble polymers produced by polymerization of some carboxyl group-containing monomers such as acrylic acid, maleic anhydride, itaconic acid (IA), etc. Due to the role of $-\text{COOH}$ group, carboxylic acid polymers not only have strong chelating ability for cationic contaminants, but also have good adsorption effect on suspended particles in water. Itaconic acid (IA) is a non-petroleum based monomer derived from algae fermentation, and its molecular structure contains two carboxyl groups. Moreover, IA monomers can be easily polymerized to form highly hydrophilic polymer chains rich in carboxyl groups (Liu et al., 2018a; Sakthivel et al., 2016).

It is expected to achieve such chitosan derivatives with good hydrophilicity, tunable molecular weight and abundant carboxyl groups, which might have robust potentials in wide field of wastewater treatment. Nevertheless, very little work focus on preparing such chitosan derivatives that can be used as both flocculants and adsorbents to remove colloidal particles and dyes. Ultraviolet-initiated graft copolymerization was a more efficient, energy-saving and economical method (Li et al., 2017b; Liao et al., 2014). The aims of this work were to prepare a chitosan-based polymer flocculant by ultraviolet-initiated graft copolymerization taking chitosan, acrylamide and itaconic acid as raw materials, and to evaluate the adsorption/flocculation performance in application of removing kaolin clay particles and decolorization of wastewater. Herein, the polymers were characterized by Fourier transform-infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), magnetic resonance spectrometry (^1H NMR) and scanning electron microscopy (SEM). In kaolin clay flocculation and crystal violet dye decolorization experiments, the flocculation and adsorption properties of chitosan (CS), chitosan grafted polyacrylamide (CS-g-PAM) and chitosan grafted poly (acrylamide-itaconic acid) (CS-P(AM-IA)) were compared respectively in order to highlight the roles of ionic groups and high molecular weight.

2. Experimental section

2.1. Materials

Chitosan (CS, 100–200 mPa·s viscosity) and Itaconic acid (98.5% purity) was obtained from Cheng Du Micxy Chemical Co. Ltd. The monomer acrylamide (AM, 98.5 wt%) was purchased from Lanjie Tap Water Company (Chongqing, China). 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-044) used as initiator was obtained from Ruihong Biological Technology (Shanghai, China). Kaolin was purchased from Guangfu Fine Chemical Institute (Tianjin, China). Crystal violet (CV) and absolute ethanol were obtained from Chuandong Chemical Co. Ltd. (Chongqing, China). All reagents were used without further purification. Ultra-pure water (18 M Ω ·cm) was used as solvent for all syntheses.

2.2. Preparation of CS-g-P(AM-IA)

As depicted in Fig. 1a, CS-g-P(AM-IA) was synthesized through UV-induced graft copolymerization taking acrylamide (AM), itaconic acid (IA) and chitosan (CS) as raw materials. 3 g chitosan was pre dissolved in 100 mL 1.0 wt% acetic acid water solution. An equimolar amount of IA and NaOH were dissolved in a quartz reactor with a certain amount of deionized water. Afterwards, 3.3 g AM monomers, 0.028 g initiator V-044 and 20 mL 3.0 wt% chitosan aqueous solution were added into the quartz reactor, and then primary precursors were stirred until completely dissolved. The reaction solution was deoxygenated by bubbling with pure N $_2$ (99.99%) for 15 min. The quartz reactor was immediately sealed and exposed to high-pressure ultraviolet light for 90 min. After irradiation, the resulting hydrogel was aged for two hours and purified with acetone. Finally, the purified substance was dried in a vacuum oven at 60 °C to constant weight.

2.3. Characterization

FTIR (Nicolet IS10) was carried out on a spotlight 200 FT-IR spectrometer in the wave number range from 4000 to 400 cm^{-1} . ^1H NMR spectra was recorded by Avance-500 NMR spectrometer (Bruker, Switzerland) in deuterium oxide (D $_2$ O) with tetramethylsilane as internal standard. XRD patterns were obtained with an X-ray diffractometer (XRD, DMAX/2C) using graphite monochromatized Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). SEM analysis was performed on MIRA 3 LMU SEM system (TES-CAN Company, Czech Republic). zeta potential and floc size distribution were measured by ZS90 Malvern potential analyzer (Malvern

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