



Ultraviolet-assisted synthesis of polyacrylamide-grafted chitosan nanoparticles and flocculation performance



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ABSTRACT

In the present work, a new flocculant, polyacrylamide-grafted chitosan nanoparticles (NCS-g-PAM), was synthesized by the copolymerization of acrylamide (AM) and chitosan nanoparticle (NCS) under ultraviolet irradiation using 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as photo-initiator. The NCS was prepared by the ionic gelation between chitosan and sodium triphosphate. The structure and morphology of NCS-g-PAM were characterized by Fourier Transform Infrared spectroscopy (FT-IR), X-ray diffraction, ¹H-nuclear magnetic resonance spectrometry, scanning electron microscopy, and thermogravimetric analysis. The factors affecting the intrinsic viscosity and the yield of copolymer were studied, which showed that the optimum conditions for the synthesis of NCS-g-PAM were $m_{AM}:m_{NCS} = 8:1$, 0.15 g of initiator dosage, $m_{CS}:m_{TPP} = 4.5:1$, 1 min of ultrasonication time, 4 h of illumination time, and 30 min of stirring time. The NCS-g-PAM was found to be more effective than NC-g-PAM in the flocculation of both kaolin suspension and Cu²⁺ simulated wastewater. With 5 mg/L of polyaluminium chloride (PAC) coordinated and 1 mg/L of NCS-g-PAM it was confirmed to be appropriate for flocculating kaolin suspension.

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1. Introduction

One of the severe environmental issues for China to face is the increasing water pollution, which is the consequence of the rapid development of various industries (Hu and Cheng, 2013). To solve this issue, numerous processes for the purification of wastewater have been developed. In particular, flocculation is regarded as an important purification technique because of its low treatment cost, high efficiency, and nominal instrumentation compared with other processes (Bharti, Mishra, & Sen, 2013; Zheng, Ma et al., 2014; Zheng, Sun et al., 2014).

Flocculation is involved in the physical aggregation process of many finely divided or dispersed particles in wastewater to form larger flocs so they are separated from the wastewater through settling (Chang, Hao, & Duan, 2008; Pal, Ghorai, Dash, Ghosh, &

Udayabhanu, 2011). The chemical agents applied in flocculation are known as flocculants, which greatly influence flocculation performance and treatment efficiency. At present, traditional inorganic metal-based flocculants and synthetic polymeric flocculants are two of the most extensively used types (Yang, Yan et al., 2013; Yang, Yang et al., 2013). However, studies have reported that traditional flocculants may be potentially harmful to human health and cause secondary pollution to the environment (Pourrezaei et al., 2011; Shi, Ju, & Zhang, 2012). Therefore, the novel environmentally friendly flocculants are urgently needed.

Considerable attention has recently been focused on the natural polymer flocculants in the fields of wastewater treatment because of their biodegradability, environmental friendliness, and extensive sources in nature (Renault, Sancey, Badot, & Crini, 2009). The natural polymer flocculants include starch (Banerjee et al., 2012; Mishra, Mukul, Sen, & Jha, 2011), chitosan (CS) (Wang, Chen, Yuan, Sheng, & Yu, 2009; Yang et al., 2011), cellulose (Liu, Yang, Zhang, Zhu, & Yao, 2014), and guar gum (Mishra and Sen, 2011). Among these flocculants, the CS is obtained from chitin (the most abundant natural polymer except for cellulose on the earth), which is one of the most promising candidates as natural flocculant. It has an outstanding sorption performance due to the presence of pri-

Abbreviations: AM, acrylamide; PAM, polyacrylamide; CS, chitosan; NCS, chitosan nanoparticles; TPP, sodium triphosphate; UV, ultraviolet; Irgacure2959, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone.

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many amino groups (Wang, Wang et al., 2009). It shows that those nanomaterials that hold large surface areas and activated function sites are good qualities (Simate, Iyuke, Ndlovu, & Heydenrych, 2012; Zhao et al., 2011). In fact, the previous studies have already proven that the CS nanoparticle (NCS) can be used for the sorption of metal ions, anionic dyes, and protein (Amidi et al., 2006; Hu, Zhang, Chan, & Szeto, 2006; Qi and Xu, 2004). However, the NCS as a flocculant has not been reported which is due to its contained-low molecular weight. Grafting polymerization is an efficient method for overcoming this drawback (Yang, Yan et al., 2013; Yang, Yang et al., 2013). The high-molecular-weight polyacrylamide (PAM) has shown excellent flocculation performance significantly enhancing bridging effect in the flocculation process, because of its long branches and high intrinsic viscosity. Therefore, grafting the PAM onto the surface of the NCS to form a new nano-flocculant may be interesting.

In general, the various methods for grafting copolymer synthesis differ in the style of free radical sites generation on the preformed polymer (Sinha, Mishra, & Sen, 2013). At present, the free radical sites to further initiate graft polymerization can be created by numerous techniques, such as chemical free radical initiators (Yang, Yan et al., 2013; Yang, Yang et al., 2013), high-energy radiation (such as gamma ray and microwaves) (Wang, Wang et al., 2009; Rani, Mishra, & Sen, 2013), and ultraviolet (UV) radiation (Guan et al., 2014; Liao et al., 2014; Zheng et al., 2013; Zheng, Ma et al., 2014; Zheng, Sun et al., 2014). The UV-initiation method needs lower reaction temperature, shorter reaction time, and fewer initiators, but it can achieve higher reaction rate as compared with other methods (Guan et al., 2014; Liao et al., 2014; Zheng, Ma et al., 2014; Zheng, Sun et al., 2014). In addition, the UV-initiation method is an easily manipulated and environmentally friendly process. Ma et al. prepared a novel anion PAM under UV initiation for removal of dioctyl phthalate and compared their flocculant with other anion PAM products prepared by thermal initiation in a water bath. The results indicated that the UV initiation performed significant enhancement function in increasing the polymerization degree of the PAM, as well as the thermal stability (Zheng, Ma et al., 2014; Zheng, Sun et al., 2014). Liao et al. have successfully synthesized a cationic PAM through UV-initiated method, which was used for sludge dewatering. The results showed that the porous structure of the copolymer is conducive for adsorbing and bridging between the copolymer molecules and the sludge particles (Liao et al., 2014).

With all the aforementioned factors taken into account, in the current work, a novel grafting flocculant nano-CS-graft-PAM (NCS-g-PAM) was synthesized through UV-initiated polymerization. The factors such as mass ratio, photo-initiator dosage, and illumination time were investigated to optimize the synthetical conditions. The structure of the obtained copolymer was characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD), ^1H nuclear magnetic resonance (^1H NMR) spectra, field-emission scanning electron microscopy (FESEM), and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

CS (with the degree of deacetylation of 80%–95% and viscosity of 50–800 mPa·s), acrylamide (AM), sodium tripolyphosphate (TPP), and sodium chloride (NaCl) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetic acid (wt.% = 36%) was obtained from Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Ethanol and acetone were obtained from Zhenqin Chemical Reagent Co., Ltd (Shanghai, China). The photo-initiator 2-hydroxy-4'-(2-hydroxyethoxy)-2-

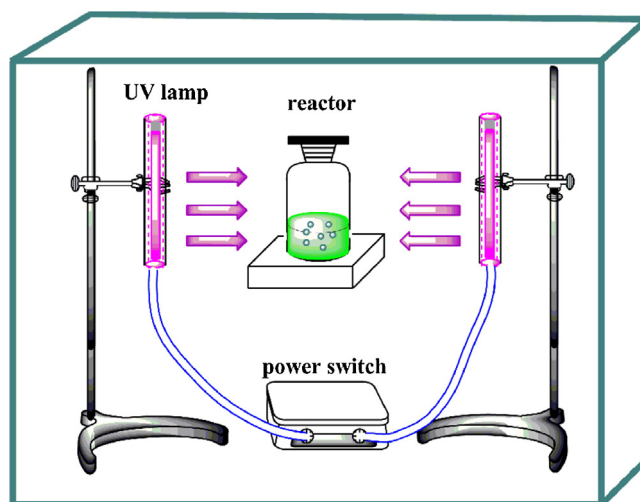


Fig. 1. Schematic of the experimental setup.

methylpropiophenone (Irgacure2959) was supplied by Changzhe Biological Technology Co., Ltd. (Shanghai, China). Except for AM and TPP, all reagents that were used in this study were of analytical grade and used directly without any further purification.

2.2. Synthesis of NCS-g-PAM

2.2.1. Preparation of chitosan nanoparticles

NCS were prepared using a method based on ionic gelation between CS and TPP, which has been reported in numerous published works (Gokce, Cengiz, Yildiz, Calimli, & Aktas, 2014; Rampinoa, Borgogna, Blasi, Bellich, & Cesàro, 2013; Rattanawongwiboon, Haema, & Pasanphan, 2014; Shukla, Mishra, Arotiba, & Mamba, 2013; Kashyap, Xiang, & Heiden, 2015). Nanoparticles are formed with intermolecular and intramolecular links between positively charged amino groups of CS and negatively charged phosphate groups of TPP. In this study, 0.2 g CS was dissolved in 15 mL of 1% (wt) acetic acid with magnetic stirring. TPP was dissolved in deionized water to a final concentration of 5 mg/mL. Then, 8 mL of the TPP solution (weight ratio of CS: TPP was 5:1) was drop-wise added to the CS solution under vigorous magnetic stirring at room temperature. The resulting suspension was then left to gelify for 30 min. Finally, the solution was ultrasonicated for 1 min to break any aggregations and reduce particle size. 8.7 mg/mL NCS solution was prepared for subsequent grafting polymerization of PAM-g-NCS. Moreover, Nanoparticle solutions were air-dried for further characterization.

2.2.2. Polymerization of NCS-g-PAM

Polymerization was performed in a 125 mL glass vessel. Fig. 1 shows a schematic of the experimental setup. Two 48 W low-pressure mercury lamps were used as UV light source for the copolymerization process.

1.6 g of AM monomer and 0.15 g of the photo-initiator Irgacure2959 were added into the above prepared NCS solution (8.7 mg/mL). After the solution was completely dissolved under magnetic stirring, purified nitrogen was bubbled through the solution for 20 min to remove oxygen. Then, the reaction vessel was immediately sealed and irradiated by UV source for 3–4 h at ambient temperature. Thereafter, the sample solution was precipitated in a mixed solution of acetone and ethanol with a volume ratio of 2:1. Finally, the solid product was washed and then dried in an oven at 105 °C for 24 h until constant weight was obtained.

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