Research article

Scale-inhibition and flocculation dual-functionality of poly(acrylic acid) grafted starch

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ABSTRACT

Natural-polymer based water treatment agents have recently received much more attention due to their environmental friendliness, widespread availability, and prominent structural features. Starch-*graft*-poly(acrylic acid) (St-*g*-PAA) is a simple natural-polymer based material that can be obtained easily by a one-step graft copolymerization. When used as a water treatment agent, St-*g*-PAA exhibits both effective scale-inhibition performance and high turbidity removal efficiency. The scale-inhibition efficiency of St-*g*-PAA against calcium carbonate ($CaCO_3$) is approximately 94% at the optimal dose in a static test of approximately 40 mg/L. Dispersion, crystal lattice distortion, and chelating effects all play important roles in the scale inhibition. When St-*g*-PAA is used as a coagulant aid for polyaluminum chloride (PAC) in the flocculation of a real hairwork wastewater, the highest reduction of the optimal PAC dose is more than 30% while the turbidity reduction is about 97% at the same time, both floc size and compactness increase, and the final settling efficiency also improves evidently. The efficient bridging flocculation effects account for the effective turbidity removal. The prominent scale-inhibition and flocculation dual-functionality of St-*g*-PAA is intrinsically ascribed to its distinct anionic linear branched-chain structure.

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1. Introduction

Water treatment agents play an important role in the purification of industrial and domestic wastewaters (Li, 2005; Metcalf and Eddy, 2003). On the basis of various functional characteristics, water treatment agents can be divided into coagulants/flocculants, adsorbents, bacteriostatic agents, scale inhibitors, corrosion inhibitors, etc. (Li, 2005). Although most of the traditional water treatment agents have proven effective, they have always been blamed for secondary pollution and potential health risks to human beings, such as residual metal ions of inorganic coagulants, toxic monomers of synthetic polymeric flocculants, the eutrophication effect of phosphorus-containing antiscalants, noxious disinfection by-products of halogen-containing bactericides (Bolto and Gregory, 2007; Goy et al., 2009; Hasson et al., 2011; Ippolito et al., 2011; Werschkun et al., 2012). There is no doubt that the energetic development of environmentally friendly and highly efficient water treatment agents is a major trend, which has a great prospect for real-world application. Moreover, if one agent contains two or more functions, it can significantly improve the application efficiency and reduce costs. Therefore, it is a very interesting topic to develop dual-functional or multi-functional water treatment agents containing coagulation/flocculation, bacteriostasis/sterilization, and scale inhibition (Huang et al., 2016, 2017; Jensen and Kelland, 2012; Liu et al., 2017a; Tripathy et al., 2009; Xiao, 2008). Among them, coagulation/flocculation is generally the fundamental one, since coagulation/flocculation process is regarded as one of the most important and widely used treatment processes of raw water (de Godos et al., 2011; Hameed et al., 2016; Teh and Wu, 2014) and industrial wastewaters (Du et al., 2017; Sanghi et al., 2006; Teh et al., 2017) due to its simplicity and effectiveness.

Based on the structure→activity relationship, although there are many differences between the various types of water treatment agents in terms of functional groups, molecular-weight range, and the application mechanism, some common features still exist. For example, quaternary ammonium bactericides and strong cationic flocculants, which both contain a large number of quaternary ammonium salt groups, efficient affect sterilization and charge neutralization flocculation because most bacteria and colloidal particles in water have negative surface charge (de Godos et al., 2011; Huang et al., 2016, 2017; Liu et al., 2017a; Sajomsang et al., 2010; Xiao, 2008). Besides, both organic polymer-based scale

inhibitors and anionic flocculants usually contain anionic groups such as carboxyl groups and sulfonic groups (Jensen and Kelland, 2012; Tripathy et al., 2009; Wang et al., 2017; Xiao, 2008). These similarities in structure make it possible to develop dual-function or multi-function water treatment agents.

In recent years, natural polymer-based water treatment agents have drawn wide attention due to their widespread availability, low cost, environmental friendliness, and biodegradability (Bolto and Gregory, 2007; Chauhan et al., 2012; Guo et al., 2013; Kirboga and Oner, 2012; Lakshtanov et al., 2011; Rinaudo, 2006; Umoren and Eduok, 2016; Yang et al., 2016). Natural polymers have many active groups, such as hydroxyl groups, which can be chemically modified easily by introducing various functional groups onto their backbones to overcome poor solubility and satisfy different application purposes, such as esterification, etherification, and graft copolymerization (Bolto and Gregory, 2007; Rinaudo, 2006; Shak and Wu, 2017; Yang et al., 2016; Zhu, 2015). Therefore, the development of multi-functional natural-polymer based water treatment agents has great potential significance.

Starch, a very popular natural polymer, has attracted much more interest due to its ease of sourcing and low cost. Many starch derivatives can be easily prepared and have been proved highly effective as water treatment agents, including multi-functional ones (Bolto and Gregory, 2007; Guo et al., 2013; Huang et al., 2016, 2017; Liu et al., 2017a, 2017b; Wang et al., 2013, 2017; Wu et al., 2016). In our previous work (Huang et al., 2016, 2017; Liu et al., 2017a), several cationic starch-based materials were obtained, all of which exhibit both effective flocculation and sterilization performance for water treatment. The development of dual-functionality starch and starch derivatives for scale inhibition and flocculation represents an under researched area.

Starch-graft-poly(acrylic acid) (St-g-PAA) is a very simple natural-polymer based material (Gok et al., 2017; Jiraprasertkul et al., 2006; Zhu et al., 2009) and can be easily prepared by one-step graft copolymerization (Liu and Wei, 2016). Because it contains abundant carboxyl groups and branch-chain structural features, St-g-PAA is well suited to the dual-functions of scale inhibition and flocculation. In this study, a St-g-PAA has been tested as a scale inhibitor for the inhibition of calcium carbonate ($CaCO_3$) and as a coagulant aid for polyaluminum chloride (PAC) for the flocculation of real hairwork wastewater. Fourier transform infrared spectroscopy (FTIR) and ^1H nuclear magnetic resonance (^1H NMR) were used to characterize the structure of St-g-PAA. The scale-inhibition mechanisms of St-g-PAA were further investigated using a scanning electron microscope (SEM) and X-ray diffraction (XRD) for the characterization of the crystal morphology and structure of $CaCO_3$. The flocculation performance and mechanisms of St-g-PAA were evaluated according to the turbidity removal efficiency and floc properties.

2. Materials and methods

2.1. Materials

Corn starch (St, weight-average molecular weight of ~1.5 × 10^5 g/mol) was purchased from Binzhou Jinhui Corn Development Co., Ltd. (Binzhou, China). Acrylic acid (R.G.) was obtained from Shanghai Taitan Science and Technology Co., Ltd. (Shanghai, China). Calcium chloride (A.R.) was sourced from Shantou Xilong Chemical Reagent Co., Ltd. (Shantou, China). Ammonium persulfate (A.R.) and sodium borate (A.R.) (Shanghai Lingfeng Chemical Reagent Co., Ltd.) were used without further treatment (Shanghai, China). All other chemicals were reagent grade and were obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Polyaluminum chloride (PAC, $[Al_2(OH)_nCl_{6-n}]_m$,

$n = 3.6$–5, $m < 10$, Al_2O_3 content $\geq 28\%$) was used directly without further purification. Distilled water was used in all experiments.

2.2. Preparation and characterization of St-g-PAA

The process to synthesize St-g-PAA was performed according to a previously published procedure (Liu and Wei, 2016). The graft monomer of acrylic acid was extracted and purified by vacuum distillation before use. Ammonium persulfate was used as an initiator. After a full gelatinization of the starch in a 250-mL flask with four-necks, the initiator and graft monomer were added separately at an interval of 5 min. All reactions occurred under a nitrogen atmosphere. The product was dewatered in 95% ethanol, then filtered and washed with distilled water. Finally, the crude product was purified further by Soxhlet extraction using acetone. After drying in a vacuum oven at 60 °C until constant weight was achieved, the graft copolymer St-g-PAA was obtained.

FTIR and ^1H NMR spectra of starch and St-g-PAA were measured by a Bruker model IFS 66/S FTIR spectrometer and a Bruker AVANCE model DRX-500 NMR spectrometer. The spectral range for the FTIR was 600 cm^{-1} to 4000 cm^{-1}. ^1H NMR measurements were made at 500 MHz, with D_2O as the solvent.

Additionally, the grafting ratio of St-g-PAA was 41.3% based on Eq. (1) (Huang et al., 2017).

$$Grafting\ ratio(\%) = \frac{W_{PAA}}{W_{St}} \times 100\% \qquad (1)$$

where W_{PAA} and W_{St} are the weights of the PAA branches and the starch backbone.

2.3. Scale-inhibition performance of St-g-PAA

The inhibition efficiency for St-g-PAA against $CaCO_3$ scale was evaluated according to the National Standard of China (GB/T 16632-2008) using the static scale-inhibition test method. The prepared $CaCl_2$ and $NaHCO_3$ solutions were mixed in a 250-mL Erlenmeyer flask, in which the molar concentrations of Ca^{2+} and HCO_3^- were both 5.0 mmol/L. Then, a certain amount of St-g-PAA was added to the mixture under consistent stirring. The samples were heated to 70 °C in a water bath for 10 h. After the reaction, the specimens were cooled to room temperature. An EDTA standard solution was used to titrate and determine the concentration of Ca^{2+} in the supernatant, and a blank test was conducted simultaneously to calculate the scale-inhibition efficiency of St-g-PAA against $CaCO_3$ scale, as shown in Eq. (2) (Chen et al., 2015; Wang et al., 2017).

$$Inhibition\ efficiency(\%) = \frac{V2 - V1}{V0 - V1} \times 100\% \qquad (2)$$

where V_0 (mL) is the consumed volume of EDTA solution during titration of the synthetic water sample without the addition of scale inhibitors and the incubation treatment, while V_1 and V_2 (mL) are the consumed volumes of EDTA solution without and with scale inhibitor after a 10-h reaction at 70 °C, respectively. All the inhibition tests were conducted in triplicate, and the final results represent the average values of the three runs. The error bar representing the relative deviation was less than 5.0%.

SEM images and XRD patterns of the $CaCO_3$ scale deposits in the absence and in the presence of St-g-PAA were carried out using an FEI Quanta 250 FEG SEM and a Shimadzu model XRD-6000 X-ray diffractometer. The SEM was operated under an acceleration voltage of 5-kV. XRD was carried out by Cu Kα radiation ($\lambda = 0.15418$ nm), with a voltage of 40 kV and a current of 30 mA.