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# Evaluation of chain architectures and charge properties of various starch-based flocculants for flocculation of humic acid from water

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ABSTRACT

Three different starch-based flocculants with various chain architectures and charge properties have been prepared through etherification, graft copolymerization, or their combination. Two of the flocculants (starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] and starch-3-chloro-2-hydroxypropyl triethyl ammonium chloride, denoted as STC-*g*-PDMC and STC-CTA respectively) are cationic, and another one (carboxymethyl starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride], denoted as CMS-*g*-PDMC) is amphoteric. Those three flocculants have shown far different flocculation efficiency and floc properties for the removal of humic acid (HA) from water due to their distinct structural features. The effects of pH, flocculant dose, and initial HA concentration have been studied systematically. Accordingly, STC-*g*-PDMC and CMS-*g*-PDMC with strongly cationic branch chains have much better flocculation performance than polyaluminum chloride (PAC) and STC-CTA, the latter of which features linear chain architecture and strongly cationic pieces lying on its chain backbone. It indicates that the architecture of cationic branch chains plays an important role in HA flocculation due to their significantly enhanced bridging effects. Moreover, STC-*g*-PDMC has higher HA removal efficiency and better floc properties than CMS-*g*-PDMC, suggesting that charge neutralization effects make notable contributions to HA removal and that the additional anionic pieces on CMS-*g*-PDMC can weaken its flocculation performance. In addition, STC-*g*-PDMC used as coagulant aid for PAC has also been tried, which observably reduces the optimal dose of the inorganic coagulant.



## 1. Introduction

Starch-based flocculants (Bolto and Gregory, 2007) have received much more attentions in the field of water treatment in recent decades due to their significant characteristics of widespread availability, low cost, environmental friendliness, and biodegradability. Although the traditional inorganic and synthetic polymeric flocculants are widely used now, they have always been blamed for the residual metal ions as well as toxic organic monomers (Bolto and Gregory, 2007; Ippolito et al., 2011). However, starch also has many defects in practical use including poor water solubility, low molecular weight, and lack of charge property, causing lower quality and efficiency in water purification. Therefore, many kinds of modified starch flocculants have been manufactured and reported to be able to further improve its flocculation performance (Krentz et al., 2006; Pal et al., 2005; Sen et al., 2009; Wang et al., 2013) by various chemical modification methods such as esterification, etherification, and graft copolymerization (Lin et al., 2012; Rath and Singh, 1997; Wei et al., 2008).

As is known, the final application performance of a material, including the flocculant, is highly dependent on their molecular structures (Ashby et al., 2013; Ravve, 2013; Wessel, 2004), apart from external environmental parameters such as pH, temperature and dose (Khayet et al., 2011; Li et al., 2004). Therefore, as for flocculants, it is significantly important to build and effectively exploit the structure-activity relationships, as these greatly influence the selection and design of high-performance flocculants in the decontamination of targeted pollutants. However, little work concerning this strategy has been reported in the field of flocculation.

Moreover, far different from small molecular-weight compounds, the structures of polymer materials including starch are quite complicated and contain multiplied levels. Besides the type and chemical composition of the repeating units, the shape and architecture of a macromolecule are also important factors during

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application (Elias, 1984; Ravve, 2013; Sperling, 2005). The structural multiplicity of the polymer materials would result in their varied application performance. As for the research topic related to the development of a novel and high-performance polymeric flocculant, most previous work focused on the design and selection from the perspective of the aforementioned former structural level, types of functional groups and chemical compositions of the flocculants (Lin et al., 2012; Rath and Singh, 1997; Vandamme et al., 2010; Wei et al., 2008; Yuan et al., 2010). However, little work has been done to study the effects of the chain architectures of the polymeric flocculants which have a really great impact on the flocculation performance due to the distinct long-chain feature of macromolecules. Different chain architectures of polymers, including linear, grafting/branching, and star-like forms, would have diverse effects (Elias, 1984; Ravve, 2013; Sperling, 2005). The similar polymers with even the same functional groups but distributed at various positions, the backbone or the side chain of polymers, sometimes have significantly different application performance.

In this work, three starch-based flocculants all containing the strongly cationic quaternary ammonium salt groups but at different positions have been designed and prepared, which bear various chain architectures, i.e. STC-*g*-PDMC with positive charges on branch chains, STC-CTA with positive charges on starch backbone, and amphoteric CMS-*g*-PDMC with positive charges on branch chains but a few negative pieces on starch backbone. The effects of chain architectures and charge properties of various starch-based flocculants on flocculation of humic acid (HA) and its floc properties have been investigated in terms of several environmental parameters including pH, dose, and initial HA concentration. HA is a type of water-soluble organic matters in nature, which not only causes yellowish color and undesirable smell of the water (Bratskaya et al., 2004), but is also the main precursor of many disinfection by-products (Richardson et al., 2007). Efficient removal of HA from water remains a thorny issue and has become a hot research topic due to its harm to water environment quality and the poor treatability (Wang and Wang, 2006; Kretzschmar et al., 1997; Lipczynska-Kochany and Kochany, 2008; Yuan and Zydney, 1999). Accordingly, the flocculation performance and mechanisms of aforementioned various starch-based flocculants for HA removal have been studied in detail in terms of their structural characteristics, especially chain architectures and charge properties. The flocculation behavior of polyaluminum chloride (PAC) has been studied together for comparison. Moreover, the combined flocculation using PAC as a coagulant and STC-*g*-PDMC as a coagulant aid in HA flocculation have also been tried.

## 2. Materials and methods

### 2.1. Materials

Starch (weight-average molecular weight of ~1.5 × $10^5$ g/mol) was purchased from Binzhou Jinhui Corn Development Co., Ltd. Chloroacetic acid (C.P.) was obtained from Zibo Lushuo Economic Trade Co., Ltd. (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC, C.P.) was from Shanghai Bangcheng Bilogical Technol. Co., Ltd. while (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CTA, C.P.) was purchased from Wuhan Yuancheng Sci. and Technol. Development Co., Ltd. Potassium persulfate (A.R., Shanghai Lingfeng Chemical Reagent Co., Ltd.), the powdered humic acid (sodium salt, Aladdin Industrial Co. Ltd.), and polyaluminum chloride (PAC, $[Al_2(OH)_nCl_{6-n}]_m$, n = 3.6–5, m < 10, $Al_2O_3$ content > 28%) were used directly without further purification in this study. All other chemicals were obtained from Nanjing Chemical Reagent Co., Ltd.

### 2.2. Preparation and characterization of starch-based flocculants

The synthetic routes of STC-*g*-PDMC, STC-CTA, and CMS-*g*-PDMC were determined according to the previous literatures (Li et al., 2015; Sen et al., 2009; Wang et al., 2013) and described in detail in Scheme 1. Briefly, STC-*g*-PDMC was prepared by grafting copolymerization under nitrogen protection and DMC was the grafting monomer while potassium persulfate (KPS) was used as initiator (Wang et al., 2013). STC-CTA was obtained by etherification and CTA was the etherifying agent (Li et al., 2015). A two-step method was used to prepare CMS-*g*-PDMC by combination of etherification and graft copolymerization. Carboxymethyl starch (CMS) was prepared first and chloroacetic acid was used as the etherifying agent, making water solubility of starch improve markedly. Then PDMC chains were grafted onto CMS backbone in a homogeneous solution using KPS as initiator (Sen et al., 2009; Wang et al., 2013). The three modified starch flocculants were all precipitated in acetone. The obtained solid products were filtered and washed by acetone for three times. Finally, the samples were extracted in a Soxhlet apparatus for 72 h, using acetone as solvent, to remove all the impurities, and then vacuum dried at 45 °C, thereby obtaining the final products. Moreover, the extents of the functional groups in those starch-based flocculants have been estimated by the colloidal titration which was described in detail in our previous work (Zhang et al., 2012). The extents of positive quaternary ammonium salts in STC-*g*-PDMC, STC-CTA, and CMS-*g*-PDMC are approximately 2.21, 1.16, and 1.72 mmol/g respectively, while that of carboxymethyl groups in CMS-*g*-PDMC is about 1.07 mmol/g.

The fourier transform infrared (FTIR) and $^1$H nuclear magnetic resonance ($^1$H NMR) spectra of the three final products were measured by a Bruker Model IFS 66/S FTIR spectrometer and a Bruker AVANCE Model DRX-500 respectively. The zeta potentials of three flocculants' aqueous solutions with a concentration of 1.0 g/L were recorded by a Malvern Model Nano-Z Zetasizer in a wide pH range from 2.0 to 10.0 adjusted by dilute HCl or NaOH aqueous solutions.

### 2.3. Flocculation experiments

HA was selected as the target contaminant here and a stock solution was prepared by dissolving 1.0 g of HA into 1.0 L of 1.0 × $10^{-4}$ mol/L NaOH solution (Kim, 2015). The actually used HA solutions was diluted to desired concentrations (10, 20, 50, and 100 mg/L respectively), then filtered by glass-fiber filters with a pore size of 0.45 μm.

Jar tests were carried out using 250-mL jars and a six-place programmed paddle mixer model of TA6 (Wuhan Hengling Tech. Co. Ltd.) in water bath at the constant temperature of 25 °C. After the pHs of the HA solutions were adjusted to desired levels by diluted HCl or NaOH aqueous solutions, the designed doses of flocculants were added into the synthetic wastewater. The ionic strength of each solution was kept constant. The detailed flocculation procedure consisted of three steps. (1) The solutions were mixed by a 2-min stir at a high speed of 200 rpm, (2) followed by a slow stir at 50 rpm for 20 min, and (3) finally settled at least 30 min.

After flocculation, the supernatants were taken out for determination of the residual HA concentrations using a UV-1800 spectrometer (Shimadzu Corporation, Japan) in combination with previously prepared calibration curves at the wavelengths of 254 nm. The HA removal percentage was calculated as the following equation: