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Evaluation of the starch-based flocculants on flocculation of hairwork wastewater

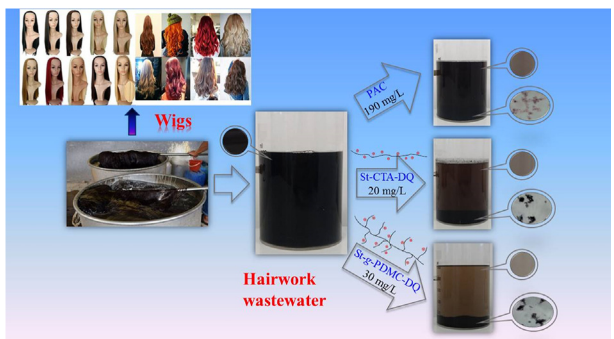
Qing Du, Hua Wei, Aimin Li, Hu Yang *

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, PR China

HIGHLIGHTS

- Two versions of starch-based flocculants with different structures have been prepared.
- Flocculation of hairwork wastewater was studied.
- Effects of cationic contents and chain architectures have been investigated.
- Patching mechanism plays an important role in flocculation process.
- The structure-activity relationship of starch-based flocculants has been discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

China is the world's largest producer of wigs, and the manufacturing generates large quantities of hairwork effluents. Coagulation/flocculation is an important step in the water treatment process. In this study, two versions of starch-based flocculants were successfully prepared through etherification and graft copolymerization, respectively. Starch-3-chloro-2-hydroxypropyl triethyl ammonium chloride (St-CTA-DQ) and starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] (St-*g*-PDMC-DQ) both contain strongly cationic quaternary ammonium salt groups, but have differing cationic contents, specifically, the degree of substitution (DS) and grafting ratio (*G*). Furthermore, the additional functional groups were distributed on different chain sites (the starch backbone for St-CTA-DQ, and the branch chains for St-*g*-PDMC-DQ). These two flocculants demonstrated superior efficiency for turbidity and UV_{254} removal in hairwork wastewater as well as better floc properties compared to polyaluminum chloride. The effects of pH, flocculant dose, and cationic group contents (DS and *G*) were systematically investigated. Consequently, it was determined that a higher cationic content in both the flocculants led to better flocculation performance as well as increased removal rates of both turbidity and UV_{254}. This was primarily due to improved charge neutralization, which highlighted the preference towards a lower optimal dose. In addition, flocculation performance worsened as the pH level increased. Overall, St-*g*-PDMC-DQ exhibited similar flocculation performance to St-CTA-DQ. However, the wastewater treated by St-*g*-PDMC-DQ showed lower residual turbidity than when treated by St-CTA-DQ. This was attributed to the distinct branch chain architecture of St-*g*-PDMC-DQ, which was beneficial for coagulating the uneasily flocculated contaminants in water, such as smaller-sized colloids and water-soluble organic substances. Flocculant structural factors, specifically charge properties and chain architecture, heavily affected the final flocculation performance.

* Corresponding author.
E-mail address: yanghu@nju.edu.cn (H. Yang).

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1. Introduction

The demand for wigs prompted the rapid development of the hairwork industry. China is leading wig production, accounting for >70% of the total global supply (Shang, 2015). The most common wig manufacturing workflow includes pickling, neutralizing, rinsing, and dying (Li and Li, 2014). Thus, the hairwork industry consumes massive quantities of water and generates large amounts of effluents. However, these hairwork effluents are high in chromaticity, odor, turbidity, chemical oxygen demand (COD), ammonia nitrogen (NH_3–N), and many toxic substances, such as colorants and surfactants. As these are not easily biodegradable, it accumulatively results in water quality degradation (da Silva et al., 2016; Yeap et al., 2014). From an environmental sustainability standpoint, the treatment of these effluents from hairwork manufacturing plants is of considerable interest to the scientific community. The typical wastewater treatment process adopted by local wig plants includes air stripping, electrolysis, coagulation/flocculation, pH adjustment, hydrolysis acidification, anaerobic process, and biocontact oxidation (Li and Li, 2014).

Among the sewage treatment processes, coagulation/flocculation is a crucial step (Bratby, 2016; El-Gohary et al., 2010; Lee et al., 2014). It has proven very useful in the treatment of wastewater discharged from various industries, including paper mills, textile mills, dye plants, and hospitals (Ahmad et al., 2007; El-Gohary and Tawfik, 2008; Gautam et al., 2007; Yeap et al., 2014). The final coagulation/flocculation performance is usually largely dependent on the coagulants/flocculants selected (Bratby, 2016; Lee et al., 2014; Yang et al., 2016). Although traditionally inorganic-metal-based and synthetic-organic-polymeric flocculants were widely used, they are known contributors to secondary pollution and health risks due to the residual metal ions, as well as the release of toxic organic monomers into the target water (Bolto and Gregory, 2007; Bratby, 2016; Ippolito et al., 2011). Furthermore, a higher dose of inorganic-metal-based coagulants is usually needed in practice, which produces more sludge. As a result, we aimed to develop new environmentally friendly flocculants.

Recently, natural polymer-based flocculants have gained interest in the field of water treatment because of their widespread availability, low cost, environmental friendliness, and biodegradability (Bolto and Gregory, 2007; Rinaudo, 2006). Among the numerous natural polymer-based flocculants, chitosan, cellulose, starch, and their derivatives have proved highly effective (Bolto and Gregory, 2007; Cai et al., 2015; Guibal et al., 2006; Huang et al., 2016; Wu et al., 2016; Yang et al., 2016). However, the higher cost of chitosan and the greater difficulty in modifications of cellulose due to its poor water solubility limit their practical applications in water treatment (Bolto and Gregory, 2007; Cai et al., 2015; Rinaudo, 2006; Yang et al., 2016). By contrast, starch is not only an inexpensive and abundant natural resource, it is also easily chemically modified by introducing various functional groups onto its backbone to satisfy different application purposes, such as esterification, etherification, and graft copolymerization (Lin et al., 2012; Rath and Singh, 1997; Wei et al., 2008; Wu et al., 2016). In fact, many starch-based flocculants with good flocculation performances have been obtained (Huang et al., 2016; Krentz et al., 2006; Sen et al., 2009; Song et al., 2009; Wang et al., 2013; Wu et al., 2016, 2017). In those previous reports (Huang et al., 2016; Krentz et al., 2006; Sen et al., 2009; Song et al., 2009; Wang et al., 2013; Wu et al., 2016, 2017), the effects of many external environmental parameters, such as pH, temperature, and dose, on the flocculation performance of the starch-based flocculants have been extensively studied.

However, the molecular structure of materials including coagulants/flocculants has a great effect on their final performances (Ashby et al., 2013; Ravve, 2013; Yang et al., 2016). In coagulation/flocculation process of water treatment, the design or selection of coagulant/flocculant, highly depending on its structure–activity relationship, is important for efficient decontamination of target wastewater. When considering polymeric flocculants, the type, contents, and distribution of additional functional groups are critical structural factors (Razali and Ariffin, 2015; Wu et al., 2016, 2017; Yang et al., 2012a). Given that most inorganic and organic suspended colloids in water contain negative charges, cationic groups are usually introduced onto the flocculants to enhance the charge neutralization capability. Hence, the cationic contents of those polymeric flocculants, that is, the degree of substitution (DS) or grafting ratio (G), are important (Razali and Ariffin, 2015; Yang et al., 2012a). In addition, those additional functional groups distributed different chain sites usually resulted in various chain architectures as well as specific application performances (Wu et al., 2016, 2017). Nevertheless, current research efforts are limited concerning the application of starch-based flocculants with different structural factors for treatment of various wastewaters including hairwork effluents.

In this study, two versions of novel starch-based flocculants were successfully prepared: starch-3-chloro-2-hydroxypropyl triethyl ammonium chloride (St-CTA-DQ) and starch-*graft*-poly[(2-methacryloyloxyethyl) trimethyl ammonium chloride] (St-*g*-PDMC-DQ). Both flocculants contained strongly cationic quaternary ammonium salt groups, but they were distributed on different chain sites (starch backbone for St-CTA-DQ and branch chains for St-*g*-PDMC-DQ). Moreover, for each version of starch-based flocculants, four variations with different cationic contents were further obtained. Fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR), and zeta-potential (ZP) measurements were used to characterize the structure and solution properties of the starch-based flocculants. In addition to two environmental parameters, pH and flocculant dose, the effects of structural factors, i.e., cationic group contents and distributions, on the flocculation of the hairwork effluents were investigated systematically. Accordingly, flocculation mechanisms were discussed in detail. Lastly, the flocculation behavior of polyaluminum chloride (PAC) was also studied for comparison.

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. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA, C.P.) and 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC, C.P.) were obtained from Wuhan Yuancheng Science and Technology Development Co., Ltd. and Shanghai Bangcheng Biological Technol. Co., Ltd., respectively. Ammonium persulfate was acquired from Shanghai Lingfeng Chemical Ragent Co., Ltd. Polyaluminum chloride (PAC, $[Al_2(OH)_nCl_{6-n}]_m$, $n = 3.6$–5, $m < 10$, Al_2O_3 content ≥28%) was used directly without purification in this study. All other chemicals were purchased from Nanjing Chemical Reagent Co., Ltd. Distilled water was used in all experiments.

2.2. Raw wastewater

Xuchang, Henan Province of China, is one of the most important wig manufacturing bases (Shang, 2015), and wastewater from a hairwork manufacturing plant located there was collected and used as raw water without any pretreatment. The wastewater was preserved at 4 °C in a refrigeration unit. The wastewater had a very dark red color and strong odor, and the main characteristics are described in Table 1. Accordingly, the hairwork wastewater showed the characteristics of high COD, turbidity, and suspended solid (SS). Particle size and distribution were analyzed using a Malvern Mastersizer 3000 system, and details are shown in Supporting information Fig. S1. The median particle size [d(0.5)] was about 1.07 μm, indicating that the hairwork wastewater mainly contained larger particles.