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Cationic xylan- (2-methacryloyloxyethyl trimethyl ammonium chloride) polymer as a flocculant for pulping wastewater

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ABSTRACT

In this work, pulp mill wastewater was treated with a novel polymer flocculant, which was synthesized through polymerizing (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC) and xylan. Xylan-DMC polymer removed 94.5% of turbidity, 61.7% of chemical oxygen demand (COD), 45.0% of lignin, 65.7% of sugar and 73.5% of biological oxygen demand (BOD) from the wastewater at the polymer concentration of 500 mg/L. The flocculation mechanism was fundamentally assessed with determining hydrodynamic size and chord length of flocs in the wastewater at different dosages of xylan-DMC polymer in the system. By adding polymers, the number of flocs with a small chord length (10–50 μm) decreased, while that with a large chord length (150–300 μm) increased, indicating the small particles agglomerated via bridging induced by the polymer. The sedimentation of formed flocs was quantitatively investigated by a vertical scan analyzer and the results depicted that the flocs could settle readily from the system.

1. Introduction

Wastewater produced in the pulping industry contains fine suspended and dissolved solids, inorganic and organic particles and other impurities, which are difficult to settle due to their small sizes and surface charges. The removal of these colloidal particles from the wastewater becomes a serious challenge for industry (Lee, Robinson, & Chong, 2014; Nasser & James, 2006). Colloids in the wastewater are usually negatively charged, and hence flocculation process with cationic flocculants is one of the most widely used techniques for treating wastewater (Teh, Budiman, Shak, & Wu, 2016).

However, commonly used synthetic cationic polymers, such as poly (2-methacryloyloxyethyl) trimethyl ammonium chloride (PDMC) and poly (diallyldimethyl ammonium chloride) (PDADMAC) are expensive and resistant to biodegradation, which hampers their uses in industry and introduces environmental problems (Bolto & Gregory, 2007). In this respect, there is an increasing demand for more environmentally friendly and effective flocculants in industry.

Recently, the flocculants produced by grafting cationic synthetic polymers onto biodegradable polysaccharide backbones have received great attentions (Constantin, Mihalcea, Oanea, Harabagiu, & Fundueanu, 2011; Dax et al., 2014; Wang et al., 2014). In the past, many flocculants, such as hydroxypropyl methyl cellulose grafted with polyacrylamide (HPMC-g-PAM) (Das, Ghorai, & Pal, 2013), PDADMAC grafted cassava starch (Razali & Ariffin, 2015), PDMC grafted starch (PDMC-g-STC) (Wang, Yuan, Wang, & Yu, 2013) and PDMC grafted chitosan (PDMC-g-chitosan) (Wang, Chen, Ge, & Yu, 2007; Wang, Chen, Yuan, Sheng, & Yu, 2009) were produced and their flocculation performance was assessed in kaolin suspensions or various pulping and municipal wastewaters. The turbidity of a kaolin suspension decreased to 25 NTU from 600 NTU when 0.1 mg/L of PDMAC-g-STC was added to the suspension (Wang et al., 2013). Wang et al. (2009) reported that 99.4% of turbidity, 81.3% of lignin and 90.7% of COD could be removed from a pulp mill wastewater at 17.8 mg/L concentration of PDMC-g-chitosan in the effluent. In the study conducted by Pal, Ghorai, Dash, Ghosh, and Udayabhanu (2011), 0.5 mg/L of polyacrylamide grafted carboxymethyl guar gum (PAM-g-CMG) was able to decrease the turbidity, suspend solids and COD from 64 to 9 NTU, 350 to 30 mg/L and 540 to 210 mg/L, respectively (Pal et al., 2011). In our previous study, a novel polymer was synthesized via polymerizing DMC and xylan (xylan-DMC) and the copolymer was utilized as a flocculant in removing anionic dyes from solution systems as well as kaolin and bentonite from suspension systems (Wang, Hou, Kong, & Fatehi, 2015; Wang, Konduri, Hou, & Fatehi, 2016). The results indicated that xylan-DMC removed 98% of azo-dye (Orange 16) at the concentration of 160 mg/L in the solution (S. Wang et al., 2015). The removals of kaolin and bentonite particles were 78.5% and 97.1%, respectively, at the xylan-DMC concentration of 16 mg/L (Wang et al., 2016). However, the

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properties of pulping wastewater, dye solutions and clay suspensions are very different. Pulping wastewater contains polymeric and monomeric organic materials with slightly negative zeta potential originating from carboxylate group attached to the organic materials (Razali, Ahmad, Ahmad, & Ariffin, 2011). Dye pigments are generally water soluble and highly charged (Fang, Cheng, & Xu, 2010) and clay suspensions contain inorganic particles that are substantially larger than the particles in pulping wastewaters (Wang et al., 2016). It is well known that the properties of particles significantly impact the process employed for their separation from colloidal systems. As there was no report regarding the application of this novel polymer (xylan-DMC) in treating pulping wastewater, it was not clear if this polymer could act as a flocculant for pulping wastewater. The first objective of this study was to evaluate if xylan-DMC could be an efficient flocculant for pulping wastewater.

Flocculation phenomenon occurs when small particles agglomerated into larger flocs, which helps their settlement and separation from solutions. Monitoring the growth of the aggregated particles, the behavior of agglomerated constituents in solutions and the sedimentation performance of the aggregated particles are crucial in assessing and understanding flocculation processes (Blanco, De La Fuente, Negro, Minte, & Tijero, 2002; Zhou & Franks, 2006). One method to identify the mechanism of flocculation is to evaluate the de-flocculation/re-flocculation of aggregated particles formed at different shear forces in solutions (Blanco, Negro, & Tijero, 2002). In the present study, focused beam reflectance measurement (FBRM) was used to monitor the size, numbers and reversibility of formed flocs in flocculation process (Hukkanen & Braatz, 2003; Kail, Marquardt, & Briesen, 2009; Marugán et al., 2008; Negro, Sánchez, Fuente, Blanco, & Tijero, 2006), and a vertical scan analyzer was employed to study the sedimentation performance of the formed flocs in the wastewater system (Kaombe, Lenes, Toven, & Glomm, 2013).

For the first time, the application of xylan-DMC polymer in the pulping wastewater was analyzed comprehensively, and the flocculation mechanism was investigated fundamentally in this work. Furthermore, the changes in the particle size and the settlement of the flocs were monitored, which are critical in developing an industrially attractive flocculation process for treating wastewater.

2. Methods and materials

2.1. Materials

Xylan from beechwood, [2-(methacryloyloxy) ethyl] trimethyl ammonium chloride solution (DMC), 80 wt.% in H_2O, sodium chloride, potassium persulfate (≥99.0%), ethanol (99.5%) and sodium nitrate (> 99.0%) were all purchased from Sigma-Aldrich company. Anionic polyvinyl sulfate (PVSK) was provided from Wako Pure Chem. Ltd. Japan and diluted to 0.0055 mol/L prior to use. Polydiallyldimethyl ammonium chloride (PDADMAC) was obtained from Sigma Aldrich Company and diluted to 0.0055 mol/L prior to use. Thermomechanical pulping spent liquor, which was generated via hot water treatment of wood chips prior to their refining, was collected from a pulp mill located in Northern Ontario, Canada. This wastewater was denoted TMPL in this work, and kept in a refrigerator at 4 °C in closed plastic barrels prior to use. Silicon oil was supllied by Formulaction company and used as received for calibrating the vertical scan analyzer.

2.2. Preparation of cationic xylan-DMC polymer

Xylan-DMC was synthesized as described in a previous study (S. Wang et al., 2015). 1 g of xylan was dissolved in 40 mL of water in a 250 mL three-neck glass flask to generate 25 g/L xylan solution. The flask was kept in a water bath at 30 °C and was deoxygenated using nitrogen atmosphere for 30 min. Then, a certain amount of DMC was added drop-wisely to the solution to generate a 3 mol/mol DMC/xylose ratio and the pH was adjusted to 7 with 0.1 mol/L NaOH. Then, 0.03 g of potassium persulfate was added to the system as an initiator and the polymerization was performed at 80 °C under nitrogen environment for 3 h. The solution was cooled to room temperature and mixed with ethanol to precipitate xylan-DMC polymer. The suspension was centrifuged at 3500 rpm for 10 min and the precipitated xylan-DMC polymer was dried at 105 °C and used as a flocculant for removing organics from the wastewater.

2.3. Flocculation

In this set of experiments, 10 g/L of xylan-DMC and xylan solutions was prepared via mixing the polymers with deionized water at room temperature. Different dosages (0–800 mg/L based on TMPL) of the polymer solutions were added to 50 mL of TMPL in 125 mL Erlenmeyer flasks. Then, the flasks were sealed and shaken at room temperature and 100 rpm for 30 min. After flocculation, the suspensions were centrifuged at 3000 rpm for 5 min and the filtrates were collected for analyses.

The numbers and size of particles in the suspensions at different polymer dosages were analyzed using a focused beam reflectance measurement (FBRM) (Particle Track E25 probe Mettler-Toledo AutoChem, USA). The methodology of FBRM is based on the application of a highly-focused laser beam scanning across particles in a suspension (Wang et al., 2014). This technique provides the chord length of the particles in a real time (Negro et al., 2006). In this set of experiments, the FBRM probe was inserted into a 500 mL glass beaker containing 200 mL of TMPL samples. Different dosages of xylan-DMC polymers were gradually added to the system, and the chord lengths of flocs were monitored at an agitation intensity of 250 rpm as described in the previous study (Fatehi, Gao, Sun, & Dashtban, 2016). In another set of experiments, 500 mg/L of xylan-DMC polymer was maintained in a 200 mL TMPL sample that was stirred at 250 rpm and then the measurement was conducted. Afterward, the stirring intensity was increased to 750 rpm to break the formed flocs (i.e., de-flocculation process). After reaching a steady state condition, the agitation intensity was reduced to 250 rpm to evaluate the re-flocculation of particles in the FBRM analysis.

2.4. Sedimentation analysis

The sedimentation of TMPL suspension in the presence and absence of xylan-DMC polymer was investigated using a vertical scan analyzer, Turbiscan Lab Expert (Formulaction Inc., France). In this set of experiments, 20 mL of TMPL suspensions with desired flocculant dosages was contained in cylindrical glass cells. The cells were vertically scanned with electro luminescent diode light source at 880 nm wavelength every 25 s for 1 h at 30 °C. Two synchronous optical sensors receive light transmitted through the sample (180° from the incident light, transmission sensor), and light backscattered by the sample (45° from the incident light, backscattering detector). The light passes through a transmission zone of the samples, while it cannot pass through the sediment zone of the samples (He, Zhang, & Fatehi, 2016). The higher transmission zone implies a clearer suspension due to the sedimentation of particles (Konduri & Fatehi, 2017). Based on the data collected, the clarity in the transmission zone of the samples was assessed with respect to the transition of silicon oil used for calibrating the instrument and the results were analyzed by Turbisoft 2.1 software (Kaombe et al., 2013; Qin, Yu et al., 2016).

2.5. Molecular weight analysis

Xylan and xylan-DMC polymer (at 5 g/L concentration) in 0.1 mol/L sodium nitrate solutions were prepared by stirring the solutions of the polymers at 300 rpm for 24 h, and then the solution was filtered with a 0.2 μm nylon filter. The filtered solutions were used for molecular