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Synthesis, characterization of a novel lignin-based polymer and its behavior as a coagulant aid in coagulation/ultrafiltration hybrid process

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ABSTRACT

A novel lignin-based flocculant was introduced in recycling of the biomass existing in papermaking sludge. The product, lignin-diallyl dimethyl ammonium chloride-acrylamide (LDA) was characterized as a cationic macromolecule polymer with broad structure. To demonstrate its efficiency, LDA was used as coagulant aid with polyferric chloride (PFC) and polyaluminum chloride (PAC) to remove humic acid by coagulation–ultrafiltration processes. Results showed that coagulation aid effect of LDA was not affected by the type of metal salts and removal ratios of dissolved organic carbon were maximum 15.1% and 11.9% larger than single PFC and PAC coagulation, respectively. More concentrated flocs with larger size and open structure as well as low fractal dimension were formed by dual-coagulants. In PFC coagulation system, LDA could absorb negative charge on the surface of Fe(III) coagulated flocs efficiently and achieve the maximum floc strength accordingly. In the ultrafiltration experiment, cake layer fouling was demonstrated to be the foremost fouling mechanism. PAC combined used with LDA resulted in the minimum membrane fouling due to the formation of looser flocs as well as more concentrated floc size distribution. Overall, LDA brought in charge neutralization and absorption bridging effect and played a positive role in coagulation–ultrafiltration processes.

1. Introduction

Coagulation/flocculation processes are preferentially applied to remove dissolved and suspended organic wastes because of their high efficiency on treating a wide range of water types with relatively low cost (Semerjian and Ayoub, 2003). Coagulation based on hydrolytic metal salts has been widely used. The most common coagulants are polymeric aluminum and ferric salts, which also have drawbacks such as neurotoxicity of residual aluminum (Iddon and Scrowston, 1970) and chromaticity color or aggressive action caused by ferric-based salts (Bretherick, 1990b). Previous studies demonstrated that the application of organic coagulant aid in combination with traditional inorganic coagulants could not only lower the consumption of metal salts, but also satisfy higher requirement of dissolved organic matter (DOM) removal (McCurdy et al., 2004; Yan et al., 2007). Recently, there is a growing interest in the development of novel flocculants by utilizing industrial and agricultural wastes as eco-friendly materials.

Lignin is a principal renewable biomass composed of methoxylated phenylpropane structures so that be widely used as a starting material of chemosynthesis, especially polymers (Heitner et al., 2010; Lee et al., 2013; Pingali et al., 2014). Zhang et al (Zhang et al., 2013). reported a novel lignin-based polyampholyte and its decolorization effect of acid black dye. In Fang et al (Fang et al., 2010), dimethylamine, acetone and formaldehyde were grafted onto lignin to form a cationic flocculant. However, these products were mainly made by commercial lignin and plentiful chemicals or prepared in multistage reaction processes, which limited the application of lignin-base cationic flocculants. Papermaking sludge, as a by-product of pulp and paper mill wastewater treatment processes, is believed to be one of the uppermost manufacturing wastes in the future (Kallas and Munter, 1994). Traditional disposal methods such as landfill, combustion and biocompost are liable to cause huge economic burdens as well as long-term ecological pollution (Kirkland et al., 2002). On the other hand, papermaking sludge has the potential for offering raw materials to

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produce commercial chemicals due to its high lignin and cellulose fibers contents (Ye et al., 2012). Heretofore, the report on polymerization of papermaking sludge-based flocculant was still limited. Rong et al (Rong et al., 2013). synthesized a neutral flocculant based on lignin from papermaking sludge and proved its combination with aluminum salts achieved a higher dissolved organic carbon (DOC) removal efficiency than single use of aluminum salts. In general, a flocculant with higher cationic could remove more negative micro particles (Guibal and Roussy, 2007). Based on previous reports, preparation of cationic flocculant generated from papermaking sludge has not been studied. In this paper, the preparation of a novel cationic flocculant with the advantage of easy operation and high efficiency was introduced. The product, LDA was synthetized by grafting diallyl dimethyl ammonium chloride (DADMAC) and acrylamide (AM) onto lignin. Moreover, LDA was characterized by fourier transform infrared spectra (FTIR), scanning electron microscope (SEM), energy dispersive X-ray (EDX), molecule weight and zeta potential.

Floc properties, such as floc strength, structure and floc size distribution are usually used to measure the degree of flocculation (Cockerill, 1973), which also shows significant effects on membrane fouling during coagulation–ultrafiltration (C-UF) processes (Barbot et al., 2008). Membrane treatment has been applied in advanced water treatment gradually. So studies of the relationship between membrane fouling and floc properties are meaningful. Generally, stronger flocs are less compressible, so that can resist applied stresses during sedimentation and ultrafiltration to avoid the reduction of coagulation efficiency (Cockerill, 1973; Liu et al., 2011). As a quantitative index describing flocs structure, fractal dimension (D_f) is directly proportional to floc compactness (Park et al., 2006). Previous studies (Li et al., 2015)demonstrated that addition of LDA could enlarge floc size observably, but the relationship between other floc properties and membrane fouling was not analyzed.

In this study, LDA was used as coagulant aid of polyferric chloride (PFC) and polyaluminum chloride (PAC) in simulative low-molecular-weight humic acid (HA) synthetic water treatment to demonstrate its flocculation efficiency and effects on membrane fouling. In addition, coagulation and flocculation mechanisms under different conditions were discussed in detail.

2. Materials and methods

2.1. Preparation of flocculants and coagulants

2.1.1. Synthesis of LDA

LDA was synthetized by grafting DADMAC and AM onto lignin contained in papermaking sludge (Fig. 1). Dried sludge containing lignin (40–45 wt.%) and cellulose (5–10 wt.%) was obtained from an alkaline papermaking mill in the Shandong Province, China (Rong et al., 2013). Synthetic processes of LDA were as follows: i) 2.0 g papermaking sludge was added into NaOH solution under the pH of 12.0 and then centrifuged to obtain lignin supernatant (Sescousse et al., 2010); ii) collected supernatant was transferred into a three-necked flask after adjusting pH to alkalescence and then stirred continuously at 60–70 °C. With N_2 inlet, 0.05 g of $K_2S_2O_8$ and 0.05 g of edetate disodium were successively added. iii) After 20 min of reaction, mixed solution containing 2.5 g AM and 8 ml DADMAC (60.0 wt.%) was added into the reactor dropwise; iv) After 3–4 h of reaction, the product was extracted with acetone, soxhlet extracted by acetone/ethanol mixed liquor and washed with ethanol, finally vacuum dried at 50 °C. LDA solution was dissolved to 1.0 g/L and stored at 4 °C for further use.

2.1.2. Preparation of PFC and PAC

PFC stock solution with B value ($[OH^-]/[Fe^{3+}]$ mole ratio) of 0.5 was prepared by adding predetermined amount of Na_2CO_3 solution to $FeCl_3 \cdot 6H_2O$ solution dropwise and then $Na_2HPO_4 \cdot 12H_2O$ was added as a stabilizer. The mixture was stirred continuously until no sediment existing (Gao et al., 2011). PAC was synthesized by titration and B value (the mole ratio of $[OH^-]/[Al^{3+}]$) of the stock solution was 2.0 (Rong et al., 2013). These two products were diluted to the final Fe and Al concentration of 10.0 g/L. In this study, coagulant dosages were calculated as Fe or Al content (mg/L).

2.2. Structural characterization of LDA

Alkali lignin (AL), which was extracted from papermaking sludge by alkali-acid treatment, and LDA were contrastively characterized through following techniques. FTIR spectra were recorded on Perkin–Elmer "Spectrum BX" spectrometer ranging from 4000 to 400 cm^{-1} with a 1.0 cm^{-1} resolution. SEM was examined via JEOL JSM-6700F scanning electron microscope with the magnification of 5000. During SEM observation, EDX was measured to identify elemental percentages using Oxford INCA X-sight elemental analyzer. Molecule weight was acquired by Waters 1515 gel chromatography apparatus, US and 0.1 mol/L of $NaNO_3$ was used as the mobile phase. Digital viscometer (NDJ-5S, Shanghai, China) was used to measure the viscosity of products. Zeta potential was measured via Zetasizer 3000HSa, Malvern Instruments, UK.

2.3. HA–kaolin synthetic water

Water sample was synthesized by HA and kaolin stock solution, which were prepared based on previous reported methods (Rong

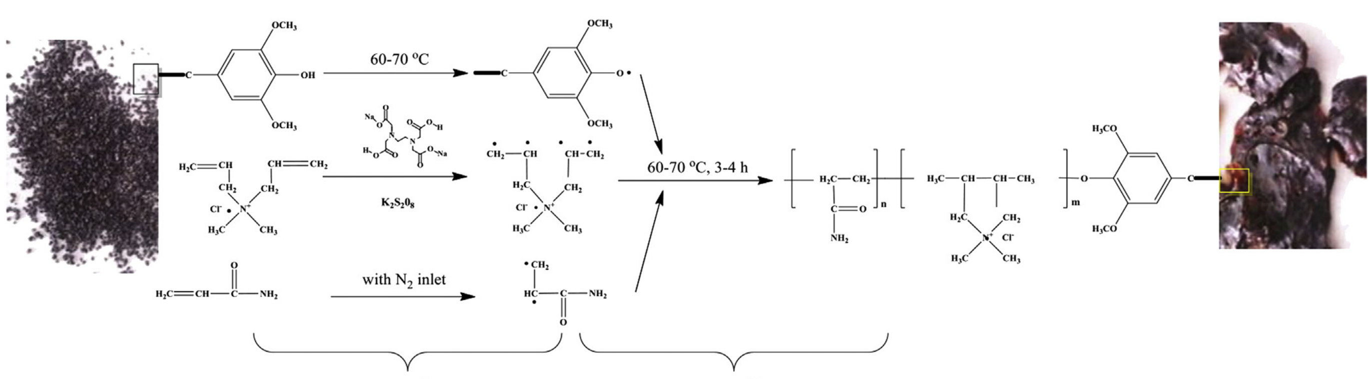

Fig. 1. Synthesis route of LDA.