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Effects of papermaking sludge-based polymer on coagulation behavior in the disperse and reactive dyes wastewater treatment

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HIGHLIGHTS

- Lignin-based flocculant (LBF) was prepared from papermaking sludge.
- Primary mechanism affecting floc properties under different conditions was studied.
- Addition of LBF improved the floc properties significantly at pH 9–10.
- Bridging effect of LBF played a more important role in the increase of floc size.
- Flocs in dual-coagulation were hard to be broken under the strong force condition.

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ABSTRACT

In this study, papermaking sludge was used as the raw biomass material to produce the lignin-based flocculant (LBF) by grafting quaternary ammonium groups and acrylamide. LBF was used as a coagulant aid with polyaluminum chloride (PAC) to treat reactive and disperse dyes wastewater. Effects of dosing method, pH, hardness and stirring speed on the coagulation behavior and floc properties were studied. Results showed that the superior coagulation efficiency and recovery factor were achieved by PAC + LBF compared with PAC and LBF + PAC. The primary mechanisms of LBF in the treatment of disperse and reactive dye solutions were charge neutralization and bridging effect, respectively. In the dual-coagulation, the impact of pH on the coagulation efficiency was weak during pH range of 5–9. Moderate hardness could enhance the floc properties due to the decrease of electrostatic repulsion and the chelation of Ca(II) and LBF. Besides, flocs coagulated by PAC + LBF had a stronger anti-crush ability.

1. Introduction

In the treatment of multifarious water samples, coagulation process is considered to be one of the most widely used pretreatment technologies to remove organic matter due to the high efficiency and low cost (Aljuboori et al., 2013; Pramanik et al., 2015). Conventional chemicals are mainly pre-polymerized aluminum or iron-based salts, such as polyaluminum chloride (PAC) and polyferric sulfate (PFS) (Yang et al., 2014a). Besides the neurotoxicity of residual aluminum (Yang et al., 2011b) and the chromaticity/corrosivity of ferric irons (Zhu et al., 2015), there also exist drawbacks in the application of metal based chemicals: the coagulation efficiencies are limited in the treatment of the special water samples (too high/low pH); the dosages are too large, and thus the cost are relatively high and a large volume of sludge is produced accordingly (Lin et al., 2015). Therefore, novel organic flocculants with high efficiency have been concerned and developed gradually, especially making full use of the biodegradable biomass. Li et al. (2016b) and Aljuboori et al. (2013) reported the production of polysaccharide-based compound bioflocculants and demonstrated their flocculating rates in the kaolin suspension, but the optimized pH range was narrow and the solubility of the products was limited. Yang et al. (2014a, 2014b) reported that the amphoteric chitosan-based flocculant which contained carboxymethyl and quaternary amine groups was efficient in the removal of particles and breaking cell walls. Zhu et al. (2015) reported the synthesis of dicarboxyl cellulose flocculant via Schiff-base route and the product exhibited the steady flocculating behavior in kaolin suspension and paper mill effluent. Lin et al. (2015) reported a novel starch-based composite flocculant, which had a superior sludge dewatering performance to polyacrylamide

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(PAM). Fang et al. (2010) prepared a lignin-based cationic polyelectrolyte through grafting dimethylamine, acetone and formaldehyde onto hydroxymethylated lignin. Above all, these studies of modified biomass-based flocculants were focused on the effects of dosage and pH on coagulation efficiencies. Floc property (e.g., floc size, anti-shear ability, fractal dimension) is a significant index to evaluate coagulation behavior. And it has been demonstrated to be related with coagulation performance and the cost of water treatment (Dong et al., 2015). So evaluation of floc structural indexes would be beneficial for the application of novel chemicals in actual water and wastewater treatment. So far, the study of floc structural properties of biomass-based flocculants under different water qualities and hydraulic conditions was still limited, especially the dominating mechanisms under the given conditions.

Compared with dosing metal salts or organic flocculants alone, the combination of metal salts and flocculants (denoted as dual-coagulants) could enhance the removal ratios of organic matter and decrease the chemical cost (Li et al., 2016a; Sun et al., 2016). Therefore, the dual-coagulants have been widely used in the treatment of actual polluted water. Based on our previous studies, cationic lignin-based flocculant (LBF) with high efficiency and low cost was prepared in the recycling of papermaking sludge (Li et al., 2016b). In this study, LBF was used as a coagulant aid with polyaluminum chloride (PAC) to treat simulated textile and dyeing wastewater. Textile and dyeing industry is one of the biggest consumption industries of water and complex chemicals during dyeing processes (Bu et al., 2016; Li et al., 2013). Effluent from dyeing industries contains different kinds of dyes with high molecular weight and complex structure, which leads to the low biodegradability (Shi et al., 2007; Zhang et al., 2008). Meanwhile these effluents contain the high concentration of inorganic salts, acids and bases, which hinder treatment efficiency and increasing the cost (Kim et al., 2004). In this study, disperse and relative dyes solutions were chosen as simulative dyes wastewater.

The objectives of this study are: (i) to investigate the coagulation behavior of PAC + LBF dual-coagulants in the treatment of disperse yellow and relative blue; (ii) to study effects of dosing sequence, initial pH and hardness on coagulation performance; (iii) to demonstrate the factors influencing the floc properties under the given conditions; (iv) to analyze dominating coagulation mechanisms and interaction under the given conditions.

2. Materials and methods

2.1. Preparation of chemicals and simulative solutions

In this study, all reagents used were of analytical grade and used without further purification. Polyaluminum chloride with the basicity of 66.7% (the percentage of $[OH^-]/[Al^{3+}]+[OH^-]$) was chosen as the coagulant and prepared by titration (Li et al., 2016b). The concentration of the stock solution was set at 10 g·Al/L. The dosage of PAC was calculated by the content of Al. LBF was made from the alkaline papermaking sludge (the lignin content >40%) by addition polymerization (Li et al., 2016b). Firstly, the lignin extraction solution was acquired by dissolving the papermaking sludge into the alkaline solution (pH > 11) and then high-speed centrifugation. And then LBF was synthesized by grafting dimethyl diallyl ammonium chloride and acrylamide in the presence of potassium peroxodisulfate and EDTA-Disodium. The zeta potential and molecular weight of LBF were approx. 36.0 mV and 800 KDa at pH 6. LBF was dosed as the liquid with the concentration of 1 g/L.

Disperse yellow SE-6GFL (D-Y) and Reactive blue K-GL (R-B) were chosen as the representation of disperse and reactive dyes. The simulative dye solutions with the concentration of 100 mg/L were prepared by dosing the dye power into tap water and stirring until dissolved actually. The wavelengths of D-Y and D-B at the maximum absorbance were 445 and 598 nm, respectively. The pH of raw water was approx. 8.20.

2.2. Coagulation process

2.2.1. Jar tests

Jar tests with unit volume of 1.0 L were performed by a program-controlled jar tester (Zhongrun Water Industry Technology Development Co. Ltd.). Based on the previous optimization experiments, the coagulation processes contained three regions: rapid mixing (200 rpm), slow mixing (35 rpm, 12.5 min) and sedimentation (0 rpm, 15 min). For PAC coagulation system, PAC was dosed at the beginning of the rapid mixing and this region lasted for 1 min. For PAC + LBF dual-coagulation, PAC was dosed first and then LBF was added after 30 s. LBF and PAC was dosed successively at an interval of 30 s, which was denoted as LBF + PAC. To study the effect of water quality and hydraulic conditions on the coagulation behavior, the indexes including initial pH and stirring speed were chosen. Initial pH was adjusted to 5–10 by 1.0 mol/L NaOH and HCl. To simulate breakage process, a force was introduced between the slow mixing region and sedimentation. And the stirring speeds were set at 100, 200, 300 and 400 rpm. Hardness of water samples was adjusted by adding $CaCl_2$ (A.R.) and the level of total hardness was based on the concentration of $CaCO_3$ (mol/L).

2.2.2. Water quality measurement

At the end of rapid mixing, zeta potential of coagulated water was measured by Zetasizer Nano (Malvern Instruments, UK). After the sedimentation, the upper water (200 ml) was collected from 2 cm below the surface and then adjusted the pH to 7.0 for absorbance measurement (using UV-754 UV/VIS spectrophotometer, Precision Scientific Instrument Co. Ltd.). The collected water samples were filtered through a 0.45 μm fiber membrane to test dissolved organic carbon (DOC) via the total organic carbon tester (Shimadzu TOC-VCPH, Japan). The removal ratio of color and DOC was calculated by the percentage of the removal color/DOC to the raw UV and DOC (Li et al., 2016a).

2.3. Floc dynamic

2.3.1. Procedure setting

During the given coagulation process, the solution was drawn through a photometric dispersion analyzer (PDA2000, Rank Brothers Ltd.) at a flow rate of 1.2 L/h and then returned to the reactor. The output data of PDA2000, the ratio of root mean square to transmitted light intensity (*Ratio*), was recorded every second. Based on the reported studies, there exists a positive correlation linear between *Ratio* with floc size under the given conditions (McCurdy et al., 2004). Therefore, *Ratio* was used to stand for floc size in this study. To investigate floc kinetic, four phases were introduced: (i) growth stage: rapid mixing (200 rpm); (ii) Steady-state stage: slow mixing (35 rpm, 12.5 min); (iii) Breakage stage: rapid mixing (50–400 rpm, 5 min); (iv) Resteady-state stage: slow mixing (35 rpm, 12.5 min). The standard curve of floc size monitored on-line and corresponding stages were shown in Fig. S1.

2.3.2. Calculation of floc property parameters

Floc properties studied in this study included floc size, crush resistance, recovery ability and structure. Floc size is quantitatively evaluated by flocculation index (FI), which is defined as the average *Ratio* value during the given stage (McCurdy et al., 2004).