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Characterization and performance of a novel lignin-based flocculant for the treatment of dye wastewater

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ABSTRACT

The application and modification of natural lignin in water treatment have attracted significant attention recently. An environmental friendly lignin-based flocculant (LBF) with enhanced flocculation effect was prepared from paper mill sludge in this work. The flocculation performance of LBF in combination with polyaluminium chloride (PAC) was evaluated for treatment disperse dye wastewater. Structure characterizations by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) spectroscopy and X-ray powder diffraction (XRD) confirmed that acrylamide (AM) and dimethyl diallyl ammonium chloride (DADMAC) monomers were grafted onto the backbone of alkaline lignin (AL) successfully. The results demonstrated that adding LBF as the coagulant aid greatly improved the decoloration capacity. LBF was more pH-independent and shear-independent than commercial polyacrylamide (CPAM) due to the enhanced charge neutralization and bridging action. Considerable improved floc properties and color removals occurred in the presence of Ca^{2+} and Mg^{2+}. In contrast, significant decrease in flocculation performance was observed in the presence of $SO_4{}^{2-}$ with or without LBF.

1. Introduction

Approximately 7×10^5 t synthetic dyes are produced around the world each year (Song et al., 2016), which cause serious environmental pollution due to their toxicity, mutagenicity and carcinogenicity (Krishnan et al., 2017; Yao et al., 2015). Techniques such as coagulation-flocculation, adsorption, biodegradation, chemical oxidation and membrane separation are commonly used in dye wastewater treatment (Singh et al., 2015; Zhu et al., 2014). Dye removal from wastewater by sedimentation following flocculation is the traditional method. However, flocs produced by inorganic coagulants are tiny and difficult to settle (Lal and Garg, 2017), generating high concentration of residual reagent as well as vast amounts of sludge after sedimentation (Mohd Yunos et al., 2017; Renault et al., 2009). Gao et al. (2007) reported that coagulation performance could be improved by dosing organic flocculants due to the enhanced charge neutralization and bridging action. Polyacrylamide (PAM) and poly dimethyl diallyl ammonium chloride (PDADMAC) are widely used for removing various contaminants from wastewater. However, these flocculants are derived from non-renewable resources, which are difficult to be biodegraded (Quinlan et al., 2015). In addition, the high costs, including material costs and operating costs, also limit their further application in wastewater treatment. Considering the conservation of non-renewable resources, the development of environmental friendly flocculants from sustainable materials should be investigated further (Cui et al., 2017; Mohd Yunos et al., 2017).

Lignin is a widely used biopolymer with a large diversity of functional groups including aromatic, phenolic hydroxyl, alcohol hydroxyl, carbonyl, methoxy, carboxyl and conjugated double bonds (Cui et al., 2017; Wang et al., 2018). Previous studies demonstrated that dimethylamine, acetone and methane could be grafted on lignin successfully (Fang et al., 2010; Li et al., 2016; Rong et al., 2014). A cationic lignin-based flocculant could achieve 95% of color removal in dye wastewater treatment (Fang et al., 2010). Rong et al. (2014) grafted AM onto the lignin backbone and synthesized a novel neutral flocculant, which exhibited significantly higher coagulation performance in comparison with polyaluminium chloride (PAC) or polyaluminium sulfate (PAS) alone. He et al. (2016) prepared sulfomethylated softwood lignin, which eliminated 99.1% of cationic dyes from cationic dye wastewater and 90% of COD from a wastewater. However, the commercial or analytical grade lignin used in previous studies increased the cost of lignin-based products (Du et al., 2014; Wang et al., 2018), thereby limiting their further application in wastewater treatment. As a result, the utilization of low-cost natural lignin for the preparation of novel

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flocculants would be desirable to improve sustainability and decrease the cost of treatment.

Biomass of paper mill sludge is abundant, including a large amount of alkali lignin (AL). However, most paper mill sludges are disposed off by traditional methods, e.g. landfill, composting or incineration (Li et al., 2016). As a result, extracting alkaline lignin from paper mill sludges represents an environmental-friendly disposal method for the waste paper mill sludges. In addition, the extracted AL shows promise as eco-friendly alternative material in water treatment.

In this work, an environmental friendly lignin-based flocculant (LBF) was produced from the paper mill sludge, and the coagulation efficiency of LBF for disperse dye wastewater was investigated. Characteristics of LBF were analyzed by fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) spectroscopy, X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and elemental analysis. Floc properties (floc size, strength factors, recovery factors, time-weighted variance and sedimentation rate), coagulation efficiencies and coagulation mechanisms were analyzed.

2. Materials and methods

2.1. Test water and chemicals

In brief, 0.1 g of dye powder (disperse yellow, SE-6GFL, chemically pure) was added to 1 L of tap water (pH: 8.00 ± 0.02) and stirred until complete dissolution. The absorbance (λ_{max} = 445 nm) and zeta potential of the artificial dye wastewater were about 0.850 ± 0.020 and −30.0 ± 1.0 mV, respectively. The disperse dye powder (color index number: disperse yellow 201) was obtained from Jinan No. 2 Textile Dyeing Mill, China.

PAC was used as the coagulant and LBF was used as the coagulant aid in this work. PDADMAC, cationic polyacrylamide (CPAM) and compound bio-flocculant (CBF) were used for comparison with LBF. PAC was prepared by dropwise adding Na_2CO_3 fluid into $AlCl_3{\cdot}6H_2O$ solution and stirring until complete dissolution. The concentration and basicity of PAC used in this work were 10 g/L and 2.0, respectively.

The concentrations of PDADMAC, CPAM and CBF solutions used in this work were 1 g/L. They were prepared as follows: 0.1 g of PDADMAC, CPAM (purchased from Henan Lantianbishui Purification Co. Ltd., China) and CBF powder was dissolved by deionized water (100 ml) with continuous stirring until complete dissolution.

2.2. Preparation of LBF

LBF was prepared from paper mill sludge (Linyi, Shandong province of China) by the following synthesis route (Li et al., 2016): 1) lignin was extracted from paper mill sludge by the acid-alkaline method described in the supplementary information. 2) acrylamide (AM) and dimethyl diallyl ammonium chloride (DADMAC) were grafted onto the lignin backbone with the initiator potassium peroxydisulfate and the chelating agent ethylenediamine tetra acetic acid disodium salt under basic condition (pH = 7.5–8.0); 3) the mixture was reacted for 3–4 h at 70 °C in water bath with continuous N_2 purge; 4) target LBF product was then extracted with acetone and washed by Soxhlet extraction for 72 h, and then vacuum dried at 50 °C. LBF solution with the concentration of 4 g/L was prepared and used in this work. Synthesis methods are specified in the supplementary information. The extracted lignin contained 16.54% of ash, 19.27% of moisture and 80.73% of solids.

2.3. Analysis methods

The molecular structures of AL and LBF were determined by FTIR on PerkinElmer “Spectrum BX” spectrometer at the wavenumbers of 4000 to 400 cm^{-1}. ^1H NMR and ^{13}C NMR (Bruker AVANCE Model DRX-500) was operated at 500 MHz using D_2O as solvent. The positive charge density of LBF was analyzed by titration with poly (vinyl sulfate) potassium (PVSK). XRD patterns of AL and LBF were characterized by powder X-ray diffractometry (powder XRD, D8 ADVANCE, Bruker) equipped with Cu Kα radiation (40 kV and 200 mA). Surface morphologies of AL and LBF were observed using JEOL JEM-2100F TEM with an accelerating voltage of 200 kV and JEOL JSM-6700F SEM with the magnification of 5000. Thermal behaviors of AL and LBF were determined by TGA-50 thermo-gravimetric analyzer at 800 °C under N_2 atmosphere. Elemental analysis for C, H, N of AL and LBF was performed with an Element Analyzer (PE 2400 II). Loss on ignition analysis of AL was conducted in a horizontal cylindrical furnace (SKQ-3-10) at 450 °C for 4 h (the heating rate was 10 °C/min). The moisture content of AL and LBF were measured by drying at 105 °C in a vacuum oven. The cationic degree and total acid number of LBF were analyzed by silver nitrate titration and potassium hydroxide titration, respectively.

2.4. Jar test

The jar test (jar test apparatus from ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) was conducted at room temperature using the following protocol: 1) the test water was stirred rapidly (200 rpm) for 1 min, and then the coagulants/flocculants were added with 200 rpm stirring for 2 min; 2) the stirring speed was adjusted to 35 rpm and maintained for 12.5 min; 3) finally, the coagulated water was settled for 15 min. According to the dosing sequence of the coagulants/flocculants, four coagulation procedures were evaluated: PAC (added PAC alone); PAC + LBF (dosed PAC and followed by LBF); LBF + PAC (dosed LBF and followed by PAC); PAC–LBF (mixed PAC and LBF before adding and added the mixture into the dye wastewater). Color removal was calculated from absorbance, which was determined by TU-1810 ultraviolet–visible spectrophotometer (Ertugay and Acar, 2017) (Beijing Purkinje General Instrument Co., Ltd.). Coagulant water before sedimentation was collected to measure the zeta potential using a dynamic light scattering instrument (Zetasizer Nano Series, Malvern Instruments Ltd., UK).

2.5. On-line optical determination of floc dynamics

On-line optical determination of flocs was monitored real-time with a PDA 2000 (Rank Bros Ltd., Cambridge, UK) operated according to photometric dispersion principle (Hopkins and Ducoste, 2003; Moussas and Zouboulis, 2009). The water sample was transferred to the equipment with a 3 mm plastic tube, and the experimental data (Ratio) was recorded by computer automatically. Coagulation procedures were similar to jar test.

2.6. Calculation methods

Strength factor (S_f), recovery factor (R_f) time-weighted variance (TWV) and sedimentation rate represent floc properties in dye wastewater treatment. Flocculation index (FI) is used to evaluate floc size and it is defined as the average Ratio value in the given stage (Jarvis et al., 2005; Yang et al., 2013):

$$FI = \frac{\sum_{i=1}^{N}(Ratio_i \cdot time_i)}{\sum_{i=1}^{N} time_i} \tag{1}$$

where $Ratio_i$ is the Ratio value in a certain time, and $time_i$ is the counter-time, N is the number of Ratios.

$$S_f = \frac{FI_1}{FI_0} \times 100 \tag{2}$$

$$R_f = \frac{FI_2 - FI_1}{FI_0 - FI_1} * 100 \tag{3}$$

where FI_0, FI_1 and FI_2 are FI value in steady state, breakage state and re-steady state, respectively.