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Evaluation of molecular weight, chain architectures and charge densities of various lignin-based flocculants for dye wastewater treatment

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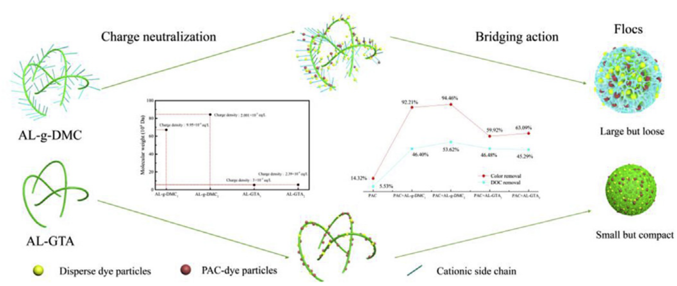
HIGHLIGHTS

- Four lignin-based flocculants were prepared from paper mill sludge.
- Flocculants with distinct molecular weight and charge densities were designed.
- Branched copolymers with high molecular weight exerted excellent color removals.
- Flocculants with same chain architectures but higher charge density performed well.
- The synergetic mechanisms and structure-activity relationships were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, four alkaline lignin (AL) based flocculants with distinct molecular weight, chain architectures and charge densities (denoted as AL-g-DMC_1, AL-g-DMC_2, AL-GTA_1 and AL-GTA_2) were prepared from paper mill sludge, which were designed via graft copolymerization of dimethyl diallyl ammonium chloride (DMC) or etherification of 2, 3-epoxypropyl trimethyl ammonium chloride (GTA). The characteristics of the aforementioned flocculants were evaluated by a series of analysis technologies, which essentially confirmed the successful introduction of quaternary ammonium groups onto the AL. The flocculation performances of the four synthesized lignin-based polymers as the coagulant aids for PAC were investigated in disperse dye (DY) wastewater treatment, and the effects of dosages, initial pH, coexisting ions, humic acid (HA) or kaolin particles were also studied. The results indicated that branched copolymers with high molecular weight like AL-g-DMC_1 and AL-g-DMC_2 exerted excellent color removals and satisfactory floc properties in comparison with linear polymers with low molecular weight (AL-GTA_1 and AL-GTA_2). Furthermore, AL-g-DMC_1 and AL-g-DMC_2 exhibited remarkable tolerance on pH alteration and coexisting ions owing to their strong bridging action.

1. Introduction

Recently, considerable increment of energy demand has promoted the development of renewable resources such as starch,

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chitosan, cellulose, hemicellulose and lignin (Wei et al., 2008; Chen et al., 2010). Among them, lignin is assigned as one of the promising natural polymers due to their biodegradability, environmental friendliness as well as availability (Naseem et al., 2016). Lignin is easily modified through graft copolymerization (Fang et al., 2010), etherification and sulphonation (He et al., 2016) on the basis of the existence of large amounts of active groups including hydroxyl and amino groups (Fang et al., 2008; Yang et al., 2015). Lignin-based products especially novel flocculants have drawn scholars' attention due to their high-performance, low-cost and eco-friendliness (Zhao et al., 2017). Large amounts of lignin-based flocculants have been prepared and investigated in previous studies, which exert superior performance in the decontamination of target pollutants. Fang et al. synthesized a lignin-based cationic polyelectrolyte by Mannich reaction, which removed 95% of anionic dyes and 89% of chemical oxygen demand (COD) (Fang et al., 2010); Rong et al. prepared a lignin-based organic polymer by graft copolymerization of acrylamide, which eliminated more than 90% of disperse yellow and reactive blue (Rong et al., 2013b); He et al. designed a sulfomethylated softwood lignin, which exhibited 99.1% of cationic dye removal and 90% of COD reduction (He et al., 2016). However, lignin used in previous studies was mostly commercial grade, which limited their further application due to the high cost. Therefore, the development and utilization of natural lignin in water/wastewater treatment are promising and meaningful.

Lignin is abundant in paper mill sludge, which can be easily extracted by chemical methods (Li et al., 2016; Veluchamy and Kalamdhad, 2017a). Paper mill sludge is difficult to dispose owing to its toxicities, vast volumes as well as the complexities of components (Veluchamy and Kalamdhad, 2017b). Techniques such as landfill and incineration are commonly used for paper mill sludge treatment (Goel and Kalamdhad, 2017; Veluchamy and Kalamdhad, 2017b), but the defects containing land wastage and secondary pollution limit their further application. Accordingly, the utilization of lignin from paper mill sludge not only provides a renewable material for wastewater decontamination but also proposes a novel method for paper sludge treatment.

The molecular structure multiplicity of the flocculants corresponds well to its final application performance (Wu et al., 2016; Liu et al., 2017). Flocculants with the same style of functional groups but distinct molecular weight, chain architectures (linear or branching) and charge properties sometimes exert dramatically different flocculation performance (Hu Wu et al., 2016; Zhouzhou Liu et al., 2017). Therefore, exploiting the structure-activity relationships of organic polymers is conducive to design the novel high-performance flocculants and optimize the application conditions in water treatment (Hu Wu et al., 2016; Qing Du et al., 2017). Previous studies with regarding to the development of effective lignin-based flocculants mostly forced on the category of functional groups and the chemical components of flocculants (Fang et al., 2010; Rong et al., 2013a; He et al., 2016). However, very little attention has been devoted to the structure-activity relationships of lignin-based flocculants in the elimination of target contaminants.

In this work, a series of eco-friendly lignin-based flocculants with distinct molecular weight, chain architectures and charge densities were prepared from the paper mill sludge. Among these flocculants, two target flocculants with the positive charges on the branch chains were synthesized through graft copolymerization of dimethyl diallyl ammonium chloride (DMC), which were named as AL-g-DMC_1 and AL-g-DMC_2. In contrast, the other two flocculants with positive charges on the backbone of the alkaline lignin (AL) were prepared by etherification of 2,3-epoxypropyl trimethyl ammonium chloride (GTA); they were defined as AL-GTA_1 and AL-GTA_2. Four lignin-based flocculants (AL-g-DMC_1, AL-g-DMC_2 AL-GTA_1 and AL-GTA_2) have observably different charge densities, which are due to the various feeding ratios of DMC or GTA monomers. Structure characteristics of AL-g-DMC_1, AL-g-DMC_2, AL-GTA_1 and AL-GTA_2 were assessed by fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR) and scanning electron microscopy (SEM). Besides, the molecular weight and the charge density of the target lignin-based flocculants were also measured. Meanwhile, the flocculation performances as well as the mechanisms of the aforementioned lignin-based flocculants for disperse yellow (DY) removal have been investigated systematically in terms of their molecular structures. The main purpose of this study was to i) propose an innovative method for paper mill sludge reutilization; ii) probe structure-activity relationships of lignin-based flocculants, which could be conducive to design efficient and economical flocculants.

2. Material and methods

2.1. Test water and chemicals

Around 0.1 g of DY powder (disperse yellow, SE-6GFL, chemically pure) was added into 1 L of deionized water and stirred until complete dissolution. Accordingly, the artificial dye wastewater (100 mg/L; $pH = 8.10 \pm 0.02$) showed the characteristics of strong electronegativity (zeta potential $= -27.69 \pm 0.05$ mV) and a very yellow color (absorbance ($\lambda_{max} = 445$ nm) $= 0.81 \pm 0.03$).

The DY particles were obtained from Jinan No. 2 Textile Dyeing Mill, China. Aluminium chloride hexahydrate, sodium carbonate anhydrous, potassium peroxydisulfate (KPS) and ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) were purchased from Sinopharm Chemical Reagent Co., Ltd. DMC with the mass fraction of 60 wt% was purchased from Shandong Luyue chemical Co., Ltd, while GTA (65 wt%) was from Shanghai Macklin Biochemical Co., Ltd. All of the chemicals were used without further purification in this work.

2.2. Preparation of lignin-based flocculants

A series of lignin-based flocculants with distinct molecular structures (molecular weight, chain architectures and charge densities) were prepared through graft copolymerization or etherification with different mass ratios of AL to each monomer (DMC and GTA). The reaction scheme of AL-g-DMC and AL-GTA is given in the Fig. 1.

The target AL-g-DMC_1 and AL-g-DMC_2 were synthesized by graft copolymerization of different amounts (5 and 15 ml) of DMC onto the AL, and the preparation procedures were given as follows (Liu et al., 2018): i) AL powder (2 g) was extracted from paper mill sludge by the acid-alkaline method, which was further purified by the repetitive extraction method (the acid-alkaline method is given in the supplementary material); ii) the initiator KPS (0.1 g) and the chelating agent EDTA-2Na (0.1 g) were successively added into the solution of AL (150 ml) at the pH level of 8.00–8.50, and then the mixture was reacted for 20 min; iii) DMC monomer (5 ml or 15 ml) was dropwise added into the mixture to enhance the reaction efficiency, and the reaction was conducted at 70 °C in the water bath for 3–4 h with the continues N_2 purge; vi) target lignin-based flocculants were then purified by soxhlet extraction for 72 h to remove the unreacted reagents and a few homopolymers of DMC, and then the samples were freeze-dried for 24 h.

The AL-GTA_1 and AL-GTA_2 were prepared through etherification by 10 and 30 g of GTA, and the synthesis steps were exhibited as follows (Kong et al., 2015): i) 2.0 g of dried AL powders were added into 150 ml of NaOH solution (1.0 mol/L) and stirred for 1 h in the water bath at 50 °C; ii) 10 or 30 g of cationic monomer, GTA, was dropwise mixed with the AL alkaline solution and stirred for 6 h to