



## Hydroxypropyl sulfonated kraft lignin as a coagulant for cationic dye

Yanzhu Guo<sup>a,b</sup>, Weijue Gao<sup>b</sup>, Pedram Fatehi<sup>b,\*</sup>

<sup>a</sup> Liaoning Key Lab of Pulp and Paper Engineering, Dalian Polytechnic University, Dalian, Liaoning Province, 116034, China

<sup>b</sup> Department of Chemical Engineering, Lakehead University, Thunder Bay, ON, P7B5E1, Canada



### ARTICLE INFO

#### Keywords:

Kraft lignin  
Lignosulfonate  
Sulfonation  
Dye removal  
Biorefining

### ABSTRACT

In this paper, kraft lignin was reacted with 3-chloro-2-hydroxypropansulfonic acid sodium (CHPS) to produce hydroxypropyl sulfonated lignin (SL). The effects of reaction conditions, e.g., the molar ratio of CHPS to lignin, the concentration of NaOH and the reaction temperature and time, on the charge density of resultant SL were investigated. The optimized conditions were found to be 80 °C, 4 h reaction time, 0.05 M NaOH concentration and 5/1 mol/mol of CHPS/lignin, which generated SL with the charge density and molecular weight of  $-3.33$  meq/g and 45,536 g/mol, respectively. The solubility of KL was 9.6 g/L while that of SL was 100 g/L at the neutral pH. The reaction mechanism between kraft lignin and CHPS was fundamentally discussed. The SL was also characterized by elemental analysis and proton nuclear magnetic resonance ( $^1\text{H}$  NMR). The thermal stability and surface activity of the SL were also evaluated and compared with those of commercially produced lignosulfonate (LSS). The efficiency of SL as a coagulant for dye (basic blue 41 and ethyl violet) removal from simulated wastewater was compared with that of LSS. The zeta potential and particle size analyses were conducted to determine the interaction mechanism of dye and lignin derivatives, and the kinetic studies confirmed their fast complexation.

### 1. Introduction

Among naturally occurring polymers, lignin is the second most abundant on earth after cellulose (Rastogi and Dwivedi, 2008). Lignin is produced commercially via two main processes of sulfite and kraft pulping. Lignosulfonates are the by-products of the sulfite pulping process. They are water soluble with an anionic charge density and have obtained uses as flocculants/coagulants in wastewater systems (He et al., 2016). However, the industrial use of lignosulfonates has been restricted by its limited supply, low purity and its limited sulfonate group (Aro and Fatehi, 2017). Kraft lignin (KL), on the other hand, is the byproduct of kraft pulping process with limited water solubility and industrial use (except as fuel) (Chakar and Ragauskas, 2004). Therefore, the sulfonation of kraft lignin can improve its water solubility, and the product may be able to replace lignosulfonate broadening its industrial uses.

In the past, cationization (Fang et al., 2010; Kong et al., 2015a; Laurichesse and Avérous, 2014; Meister and Li, 1992), carboxylation (Gan et al., 2013; Konduri et al., 2015; Lange and Schweers, 1980) and copolymerization (Ma et al., 2016; Mai et al., 2000; Vanerek and van de Ven, 2006) of lignin were studied. Sulfonation is another effective method to impart a high charge density into kraft lignin (Konduri and

Fatehi, 2015; Matsushita and Yasuda, 2005). The pKa value of sulfonate groups is below 2.0 (Espinoza-Acosta et al., 2016), which is lower than that of carboxyl groups (4.3) (Safaei Nikouei and Lavasanifar, 2011) and phenolic hydroxyl groups (close to 10.0) (Helander et al., 2013). Therefore, the pH sensitivity, especially the aqueous solubility, of lignins is extensively improved via sulfonation reaction (Konduri and Fatehi, 2015; Kong et al., 2015b). Efforts have been made on the sulfonation or sulfomethylation of kraft lignin (KL). Dilling (1991a) reported to convert KL to water-soluble sulfonated lignin via sulfuric acid treatment. However, the reactivity and sulfonation degree of the product were low due to the condensation reaction of lignin under acidic conditions (Matsushita and Yasuda, 2005). Sulfomethylation of KL with sodium sulfite or sodium bisulfite and an aldehyde (i.e., formaldehyde) under alkaline conditions were also studied (He and Fatehi, 2015; Konduri and Fatehi, 2015; Ouyang et al., 2009; Zhou et al., 2007). However, formaldehyde is not an environmentally friendly chemical. Therefore, developing a more environmentally friendly procedure for effectively sulfonating lignin is crucial in producing sulfonated lignin at commercial scales. 3-chloro-2-hydroxypropansulfonic acid sodium salt is an environmentally friendly chemical and has been used for sulfonating cellulose, starch and chitosan in the past (Song et al., 2013; Wang et al., 2015; Yin et al., 2009). Qin et al. (2015, 2016) have

\* Corresponding author.

E-mail address: [pfatehi@lakeheadu.ca](mailto:pfatehi@lakeheadu.ca) (P. Fatehi).

prepared sulfonated alkali lignin via crosslinking alkali lignin with epichlorohydrin and CHPS. However, the production of sulfonated kraft lignin only by sulfonation with CHPS has not been attempted in previous studies. Meanwhile, the effects of sulfonation reaction conditions, e.g., molar ratio of CHPS to lignin, reaction temperature and time, on the properties of the product have not been comprehensively discussed. In addition, the systematic understanding of the reaction mechanism of the CHPS and KL is unknown. One objective of this work was to investigate the reaction mechanism of CHPS and KL.

Owing to their excellent wettability and anionic charge density, lignosulfonates and sulfonated lignin have been exploited as coagulants (He et al., 2016), dispersants and concrete additives (Ouyang et al., 2009) as well as adsorbents for metals from wastewater effluents (Abu-Dalo et al., 2013). Coagulation process is preferentially applied to remove dissolved or suspended organic dyes from textile effluents because of its high efficiency and relatively low operation costs (Lee et al., 2014). Coagulants neutralize repulsive charges developed between dye particles, facilitate their aggregation and allow aggregated dyes to settle (Wahlström et al., 2017). In the past, sulfonated lignin was also used as a coagulant for water purification systems (Bolto and Gregory, 2007), while sulfomethylated kraft lignin (prepared by oxidation and sulfomethylation) was used as a coagulant for removing a cationic dye from a simulated dye solution (He et al., 2016). These studies reported the importance of charge density of sulfomethylated lignin in coagulating dyes. The second objective of this work was to study the interaction of this newly developed sulfonated lignin with cationic dyes.

In this paper, a novel sulfonated lignin with a high charge density was developed by reacting KL and CHPS under alkaline conditions. The effects of the sulfonating conditions on the charge density and molecular weight of the product were evaluated in detail. The properties of the SL were extensively studied by FTIR, TGA, NMR and GPC, tensiometer and compared with those of KL and commercial lignosulfonates. Moreover, the performance of SL, KL and commercial lignosulfonate in coagulating dye pigments in a simulated dye solution was discussed. The main novelty of this work was that the reaction mechanism of KL and CHPS were investigated comprehensively and the interaction of the product and a cationic dye was assessed in detail.

## 2. Experimental

### 2.1. Materials

Softwood kraft lignin (KL) was provided by FPInnovations' pilot plant facilities in Thunder Bay, ON, Canada. 3-chloro-2-hydroxypropansulfonic acid sodium salt (CHPS), sodium hydroxide with a 97% purity (reagent grade), polydiallyldimethyl-ammonium chloride (PDADAMAC), para-hydroxybenzoic acid, dimethyl sulfate, pyridine, deuterium oxide (D<sub>2</sub>O), deuterated chloroform (CDCl<sub>3</sub>), 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane (TMDF), cyclohexanol with a 99% purity, chromium(III) acetylacetonate, ethyl violet (EV), basic blue 41 (BB, 40% dye concentration), sodium chloride and potassium sulfate were all purchased from Sigma-Aldrich Company and directly used without purification.

Dialysis membrane with a molecular weight cut off of 1000 g/mol was purchased from Spectrum-Labs. Lignosulfonate acid (LSS), provided by Sigma-Aldrich Company, was purified by dialysis with deionized water for 2 days. After drying in the 105 °C oven, the charge density of purified LSS was determined to be −2.36 meq/g. Table 1 provides the properties of dyes used in this study, including UV absorption wavelength and standard curves used for determining the concentration of dye.

### 2.2. Sulfonation of KL by CHPS

Two grams of KL were added into a 250 mL three-neck round-bottom flask and mixed with 10 mL water by stirring at 200 rpm for

**Table 1**  
Properties of dyes.

Dyes	MW	Formula	Charge density (meq/g)	Wavelength (nm)	Standard curves
EV	492.14	C <sub>31</sub> H <sub>42</sub> N <sub>3</sub> Cl	2.65	595	y = 5.3863x + 0.1006 R <sup>2</sup> = 0.9996
BB	482.57	C <sub>20</sub> H <sub>26</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>	3.26	617	y = 6.0963x + 0.0133 R <sup>2</sup> = 0.9997

10 min. Different volumes of NaOH solution (1.0 M) were then gradually added to the solutions to control the desired concentration of NaOH in the reaction systems. The concentration of KL in the aqueous solution was 15 g/L. The flasks were then placed into a water-bath on a hot plate and the water-bath was heated to a desired temperature. Various amounts of CHPS were then added into the flasks under magnetic stirring at 500 rpm. The reactions were performed at different temperatures for different time intervals with a stirring rate of 400 rpm. After completion, the solutions were cooled to room temperature by immersing the flasks into cold water. After adjusting the pH of the solutions to 7.0 using HCl solution (20 wt.%), the mixtures were transferred into membrane dialysis tubes. The tubes were dialyzed against distilled water for 48 h to remove unreacted CHPS and salts. During the dialysis process, the distilled water was refreshed every 6 h. The final sulfonated lignin products (SL) were obtained by drying the dialyzed solution at 105 °C in an oven for 12 h.

### 2.3. Methylation of KL

In order to confirm if the phenolic or aliphatic hydroxyl groups of KL would participate in the sulfonation reaction with CHPS, the KL was methylated according to an established method (Sadeghifar et al., 2012). In this set of experiments, 1.0 g of KL and 15 mL of NaOH solution (0.7 M) were added into a 100 mL three-neck glass flask and stirred at 300 rpm for 30 min. After dissolving lignin in the NaOH solution, a desired amount of dimethyl sulfate (2.5 mol per each mol of phenolic hydroxyl group of lignin) was added to the system. After stirring at room temperature and 300 rpm for 30 min, the mixture was reacted at 80 °C for 2 h. The pH of reaction solution was controlled in the range of 11.0–11.5 by continuously adding NaOH solution (0.7 M) into the system. After the reaction, the pH of the solution was adjusted to 2.5 using HCl solution (2.0 M), which reduced the solubility of the sulfonated lignin and facilitated its precipitation. The precipitated particles were isolated by centrifugation at 3000 rpm for 30 min using a centrifuge (Sorvall ST 16, Thermo Fisher). The precipitates were then washed with distilled water several times until the pH of precipitates was close to 7.0. The final product was freeze dried for 48 h and defined as the ML.

### 2.4. Sulfonation of methylated KL by CHPS

The methylated KL was sulfonated by CHPS under the conditions of 5/1 mol/mol CHPS/lignin, 15 g/L lignin concentration, 0.05 M NaOH concentration, 80 °C and 4 h. The sulfonated products were purified by the dialysis as described in Section 2.2. This sulfonated sample was dried in a 60 °C oven and named as the SML.

### 2.5. Treatment of produced SL under alkaline condition

To explore if sulfonate group was hydrolyzed and cleaved from SL under a strong alkaline condition, the SL having 1.69 mmol/g sulfonate group, which was prepared under the optimal conditions of 5/1 mol/mol CHPS/lignin, 0.05 M NaOH concentration, 80 °C and 4 h, was treated in a glass flask in alkaline aqueous solution under conditions of 15 g/L concentration, 0.15 M NaOH concentration, 60 °C and 6 h. After

Download English Version:

<https://daneshyari.com/en/article/8879553>

Download Persian Version:

<https://daneshyari.com/article/8879553>

[Daneshyari.com](https://daneshyari.com)