Sulfonation of Hydroxymethylated Lignin and Its Application

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Abstract: To valorize kraft lignin, hydroxymethylation and sulfonation were applied on this under-utilized, but vastly available, material. The hydroxymethylation pretreatment was conducted as means to improve the reactivity of lignin. The sulfonation of hydroxymethylated kraft lignin was investigated by sulfuric acid and sodium sulfite treatments under various conditions. The modified lignin samples were characterized for their charge density, solubility, elemental components, and molecular weights. The results showed that the hydroxymethylation facilitated the sulfonation by sodium sulfite, yielding a product (SSH-lignin) with the charge density of \(-1.2 \text{ meq/g}\) and water solubility of 10 g/L under the conditions of $N_{2}SO_{3}$/lignin molar ratio of 0.49 mol/mol, 95 \textdegree C and 3 h. On the other hand, hydroxymethylation hindered the sulfonation of lignin by sulfuric acid, yielding a product (SAH-lignin) with the charge density of \(-0.46 \text{ meq/g}\) and solubility of 0.9 g/L under the conditions of $H_{2}SO_{4}$/lignin molar ratio of 14.8 mol/mol, 80 \textdegree C and 1 h. The SSH-lignin had a high adsorption on kaolinite (17 mg/g) at a lignin concentration of 40 g/L. The sulfonated lignins were also found to be effective coagulant for the cationic dye ethyl violet.

Keywords: kraft lignin; hydroxymethylation; sulfonation; adsorption; dye removal


1 Introduction

Lignin is one of the most abundant natural occurring biopolymers and provides an excellent source of inexpensive readily available chemical to create valuable products (Saito et al., 2012; Arevalo-Gallegos et al., 2017). Lignosulfonate produced from the sulfite process has long been utilized for various purposes (Liu and Peng, 2015; Aro and Fatehi, 2017). However, the amount of lignosulfonate produced is limited in the world, and thus it can not meet the demand for industry. This is because the number of sulfite pulping processes and their lignosulfonate production capacity are limited (Bleischwitz et al., 2009; Joelsson and Gustavsson, 2012). Kraft lignin, while abundant, has a very limited industrial application, as it is water insoluble and unreactive (Laurichesse and Avérous, 2014; Gellerstedt, 2015).

The sulfonation of Kraft lignin may render it with unique properties (e.g., water solubility and charge density) that are required for broadening its potential uses. Previously, sulfuric acid treatment was used as a method to sulfonate alkali lignin and hydroxymethylated alkali lignin derived from olive stone biomass, which were incorporated into a phenol/formaldehyde resin production (Zoumpoulakis and Simitzis, 2001). A study on the sulfomethylation reaction of lignin illustrated that a higher sulfur content at the ortho position on the guaiacyl phenylpropene subunit of lignin was beneficial for its application as a dispersant (He and Fatehi, 2015; konduri and Fatehi, 2015). As an unreactive material, kraft lignin may require pretreatment to allow for an efficient sulfonation.

In contrast to other wood-based materials, such as cellulose (Rajalaxmi et al., 2010), the modification of kraft lignin is challenging due to its structural complexity. The $\alpha$ position of phenyl propene subunits of kraft lignin presents the most reactive site for modification (Holmberg, 1935). However, the $\beta$-O-4 aryl ether linkages and others interconnecting bonds create significant steric hindrance or occupy the available $\alpha$ site (e.g., $\alpha$-O-4 aryl ether bonds) on lignin, which leads to further unreactivity of kraft lignin. The improvement in the reactivity of lignin would allow a greater amount of sulfonation to occur generating a sulfonate product with a high charge density.

Since 1990s, lignin has been modified via hydroxymethylation with formaldehyde to enhance its reactivity for the formation of phenol formaldehyde resins (Benar et al., 1999; Mansouri et al., 2007; Hu et al., 2011; Ma et al., 2011). Lignin can react with formaldehyde by heating under alkaline conditions. The hydroxymethylation reactions increase the bonding site through the addition of hydroxymethyl groups to the ortho positions of aromatic ring on lignin (Gosselink et al., 2004; Alonso et al., 2005).

The sulfomethylation can be conducted in one-step, i.e.,
hydroxymethylation through the addition of formaldehyde and sulfonation via using sodium sulfite simultaneously (Benar et al., 1999). Alternatively, the sulfomethylation reaction to produce sulfonated lignin products was reported to proceed in two steps of hydroxymethylation and sulfonation (Matsushita and Yasuda, 2005). In one study, the sodium sulfite treatment was conducted on hydroxymethylated acid hydrolysis lignin to produce sulfonated lignin to be used as a dispersant (Matsushita and Yasuda, 2005). However, it is not clear if the changes in properties of lignin are attributed to the hydroxymethylation. Despite available information about hydroxymethylation of non-wood and hydrolysis lignin, the hydroxymethylation of kraft lignin prior to sulfonation has not been fully studied. As wood species and their production process impact the properties significantly and thus the reactivity of lignin, available information is inconclusive for estimating the hydroxymethylation and sulfonation of kraft lignin. The main objective of this work was to study the hydroxymethylation pretreatment of kraft lignin to improve its reactivity toward its sulfonation via sodium sulfite and sulfuric acid treatments.

In this study, the hydroxymethylated lignin (H-lignin) was produced and the product was sulfonated with sulfuric acid or sodium sulfite under different scenarios. The characteristics of the products were evaluated by using a particle charge detector, conductometric titrator, elemental analyzer and gel permeation chromatography. The solubility of lignin after modification was also assessed. Based on the results, the conditions that yielded a sulfonated lignin derivative with the highest charge density and solubility were determined. The charge density and solubility were considered as key factors in determining the properties of the induced products to be used as a coagulant and functional filler. As kraft lignin is widely available, the main aim of this work was to generate results that are relevant to kraft pulping processes for their conversion into integrated forest biorefineries. The potential applications of the products were evaluated for their adsorption performance on calcium carbonate and kaolinite for functional filler production, as well as in coagulant systems for dye removal.

2 Materials and Methods

2.1 Materials

In this work, washed and dried softwood kraft lignin was supplied by FPInnovations from its pilot scale facilities in Thunder Bay, ON. Formaldehyde solution (30wt%), kaolinite, tetrahydrofuran (THF), NaOH, Na₂SO₃, acetic anhydride, pyridine, ethyl violet and poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight of 100 000–200 000 g/mol (20wt% in water) were all purchased from Sigma-Aldrich. Sulfuric acid (98% purity) was purchased from ACP company, and used as received. Anionic polyvinyl sulfate (PVSK) with a molecular weight of 100 000–200 000 g/mol (98.4wt% esterified) was provided by Wako Pure Chem. Ltd. Japan. Polytetrafluoroethylene (PTFE) filter was purchased from Fisher Scientific. The Tego@Trant A100 was supplied by Metrohm Inc. Dialysis membrane with a molecular weight cut-off of 1000 g/mol was obtained from Spectrum Labs.

2.2 Hydroxymethylation of kraft lignin

The hydroxymethylation of softwood kraft lignin was performed through the addition of dried kraft lignin (1 g) to formaldehyde solution at a CH₂O/lignin molar ratio of 0.55 mol/mol in a three-neck glass flask (Zoumpoulakis and Simitzis, 2001; Yu et al., 2013). The pH of the solution was adjusted to 10 with the addition of 2.5 mol/L NaOH, and bulked to a final fixed volume of 100 mL with deionized distilled water. The system was charged with a graham condenser and a magnetic stir bar and reacted at 95°C for 2 h. After the reaction, a 30 mL sample was taken for determining the yield of this reaction. The products were cooled to room temperature, neutralized with 1 mol/L H₂SO₄(aq) and then underwent membrane dialysis for two days, while changing water every 2 h for the first 6 h and then once a day for two days for purification. The purified solution was then dried at 60°C in an oven so that dried H-lignin was obtained.

2.3 Sulfonation of lignin with sulfuric acid

The H-lignin samples (0.5–1.0 g) were reacted with 1.5–20 g of 98% H₂SO₄ in a glass vials, vortexed at 2900 r/min for 1 min using Fisher Scientific Mini Vortexor (to ensure homogenous mixture), sealed and placed in an oil bath at a temperature of 80°C–160°C for 0.5–3.0 h. The reaction parameters were lignin/H₂SO₄(aq) molar ratio (6.5–92.6), reaction time (0.5–3.0 h) and temperature (80°C–160°C). Upon removing samples from the oil bath, the sulfonation reaction was stopped through neutralizing with NaOH (2.5 mol/L). The solutions were cooled to room temperature and unreacted sulfuric acid was separated by dialysis membranes while changing water every 2 h for the first 6 h and then once a day for two days.

2.4 Sulfonation of lignin with Na₂SO₃

In this study, 0.5–1.0 g of H-lignin samples were reacted with Na₂SO₃ in a multitude of conditions. The reaction parameters were Na₂SO₃/lignin ratio (0.2–0.7 m/m), reaction time (1–7 h), temperature (50°C–95°C) and lignin concentration (7.4–16.7 g/L). All reactions were conducted in a 500 mL three neck flask with a magnetic stirrer set at 300 r/min, which was assembled with a thermometer and a graham condenser with an effort to
eliminate the loss of sulfonation reagents through evaporation. Once the desired reactants were added, the solutions were adjusted to pH ≈ 10 with NaOH solution (2.5 mol/L) and heated to the appropriate temperature. Following the reaction, the products were removed from the reaction vessel, washed with distilled water and allowed to cool to room temperature. The solutions were then neutralized with a 0.4 mol/L H₂SO₄ solution, and allowed to cool to room temperature. The solutions were then neutralized with a 0.4 mol/L H₂SO₄ solution, and unreacted Na₂SO₃ and other contaminants were separated by dialysis membranes as explained earlier.

2.5 Analysis on degree of sulfonation

A conductometric titration was considered to determine the number sulfonated group attached to lignin. In this method, a 1wt% solution of lignin samples was prepared in distilled water and the mixture was shaken in a Boekel Scientific water bath operating at a temperature of 30°C and 100 r/min for 1 h. Then, the solution was titrated against Tego@trant A100 using a Metrohm 905 Titrand (Canada), and finally the sulfonation degree was calculated.

2.6 Charge density and solubility analyses

At first, a 1wt% solution of lignin samples was prepared by adding the lignin samples to deionized distilled water (pH=7) at room temperature. The solution was shaken for 1 h at 100 r/min at 30°C. After shaking, the solutions were centrifuged at 1000 r/min for 5 min in order to separate soluble and insoluble parts from the solution. The filtrate part was taken for charge density analysis of soluble lignin, while precipitates were dried in an oven at 60°C for charge density analysis of insoluble lignin. The charge density of soluble lignin samples was determined by direct titration, while the charge density of insoluble ones was identified by the inverse titration method using a Particle Charge Detector, Mutek PCD-04 titrator (Herrsching, Germany) and PDADMAC or PVSK standard solutions (~0.005 mol/L) as explained elsewhere (Inwood et al., 2017).

2.7 Elemental analysis

The elemental analysis of lignin samples was performed using a Vario EL Cube instrument (Germany). Lignin samples were loaded in an integrated carousel and flushed with carrier gas (He). The combustion of lignin samples was carried out, and the combusted gases were reduced in order to be identified by the instrument. The elemental analysis helped investigate the theoretical formula of lignin before and after treatment by considering the weight percentage and atomic weight of each element.

2.8 Molecular weight analysis

One hundred milligrams of dried lignin samples were suspended in 4.0 mL of acetic anhydride/pyridine 1/1 (v/v) solution stirring for 30 min at 25°C and 300 r/min, and then kept in the dark for 24 h. The resulting solution was added to 50 mL of cold water and centrifuged/washed three times. The solvent was then removed from the samples by a freeze dryer. The acetylated samples were dissolved in 10 mL of THF by stirring at 300 r/min at room temperature for 30 min and then filtered with a PTFE filter (13 mm diameter and 0.2 µm pore size). The filtered samples were used for a molecular weight analysis. The molecular weight analysis of the samples was determined using a gel permeation chromatography system, Malvern (Montreal, QC, Canada) GPCmax VE2001 Module + Viscotek TDA305 with multi-detectors (UV, RI, viscometer, low angle, and right angle laser detectors). The organic columns Poly-Analytic PAS106M, PAS103, and PAS102.5 were used for a molecular weight analysis, and HPLC-grade THF was used as solvent and eluent. The flow rate and column temperature were set at 1.0 mL/min and 35°C, respectively.

2.9 Adsorption of lignin on kaolinite

In this set of experiment, 1 g of kaolinite was added into 20 mL of lignin solution of varying concentrations (0–40 g/L) and the mixtures were shaken in a water bath for 24 h, and 100 r/min at 30°C (Pang et al., 2008). After shaking, the samples were centrifuged using a Thermo Scientific Sorvall ST 16 Centrifuge at 4000 r/min for 5 min, after which a clear supernatant was observed. The concentration of lignin remaining in solutions was measured by UV spectroscopy using a Thermo Scientific Genesys 10S UV-Vis at 205 nm and 280 nm. The adsorption amount was calculated by the difference in the concentrations of lignin in the supernatants before and after the adsorption test.

2.10 Dye coagulation analysis

In this set of experiments, a 0.1wt% solution of ethyl violet and a 0.03wt% solution of the sulfonated lignin samples was prepared. Then, 20 mL of the dye samples was added to 50 mL of centrifugal tubes. Afterward, the mixtures were shaken in a water bath at 30°C for 10 min at 100 r/min. After shaking, the samples were centrifuged using a Thermo Scientific Sorvall ST 16 Centrifuge at 2500 r/min for 10 min. The absorbance of the supernatant was measured at 595 nm for ethyl violet by Thermo Scientific Genesys 10S UV-Vis. The effectiveness of the lignin samples as coagulants was evaluated at different ethyl violet concentrations. Calibration standards for ethyl violet were created and a standard curve was utilized to determine the concentration of the dyes after the treatment with lignin samples.

3 Results and Discussion

3.1 Hydroxymethylation of lignin

The properties of unmodified and hydroxymethylated lignin are shown in Table 1. As can be seen, the molecular weight of H-lignin was marginally larger than the molecular
Weights of kraft lignin. Formaldehyde was reported to crosslink phenolic groups and lignin in acidic or basic environment (Gonçalves and Benar, 2001; Saito et al., 2012). This may also verify that polymerization occurred through the formaldehyde reagent despite optimum conditions designed to discourage this undesirable side reaction (Pang et al., 2008). The polymerization of formaldehyde with phenols and/or lignin was reported to occur via reacting at the available para or ortho positions of the phenyl propene subunits to form a tertiary functionalized network (Zoumpoulakis and Simitzis, 2001).

The elemental analysis facilitated the determination of chemical formulas for lignin samples. To allow for ease of comparison, a basis of 9 units of carbon was used. The chemical formula of softwood kraft lignin and H-lignin were determined to be C_{86.79}H_{214.1}O_{64.20}N_{0.07}S_{0.04} and C_{14.092}H_{30.90}O_{58.61}N_{0.04}S_{0.03}, respectively. The presence of sulfur in both kraft lignin and H-lignin may be indicative of impurities in unmodified kraft lignin, as unmodified kraft lignin was acid-washed with sulfuric acid prior to use. It is noted that hydroxymethylation increased the hydrogen and oxygen contents of lignin with grafting formaldehyde to the phenyl propene subunits of lignin. However, chemical formulas of lignin considering its methoxyl group is recommended for readers and will be in fact used by the authors in future studies.

### Table 1 Properties of lignin in this study

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
<th>Elemental composition (wt%)</th>
<th>Charge density (meq/g)</th>
<th>SO_3^- group (meq/g)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>Kraft lignin</td>
<td>9679</td>
<td>2141</td>
<td>4.52</td>
<td>64.20</td>
<td>5.12</td>
<td>0.07</td>
</tr>
<tr>
<td>H-lignin</td>
<td>14 092</td>
<td>3090</td>
<td>5.56</td>
<td>58.61</td>
<td>5.62</td>
<td>0.04</td>
</tr>
<tr>
<td>SAH-lignin</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>46.75</td>
<td>3.46</td>
<td>0.03</td>
</tr>
<tr>
<td>SSH-lignin</td>
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<td>2001</td>
<td>4.53</td>
<td>59.45</td>
<td>5.53</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Notes: All samples were created under optimum conditions for charge density and solubility. ND, Not detected.

The H-lignin exhibited a solubility of 55%. The charge density of H-lignin is higher than that of kraft lignin due to the addition of formaldehyde to the aromatic ring.

### 3.2 Sulfonation of H-lignin via sulfuric acid treatment

Figure 1a shows the charge density of soluble lignin (CDSL), charge density of insoluble lignin (CDIL), and solubility of sulfonated H-lignin (SAH-lignin) by H_2SO_4 as a function of sulfuric acid/lignin molar ratio. A maximum value of 0.4 meq/g was achieved for the CDSL, while solubility and the CDIL were marginal. Furthermore, the CDSL, CDIL and solubility exhibit no significant changes as the H_2SO_4/lignin molar ratio increased.

Figure 1b exhibits the CDSL, CDIL and solubility of SAH-lignin as a function of time of sulfonation reaction. It is evident that the CDSL, CDIL, and solubility remained low tested all the times. The CDIL was negligible and CDSL did not exceed 0.27 meq/g, regardless the reaction time.

Figure 1c presents the CDSL, CDIL and solubility of SAH-lignin as a function of temperature of sulfonation. Evidently, with an increase in temperature from 80°C to 140°C, the CDSL decreased from a value of 0.43 meq/g to 0.26 meq/g. The solubility and the CDIL remained negligible over the evaluated reaction temperature. This confirms the literature results that condensation reactions rely heavily on temperature and increase with time (Xie and Shi, 2011).

However, H-lignin has an initial charge density of 1.2 meq/g and a solubility of 55% prior to sulfonation. Therefore, it can be concluded that the sulfonation had a
detrimental effect on charge density and solubility, as the charge density and solubility of the H-lignin significantly dropped after sulfonation. In this respect, self-condensation of lignin under strong acidic conditions might be the main reason for such results (Matsushita et al., 2004a; Matsushita et al., 2004b; Matsushita et al., 2009).

3.3 Sulfonation of H-lignin via sodium sulfite treatment

Figure 2a shows the CDSL and the solubility of sulfonated H-lignin by Na₂SO₃ (SSH-lignin) as a function of the Na₂SO₃/H-lignin molar ratio. It is seen that the solubility increased from 75% to a maximum of 95.6% at the Na₂SO₃/H-lignin molar ratio of 0.33. A decrease in solubility is noted as the sulfonation molar ratio was increased to 0.82 mol/mol. Condensation has been found to occur in alkaline conditions (Hedjazi et al., 2009), and elemental sulfur in the solution reported to act as an inhibiting agent for alkaline condensation of lignin (Gierer, 1964; Gierer and Petterson, 1977). The charge density decreased from an initial charge density of 1.6 meq/g to 1.3 meq/g once the ratio increased from 0.67 to 1.20 Na₂SO₃/H-lignin. This decrease may be due to the presence of hydroxymethyl group on phenyl propene group being sulfonated at lower Na₂SO₃/H-lignin ratio, and occurrence of condensation at a higher Na₂SO₃/H-lignin ratio.

Figure 2b illustrates the impact of time on the CDSL and solubility of SSH-lignin. The CDSL increased from 1.08 meq/g to 1.60 meq/g as time of reaction extended from 1 h to 5 h. At shorter reaction times, the SSH-lignin was more soluble. However, extending the reaction time led to a decrease in solubility. As stated earlier, an increased reaction time favors condensation over sulfonation, which has been stated earlier to occur in alkaline conditions (Gierer, 1964; Gierer and Petterson, 1977).

Figure 2c presents the influence of reaction temperature on the CDSL and solubility of SSH-lignin. Through the examination of solubility and the CDSL, a temperature of 95°C was the optimum with the highest charge density of 1.4 meq/g and solubility of 96wt%. The optimized temperature for the sulfomethylation of sodium lignosulfonate was 95°C in the literature (Yu et al., 2013). However, a lower temperature of 85°C was reported as optimum for the sulfonation of woody biomass (Xie and Shi, 2011).

The optimum conditions for the SAH-lignin and SSH-lignin were the temperatures of 80°C and 95°C; reaction time of 1.0 and 3.0 h; H₂SO₄/lignin molar ratio of 14.8 mol/mol and Na₂SO₃/lignin molar ratio of 0.49 mol/mol, respectively.

3.4 Characterization of modified lignin

The properties of sulfonated lignin prepared under optimum conditions are shown in Table 1. The molecular weight of H-lignin decreases dramatically after sulfonation for SSH-lignin. This decrease in molecular weight can be attributed to the cleavage of large amount of ether bonds by the sulfonation of phenolic β-O-4 structure of lignin in alkaline solution (Matsushita, 2015), which will be discussed later. The molecular weight of SAH-lignin could not be measured, due to limited solubility of the lignin samples in tetrahydrofuran after acetylation. The derived chemical formula of SAH-lignin and SSH-lignin were C₉H₇.95₄O₆.90₈S₀.55₇ and C₉H₉.9₈O₃.₆₆S₀.₁₂, respectively. It is seen that oxygen is greater in the sulfonated lignin samples than kraft and H-lignin. The SAH had a greater amount of sulfur than SSH-lignin, which is due to the presence of sulfuric acid after treatment in the samples, and condensation of lignin using sulfuric acid as a catalyst would increase its overall molecular weight (Helander et al., 2013).

Lignin condensation under strong acidic conditions could be the reason for lower charge density of the SAH-lignin than that of H-lignin (Table 1). The sulfonation amount and charge density of SSH-lignin was determined to be over two times higher than those of the SAH-lignin (Inwood et al., 2017). The lower charge density of the SSH-lignin than that of H-lignin could be attributed to the loss of hydroxyl groups in condensation reaction under alkaline conditions (Gierer, 1964; Gierer and Petterson, 1977).
which are necessary for substitution by –SO₃⁻ groups.

3.5 Solubility

Figure 3 shows the solubility (1wt%) of lignin samples as a function of pH. Unmodified kraft lignin was only soluble under alkaline conditions at a pH higher than 10. The H-lignin exhibited improved solubility of 55% at pH 7. The SSH-lignin exhibited complete solubility over all pH ranges, because it has a large polarity originating from hydroxymethyl and sulfonated groups, which both would aid in maintaining a high solubility of lignin.

3.6 Sulfonation and hydroxymethylation reactions

The reaction schemes for sulfonation (via sulfuric acid or sodium sulfite) of hydroxymethylated are presented in Fig. 4. Lignin is an amorphous, polyphenolic, highly crosslinked polymer consisting of polyphenyl propene units joined by carbon-carbon and ether bonds. The subunits of lignin are referred to as p-hydroxyphenyl (H), guaiacyl (G), and sinapyl (S) subunits, respectively. As major components of softwood lignin are G units with trace amounts of S and small amount of H units, G and H units were drawn as the representatives in the following reaction schemes.

Fig. 4 Reaction scheme for sulfonation with hydroxymethylated lignin
With the aliphatic chain occupying the para position, the formaldehyde would react solely on the ortho position relative to the hydroxide group on lignin’s ring (Yasuda et al., 1998). Only one type of H-lignin (i-a in Fig. 4) can form via hydroxymethylation of G subunit, while two types of H-lignin (i-b and i-c in Fig. 4) could be induced from hydroxymethylaion of H subunit according to the number of ortho position substituted.

As discussed in our previous study, aromatic sulfonic group formed through the sulfonation by sulfuric acid on the ortho position of lignin’s aromatic ring under strongly acidic conditions (Cerfontain et al., 1985; Gao et al., 2019). Therefore, after the hydroxymethylation pretreatment, the occupation of both ortho positions on H-lignin i-a and i-b prevented introduction of sulfonic groups by sulfuric acid treatment, while H-lignin i-c presented the only possibility with sulfonation on its one available ortho position. This explains the relatively low charge density and sulfonic group content in the SAH-lignin (Table 1).

On the other hand, the sulfonation by sodium sulfite treatment mainly occurs on aliphatic hydroxyl groups (e.g., $\alpha$-position) as well as the phenolic $\beta$-O-4 structure of lignin under alkaline conditions (Matsushita, 2015; Aro and Fatehi, 2017; Gao et al., 2019). The sulfite group is not expected to react at the ortho position (relative to the hydroxide group) as stronger conditions are needed for aromatic substitution (Cerfontain et al., 1985). On the hydroxymethylated lignin (i.e., H-lignin i-a, i-b, i-c in Fig. 4), new reactive sites on both G and H subunits can occur for the sulfonation on the newly added hydroxymethyl group associated with the aromatic ring (Alonso et al., 2005). Thus, hydroxymethylation was demonstrated to be an effective pretreatment for the sodium sulfite treatment of lignin, resulting in its high sulfonic group content (Table 1) and solubility (Fig. 3).

## 3.7 Applications of sulfonated lignin

### 3.7.1 Adsorption performance

Fillers have been used in composites and papermaking to reduce the cost of the products and to improve their properties. However, a major problem of fillers is their compatibility with other components of composites and papermaking. Previously, various lignin species were adsorbed on activated carbon, calcium carbonate, and calcium oxide; and the products were reported to be used as modified fillers in various applications such as papermaking and composites (Fatehi et al., 2010; Fatehi et al., 2013). Therefore, the adsorption performance of the unmodified kraft lignin and the SSH-lignin samples was evaluated on kaolinite (Fig. 5) for serving for this purpose.

It can be seen from Fig. 5 that kraft lignin did not adsorb on kaolinite but did the sulfonated lignin samples. Generally, charge density, molecular weight, hydrophilicity and molecular structure of organic materials as well as the properties of adsorbents affect their adsorption performance on adsorbents. Increasing the sulfur content and molecular weight of lignin were reported to improve the adsorption of lignin (Matsushita and Yasuda, 2005). In the literature, increased charge density was noted to improve the adsorption capacity of lignocellulosic materials on calcium carbonate (Cerfontain et al., 1985). This is verified in this study, as the SSH-lignin exhibits the greatest charge density and the greatest adsorption affinity. The results showed that modified lignin samples had better adsorption than unmodified lignin. The modified kaolinite can potentially be used as fillers in composites or papermaking (e.g., container board).

Experiments were performed under the conditions of 30°C, 24 h and 100 r/min.

### 3.7.2 Dye removal

Lignin presents itself as an interesting compound to be converted to a coagulant as it degrades naturally into non-toxic monomers and shows great potential due to its large and complex polyphenolic structure (Hedges et al., 1985; Doherty et al., 2011; Zhang et al., 2013). The lignin samples synthesized in this study were also evaluated as a coagulant to remove cationic dye. Ethyl violet was chosen as a representative of cationic dyes with a charge density of 2.57 meq/g and a molecular weight of 492.14 g/mol. Figure 6 shows the impact of the SSH-lignin dosage on

Experiments were conducted under the conditions of 30°C, 10 min and 100 r/min.
ethyl violet dye removal. An optimum dye removal of 82.6% was reached at the SSH-lignin dosage of 0.2 g/L. Increasing the lignin concentration from 0.2 g/L to 0.3 g/L would produce overcharged complexes by the excess amount of available lignin in solution. These complexes would repel each other and prevent coagulation, leading to reduced dye removal (Fang et al., 2010). Kraft lignin, H- and SAH-lignin were not shown in this set of experiments due to their ineffectiveness and insolubility in neutral solutions.

### 4 Conclusions

Hydroxymethylation pretreatment hindered sulfonation \( \text{H}_2\text{SO}_4 \) while slightly favored sodium sulfite sulfonation. The sulfonation of H-lignin by sulfuric acid resulted in a product with the charge density of 0.46 meq/g and solubility of 9%, which was obtained under the conditions of 80°C, 1 h and 3.34×10^{-2} \( \text{H}_2\text{SO}_4 \)/H-lignin molar ratio. The sulfonation of H-lignin by sodium sulfate resulted in a product with the charge density of 1.2 meq/g and solubility of 100%, which was obtained under the conditions of 95°C, 3 h and 0.5 \( \text{Na}_2\text{SO}_4 \)/H-lignin molar ratio. The molecular weight of lignin samples increased after hydroxymethylation pretreatment, but it was reduced by sulfonation with sodium sulfate. The sulfonated lignin samples adsorbed considerably on kaolinite, which modified the surface of these fillers (modified fillers were produced for composite and papermaking). Furthermore, the SSH-lignin was successfully used as a coagulant for ethyl violet dye removal from a simulated solution.

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