Structural Variation of Lignin and Lignin−Carbohydrate Complex in Eucalyptus grandis × E. urophylla during Its Growth Process

Zhao, Bao-Cheng; Chen, Bo-Yang; Yang, Sheng; Yuan, Tong-Qi; Charlton, Adam; Sun, Run-Cang

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Chemosynthesis and structural characterization of a novel

lignin-based bio-sorbent and its strong adsorption for Pb (II)

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Bing Wang[a], Jia-Long Wen[a], Shao-Long Sun[a], Han-Min Wang[a], Shuang-Fei Wang[b],

Qiu-Yun Liu[c], Adam Charlton[c], Run-Cang Sun[a, *]

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[a]Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University,

No.35 Tsinghua East Road Haidian District, 100083, Beijing, China.

[b]Light Industry and Food Engineering College, Guangxi University, Guangxi 530004

China.

[c]The BioComposites Centre, Bangor University, Bangor LL57 2UW, UK.

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1   ABSTRACT:

2   The removal of heavy metals ions from wastewater by an economic, high-effective,

3   and environmentally friendly method is particularly important. In this study, an

4   effective lignin-based bio-adsorbent (SAPL-1.5), which contained specific functional

5   groups and spatial cross-linking structures, was synthesized through chemical

6   modification. SAPL-1.5 was comprehensively characterized by ^{31}P, ^{1}H, ^{13}C NMR, and

7   elemental analysis as compared to the raw lignin. The results showed that the

8   chemical reactivity of lignin was significantly improved after phenolation process,

9   and the adsorption groups were successfully grafted onto lignin macromolecule. In

10   addition, the influences of pH, SAPL-1.5 dosage, contact time, and initial Pb (II)

11   concentration on the adsorption performance was systematically investigated. The

12   highest adsorption capacity reached to 130.2 mg/g (Pb (II), 140 mg/L), and a removal

13   efficiency of 100% was achieved (Pb (II), 20 mg/L). Moreover, the adsorption

14   isotherm and adsorption kinetics indicated that the results were fitting well with the

15   Langmuir and pseudo-second-order model, respectively. Furthermore, the removal

16   efficiency of SAPL-1.5 for Pb (II) (20 mg/mL) still maintained over 85% after 5

17   cycles. Therefore, the lignin-based material obtained could be considered as a

18   promising potential adsorbent with a low cost, high performance and reutilization for

19   its application in the wastewater treatment process. It is believed that the lignin-based

20   bio-sorbent can enlarge the lignin valorization in the current biorefinery process.

21   To whom correspondence should be addressed. Tel: +86-10-62336903.

22   Fax: +86-10-62336903. E-mail:rcsun3@bjfu.edu.cn.

1. Introduction

With the development of industry, water pollution induced by heavy metals such as copper, silver, cadmium, mercury, and lead has drawn great concerns (Uddin et al., 2017; Hossain et al., 2014; Lü et al., 2013).These heavy metals are non-degradable and tend to accumulate in living organisms, which will lead to ecological and human health damage. Obviously, heavy metal ions should be removed from waste water prior to discharge them into the environment. Up to now, a variety of methods, such as chemical precipitation, electro dialysis, ion exchange, and membrane separation, have been explored to remove the toxic heavy metal ions from aqueous solutions (Reddad et al., 2012; Mohan et al., 2006; Ozmen et al., 2010). However, each method has its own disadvantage, such as high cost and energy consumption, as well as the need of large quantities of chemical additives, which resulted in the formation of by-product sludge and secondary pollution. Therefore, it is necessary to develop more effective and inexpensive methods to remove heavy metals from waste water. Based on the previous reports (Bhattacharya et al., 2008; Dodsonet al., 2015; Daset al., 2010), bio-sorption is one of the most promising method as compared to others, since it was handy, economic, and high-efficiency under low metal concentrations, which is important for deep purification of waste water. Thus, an adsorbent with low-cost and high-effective derived from an abundant and sustainable material in the nature is needed.

Biomass materials, such as cellulose, hemicelluloses, lignin, bacteria, fungi,

1   chitosan, and agricultural wastes, have many unique advantages including sustainable

2   resource, low cost, biocompatibility, and low environmental impact. Therefore, these

3   materials have been drawn great attention on the development of biomass adsorbents

4   (Das et al., 2010; Guo et al., 2008). Among the biomass materials, lignin has many

5   advantages of adsorption owing to the specific functional groups and spatial structure

6   features (Dizhbite et al., 1999; Li et al., 2016a; Brandt et al., 2013).

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8   Lignin, the second most abundant renewable material, which is next to cellulose in

9   biomass, is a phenolic polymer derived primarily from three different

10   phenylpropanoid units, such as syringyl, guaiacyl, and *p*-hydroxyphenol units (Ralph

11   et al., 2010). In the worldwide pulping industry, over 70 million tons of lignin are

12   generated as a by-product ever year. However, only 2-10% of the total lignin

13   produced is used as high value-added materials or chemicals, and the left more than

14   90% is burned as low value fuels (Dodson et al., 2015). In fact, lignin is a very

15   promising raw material available for the preparation of adsorbent, owing to its low

16   cost and toxicity, and possession of several functional groups (methoxyl, aliphatic

17   hydroxyl, phenolic hydroxyl, carboxyl, etc) (Mohan et al., 2006). Actually, lignin has

18   been identified to be an adsorbent for the adsorption of heavy metal ions (Guo et al.,

19   2008; Mohanet al., 2006; Maldhure et al., 2011; Geet al., 2014). Demirbas

20   (Demirbaset al., 2004) developed a lignin-based adsorbent with an adsorption

21   capacity of 8.2-9.0 mg/g for Pb (II) and 6.7-7.5 mg/g for Cd (II). The lignin obtained

22   from enzymatic hydrolysis residues of cornstalk showed a maximum adsorption

capacity of 20 mmol/L for Au (III) (Ge et al., 2014). However, the adsorption capacity

of unmodified lignin is usually limited by low quantity of functional groups, such as

sulfo, amino, and hydroxyl groups, therefore, modification of lignin before utilization

is highly necessary. To enhance lignin's adsorptive property, O, N or (and) S

-containing functional groups were preferred to grafted to the lignins. Generally, the

introduction of nitrogen- and sulphur-containing functional groups is expected to

enhance the redox and adsorptive property of lignins. Ge et al. (Ge et al., 2014) found

that the maximum adsorption capacity of lignin with functional groups, such as

sulfonic and amino, was as high as 45 and 53 mg/g for Cu (II) and Pb (II),

respectively. Peternele et al. (Peternele et al., 1999) modified the lignins with

carboxymethyl groups, and the adsorption capacity reached to 80.3 and 37.9 mg/g for

Pb (II) and Cd (II), respectively. These reports proved that the lignin can be used as an

adsorbent to purify the wastewater. However, the adsorption capacity or (and)

removal rate of these lignin-based biosorbents were limited, especially at low metal

ion concentrations. In addition, the adsorbents could not be easily separated and

recycled, which would restrict its applications in many fields and generate the

secondary pollution.

To our knowledge, one of the most important reasons for the limited adsorption

capacity is attributed to lower chemical reactivity of lignin from industrial and current

biorefinery process, which resulted in a handful of functional groups grafted onto the

lignin. To improve the chemical reactivity of the raw lignins, many approaches have

been developed to enhance the chemical reactivity of lignins, mainly including demethylation and phenolation (Kai et al., 2016). Phenolation is a method to introduce the phenol to lignins, further introduce more phenolic hydroxyl groups into lignins and the chemical reactivity of lignins can be significantly improved. These lignins could be developed into novel lignin-based biomaterials, such as adsorbent, antioxidant, fire retardant, and phenolic resin (Kai et al., 2016).

In this study, the lignin was activated through an improved process of phenolation before modification (Scheme 1a). The amino and sulfonic functional groups were then sequentially grafted onto phenolated lignin by mannich reaction and sulfomethylation, respectively (Scheme 1b). Considering the high toxicity and seriously damage to the nervous and reproductive system, kidneys, as well as liver, Pb (II) as a model heavy metal ion was chosen for evaluating the adsorption capacity of lignin-based adsorbent. The influences of initial concentration and pH of Pb (II), contract times, as well as reagent dosages on the adsorptive property of lignin were comprehensively investigated. The kinetic and equilibrium parameters were also calculated to investigate the adsorption performance of modified lignin.

2. Materials and methods

2.1 Materials

The alkaline lignin was obtained from the hydrothermally pretreated corn cob and provided from Shandong Longlive Bio-technology Co., Ltd, China. The general

1 process for the lignin production has been detailed described in our previous paper

2 (Yang et al., 2014). In brief, the alkaline lignin was obtained from the hydrothermally

3 pretreated corn cob. Phenol, sulfuric acid (H_2SO_4), 1, 6-hexanediamine (HD),

4 formaldehyde (HCHO), sodium hydroxide (NaOH), and carbon disulfide (CS_2) and

5 other reagents were purchased from Sigma-Aldrich (Beijing, China).

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7 *2.2 Phenolation of lignin*

8 The lignin was activated by an improved phenolation process prior to

9 ammonization and sulfuration (Scheme 1a). Simply, phenolation of alkaline lignin

10 was performed with 20 g lignin dissolved in 40 g phenol solution, and the

11 homogenous mixture was catalyzed by H_2SO_4 (2.18 mL) at 110 ºC for 20 min. After

12 the reaction completed, the mixture was slowly poured into 10 volumes of acid water

13 (pH = 2.0, adjusted by HCl) under vigorous mechanical stirring to precipitate the

14 phenolated lignin, which was then obtained by filtering, washing with ethanol

15 followed by acid water (pH = 2.0), and finally freeze-drying. The yields of phenolated

16 lignin (PL) were about 80% (based on the weight of lignin and phenol).

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18 *2.3 Chemosynthesis of lignin-based biosorbent*

19 The ammonization and sulfuration of lignin (SAPL, SAL) were obtained through

20 Mannich (Scheme 1a) and sulfuration (Scheme 1b) reaction. (i) 5.0 g L or PL and 10

21 mL 0.4 mol/L NaOH were drop into a three round bottom flask bottle. The reaction

22 was kept at room temperature for about 15 min with vigorously stirring to ensure the

complete dissolution of lignin. Subsequently, a certain amount of formaldehyde, HD,

and deionized water (Table S1) were added into the flask to form a 100 mL solution

with continuous stirring. After that, the reaction temperature was elevated to 60 $^{\circ}$C,

and the time lasted for 3 h. (ii) sulfuration: the resulting mixture was cooled down to

40 $^{\circ}$C, and a certain amount of carbon disulfide (Table S1) was slowly added into the

solution drop , and then kept for 4 h to complete the sulfuration. At the end of the

designated time, the mixture was dialyzed with dialysis bag (*Mw*=1000). After that,

all the modified lignins were freeze-dried and then stored indifferent centrifuge tubes

for the characterization and adsorption. The detailed formula of fraction of

lignin-based biosorbent was listed in Table S1.

2.4 Characterizations

In this study, elemental analysis (C, H, N and S) of the lignins was measured by PE

2400 II. NMR spectra (^{1}H, ^{13}C, 2D-HSQC, and ^{31}P NMR spectra) were performed on

a Bruker AVIII (400 M) according to previous publications (Ralph et al., 2010; Pu et

al., 2011; Wen et al., 2013;Sun et al., 2013).

2.5 Batch adsorption

All the adsorption tests were performed at 25 $^{\circ}$C to investigate the adsorptive

property of the modified lignins for the Pb (II). The aqueous solution of the metal ions

was prepared by dissolving $Pb(NO_3)_2$ in deionized water for different concentrations.

Typically, a certain amount of SPAL-1.5 was dispersed in a $Pb(NO_3)_2$ aqueous

solution (50 mL). Then, the mixture was incubated in water bath at 25 °C with

constant stirring for given time. As the predetermined time arrived, 5 mL supernatant

solutions were pipetted and then filtered through 0.22 mm membranes for the

detection of Pb (II). The concentrations of the initial and residual ions were

determined by inductively coupled plasma (ICP) spectrometer (ICP-8000,

PerkinElmer), respectively. In this study, the factors affect the adsorption capacity (Qe)

and removal efficiency (R, %) for Pb (II) including the pH, initial concentration of the

Pb (II) aqueous solution, lignin dosage, as well as the contact time of SAPL-1.5 in

$Pb(NO_3)_2$ aqueous solution were thoroughly investigated. In addition, the pH of

$Pb(NO_3)_2$ aqueous solution was adjusted by 0.1 M HNO_3 and NaOH. The removal

efficiency (formula 1) and adsorption capacity (formula 2) were calculated based on

the following equations:

$$\mathbf{R} = \frac{\mathbf{C_0 - C_e}}{\mathbf{C_0}} \times \mathbf{100\%} \qquad \qquad \mathbf{(1)}$$

$$\mathbf{Q_e} = \frac{\mathbf{C_0 - C_e}}{\mathbf{m}} \times \mathbf{V} \qquad \qquad \mathbf{(2)}$$

where R and Q_e represent the removal efficiency (%) and adsorption capacity at

equilibrium (mg/g), respectively. C_0 and C_e are the initial and equilibrium

concentrations of metal ions (mg/L); V is the volume of the Pb (II) solutions (L), and

m is the dry weight of SAPL-1.5 (g). All experiments were performed in duplicate and

the results presented in the manuscript were the mean values.

2.6 Regeneration of SAPL-1.5

To investigate the reusability of SAPL-1.5, regeneration experiment was conducted

1   in the current study. In brief, the metallic-loaded SAPL-1.5 was transferred into 0.1 M

2   HNO_3 aqueous solution (100 mL) with stirring for 120 min at room temperature. The

3   insoluble solids were filtered and washed with distilled water and then poured into 0.1

4   M NaOH aqueous solution (100 mL) with stirring for 120 min at room temperature.

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3. Results and discussion

3.1 Characterization of lignins with or without modification

8   ^{31}P NMR spectroscopy is a facile and direct analysis tool for quantifying the

9   different hydroxyl groups (carboxyl groups, phenolic hydroxyl, and aliphatic

10   hydroxyl) in lignin (Pu et al., 2011; Granata et al., 1995). Generally, the content of

11   active sites was related to the type of lignins because G- and H-type lignins contain

12   one and double active sites, respectively. Therefore, in this study, the changes of

13   varios hydroxyl groups in these lignins were measured by ^{31}P-NMR spectra (Figure1

14   and Table 1). As shown in Figure 1, the intensity of the signals at 138.4-137.1 ppm

15   referring to *p*-hydroxyphenyl units was significantly increased as compared to that of

16   L, implying that the phenol was successfully grafted onto the lignin. By contrast, the

17   intensity of the signals belonging to aliphatic hydroxyl groups (Al-OH) in PL

18   (146.0-149.0 ppm) was observably reduced. In addition, the quantitative data inTable

19   1 showed the distribution of the varied hydroxyl groups (Al-OH, S-OH, G-OH, H-OH,

20   and -COOH) and active sites of the lignins. The content of Al-OH was decreased to

21   0.24 mmol/g in PL from 1.48 mmol/g in L, which is probably that the phenolation

22   reaction occurred in the side-chain of lignin under the acidic conditions. Furthermore,

the increased content of condensed syringyl (5-substituted, 144.5-143.2 ppm) phenolic moieties (0.23 to 0.25 mmol/g) is attributed to the occurrence of a minimal amount of condensation reaction. Actually, the condensation reaction could be also reflected by the slightly increase of molecular weight (FigureS1). Furthermore, the decreased of G-type OH groups content (1.16-0.98 mmol/g) implied that the demethylation and condensation reaction occurred during the phenolation process. It should be noted that the content of H-type OH was increased from 0.68 (L) to 3.14 mmol/g (PL), suggesting that the phenol was successfully grafted onto lignin. Especially, the results showed that the content of active sites in PL was three times higher than those in L. Therefore, it could be concluded that the chemical reactivity of lignin was significantly improved after phenolation, which would be beneficial for the chemical modification of raw lignin.

Subsequent 2D-HSQC spectra of lignin and phenolated lignin (Figure S2) also provide some evidences for the successful phenolation of lignin in the present study. As compared to the spectrum of L, only small correlated signals for β-O-4 linkages were disappeared in the spectrum of PL. In fact, the intensity of the signals appearing in the spectrum of L was weaken as compared with that of PL, which was attributed to the low content of C_9-units in PL. Referring to the aromatic region of the L and PL, it was found that no obvious changes of the signals for S and G units occurred expected for the disappeared signals for dissociative p-coumric acid (p-CA). This suggested that the dissociative p-coumric acid, which was coprecipitated with the alkaline lignin,

was removed after phenolation process. Besides, the enlarged signals for H-type

lignin units indicated of successful phenolation of phenol onto lignin. Considering the

unchanged signals for S and G units as well as the reduced aliphatic OH groups in the

PL, it was speculated that the phenolation was mainly condensed with the side-chain

of the lignin rather than aromatic rings in the present study.

In the ^{1}H NMR spectrum of phenolated lignin, large amplification of the peak

belonging to aromatic protons (6.0-7.4 ppm) could be detected (Figure 2). It was

observed that the intensity of aromatic protons was increased in PL as compared to

that in L, suggesting that the phenol was successfully grafted onto lignins, which was

in accordance with the results of the above ^{31}P NMR, 2D-HSQC, and the following

^{13}C NMR spectra. However, the intensity of signals (3.4-3.9 ppm) assigned to α and

γ-H was decreased in PL, implying that the phenolization appeared in the side chain

of lignin as illustrated in scheme 1a, which was proved by 2D-HSQC and ^{31}P-NMR

spectra. However, it was found that the HCHO replaced the aromatic protons through

mannich reaction, which resulted in the decrease of the aromatic signals (6.0-7.4 ppm)

intensity in APL-1.5 and SAPL-1.5. Furthermore, it should be noted that the newly

appeared signals at 1.46 and 2.75 ppm are assigned to the H of the introduced HD in

SAPL-1.5, implying that the HD was successfully grafted onto lignin.

To further investigate the mechanism of the chemical modification of lignin, ^{13}C

NMR spectra of lignins and its derivatives (L, PL, and SAPL-1.5) were performed,

and the results are given in Figures 3 and S3. The detail assignments of the lignin could be achieved according to the previous publications of the NMR characterization of lignins (Ralph et al., 2010; Sun et al., 2013). In the aromatic regions (153-103 ppm) of the three samples, the S-type units are detected at 152.3, 147.6, 138.3, and 104.4 ppm, derived from etherified $S_{3,5}$, non-etherified $S_{3,5}$, etherified S_4, and $S_{2,6}$, respectively. In addition, the G-type units give signals at 148.3 ppm (C-3, etherified), 147.5 ppm (C-4, etherified), 144.3 ppm (C-4, non-etherified), 135.9 ppm (C-1, etherified), and 118.9 ppm (C-5). Apart from the signals represented for the S and G units, the H unit was also clearly distinguished according to the previous publications (Ralph et al., 2010; Sun et al., 2013).Furthermore, an obvious signal belonging to the C-8 of dissociated p-coumaric acid (p-CA) appeared at 168.1 ppm in the spectrum of lignin (Sun et al., 2013.Cui et al., 2011). After the phenolation, it was found that the signal for dissociated p-CAwas disappeared, suggesting that the lignin was purified during the phenolation process. In addition, it was observed that the intensity of the signal at 128.2 ppm assigned to $H_{2,6}$ was obviously increased. However, the signal of $H_{2,6}$ was shifted upfield and the intensity was then decreased due to the substitution of $H_{2,6}$ during the mannich reaction. Meanwhile, the decreased intensity of G_5 signal in SAPL-1.5 also verified the occurrence of the substitution reaction at G_5 position. Moreover, considering the newly appearance signals attached to the carbon of CH_2 (42-45, 26-30 and 57.3 ppm) and C=S (201.9 ppm) in SAPL-1.5, it could be concluded that HD was successfully grafted onto lignin, which was consistent with the following elemental analysis.

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2   Elemental analysis (Table 2) was performed to investigate the quantitative changes

3   of the C, H, N, and S contents in lignins, which were affected by the different molar

4   ratios among L, HCHO, HD, and CS_2, as well as the phenolation. The results showed

5   that the content of N and S was elevated with the increment of the molar ratios

6   between lignin and reactants (HCHO, HD, and CS_2). As compared to SAL-1.5, the

7   content of C in SAPL-1.5 significantly declined. However, the S and N contents were

8   obviously enhanced to 8.38 and 11.98%, respectively. Therefore, it could be

9   concluded that the chemical reactivity was enhanced by phenolation and resulted in

10   more CS_2 were grafted onto lignin, which would provide abundant adsorption sites for

11   the adsorption of metal ions. In this study, considering the economic value, SPAL-1.5

12   instead of SAPL-2 was chosen for investigating the adsorption property of Pb (II) in
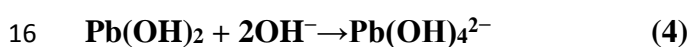
13   the following experiment.

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15   *3.2 Adsorption of Pb (II)*

16   *3.2.1 Effect of the initial pH*

17   The initial pH value of metal ions aqueous solution is a critical factor in influencing

18   the adsorption performances, since it affected the surface charge of SAPL-1.5, the

19   degree of ionization, and speciation of adsorbate (Ge et al., 2014). In this study, the

20   adsorption capacity of Pb (II) by SAPL-1.5 was performed with the pH between2.0

21   and 6.0. In addition, the initial Pb (II) concentration was 20 mg/L, and the constant

22   time maintained 90 min. As shown in Figure 4a, the adsorption capacity enhanced

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1   with the increase of pH, and reached to the maximum value when the pH was 5.0. The

2   reason for the limited adsorption capacity at low pH was that the strong competition

3   for the adsorption sites of lignins would occurred between the constant Pb (II) ions

4   andthe high H^+ ions (Li et al., 2016b; Mahmoud et al., 2015). However, as the pH

5   enhanced, the declined H^+ ions would weaken the competition, and consequently

6   enhanced the metallic ions uptake. However, too higher pH of the solution would

7   resulted in the secondary reaction productions, such as $Pb(OH)_2$ and $Pb(OH)_4^{2-}$,

8   which could affect the adsorption process and reduced the adsorption capacity.

9   Actually, the Pb (II) adsorption process was divided into three stages based on the

10   different pH conditions (Yang et al., 2011a; Yang et al., 2011b; Dlamini et al., 2012).

11   In detail, precipitation or hydrolyses began to appear as the pH was higher than 6.0,

12   surficial deposition occurred when the pH decreased to 5.0 from 6.0, and competitive

13   adsorption between H_3O^+ and Pb (II) appeared as the pH further reduce to 5.0. The

14   hydrolysis reaction of Pb (II) is described in equation 3 and 4.

15   $$\mathbf{Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2} \qquad \mathbf{(3)}$$

16   $$\mathbf{Pb(OH)_2 + 2OH^- \rightarrow Pb(OH)_4^{2-}} \qquad \mathbf{(4)}$$

17   The zeta potential of lignin is also an important parameter to evaluate the

18   absorbability. As shown in Figure 4b, the zeta potential decreased with the increase of

19   pH, and the zero charge of SAPL-1.5 appeared at pH 3.0. With the pH further

20   decreased to 5.0, the negative charges reached to 20.5, which was significantly higher

21   than those of other chemical modification lignins that have been previously reported

22   (Ge et al., 2014; Li et al., 2015). Furthermore, the more negatively charged surfaces of

1 SAPL-1.5 at higher pH value would providemore stable environment for lignin-based

2 adsorbent. Therefore, for acquiring the highest adsorption capacity of heavy metals

3 and avoiding the occurrence of precipitation of $Pb(OH)_2$ and $Pb(OH)_4^{2-}$, the batch

4 adsorption experiment of Pb (II) was performed at pH value of 5.0.

5

6 *3.2.2 Effect of SAPL-1.5 dosages*

7   In this study, the effect of SAPL-1.5 dosages on the adsorption capacity and

8 removal efficiency was performed at pH 5.0 with an initial ion concentration of 20

9 mg/L at a temperature of 25 °C for a contact time of 40 min, and the results are given

10 in Figure 5. In low dosages, it showed the high adsorption capacity, which was mainly

11 due to the increased ratio of the adsorbent to metal ions. However, it was observed

12 that the adsorption capacity decreased with increase of SAPL-1.5 dosages. This could

13 be explained by the generation of substantial unsaturated adsorption sites which

14 resulted from the higher SAPL-1.5 dosages. By contrast, the removal efficiency of Pb

15 (II) obviously enhanced with the increase of SAPL-1.5 dosages, and reached to

16 maximum value (100%) at a dosage of 0.03 g/50mL. The reason for the increase of

17 removal efficiency was probably attributed to the additional adsorption sites and the

18 contact area that provided by the higher SPAL-1.5 content, while the number of metal

19 ions was kept constant under a low concentration of Pb (II) (20 mg/L) (Bansal et al.,

20 2009; Li et al., 2015).

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22 *3.2.3 Effect of initial lead concentration*

1   To evaluate the adsorption capacity of SPAL-1.5 for lead ions, adsorption isotherms

2   were measured with the initial lead concentrations of 20-160 mg/L at a pH of 5.0, for

3   an SAPL-1.5 dosage of 0.03 g/50 mL, at a temperature of 25 $^{\circ}$C, and a contact time of

4   90 min. As can be seen from Figure 6a, the adsorption capacity (calculated as formula

5   3) increased with the increase of initial Pb (II) concentration, and the maximum

6   adsorption capacity reached to over 130 mg/g, which was obviously higher than those

7   of other lignins presented in Table 3. The reason for the elevated adsorption capacity

8   was that the higher lead concentration would provide more contracting surface of Pb

9   (II) to SAPL-1.5. However, the adsorption capacity began to flatten as the initial lead

10   concentrations reached to 140 mg/L. This was that the limited adsorption sites were

11   sufficiently occupied by an excess of Pb (II) ions, and then resulted in polymer chain

12   shrinking (Pehlivan et al., 2006). In addition, the Langmuir and Freundlich isotherm

13   models were used to fit the adsorption data in this study, respectively (Figure6b). The

14   two isotherm models has be described in supporting information (Formula S1 and S2).

15   As shown in Figure 6b and Table 4, the adsorption capacity for Pb (II) is in good

16   agreement with the Langmuir adsorption model ($R_1^2 = 0.9940$) rather than Freundlich

17   model ($R_2^2 = 0.9677$). The adsorption capacity ($Q_m = 130.2$ mg/g) was closed to the

18   maximum adsorption ($Q_e = 136.9$ mg/g), suggesting that the adsorption behavior of

19   SAPL-1.5 occurred on the surface is homogeneous and that the adsorption can be

20   characterized as monolayer manner (Langmuir et al., 1918).

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1   *3.2.4 Effect of contact time*

2   The contact time between SAPL-1.5 and Pb (II) is also a vitally important

3   parameter for evaluating the adsorption properties of adsorbents. To determine an

4   optimum contact time between SAPL-1.5 and Pb (II) ions, the adsorption process was

5   completed under the condition of a Pb (II) concentration of 80 mg/L, a dosage of 0.03

6   g, a temperature of 25 ^{o}C, and a pH of 5.0. Meanwhile, the samples were collected

7   every 10 mins for 8 times. As shown in Figure 7, the adsorbing capacity rapidly

8   increased within the initial 10 mins, and then the growth rate became slow and finally

9   flatten in 40 min. The fast adsorption could be ascribed to the large number of

10   effective adsorption sites on the surface of SAPL-1.5 (Ge et al., 2014; Songet a., 2015;

11   Say et al., 2008; Cui et al., 2015). In detail, the good dispersibility of SAPL-1.5 and

12   high-efficiency chelating ability of C-S^{-} towards metallic ions is the most important

13   reason. Besides, the electrostatic attraction of hydroxyl groups (original and grafted

14   hydroxyl groups, as well as carboxyl groups) were probably another important reason

15   for the rapid adsorption (Aboutalebi et al., 2011; Karnitz et al., 2007)

16   In this study, the adsorption kinetics was examined through the calculation of

17   pseudo-first-order and pseudo-second-order model. The two kinetic rate equations has

18   be described in supporting information (Formula S3 and S4). The fitting results are

19   presented in Figure7 and Table 5. In this study, a particular high correlation

20   coefficient ($R_2^2 > 0.9978$) between t and t/Q_t implied that the pseudo-second-order

21   model was more suitable for adsorption description. Thus, it can be concluded that the

22   adsorption process of SAPL-1.5 is primarily due to chemisorption, such as, ion

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1 exchange, chelation electrostatic forces and valence forces.

2

3 *3.2.5 The reusability of SAPL-1.5*

4 The reusability of the adsorbent plays an important role in evaluating the potential

5 commercialization of the adsorbent. Thus, the adsorption-desorption ability of

6 SAPL-1.5 was realized through 0.1 M HNO_3 and NaOH aqueous solution according

7 to the description of methods section, and the results were presented in FigureS4. It

8 was found that the removal efficiency for Pb (II) (20 mg/mL) still maintained above

9 85% after 5 cycles, and the average removal efficiency for Pb (II) (20 mg/mL)

10 reached to 93.9%. In short, all these results demonstrated that the SAPL-1.5 is a

11 promising bio-sorbent in reducing pollution of Pb (II) ions for waste water treatment.

12

13 **4. Conclusion**

14 An effective bio-adsorbent (SAPL-1.5) was synthesized and fabricated from the

15 renewable resource−lignin. The fundamental chemistry and adsorptive behaviors were

16 systematically investigated. SAPL-1.5 exhibited excellent adsorption performance for

17 Pb (II), which is mainly attributed to the strong electrostatic attraction between heavy

18 metal ions and sulfuric and oxygenic functional groups. The results showed that the

19 maximum adsorption capacity and removal efficiency of the SAPL-1.5 reached to

20 130.2 mg/g and 100% for Pb (II), respectively. In addition, the adsorption kinetics and

21 adsorption isotherm were fitted well with the Langmuir model and

22 pseudo-second-order. Furthermore, the adsorbent of SAPL-1.5 presented outstanding

cycling capability. Considering the potential economic and eco-friendly alternative for heavy metal removal, it can be concluded that SAPL-1.5 would become a promising bio-adsorbent for water purification. More importantly, the present study owns good scientific merit, which not only provides the theoretical foundation for lignin valorization in biosorption process, but also extends the further application of lignin in current biorefinery scheme.

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