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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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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 , ^1H , ^{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.

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1 **1. Introduction**

2 With the development of industry, water pollution induced by heavy metals such as
3 copper, silver, cadmium, mercury, and lead has drawn great concerns (Uddin et al.,
4 2017; Hossain et al., 2014; Lü et al., 2013). These heavy metals are non-degradable
5 and tend to accumulate in living organisms, which will lead to ecological and human
6 health damage. Obviously, heavy metal ions should be removed from waste water
7 prior to discharge them into the environment. Up to now, a variety of methods, such
8 as chemical precipitation, electro dialysis, ion exchange, and membrane separation,
9 have been explored to remove the toxic heavy metal ions from aqueous solutions
10 (Reddad et al., 2012; Mohan et al., 2006; Ozmen et al., 2010). However, each method
11 has its own disadvantage, such as high cost and energy consumption, as well as the
12 need of large quantities of chemical additives, which resulted in the formation of
13 by-product sludge and secondary pollution. Therefore, it is necessary to develop more
14 effective and inexpensive methods to remove heavy metals from waste water. Based
15 on the previous reports (Bhattacharya et al., 2008; Dodson et al., 2015; Daset al.,
16 2010), bio-sorption is one of the most promising method as compared to others, since
17 it was handy, economic, and high-efficiency under low metal concentrations, which is
18 important for deep purification of waste water. Thus, an adsorbent with low-cost and
19 high-effective derived from an abundant and sustainable material in the nature is
20 needed.

21

22 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).

7
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; Mohan et al., 2006; Maldhure et al., 2011; Geet et al., 2014). Demirbas
20 (Demirbas et 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

1 capacity of 20 mmol/L for Au (III) (Ge et al., 2014). However, the adsorption capacity
2 of unmodified lignin is usually limited by low quantity of functional groups, such as
3 sulfo, amino, and hydroxyl groups, therefore, modification of lignin before utilization
4 is highly necessary. To enhance lignin's adsorptive property, O, N or (and) S
5 -containing functional groups were preferred to grafted to the lignins. Generally, the
6 introduction of nitrogen- and sulphur-containing functional groups is expected to
7 enhance the redox and adsorptive property of lignins. Ge et al. (Ge et al., 2014) found
8 that the maximum adsorption capacity of lignin with functional groups, such as
9 sulfonic and amino, was as high as 45 and 53 mg/g for Cu (II) and Pb (II),
10 respectively. Peternele et al. (Peternele et al., 1999) modified the lignins with
11 carboxymethyl groups, and the adsorption capacity reached to 80.3 and 37.9 mg/g for
12 Pb (II) and Cd (II), respectively. These reports proved that the lignin can be used as an
13 adsorbent to purify the wastewater. However, the adsorption capacity or (and)
14 removal rate of these lignin-based biosorbents were limited, especially at low metal
15 ion concentrations. In addition, the adsorbents could not be easily separated and
16 recycled, which would restrict its applications in many fields and generate the
17 secondary pollution.

18

19 To our knowledge, one of the most important reasons for the limited adsorption
20 capacity is attributed to lower chemical reactivity of lignin from industrial and current
21 biorefinery process, which resulted in a handful of functional groups grafted onto the
22 lignin. To improve the chemical reactivity of the raw lignins, many approaches have

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

7
8 In this study, the lignin was activated through an improved process of phenolation
9 before modification (Scheme 1a). The amino and sulfonic functional groups were then
10 sequentially grafted onto phenolated lignin by mannich reaction and sulfomethylation,
11 respectively (Scheme 1b). Considering the high toxicity and seriously damage to the
12 nervous and reproductive system, kidneys, as well as liver, Pb (II) as a model heavy
13 metal ion was chosen for evaluating the adsorption capacity of lignin-based adsorbent.
14 The influences of initial concentration and pH of Pb (II), contact times, as well as
15 reagent dosages on the adsorptive property of lignin were comprehensively
16 investigated. The kinetic and equilibrium parameters were also calculated to
17 investigate the adsorption performance of modified lignin.

18 19 **2. Materials and methods**

20 *2.1 Materials*

21 The alkaline lignin was obtained from the hydrothermally pretreated corn cob and
22 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).

6

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 °C 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).

17

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

1 complete dissolution of lignin. Subsequently, a certain amount of formaldehyde, HD,
2 and deionized water (Table S1) were added into the flask to form a 100 mL solution
3 with continuous stirring. After that, the reaction temperature was elevated to 60 °C,
4 and the time lasted for 3 h. (ii) sulfuration: the resulting mixture was cooled down to
5 40 °C, and a certain amount of carbon disulfide (Table S1) was slowly added into the
6 solution drop , and then kept for 4 h to complete the sulfuration. At the end of the
7 designated time, the mixture was dialyzed with dialysis bag ($M_w=1000$). After that,
8 all the modified lignins were freeze-dried and then stored indifferent centrifuge tubes
9 for the characterization and adsorption. The detailed formula of fraction of
10 lignin-based biosorbent was listed in Table S1.

11

12 *2.4 Characterizations*

13 In this study, elemental analysis (C, H, N and S) of the lignins was measured by PE
14 2400 II. NMR spectra (^1H , ^{13}C , 2D-HSQC, and ^{31}P NMR spectra) were performed on
15 a Bruker AVIII (400 M) according to previous publications (Ralph et al., 2010; Pu et
16 al., 2011; Wen et al., 2013; Sun et al., 2013).

17

18 *2.5 Batch adsorption*

19 All the adsorption tests were performed at 25 °C to investigate the adsorptive
20 property of the modified lignins for the Pb (II). The aqueous solution of the metal ions
21 was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ in deionized water for different concentrations.
22 Typically, a certain amount of SPAL-1.5 was dispersed in a $\text{Pb}(\text{NO}_3)_2$ aqueous

1 solution (50 mL). Then, the mixture was incubated in water bath at 25 °C with
2 constant stirring for given time. As the predetermined time arrived, 5 mL supernatant
3 solutions were pipetted and then filtered through 0.22 mm membranes for the
4 detection of Pb (II). The concentrations of the initial and residual ions were
5 determined by inductively coupled plasma (ICP) spectrometer (ICP-8000,
6 PerkinElmer), respectively. In this study, the factors affect the adsorption capacity (Q_e)
7 and removal efficiency (R , %) for Pb (II) including the pH, initial concentration of the
8 Pb (II) aqueous solution, lignin dosage, as well as the contact time of SAPL-1.5 in
9 $Pb(NO_3)_2$ aqueous solution were thoroughly investigated. In addition, the pH of
10 $Pb(NO_3)_2$ aqueous solution was adjusted by 0.1 M HNO_3 and $NaOH$. The removal
11 efficiency (formula 1) and adsorption capacity (formula 2) were calculated based on
12 the following equations:

13
$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

14
$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

15 where R and Q_e represent the removal efficiency (%) and adsorption capacity at
16 equilibrium (mg/g), respectively. C_0 and C_e are the initial and equilibrium
17 concentrations of metal ions (mg/L); V is the volume of the Pb (II) solutions (L), and
18 m is the dry weight of SAPL-1.5 (g). All experiments were performed in duplicate and
19 the results presented in the manuscript were the mean values.

20

21 *2.6 Regeneration of SAPL-1.5*

22 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 HNO₃ 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.

5

6 **3. Results and discussion**

7 *3.1 Characterization of lignins with or without modification*

8 ³¹P 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 various hydroxyl groups in these lignins were measured by ³¹P-NMR spectra (Figure 1
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 in Table
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,

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

13
14 Subsequent 2D-HSQC spectra of lignin and phenolated lignin (Figure S2) also
15 provide some evidences for the successful phenolation of lignin in the present study.
16 As compared to the spectrum of L, only small correlated signals for β -O-4 linkages
17 were disappeared in the spectrum of PL. In fact, the intensity of the signals appearing
18 in the spectrum of L was weaken as compared with that of PL, which was attributed to
19 the low content of C₉-units in PL. Referring to the aromatic region of the L and PL, it
20 was found that no obvious changes of the signals for S and G units occurred expected
21 for the disappeared signals for dissociative *p*-coumric acid (*p*-CA). This suggested
22 that the dissociative *p*-coumric acid, which was coprecipitated with the alkaline lignin,

1 was removed after phenolation process. Besides, the enlarged signals for H-type
2 lignin units indicated of successful phenolation of phenol onto lignin. Considering the
3 unchanged signals for S and G units as well as the reduced aliphatic OH groups in the
4 PL, it was speculated that the phenolation was mainly condensed with the side-chain
5 of the lignin rather than aromatic rings in the present study.

6

7 In the ^1H NMR spectrum of phenolated lignin, large amplification of the peak
8 belonging to aromatic protons (6.0-7.4 ppm) could be detected (Figure 2). It was
9 observed that the intensity of aromatic protons was increased in PL as compared to
10 that in L, suggesting that the phenol was successfully grafted onto lignins, which was
11 in accordance with the results of the above ^{31}P NMR, 2D-HSQC, and the following
12 ^{13}C NMR spectra. However, the intensity of signals (3.4-3.9 ppm) assigned to α and
13 γ -H was decreased in PL, implying that the phenolization appeared in the side chain
14 of lignin as illustrated in scheme 1a, which was proved by 2D-HSQC and ^{31}P -NMR
15 spectra. However, it was found that the HCHO replaced the aromatic protons through
16 mannich reaction, which resulted in the decrease of the aromatic signals (6.0-7.4 ppm)
17 intensity in APL-1.5 and SAPL-1.5. Furthermore, it should be noted that the newly
18 appeared signals at 1.46 and 2.75 ppm are assigned to the H of the introduced HD in
19 SAPL-1.5, implying that the HD was successfully grafted onto lignin.

20

21 To further investigate the mechanism of the chemical modification of lignin, ^{13}C
22 NMR spectra of lignins and its derivatives (L, PL, and SAPL-1.5) were performed,

1 and the results are given in Figures 3 and S3. The detail assignments of the lignin
2 could be achieved according to the previous publications of the NMR characterization
3 of lignins (Ralph et al., 2010; Sun et al., 2013). In the aromatic regions (153-103 ppm)
4 of the three samples, the S-type units are detected at 152.3, 147.6, 138.3, and 104.4
5 ppm, derived from etherified S_{3,5}, non-etherified S_{3,5}, etherified S₄, and S_{2,6},
6 respectively. In addition, the G-type units give signals at 148.3 ppm (C-3, etherified),
7 147.5 ppm (C-4, etherified), 144.3 ppm (C-4, non-etherified), 135.9 ppm (C-1,
8 etherified), and 118.9 ppm (C-5). Apart from the signals represented for the S and G
9 units, the H unit was also clearly distinguished according to the previous publications
10 (Ralph et al., 2010; Sun et al., 2013). Furthermore, an obvious signal belonging to the
11 C-8 of dissociated *p*-coumaric acid (*p*-CA) appeared at 168.1 ppm in the spectrum of
12 lignin (Sun et al., 2013. Cui et al., 2011). After the phenolation, it was found that the
13 signal for dissociated *p*-CA was disappeared, suggesting that the lignin was purified
14 during the phenolation process. In addition, it was observed that the intensity of the
15 signal at 128.2 ppm assigned to H_{2,6} was obviously increased. However, the signal of
16 H_{2,6} was shifted upfield and the intensity was then decreased due to the substitution of
17 H_{2,6} during the mannich reaction. Meanwhile, the decreased intensity of G₅ signal in
18 SAPL-1.5 also verified the occurrence of the substitution reaction at G₅ position.
19 Moreover, considering the newly appearance signals attached to the carbon of CH₂
20 (42-45, 26-30 and 57.3 ppm) and C=S (201.9 ppm) in SAPL-1.5, it could be
21 concluded that HD was successfully grafted onto lignin, which was consistent with
22 the following elemental analysis.

1

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 CS₂, 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 CS₂). 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 CS₂ 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.

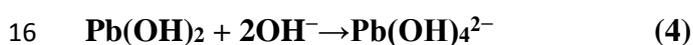
14

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 between 2.0
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

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 and the 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)₄²⁻,
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 H₃O⁺ 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.



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 provide more 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 $\text{Pb}(\text{OH})_2$ and $\text{Pb}(\text{OH})_4^{2-}$, 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).

21

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 °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).

21

22

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 °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; Song et al., 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

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 HNO₃ 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

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

7

8

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14

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