1. Introduction

Water body loaded with heavy metals is an important environmental problem due to the heavy metals could be bio-accumulated and further cause ecological damage [1]. Although copper is important to human beings, it also injures health at high concentration [2]. After enriching via food chain, the excess Cu(II) could be assimilated into human body and trigger various diseases of gastrointestinal discomfort, liver and kidney damage [3, 4]. The discharge permissible concentration for Cu(II) in drinking water is 2.0 mg/L according to the World Health Organization (WHO) [5]. In China, the three-level discharged concentration of Cu(II) from wastewater is ruled as 2.0 mg/L (GB 8978-1996). However, the concentrations of Cu(II) in most industrial wastewater far exceed 2.0 mg/L. For example, the concentration of Cu(II) is approximately 50 mg/L discharged from electroplating industry [6] and 20 mg/L in washing water of circuit board production [6]. Therefore, it is necessary to control the contamination of Cu(II) in the aquatic environment. By far, various approaches have been developed for removing heavy metals from aqueous solution, such as coagulation flocculation [7], precipitation filtration [8], solvent extraction [9], reverse-osmosis [10] and adsorption [11]. Of these technologies, adsorption could be used as a promising method, attributing to the advantages of easy accessibility and cost effectiveness [12]. Currently, considerable research has focused on designing and fabricating a series of adsorbents with chemical activity and versatile functional groups by using biomass as raw materials due to their extensive sources, environmental friendliness and low cost [13].

Lignin is the second largest biomass after cellulose in the nature [14, 15]. As an industrial by-product, lignin is generated from pulp- ing and bio-refinery on a large scale [16]. It was reported that approximately 70 million tons of lignin was produced from pulping.
worldwide in 2017 [17, 18]. Lignin can be exploited as a kind of adsorbent for removing heavy metals from aqueous solution [17, 19-21], but before the practical use lignin needs to be modified. For instance, Zhang et al. [22] used monochloroacetic acid and amine reagents as modifiers to make lignin carry oxygen- and nitrogen-containing functional groups including hydroxy (-OH), carboxyl (-COOH) and amine (-NH2). The modified lignin reduced 50 mg/L Cu(II) to 15 mg/L after 720 min [22]. Xu et al. [23] fabricated a kind of aminated lignin, in which amine substance was used to ornament lignin and consequently the nitrogen-containing groups of -NH and -NH2 were introduced; the aminated lignin reduced 50 mg/L Cu(II) to 8.5 mg/L after 360 min. Chakraborty and Tare [24] adopted xanthates to modify lignin with the functional groups of -CSS- and -COC, and then treated Cu(II)-loaded water (20 mg/L). After 720 min, approximately 16 mg/L of Cu(II) was detected in aqueous solution. Although these modified lignins could remove a certain percentage of Cu(II), all the residual Cu(II) still exceeded the discharge standard of 2.0 mg/L.

In our previous work, polyethyleneimine (PEI) and carbon disulfide (CS2) were applied as the reagents to modify alkaline lignin (named as AL-PEI-CS2), in which -NH, -NH2 and -CSS- groups functionalized the network of alkaline lignin [25]. The removal efficiency of Cu(II) was investigated, in which seven metal ions including Cu(II), Pb(II), Cd(II), Zn(II), Ca(II) and Mg(II) coexisted in aqueous solution (pH = 6.0). All the initial concentrations for the seven ions were set at 2.0 mg/L. After 300 min, it was found that the residual concentration of Cu(II) was only 0.06 mg/L far below the discharge permissible concentration (2 mg/L). However, the adsorption mechanism of AL-PEI-CS2 towards Cu(II) has not been studied systematically. In this work, the adsorption kinetics, adsorption isotherm, the binding interaction between AL-PEI-CS2 and Cu(II), as well as the reusing ability were investigated with the initial concentration of Cu(II) closed to that in real wastewater and the residual concentration of Cu(II) against WHO’s standard. This work aims at preparing a kind of modified alkaline lignin for treatment of Cu(II)-loaded wastewater and providing an insight into the treatment of wastewater contaminated by heavy metals by the biomass-based adsorbent.

2. Chemicals and Methods

2.1. Chemicals

The analytical grade of AL was brought from Bailaibo Technology Co. LTD (Beijing, China). PEI (branched, Mn = 70,000, 30 w/v aqueous solution) was obtained from Shanghai Xinrui Biotecnology Co., LTD (Shanghai, China). Other analytical grade reagents of sodium hydroxide (NaOH), hydrochloric acid (HCl), formaldehyde (HCHO), CS2 and ethanol were all provided by Chongqing Zinguang Chemical Co. LTD (Chongqing, China). Standard solutions (all in 1,000 mg/L) of copper nitrate (Cu(NO3)2), potassium nitrate (KNO3), calcium nitrate (Ca(NO3)2), sodium nitrate (NaNO3) and magnesium nitrate (Mg(NO3)2) were all supplied by the Guangzhou Analysis test center Keli Technology Development Co. LTD (Guangdong, China). Ultrapure water was prepared from a FAMO-10 equipment (resistivity = 18.25 mΩ-cm, Nanjing Quankun Biotechnology Co. LTD, China).

2.2. Preparation of AL-PEI-CS2 and Characterization

The modified alkaline lignin, named as AL-PEI-CS2, was prepared via the same method as described in our previous work [25]. AL was employed as the raw material and two reagents (PEI and CS2) as the modifiers in order to introduce nitrogen- and sulfur-containing functional groups. Briefly, three grams of AL were dissolved into 90 mL of ultrapure water in a 300-mL three-neck flask. The solution pH was adjusted at 13.0 via 0.1 mol/L of NaOH. The flask was placed on a magnetic stirring apparatus for agitating 30 min at room temperature. Ten milliliters of HCHO and 10 mL of PEI were dropwise added into the flask, in which the temperature of the apparatus was set at 90°C for sustaining 5 h and then cooled to 40°C. CS2 (15 mL) was added into the flask drop by drop. After 3 h, the precipitates in the flask were collected by centrifugation (TD-4M, Jinan Oulaibo Scientific Instrument Co., Ltd, China) at 5,000 rpm and 25°C. Ethanol and ultrapure water were used for washing the precipitates until the filtrate pH ranged from 6.0 to 7.0. The precipitates were dried via vacuum freeze dryer (FD-1A-50, Jiangsu Tianling Instrument Co., Ltd, China) at -60°C for 6 h. Finally, a kind of red-brown powders was obtained (AL-PEI-CS2) and stored in a centrifuge tube (φ = 2.5 cm, Jinan Oulaibo Electronic Commerce Co., Ltd) at room temperature for further use.

The morphology of AL and AL-PEI-CS2 (coated with Au powders) was analyzed through scanning electron microscope energy (VEGAIIXMU, Germany) coupled with dispersive spectroscopy (OXFORD, England) (SEM-EDS). Fourier transform infrared spectroscopy (FT-IR) (Nicolet NEXUS 750, USA) was operated under the condition of resolution 4 cm⁻¹ and scans number 16. X-ray photoelectron spectroscopy (XPS) spectra was run by using Mg and Kα as X-ray sources (1253.6 eV protons) (Thermo Scientific K-Alpha, USA). All the binding energies of XPS spectra were calibrated based on C 1s at 284.6 eV. Zeta potential (Malvern Zetasizer Nano S90, England) was conducted by adding 10 mg of AL-PEI-CS2 into 10 mL of aqueous solutions (pH = 1.0, 3.0, 4.0, 5.0, 6.0 and 9.0); after ultrasonic for 1 h and standing for 24 h, the samples of the solutions were measured. The specific surface areas were analyzed at 77 K via N2 adsorption-desorption isotherms (ASAP2460, McMurakit Instrument Co., Ltd, USA).

2.3. Adsorption Performance Evaluation

2.3.1. Monitoring the residual concentration of Cu(III) at different solution pH

The initial concentration of Cu(II) was 50 mg/L. The values of solution pH varied from 1.0 to 6.0 adjusting by 0.1 mol/L of HCl or NaOH. Fifty milliliters of Cu(II) solution and 0.0500 g of AL-PEI-CS2 were put into a 250-mL conical flask, and then covered with parafilm (Huimin Tengjie Plastic Industry Co., Ltd, China). The flasks were placed on a shaker (HYQ45, Wuhan Huicheng Biological Technology Co. LTD, China) at 25°C and 140 rpm. After 180 min, 5 mL of sample was withdrawn (Finnpipette™ F1, Thermo Fisher Scientific Co., Ltd, USA) and passed through 0.45 μm nylon membrane filter (Guzhou Tongn Experimental Instrument Co., Ltd, China). The filtrate was collected for monitoring the residual concentration of Cu(II) via the inductively coupled plasma optical
emission spectrometry (ICP-OES) (Thermo, USA). Three parallel tests were carried out and error bars were used to analyze the data depicting 95% confidence intervals. The control experiments were performed in the absence of AL-PEI-CS₂ to determine if the loss in Cu(II) happened through other pathways (e.g., adsorption on the flask wall, evaporation, or sorbed by the filter paper).

2.3.2. Monitoring the residual concentration of Cu(II) at the presence of cations
Four cations of K(I), Na(I), Ca(II) and Mg(II) were used. As for each cation, 2.5 or 5 mL of standard solution (1,000 mg/L) was mixed with Cu(II) solution (2.5 mL, 1,000 mg/L) in a 250-mL conical flask. The mixed aqueous solution was diluted to be 50 mL with adjusted pH as 5.03, in which \( C_0 \) of Cu(II) was obtained as 50 mg/L. The value of \( C_0 \) for each cation was 50 and 100 mg/L, respectively. Then 0.0500 g of AL-PEI-CS₂ was added into the flask for the adsorption experiments. Three parallel tests were carried out and error bars were used to analyze the data depicting 95% confidence intervals. Other operations were the same as those mentioned in Section 2.3.1.

2.3.3. Monitoring the residual concentration of Cu(II) under different contact times and initial concentrations
Fifty milliliters of Cu(II) solutions (5, 10, 15, 20, 30 and 50 mg/L) and 0.0500 g of AL-PEI-CS₂ were put into a 250-mL conical flask, respectively. All the solution pH values were set at 5.03. The flasks were placed on a shaker at 25°C and 140 rpm. At certain intervals, 5 mL of the sample was withdrawn. Three parallel tests were carried out and error bars were used to analyze the data depicting 95% confidence intervals. Other operations were the same as those mentioned in Section 2.3.1.

Adsoncentration of Cu(II) at time \( t \) was calculated by the following equations:

\[
\text{Removal efficiency} \, (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (3)
\]

where \( C_0 \) (mg/L) is the initial concentration of Cu(II); \( C_t \) (mg/L) is the residual concentration of Cu(II) at time \( t \); \( V \) (L) and \( M \) (g) are the volumes of Cu(II) solution and the mass of AL-PEI-CS₂, respectively.

3. Results and Discussion

3.1. Characterization of the Modified Alkaline Lignin
As presented in Fig. S1(a), the color of the raw AL was black while changed into yellow-brown after modification. SEM pictures exhibited that AL was composed of large blocks whereas the particles of AL-PEI-CS₂ were relatively small and incompact (Fig. S1b). According to N₂ absorption-desorption isotherm (Fig. S1c), the BET specific area of AL-PEI-CS₂ was calculated to be 1.656 m²/g, almost 16 times higher than that of raw AL (0.102 m²/g). FT-IR spectra displays that AL contained the functional groups of -OH as aromatic ring skeleton (1,592/1,509 cm⁻¹) [27] as well as amniotic ring skeleton (1,592/1,509 cm⁻¹) [27] (Fig. 1a). As for AL-PEI-CS₂, four new peaks corresponding to -NH₂ (1,662 cm⁻¹) [28], C=N (1,366 cm⁻¹) [29], C=S (1,081 cm⁻¹) [30] and C-S (855 cm⁻¹) [31] were recorded. In addition, the stretching vibration of -NH can also be discovered at 3,431 cm⁻¹ for AL-PEI-CS₂ [19]. Besides FT-IR, the technology of XPS was adopted. Fig. 1b shows full scan survey XPS spectra for AL and AL-PEI-CS₂. Different
from the three peaks of C 1s, O 1s and S 2p carried by AL, one new peak of N 1s was detected in AL-PEI-CS2 (Fig. 1(b)). As for the discovery of S 2p in AL, it was due to the usage of sodium sulfide (Na2S) during its preparation [20]. As depicted in Fig. 1(c), the spectra of O 1s were determined as C-O (532.6 eV) [32] and O-H (531.7 eV) [32]. According to Fig. 1(d), N 1s spectra corresponded to N-CS2 (403.9 eV) [33, 34] and -NH/-NH2 (399.5 eV) [19]. Fig. 1(e) was the binding energy of S 2p, which belonged to C=S (168.6 eV) [33] and C-S (163.2 eV) [33]. Considering the results from FT-IR and XPS, the nitrogen-, sulfur- and oxygen-containing groups of the modified alkaline lignin were determined as -OH, -NH, -NH2, and -S-C=S- (-CSS-), which would serve as the adsorption sites for removal of metal ions from aqueous solution.

3.2. Evaluation on Adsorption Performance of the Modified Alkaline Lignin

3.2.1. Residual concentration of Cu(II) at different solution pH

As for effluent discharged from mine wastewater, electroplating wastewater and washing water of circuit board production, the pH value generally ranges from 2.0 to 5.0 [35]. Therefore, the solution pH in this study was set at 1.0 to 6.0. As seen from zeta potential curve (Fig. 2(a)), surface of the modified alkaline lignin (AL-PEI-CS2) would be positively charged at solution pH < 3.1 while negatively charged at solution pH > 3.1 (pH_{pzc} = 3.1). Fig. 2(b) exhibits the dissociation forms of copper at different solution pH values, in which Cu^{2+} ions exist as the main species accompanied by a little amount of CuOH^{+} ions when pH value is less than 6.0. It can be assumed that electrostatic attraction would occur between AL-PEI-CS2 and Cu(II) when the solution pH varies from 3.1 to 6.0. The higher solution pH is, the stronger the electrostatic attraction happens. The adsorption ability of AL-PEI-CS2 towards Cu(II) is supposed to follow the sequence (in pH) of 6.0 > 5.0 > 4.0 > 3.0 > 1.0. In order to verify such a sequence, the adsorption experiments for Cu(II) over AL-PEI-CS2 at different pH values were conducted.

As displayed in the insert of Fig. 2(a), the adsorption capacity \( q_t \) and the removal efficiency was 45 mg/g and 92% for Cu(II) at pH of 1.30 and then increased to 49 mg/g and 98% at pH of 5.65 when the initial concentration \( C_0 \) of Cu(II) was 50 mg/L and the contact time was 180 min, respectively. The possible reason for this result was the excess protons (H\(^+\)) resulted in the protonation of the functional groups carried by AL-PEI-CS2 at lower pH, and consequently the electronic attraction between Cu\(^{2+}\) ions and AL-PEI-CS2 weakened, whereas the deprotonation occurred to improve the adsorption at a higher pH value [36, 37].

In order to verify the change in solution pH before and after adsorption, the values of pH_{initial} were set as 1.30, 3.15, 4.14, 5.03 and 5.65. When pH_{initial} equaled to 1.30, the value of pH_{final} was measured to be 1.33 (insert in Fig. 2(b)). As shown in Fig. 2(a), at the condition of pH lower than pH_{pzc} (3.1), the surface of AL-PEI-CS2 is charged positively, which means that H\(^+\) promoted the functional groups of -OH, -NH, -NH2 and -CSS- [36, 37] and consequently the amount of protons in solution decreased. This
might explain why the value of $\text{pH}_{\text{final}}$ (1.33) was higher than that of $\text{pH}_{\text{initial}}$ (1.30). When $\text{pH}_{\text{initial}}$ was set at 3.15, 4.14, 5.03 and 5.65, the values of $\text{pH}_{\text{final}}$ ascended to 4.65, 5.35, 5.85 and 6.01. The possible reason is that at the condition of pH higher than pH$_{\text{pzc}}$ (3.1) the negatively charged AL-PEI-CS$_2$ would interact with proton via electronic attraction, and therefore, result in the increase in pH$_{\text{final}}$. Interestingly, the difference between pH$_{\text{final}}$ and pH$_{\text{initial}}$ was 1.5, 1.21, 0.82 and 0.36 (insert in Fig. 2(b)), suggesting more protons retained in solution at higher pH$_{\text{initial}}$. The decreasing trend might attribute to increasing CuOH$^+$ amounts at relatively higher initial solution pH (Fig. 2(b)). CuOH$^+$ might compete with proton and interact with AL-PEI-CS$_2$.

The residual concentration of Cu(II) ($C_r$) was measured to be 4.55, 3.95, 2.8, 1.2 and 1.0 mg/L corresponded to solution pH of 1.30, 3.15, 4.14, 5.03 and 5.65. It was discovered that when solution pH was limited in the range of 5.03 to 5.65, the residual concentration of Cu(II) in the effluent can meet with the standard of 2 mg/L regulated by WHO and Chinese government. Ge et al. [19] adopted a kind of amino and sulfonic ornamented lignin (ASL) as the adsorbent, in which the removal efficiency of Cu(II) was 60%, 61%, 62%, 63% and 70% when the value of solution pH was 3.0, 4.0, 5.0, 6.0 and 7.0 (Fig. 2(c)), respectively. Accordingly, the $C_r$ value of Cu(II) at 90 min was 20, 19.5, 19, 18.5 and 15 mg/L with $C_0$ of 50 mg/L (Fig. 2(c)) [19]. Todorciuc et al. [38] employed the raw lignin derived from wheat straw to adsorb Cu(II) ($C_0 = 38.6$ mg/L) (Fig. 2(c)). The residual concentration was 36.1, 28.6, 26.6 and 3.6 mg/L with solution pH being 2.0, 3.0, 4.0 and 6.0 as well as $t$ being 180 min (Fig. 2(c)) [30], respectively. Xu et al. [23] used a kind of aminated lignin (AL) to remove Cu(II) from water. The value of $C_r$ for Cu(II) at 150 min was detected to be approximately 70, 68, 65, 57, 45 and 34 mg/L corresponded to the solution pH of 3.0, 3.5, 4.0, 4.5, 5.0 and 5.5 as $C_0$ of Cu(II) was 100 mg/L (Fig. 2(c)), respectively. As seen from these results, it can be concluded that the removal ability of AL-PEI-CS$_2$ for Cu(II) is ideal at a wide pH range from 1.0 to 6.0, especially at pH of 5.0 and 6.0.

### 3.2.2. Residual concentration of Cu(II) at the presence of cations

The influences of K(I), Na(I), Ca(II) and Mg(II) on the removal of Cu(II) by AL-PEI-CS$_2$ were conducted as these cations naturally exist in the aqueous environment. As displayed in Fig. S2, the dominant speciation of K(I), Na(I), Ca(II) and Mg(II) is K$^+$, Na$^+$, Ca$^{2+}$ and Mg$^{2+}$ when solution pH is less than 8.0, respectively. These cations might compete with Cu(II) during the adsorption process. In this research, the initial concentrations of K(I), Na(I), Ca(II) and Mg(II) were set at 0, 50 and 100 mg/L since these ions exist in the natural aqueous environment with the concentration of 0.2 to 167.4 mg/L [39]. Fig. S3 shows that the removal capacity of AL-PEI-CS$_2$ towards Cu(II) was not obviously affected by K(I), Ca(II), Na(I) and Mg(II). Even coexisted with the four cations, all the residual concentrations of Cu(II) almost meet with the standard of 2.0 mg/L regulated by WHO and Chinese government (Fig. 3(a)).

Fig. 3(a) compares the Cu(II) $C_r$ between AL-PEI-CS$_2$ and nanotubes synthesized by Liu et al. [40]. It was found that when the initial concentrations of these cations, the initial concentration
of Cu(II) and the contact time were close, the Cu(II) \( C_r \) for nanotubes were almost 20 to 30 times higher than those for AL-PEI-CS and far beyond the discharged standard of 2 mg/L. Similar phenomenon was also observed for hydrogel prepared by Zhang et al. [41] (Fig. 3(b)).

As for the three adsorbents (AL-PEI-CS, nanotubes and hydrogel), the monovalent cations including Na(I) and K(I) slightly affected the value of \( C_r \) while the influences of bivalent cations such as Ca(II) and Mg(II) were higher. The hydration free energy follows the order of K\(^+\) (-1,095 kJ/mol) > Na\(^+\) (-1,097 kJ/mol) > Ca\(^{2+}\) (-1,588 kJ/mol) > Mg\(^{2+}\) (-1,900 kJ/mol) [42, 43]. Cheng et al. [44] pointed out that higher hydration free energy tends to keep metal ions in aqueous solution, that is, prevents the transfer of the ions from bulk solution to the adsorbent surface. Therefore, Ca(II) and Mg(II) are easier to attach on the surfaces of AL-PEI-CS, nanotubes and hydrogel than Na(I) and K(I), and consequently, competition of bivalent cations for adsorption would be more fierce.

### 3.2.3. Residual concentration of Cu(II) under different contact times and initial concentrations

Fig. 4(a) shows that all the values of adsorption capacity (\( q_t \)) increased significantly from 0 to 60 min and then slightly from 60 to 120 min. After 120 min, the values of \( q_t \) kept almost unchanged even the contact time was prolonged to 180 min. The equilibrium time was determined as 180 min. According to the insert in Fig. 4(a), the adsorption efficiencies of Cu(II) over AL-PEI-CS reached 93% (\( C_0 = 5 \) mg/L), 95% (\( C_0 = 10 \) mg/L), 95% (\( C_0 = 15 \) mg/L), 95% (\( C_0 = 20 \) mg/L), 94% (\( C_0 = 30 \) mg/L), and 96% (\( C_0 = 50 \) mg/L) at 180 min, respectively. The values of \( C_r \) was observed to be as low as 1.72, 0.98, 1.15, 1.77, 1.76 and 1.86 mg/L corresponding to \( C_0 \) of 5, 10, 15, 20, 30 and 50 mg/L at the contact time of 20, 40, 90, 90, 180 and 180 min (Fig. 4(b)), respectively. These results demonstrated that all the Cu(II) \( C_r \) can meet with the standard of 2 mg/L within the initial concentration range of 0 to 50 mg/L. As for lower \( C_0 \) (5 and 10 mg/L), even at the initial stage (0 to 40 min) the values of \( C_r \) were less than 2 mg/L. It was noted here that at the equilibrium time of 180 min, the Cu(II) \( C_r \) was finally determined to be 0.32, 0.45, 0.65, 0.94, 1.76 and 1.86 mg/L when the initial concentration was 5, 10, 15, 20, 30 and 50 mg/L, respectively.

Descriptions on the adsorption kinetics and isotherm of Cu(II) onto AL-PEI-CS were given in Text S1. As displayed in Text S1, it showed that experimental data were well fitted by pseudo-second-order kinetic, suggesting the adsorption of Cu(II) over AL-PEI-CS was chemisorption. Boyd’s film-diffusion model proved the adsorption rate of Cu(II) onto AL-PEI-CS was determined by film diffusion. The maximum adsorption capacity (\( q_m \)) of Cu(II) was obtained as 58 mg/g by using the Langmuir isothermal model. Table 1 compares the adsorption capacity for different lignin-based adsorbents towards Cu(II) according to \( q_m \) values and the contact time to reach equilibrium, while Table 2 according to the residual concentration of Cu(II) at equilibrium. As seen from in Table 1, the value of \( q_m \) for AL-PEI-CS was higher than adsorbents VI to XII by approximately 1.04, 1.27, 1.30, 3.23, 6.34, 6.87 and 207 times, respectively. It was observed that \( q_m \) of AL-PEI-CS was lower than adsorbents II to IV, whereas the contact time to reach
Fig. 4. (a) The influence of contact time on the adsorption of Cu(II) over AL-PEI-CS2 under different initial concentrations (insert: the removal efficiency of Cu(II) at 60, 120 and 180 min); and (b) the values of Cr at different contact times when C0 of Cu(II) ranged from 0 to 50 mg/L.

3.2.4. Residual concentration of Cu(II) during the regeneration process

In order to evaluate the reusing ability of AL-PEI-CS2, a four-adsorption-desorption-cycle was designed. As presented in Fig. S5, the values of qₑ was 49.9, 49.1, 49.9, 49.0 and 48.8 mg/g for fresh AL-PEI-CS2 and the regenerated AL-PEI-CS2 at cycles 1 to 4, respectively. Compared to fresh AL-PEI-CS2, the decrease ratio in the qₑ value corresponding to cycles 1 to 4 was only 1.6%, 2.0%, 1.8% and 2.2%, respectively. Excitingly, the Cu(II) Cr was as low as 1.9, 2.1, 2.0 and 2.2 mg/L for cycles 1 to 4, basically meeting with the maximum acceptable limit (2 mg/L) regulated by WHO and Chinese government. These results illustrated that the reusing ability of AL-PEI-CS2 is acceptable.

3.3. Adsorption Mechanism

SEM-EDS exhibits the uptake of Cu(II) by AL-PEI-CS2 (Fig. S6). FT-IR spectra of AL-PEI-CS2 and AL-PEI-CS2-Cu(II) complexes were displayed in Fig. 5(a). Compared to AL-PEI-CS2, the peaks centered at 1,662 (-NH₂) and 855 cm⁻¹ (C-S) weakened for AL-PEI-CS2-Cu(II) complexes, indicating that the groups of -NH₂ and -CSS- were responsible for the uptake of Cu(II). XPS technology was employed to further confirm the adsorption mechanism. Fig. 5(b) presents that one peak of Cu 2p for AL-PEI-CS2-Cu(II) complexes was recorded. The characteristic peaks of Cu 2p centered at 951.8 and 931.9 eV were assigned to Cu 2p½ and Cu 2p½/2 (Fig. 5(c)) [52], respectively. The high-resolution spectra for S 2p displayed that the binding energy of C=S and C-S groups in AL-PEI-CS2 shifted from 163.2 eV to 162.8 eV and 168.6 eV to 167.2 eV in AL-PEI-CS2-Cu(II) complexes (Fig. 5(d)). A new peak of 168.7 eV emerged in AL-PEI-CS2-Cu(II) complexes, which was attributed to S-Cu. These results demonstrated that S atom of the -CSS- group in AL-PEI-CS2 accounted for binding with Cu(II) [53]. The binding energies of N 1s for -N-CS2 (403.9 eV) and -NH/-NH2 groups carried by AL-PEI-CS2 were observed to be shifted to 400.9 eV and 399.2 eV in AL-PEI-CS2-Cu(II) complexes, respectively, which may be due to the groups of C-N and -NH/-NH2 interacted with Cu(II) [19]. As shown in Fig. 5(f), the peaks at 532.6 and 531.7 eV (correspondingly assigned to the functional groups of C=O and -OH) moved to 532.4 and 531.2 eV. Moreover,

| Adsorbents                          | t (min) | pH | T (°C) | qₑ (mg/g) | Ref.   |
|-------------------------------------|---------|----|--------|-----------|--------|
| I AL-PEI-CS2                         | 180     | 5.0| 25     | 58        | This work |
| II Annealed freeze-dried lignin      | 2,880   | n  | n      | 290       | [45]    |
| III Kraft lignin                     | 2,880   | 4.5| 25     | 87.1      | [46]    |
| IV Fe₃O₄@SiO₂-NH-MFL                 | 720     | 6.0| n      | 70.6      | [22]    |
| V N-acetyl-L-cysteine-lignin (CFL)   | 120     | 6.0| 15     | 68.7      | [33]    |
| VI Aminated epoxy-lignin             | 50      | 6.0| 30     | 55.4      | [47]    |
| VII Lignin-DETA-SO₃                  | 60      | 6.0| 25     | 45.4      | [19]    |
| VIII Aminated lignin                 | 360     | 5.5| 30     | 42.6      | [23]    |
| IX Silanization/amination of lignin (SAL) | 150 | 6.7| 25     | 17.8      | [48]    |
| X Lignocellulosic hydrogel           | 1,440   | 6.0| 25     | 9.14      | [49]    |
| XI Kraft lignin                      | 360     | n  | 35     | 8.44      | [50]    |
| XII Lignin/chitin films              | 2,880   | n  | n      | 0.28      | [51]    |
a new peak at 529.9 eV was assigned to O-Cu. These results indicated that the oxygen containing functional groups participated in the adsorption process. Combined FT-IR with XPS spectra, it can be concluded that the groups of -OH, -NH₂, -NH, C-N, and -CSS- carried by AL-PEI-CS₂ served as the adsorption sites.

In order to explain the advantage of AL-PEI-CS₂ over other lignin-based adsorbents presented in Table 2, the functional groups of these materials were given. An obvious difference lies in the existence of -CSS- group for AL-PEI-CS₂. In our previous study [37], a kind of modified alkaline lignin (FLAL) was prepared, in which alkaline lignin was used as raw material, and carbon disulfide (CS₂) was employed as the modifier. The functional groups of -CSS-carried by FLAL was proved to be the primary adsorption site for Pb(II) and Cu(II). According to the traditional theory [43, 44], the adsorption ability of FLAL towards Pb(II) should be higher than Cu(II) as the hydration radius of Pb(II) (4.01 Å) is less than Cu(II) (4.19 Å). It is well known that lower hydration radius is beneficial to adsorption. In contrast, FLAL exhibited better removal performance for Cu(II) than for Pb(II). The reason was that the bond energy between the functional group of -CSS- and Cu(II) was lower than that of Pb(II) based on DFT calculations. Thus, we pointed out that not only the physio-chemical property of sorbate...
but also the functional group of adsorbent determines the adsorption performance. On the basis of our previous research, we hypothesized that it might be the existence of the -CSS- group that makes AL-PEI-CS₂ work well with the residual concentration of Cu(II) meeting with the standard of 2 mg/L under variously operating conditions.

4. Conclusions

In this work, the adsorbent AL-PEI-CS₂ was used to remove copper from aqueous solution and its performance was evaluated based on the residual concentration (Cₜ) of Cu(II) under various operating conditions including solution pH, coexisting cations, contact time, and the initial concentrations of Cu(II). When the solution pH ranged from 5.03 to 5.65, the values of Cₜ were measured to be 1.2 and 1.0 mg/L, lower than the discharged standard of 2.0 mg/L regulated by WHO and Chinese government. Under the situation of Cu (II) coexisting with K(I), Na(I), Ca(II) and Mg(II), the values were determined to be 1.96 (or 2.06), 1.53 (2.18), 1.97 (1.71) and 1.55 (2.53) mg/L when the initial concentrations of the four cations were 50 (or 100) mg/L, respectively. At the contact time of 180 min, the values of Cₜ were 0.32, 0.45, 0.65, 0.94, 1.76 and 1.86 mg/L corresponding to the initial copper concentrations of 5, 10, 15, 20, 30 and 50 mg/L, respectively. Even AL-PEI-CS₂ was regenerated for four times, the values of Cₜ were as low as 1.9, 2.1, 2.0 and 2.2 mg/L for cycles 1, 2, 3 and 4 at the initial concentration of Cu(II) of 51 mg/L and contact time of 180 min. Compared to other lignin-based adsorbents based on qₑ, equilibrium time and Cₜ at equilibrium, AL-PEI-CS₂ exhibited higher application potential to the treatment of Cu(II)-loaded wastewater. Adsorption mechanism revealed that -OH, -NH₂, -NH, C-N and -CSS- contributed to the uptake of copper ions.

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Author Contributions

C.L.Z (Associate Professor) contributed to conceptualization, review, editing and funding acquisition. Q.R.W (Ph.D. student) conducted conceptualization, investigation, formal analysis and original draft. Y.J.D (Senior Engineer) was responsible for data curation. B.Z (Professor) offered funding acquisition. Y.Y.Z (Ph.D. Assistant Professor) collected resources. T.C.Z (Professor) was in charge of sources.

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