Construction of a Carbon/Lignosulfonate Adsorbent to Remove Pb$^{2+}$ and Cu$^{2+}$

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ABSTRACT: Removing heavy metal ions from water is an important issue to improve water quality. However, using cost-effective and more environmentally friendly adsorbents to achieve efficient adsorption capacity remains a challenge. Carbon spheres were prepared by the hydrothermal method and then combined with sodium lignosulfonate to form a lignosulfonate carbon (C/SL) adsorbent. C/SL achieved the adsorption of Pb$^{2+}$ and Cu$^{2+}$ after 60 min (the adsorption capacity was 281 mg g$^{-1}$ for Pb$^{2+}$ and 276 mg g$^{-1}$ for Cu$^{2+}$) and had good selectivity and reusability (5 cycles). The simulated experimental data show that the pseudo-second-order kinetics and Langmuir isotherm are closer to the actual adsorption. Thermodynamic studies show that the adsorption of Pb$^{2+}$ and Cu$^{2+}$ is enhanced by the spontaneous process at higher temperature. This study also shows that functional groups such as hydroxyl and amino groups play an important role in the adsorption process.

INTRODUCTION

Water is the matter basis for human survival, but various types of water pollution endanger the lives of people all over the world. The price of industrial development is often environmental pollution, and water pollution of heavy metal ions is one of the most difficult problems to solve.\(^1\)−\(^5\) Heavy metal ions are highly toxic, cannot be degraded, and are easily enriched in the food chain, threatening the life and health of higher organisms.\(^6\)−\(^8\)

How to solve this kind of water pollution has become an urgent problem for countries all over the world.

The chemical precipitation method,\(^9\) ion exchange method,\(^10\) membrane treatment method,\(^11\) and adsorption method\(^12\)−\(^14\) are commonly used techniques for solving heavy metal ions. The first three technologies are mature, but they have many technical defects that cannot be avoided, are expensive, and have poor stability. Therefore, scholars use the adsorption method as a breakthrough to solve this problem.\(^15\),\(^16\) The adsorption method has the advantages of simple operation, high efficiency, and good environmental compatibility, so it is widely used by scholars.\(^17\)

Nowadays, the common adsorbents are mainly nonmetallic, metal oxides (such as alumina, silica gel, natural clay, and molecular sieve), and various activated carbon adsorbents modified by physical or chemical methods with carbon as raw materials.\(^18\)−\(^32\) Due to the excellent adsorption capacity, thermal stability, and chemical stability of carbon adsorbent materials, it is very suitable to use carbon adsorbent materials for the treatment of heavy metal ion wastewater.

The excellent properties of carbon are widely used as adsorbents. Activated carbon\(^33\)−\(^35\) and carbon nanotubes (CNTs)\(^15\),\(^22\) are commonly used as adsorbents. Activated carbon\(^26\)−\(^29\) has great adsorption capacity for heavy metal ions, but its disadvantages are high price, short service life, and high operation cost. Heavy metal ions are exchanged with the surface of activated carbon to achieve the purpose of removal. Some scholars have found that −OH and −COOH on the surface of activated carbon can coordinate with ions, resulting in the deposition of ions on the surface of activated carbon. Zhu et al.\(^13\) treated dimethylaminoethyl methacrylate with activated carbon made of rice husk to obtain the PDMAEMA-RHC composite for treating copper ions. It was found that the pore diameter of the PDMAEMA-RHC adsorbent was 3.8 nm, the surface area was 789 m$^2$ g$^{-1}$, and the adsorption capacity of copper ions was 31 mg g$^{-1}$. Imamoglu et al.\(^14\) activated the hazelnut shell with zinc chloride and then introduced nitrogen to prepare activated carbon. Its surface area is 1092 m$^2$ g$^{-1}$. The adsorption capacity of the adsorbent for copper ions is 6.6 mg g$^{-1}$ and for lead ions is 13.1 mg g$^{-1}$. A CNT is a carbon material with small size, large specific surface area, and high mechanical strength. CNTs are cylindrical carbon tubes formed by curling graphite sheets. The hollow layered structure of multiwalled CNTs makes it a good adsorbent. Li et al.\(^15\) loaded Al$_2$O$_3$ on CNTs to form a composite material, which has a good treatment effect on heavy metal ions, and the adsorption capacity for lead ions is 17.5 mg g$^{-1}$.

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Compared with other carbon materials, hydrothermal carbonization is a more green and environmentally friendly technology.\textsuperscript{1,16} The main reason is that the hydrothermal carbonization process is a process of reducing carbon, which can reduce the release of carbon dioxide, thereby reducing the greenhouse effect to achieve the purpose of protecting the environment.\textsuperscript{21} The main reason is that the hydrothermal carbonization process is a process of reducing carbon, which can reduce the release of carbon dioxide, thereby reducing the greenhouse effect to achieve the purpose of protecting the environment. Simultaneously, the cost of the hydrothermal carbon material is cheaper and the surface of the prepared carbon material contains a large number of oxygen-containing functional groups; so, the carbon material prepared by the hydrothermal method can be used in many fields.\textsuperscript{30,31} The main application areas of hydrothermal carbon materials include environmental applications,\textsuperscript{20} catalyst applications,\textsuperscript{26} electro-chemical applications,\textsuperscript{28} and biological applications.

There is no doubt that natural molecules, cellulose, polysaccharide, protein, lignin, and so on are the best carbon source of hydrothermal carbon. A large amount of lignosulfonate will be produced in the process of papermaking, pulping, and bioethanol production. However, lignosulfonate is not fully utilized and treated as waste, resulting in a waste of resources. Lignosulfonate has a high carbon content, so it is suitable to use it as a carbon source. It not only makes rational use of resources but also reduces the cost of adsorbent manufacturing. Kang et al.\textsuperscript{32} conducted hydrothermal carbonization experiments on cellulose, lignin, D-xylose, and wood powder at 225−265 °C. It was found that the yield trend of raw materials was lignin > wood powder > cellulose > D-xylose.

In this paper, hydrothermal carbon is synthesized with sodium lignosulfonate (SL) as the carbon source and then combined with SL to form the modified lignosulfonate adsorbent. Heavy metal ions are treated by adsorbents, and their adsorption properties are evaluated by various characterization methods. Different factors are set up to evaluate the adsorption performance and adsorption mechanism of the adsorbent. Lignosulfonate is a kind of waste. The modified lignosulfonate is used to produce the polymer adsorbent and composite adsorbent with excellent performance, which not only completes the reuse of waste but also reduces the consumption of other resources. This waste reuse of lignosulfonate can save natural resources, treat polluted wastewater, and protect natural resources and natural environment.

## RESULTS AND DISCUSSION

Figure 2 shows the scanning electron microscopy images, infrared spectrum, X-ray diffraction (XRD) diffraction pattern, and Raman spectrum before and after the reaction. Figure 2A shows the structure of hydrothermal carbon, which is spherical in different sizes, similar to the grape structure, confirming that the chemical structure is spherical. It is shown from Figure 2B that after compounding with lignosulfonate, spherical carbon is covered, and the surface is uneven, showing a stacking phenomenon. Figure 2C shows the element distribution diagram of the adsorbent. The adsorbent contains C, N, O, S, and Na elements, in which the N element is introduced by Mannich reaction of lignosulfonate.

In Figure 2D, it can be seen that the characteristic absorption peak of SL, 3408 cm\(^{-1}\), is the O−H stretching vibration absorption peak; 2935 cm\(^{-1}\) is the tensile vibration peak of C−H; 1605, 1513, and 1462 cm\(^{-1}\) are the C=C stretching vibration peaks in the aliphatic ring; 1210 cm\(^{-1}\) is the absorption peak of the sulfonic acid group; and 1039 cm\(^{-1}\) is the characteristic peak of fatty ether. The infrared absorption peak of C/SL includes the characteristic absorption peak of SL, as well as other absorption peaks. 811 cm\(^{-1}\) is the out-of-plane bending vibration peak of N−H, which is introduced by the amino group in triethylenetetramine; 1657 cm\(^{-1}\) is the characteristic absorption peak of C==O; and 1280 cm\(^{-1}\) is the stretching vibration peak of C−N, which is a new group generated after compounding with the carbon sphere, confirming that the carboxyl group on the carbon ball reacts with the amino group. Figure S1 shows the infrared spectrum of C/SL adsorption of Pb\(^{2+}\) and Cu\(^{2+}\). It is clear that some of the absorption peaks of the hydrogel with heavy metal ions have shifted. Pb\(^{2+}\) and Cu\(^{2+}\) will chelate with O and N elements to form coordination bonds, which will change the electron cloud density and cause the shift of the bond vibration band.\textsuperscript{34}
As can be seen from Figure 2E, the two diagrams show large diffraction peaks only at 23°. The C/SL adsorbent has a carbon peak similar to hydrothermal carbon, indicating that SL and hydrothermal carbon are successfully combined, and the
diffraction of the two substances is consistent with that of amorphous carbon.35

Raman spectroscopy is often used to characterize the properties of carbon materials. Figure 2F shows that hydrothermal carbon and C/SL adsorbent have two absorption peaks. The left peak is D-band, which is the absorption peak caused by carbon atom lattice defects, and the right peak is G-band, which is the in-plane stretching vibration of carbon atom sp² hybridization. This indicates the existence of sp² and sp³ hybrid carbon atoms, structural defects, and oxygen-containing functional groups in C/SL.36 The calculated $I_D/I_G = 0.59$ can also draw the conclusion that the carbon ball of SL is amorphous carbon, which is consistent with the results of XRD analysis.

The dose of the adsorbent directly affects the cost issue. As can be seen from Figure 3A,B, the adsorbent dose increases and the adsorption capacity decreases. The metal ion concentration in the capacity is constant, the dose of the adsorbent added increases, and only a small number of adsorption sites are used, resulting in the reduction of the average adsorption capacity of the C/SL adsorbent. However, the removal rate of metal ions is also increasing until it is close to 100%. For these results, adsorption experiments were carried out at a dose of 0.01 g.30

The pH of the environment have a great effect on the performance of the adsorbent. When the initial concentration of Pb²⁺ and Cu²⁺ is 40 mg L⁻¹, the theoretical pH at which the precipitate begins to appear is 5.97 and 6.23, respectively. It is known from the experiment that when pH does not exceed 7, the effect of C/SL on Pb²⁺ and Cu²⁺ is larger than the effect of OH⁻ (in Figure S2). Therefore, this paper reports only the performance of C/SL at pH < 7. It can be seen from Figure 3C that when pH < 6, the performance of C/SL is seriously affected by H⁺. On the one hand, H⁺ is easy to combine with C/SL to occupy the adsorption site, and on the other hand, C/SL has a positive charge, which repels heavy metal ions (in Figure S3). When pH > 6, the adsorption capacity of C/SL for two ions increase rapidly. This may be because the concentration of H⁺ substantial reduction and the surface charge of C/SL change from positive to negative.30,31 Compared with Figure 3C,D, the effect of pH on SL is basically the same as that of C/SL, indicating that H⁺ also has a great impact on SL adsorption performance.

It can be seen from Figure 4A,B that in the presence of nitrate ions, C/SL adsorbs the least Pb and Cu, followed by chloride ions, and in the presence of sulfate ions, the adsorption capacity of Pb and Cu is the largest. Li et al.37 found that after adsorbing HPO₄²⁻, F⁻, SO₄²⁻, Cl⁻, and NO₃⁻ (pH 3.5~8.0), the clay of Latosol ζ. The potential has a negative shift in the order of HPO₄²⁻ > F⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻. This shows that the
adsorption of heavy metal ions will increase with the increase of adsorbent electronegativity. It can be proved that the adsorption of C/SL on sulfate is better than that of chloride and nitrate under the presence of different accompanying anions. For Cu, under certain conditions, heavy metals can form composite ions with anions in the solution, which changes the activity of free heavy metal ions in the solution, thus affecting the adsorption of heavy metals. Cl\(^{-}\) and Cu form CuCl\(^{+}\) complex ions, which reduces the degree of hydration of ions and the average charge of ions, resulting in lower solvation energy and energy barrier. Therefore, this complex ion is easier to be adsorbed by C/SL, making the adsorption capacity of C/SL for copper chloride greater than that of copper nitrate.\(^{38}\) The coordination adsorption of SO\(_4^{2-}\) with variable charge points enhances the negative charge on the surface and increases the adsorption capacity. Due to the abovementioned reasons, the adsorption of sulfate > chloride > nitrate in C/SL.

In Figure 4C, the adsorption efficiency of the C/SL adsorbent for different ions is different; Pb\(^{2+}\) (98%), Cd\(^{2+}\) (97%), Cd\(^{2+}\) (62%), Co\(^{2+}\) (81%), and Cr\(^{3+}\) (70%). Figure 4D shows the selective adsorption of the C/SL adsorbent for the bivalent heavy metal ions. The preferential adsorption efficiencies of Pb\(^{2+}\) and Cu\(^{2+}\) are 91% and 83%, respectively. Adsorption efficiency is ranked as Pb > Cu > Co > Cd > Cr. The cause of selective adsorption may refer to the electronegativity of the metal (2.33 for Pb, 1.90 for Cu, 1.88 for Co, 1.69 for Cd, 1.66 for Cr).

Figure 5 shows the adsorption of Pb\(^{2+}\) and Cu\(^{2+}\) by C/SL and SL with contact time. The adsorption equilibrium time of Pb\(^{2+}\) and Cu\(^{2+}\) on SL needs at least 60 min, and the removal efficiencies of Pb\(^{2+}\) and Cu\(^{2+}\) are 43.5 and 39.5%, respectively. In contrast, it takes 60 min to reach equilibrium on C/SL, and the removal rates of Pb\(^{2+}\) and Cu\(^{2+}\) are almost 100%. The porous structure of C/SL accelerates the diffusion of metal ions in the particles, so as to realize rapid adsorption.

According to the equilibrium time data, the pseudo-first-order and pseudo-second-order models were used to analyze the adsorption rate. Table S2 lists the relevant parameters calculated from the two models. For SL data, the correlation coefficient of the pseudo-first-order model (\(R^2 = 0.977\) for Pb\(^{2+}\) and 0.994 for Cu\(^{2+}\)) is greater than that of the pseudo-second-order kinetic model, which is 0.939 for Pb\(^{2+}\) and 0.989 for Cu\(^{2+}\), indicating that there are enough adsorption sites on SL to adsorb Pb\(^{2+}\) and Cu\(^{2+}\). On the contrary, for the data of C/SL, the correlation coefficients of the pseudo-first-order model (\(R^2 = 0.955\) for Pb\(^{2+}\) and 0.866 for Cu\(^{2+}\)) are less than 0.999 for Pb\(^{2+}\) and 0.999 for Cu\(^{2+}\) in the pseudo-second-order kinetic model, indicating that the adsorption sites on C/SL are limited. Pseudo-first-order and pseudo-second-order kinetics can describe the data as a generalized rate control step, but they cannot provide a comprehensive view of adsorption in a series of different steps. When metal ions enter the adsorbent from the solution, the diffusion in pores and particles is usually rate-limited. Intraparticle diffusion has three different linear regions over the entire...
time range (Figure S4). As can be seen from Figure S4, the curves of equilibrium adsorption capacity ($q_e$) and $t^{0.5}$ of SL and C/SL do not pass through the origin, indicating rapid intraparticle diffusion.\textsuperscript{34,39,40}

The adsorption isotherms of C/SL at different temperatures are shown in Figure 6. The adsorption capacity increased with the increase of temperature and initial concentration. Langmuir and Freundlich isotherms are used to describe the adsorption behavior of Pb\textsuperscript{2+} and Cu\textsuperscript{2+}, and their corresponding parameters are shown in Table S3. For C/SL, the correlation coefficient of the Langmuir model ($R^2 > 0.994$) is higher than that of the Freundlich model ($R^2 < 0.981$), indicating the monolayer adsorption of Pb\textsuperscript{2+} and Cu\textsuperscript{2+} by C/SL. Therefore, the adsorption behavior of C/SL for Pb\textsuperscript{2+} and Cu\textsuperscript{2+} conforms to the Langmuir model. The maximum theoretical adsorption capacity of C/SL is as high as 283.6 mg g\textsuperscript{-1} for Pb\textsuperscript{2+} and 276.8 mg g\textsuperscript{-1} for Cu\textsuperscript{2+}, which is much higher than that of SL (105.1 mg g\textsuperscript{-1} for Pb\textsuperscript{2+} and 87.5 mg g\textsuperscript{-1} for Cu\textsuperscript{2+}) (Figure S5).\textsuperscript{41,42} In the actual adsorption process, the maximum adsorption capacity of C/SL for Pb is 281 mg g\textsuperscript{-1} and that of Cu is 276 mg g\textsuperscript{-1}. This is very close to the maximum predicted by Langmuir isotherm, which proves that the Langmuir isotherm model can better represent the actual adsorption process.

It can be seen from Figure 6 (A,B) that with the increase of temperature, the surface-active sites of the C/SL adsorbent will increase, resulting in the increase of the adsorption capacity of the C/SL adsorbent. In order to further explore the relationship between temperature and adsorption, the thermodynamic method was used to explore the adsorption heat.

The thermodynamic formula is used to fit the data, as shown in Figure 6C, and Table S4 lists the results of thermodynamic fitting parameters. In Table S4, the entropy change $\Delta S^0$ of adsorption is more than zero, which indicates that the entropy value increases in this process; the enthalpy change $\Delta H^0$ of adsorption is more than zero, which indicates that the whole adsorption process is endothermic; Gibb’s function is calculated according to the enthalpy change and entropy change, and $\Delta G^0$ is less than zero, which indicates that the adsorption process is a spontaneous process.

In order to study the removal mechanism of Pb\textsuperscript{2+} and Cu\textsuperscript{2+}, X-ray photoelectron spectroscopy (XPS) was used to study the chemical changes of Pb\textsuperscript{2+} and Cu\textsuperscript{2+} before and after adsorption. From Figure 7A, it can be seen that there were no obvious peaks in C/SL, the Pb 4f peaks appear in the spectrum of C/SL after adsorption of Pb, and the Cu 2p peaks appear in the spectrum of C/SL after adsorption of Cu (Figure 7B,C). It was revealed that the adsorption of Pb\textsuperscript{2+} and Cu\textsuperscript{2+} occurs on the surfaces of C/SL, resulting in changes in the part bonding environment.\textsuperscript{43} In the N spectrum before and after adsorption of Pb\textsuperscript{2+} and Cu\textsuperscript{2+} (as shown in Figure 7D), the $-\text{NH}_3$, $-\text{NH}_2$, and $-\text{NH}$ peaks had...
chemically changed after adsorption, and the peaks corresponding to $-\text{NH}_3$, $-\text{NH}_2$, and $-\text{NH}^-$ of C/SL underwent chemical shifts after adsorption, indicating that $-\text{NH}_3$, $-\text{NH}_2$, and $-\text{NH}^-$ on the surfaces of C/SL are chemically bonded to Pb$^{2+}$ and Cu$^{2+}$. In addition, as shown in Figure 7E, the binding energy of the O1s of C/SL is 531.13 eV, while it became 531.13 eV (Pb) and 531.49 eV after adsorption of Pb$^{2+}$ and Cu$^{2+}$, respectively. These results indicated that the O element participates in the adsorption of Pb$^{2+}$ and Cu$^{2+}$. The O element contained a solitary pair of electrons, while the transition metal had free atomic orbits. They can share electrons to form amino metal complexes. In Figure 7F, it also revealed that the S 2p binding energy peak of $\text{SO}_3^-$, $\text{S}^-\text{O}$, and $\text{C}^-\text{S}$ in C/SL-Cu moved from 169.4 to 170.43, 168.8 to 169.67, and 168.1 to 168.34 eV after biosorption, respectively. This indicated that the S atom in $\text{SO}_3^-$ took part in coordinating with metal ions. XPS results show that the adsorption is related to carboxyl, sulfonic acid, and amine groups, which form chelates with heavy metal ions. The chelating ability of the adsorbent is related to O, N, and S. Pb and Cu can be effectively removed by introducing these functional groups.

After the C/SL adsorbent adsorbs metal ions, HCl was added to desorb the adsorbent, filtered, and dried, and then, the second adsorption experiment was conducted. After five adsorption experiments, it was found that the C/SL adsorbent still has high adsorption performance. The adsorption efficiency of the adsorbent for the two ions is not less than 84%. Simultaneously, it is revealed in Figure 8 that the adsorption efficiency of the C/SL adsorbent for Pb$^{2+}$ and Cu$^{2+}$ ions is basically the same, indicating that the C/SL adsorbent has no specificity for the adsorption of two ions.

The adsorption capacity of C/SL for Pb$^{2+}$ and Cu$^{2+}$ was compared with other carbon adsorbents reported in the recent literature. Although the maximum adsorption performance of C/SL for Pb$^{2+}$ and Cu$^{2+}$ is not the best among the listed results (Table 1), C/SL can still be used as an efficient adsorbent.

## CONCLUSIONS

In this study, a low-cost C/SL adsorbent was prepared by lignosulfonate to effectively remove Pb$^{2+}$ and Cu$^{2+}$ from water. At pH 7, the maximum adsorption capacities of C/SL for Pb$^{2+}$ and Cu$^{2+}$ were 281 and 276 mg g$^{-1}$, respectively. The adsorption process conforms to Langmuir isotherm and pseudo-second-order kinetics. C/SL has good selectivity and reusability for Pb$^{2+}$ and Cu$^{2+}$, and all the hydroxyl and amino groups help to promote the accumulation of Pb$^{2+}$ and Cu$^{2+}$. The mechanism is the chelation and electrostatic force between Pb$^{2+}$ and Cu$^{2+}$ and C/SL. The results show that C/SL is an effective adsorbent for the removal of Pb$^{2+}$ and Cu$^{2+}$.

## MATERIALS AND METHODS

SL is used as the raw material for hydrothermal carbon and composites; cetyltrimethylammonium bromide (CTAB) is a
template for the preparation of hydrothermal carbon; hydrochloric acid is used to adjust the pH of the solution; absolute ethanol is used as the solvent or washing solution; glutaraldehyde and triethylenetetramine were involved in the modification of lignin sulfonate; lead nitrate, copper nitrate, chromium nitrate, cadmium nitrate, and cobalt nitrate simulate the pollution of heavy metal ions; and lead sulfate, copper sulfate, copper chloride, and lead chloride were used to study the effect of anions on adsorption performance. These chemical reagents were purchased from Shanghai Sinopharm Group Co., Ltd.

SL, CTAB, HCl, ethanol, glutaraldehyde, triethylenetetramine, lead nitrate, and copper nitrate were analytical grade and obtained from Shanghai Sinopharm Group Co., Ltd.

**Preparation of Hydrothermal Carbon.** First, 30 mL of concentrated hydrochloric acid was added to 50 mL of deionized water while stirring, and 3 g of SL was added into solution. Next, CTAB was added to the solution, stirred until dissolved, and then transferred the solution to a 100 mL reaction
kettle, and the solution reacted at a constant temperature of 180 °C for 12 h. After the reaction, the solid and liquid were separated by centrifugation, washed with deionized water and anhydrous ethanol until the washing solution was colorless, and then dried in an oven to obtain carbon materials. After drying, CTAB was removed from the carbon material by a tubular furnace (specific parameters: nitrogen protection, 5 °C min⁻¹ heating rate increased from 25 to 800 °C), then cleaned with deionized water, and finally dried to obtain hydrothermal carbon spheres.

**Preparation of Adsorbent.** According to several key elements (carbon, lignosulfonate, triethylenetetramine, and glutaraldehyde) used in the experiment, orthogonal experiments were carried out to optimize the best content of each factor (Table S1). 100 mL of deionized water, 4 g of SL, and 3 g of carbon materials were added into a three-neck flask in turn and dispersed by ultrasonication and then refluxed at 60 °C for 60 min. 50 mL of glutaraldehyde was continuously added to the abovementioned solution, and the reaction continued for 3 h. After the reaction was completed, it was filtered and washed to obtain a brown precipitate. Next, the brown solid, 6mL of CTAB, was added into a three-necked flask in turn, and the solution reacted at a constant temperature of 180 °C for 30 min. 5 mL of glutaraldehyde was continuously added to the three-necked flask to react for 3 h. After the reaction was completed, the solid and liquid were separated by centrifugation, washed with deionized water until the washing solution was colorless, and then dried in an oven to obtain carbon-coated modified SL (C/SL). The mechanism of the abovementioned solution is shown in Figure 1.

In this study, SL was used as the raw material to prepare carbon sphere materials by the hydrothermal method and template method, and its formation mechanism was speculated. In the presence of H⁺ (from HCl), SL is hydrolyzed into a monomer and dimer, and the sulfonic acid group in the monomer or dimer of hydrolyzed SL reacts with the ammonium ion in CTAB. Then, under hydrothermal conditions, the hydrolyzed SL forms spherical mesoporous carbon by dehydration polymerization. Finally, CTAB was removed by calcination at 800 °C.

SL, glutaraldehyde, and triethylenetetramine will undergo Mannich reaction under heating conditions to generate β-amino compounds (aminated lignosulfonate). The infrared spectrum of carbon spheres shows that there are carboxyl groups on the surface of carbon spheres (in Figure S1). It is speculated that the amino groups on aminated lignosulfonate react with the carboxyl groups on carbon spheres to form the C/SL adsorbent.

**Adsorption Properties of C/SL Adsorbent.** First of all, Pb²⁺ and Cu²⁺ (1000 mg L⁻¹) were prepared in a 1 L volumetric flask as the reserve for the adsorption experiment. A 50 mL beaker was added with the metal ion solution and adsorbent, and the adsorption equilibrium was maintained at a constant temperature. When studying the influencing factors, the parameters are set as follows: pH: 2–7, initial ion concentration 10–60 mg L⁻¹, adsorbent dosage 0.01–0.05 g, temperature 25–45 °C, and time 0–180 min. The ion concentration was measured by inductively coupled plasma (ICP-OES), and the adsorption capacity (qe) was calculated by eq 1.

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(1)

where \( C_0 \) is the initial concentration, \( C_e \) is the equilibrium concentration (mg L⁻¹), \( V \) is the solution volume (L), and \( m \) is the adsorbent weight (g). In order to control the correctness, all adsorption experiments of this batch were conducted in three times, and the average value was reported.

When studying the kinetic model, the parameters are set as follows: pH = 7, the metal ion concentration is 40 mg L⁻¹, the amount of the adsorbent is 0.01 g, the adsorption time is 0–180 min, and the temperature is 25 °C. When discussing thermodynamics, the experimental parameters were set as follows: pH = 7, metal ion concentration 40 mg L⁻¹, adsorbent dosage 0.01 g, adsorption time 180 min, and temperature 25–45 °C.

The nonlinear equations are pseudo-first-order (2), pseudo-second-order (3) kinetic models, Langmuir (4), Freundlich (5), Temkin (6), D-R (7–9) adsorption isotherm models, thermodynamic eqs 10 and 11, and the experimental data are fitted with Origin 9.1 software to evaluate the kinetics and adsorption capacity.

\[ q_t = q_e \left[1 - e^{-k_1 t}\right] \]  

(2)

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e^2 t} \]  

(3)

\[ \frac{q_e}{C_e} = \frac{Q_m k_L C_e}{1 + k_L Q_m} \]  

(4)

\[ q_e = k_C C_e^{1/n_e} \]  

(5)

\[ q_e = B \ln A + B \ln C_e \]  

(6)

\[ \ln q_e = -\beta e^2 + \ln q_{m,D-R} \]  

(7)

\[ \varepsilon = RT \ln \left(\frac{C_e + 1}{C_e}\right) \]  

(8)

\[ E = \frac{1}{\sqrt{2\beta}} \]  

(9)

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  

(10)

\[ \ln(q_e/C_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  

(11)

where \( k_1 \) (min⁻¹), \( k_2 \) (g mg⁻¹ min⁻¹), and \( k_p \) (mg g⁻¹ min⁻¹/2) are pseudo-first-order rate constants, pseudo-second-order rate constants, and intraparticle diffusion rate constants, respectively. \( t \) (min) is the time, \( C \) is a constant, and \( q_0 \) (mg g⁻¹) is the adsorption capacity corresponding to \( t = 0 \).\( q_{m,D-R} \) is the
maximum saturated adsorption capacity. \( K_r \) (L mg\(^{-1}\)) is the Langmuir adsorption constant related to the adsorption energy. \( K_F \) (L g\(^{-1}\)) is the Freundlich adsorption constant related to the adsorption capacity and \( n \) is the constant. \( A \) (mg L\(^{-1}\)) is the equilibrium constant related to binding energy, and \( B \) is the Temkin constant related to the adsorption heat. \( q_{n, B, R} \) (mg g\(^{-1}\)) is the theoretical maximum adsorption capacity of the D−R adsorption isotherm model, \( \beta \) (mol\(^2\) KJ\(^{-1}\)) is the D−R model constant related to the adsorption energy, and \( \varepsilon \) is Polanyi adsorption potential. \( R \) is the universal gas constant, and \( T \) (K) is the thermodynamic temperature. \( E \) (KJ mol\(^{-1}\)) is adsorption energy. \( \Delta G^\circ \) (KJ mol\(^{-1}\)) is Gibbs free energy, \( \Delta S^\circ \) (J mol\(^{-1}\) K\(^{-1}\)) is adsorption entropy change, and \( \Delta H^\circ \) (KJ mol\(^{-1}\)) is adsorption enthalpy change.

0.01 g of C/SL was added into 50 mL of ion solution and then adsorbed at room temperature for 180 min (pH: 7). After separation, the supernatant was measured to obtain the corresponding adsorption capacity. Then, 0.1 M HCl was used for desorption, and then, the adsorption of the ions was repeated five times with the same adsorption conditions as described above, and the regeneration efficiency \( r_e \) was calculated according to the experimental results.

\[
  r_e = \frac{q_n}{q_1} \times 100\%
\]  

(12)

where \( q_n \) (mg g\(^{-1}\)) is the first adsorption equilibrium adsorption capacity and \( q_1 \) (mg g\(^{-1}\)) is the nth adsorption equilibrium adsorption capacity.

### Characterization of C/SL Absorbent

The morphology of the material was characterized by QUANTA 200 scanning electron microscope. The X-ray pattern of C/SL was measured by the TDF-3200 and Cu Kα radiation source \((k = 1.540598 \AA)\). The diffraction angle of 2θ was 5°–80°, and the detection rate was 0.02° min\(^{-1}\). The composition of the sample was characterized by Raman spectroscopy (Raman, ATC0400-UV). Fourier transform infrared spectroscopy (FTIR) was used to study the surface groups on the material surface. A Thermo Scientific spectrometer, Nicolet 5700, was used with a resolution of 4 cm\(^{-1}\), a collection rate of 20 min\(^{-1}\), and a spectral range of 4000–400 cm\(^{-1}\). The samples to be tested and KBr were pressed in the ratio of 1:100. The elemental content of the sample was characterized and analyzed with an element analyzer (PerkinElmer 2400II). XPS was performed on a Kratos Axis Ultra electron microscope. The X-ray pattern of C/SL was measured, and a graph of \( pH_{\text{pzc}} \) represents the point where \( \Delta pH = 0 \).

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#### Notes

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