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Preparation of Sodium Lignosulfonate/Chitosan Adsorbent and Application of Pb²⁺ Treatment in Water

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Abstract: Industrial wastewater has brought huge disasters to water resources and soil and has seriously affected the growth of animals and plants. There is an urgent need for a green and efficient adsorbent to solve the problem of water pollution. Sodium lignosulfonate and chitosan undergo free radical polymerization to form a lignin/chitosan adsorbent, which is used to treat Pb²⁺ in water pollution. An orthogonal experiment was used to optimize the content of sodium lignosulfonate, chitosan, cross-linking agent and initiator to obtain the adsorbent with the best adsorption performance. The adsorbents were characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermal analysis and zeta potentiometry. The influence of different conditions on the adsorption of heavy metal ions by lignosulfonate/chitosan adsorbent was explored, and a kinetic and isotherm model was established. The results showed that the adsorption capacity of Pb²⁺ was 345 mg g⁻¹ when the adsorbent was 0.01 g, the concentration of heavy metal ions was 100 mg L⁻¹ and pH was 7. The adsorption process of lignosulfonate/chitosan is a kind of spontaneous adsorption mode, which is mainly composed of electrostatic adsorption and chemical adsorption.

Keywords: chitosan; lignosulfonate; adsorbent; orthogonal optimization

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1. Introduction

Water health is very important to human and environmental safety. Today's freshwater resources are extremely polluted, and water-pollution treatments have been investigated worldwide. One cause of water pollution is domestic and industrial sewage. Heavy metal ions are among the most serious pollutants [1–4], as they are rich in nature and do not easily degrade in the environment. Lead is a toxic metal that can accumulate in human and animal tissues. Its sources include paints, coatings, batteries, smelting, hardware, machinery, electroplating, cosmetics, hair dyes, glaze dishes, tableware, coal, puffed food and tap water pipes [5–7]. After entering the body through the skin, digestive tract or respiratory tract, lead interacts with various organs, causing anemia, neurological disorders and kidney damage [8,9].

Currently, lead is processed by oxidation–reduction [10], electrolysis [11], ion exchange [12] and adsorption [13–15]. The oxidation–reduction method efficiently precipitates heavy metal ions, but produces a large amount of waste residue that causes secondary pollution. The electrolysis method converts heavy metal ions into easy-to-handle valence states through the electrolytic cell principle. This method efficiently treats a large amount of sewage, but its application is limited by low cost. The ion–exchange method separates heavy metal ions through ion-exchange resins. Although the separation of heavy gold ions approaches 100%, the resin is expensive and not easily recycled. Among the above-listed methods, adsorption is the expected main method for future processing of heavy metal ions. The adsorption method has several advantages—high efficiency, economy and greenness—which are not shared by traditional methods [16–19].

Heavy metal ions can be adsorbed by various techniques such as electrostatic attraction, chelation of functional groups and ion exchange on the adsorption surface. Most physical adsorbents have an electrostatic reference, and adsorbents with fast adsorption rates can quickly and effectively remove pollutants. The functional groups of organic adsorbents chelate with metals, and many oxygen-containing functional groups form stable coordination structures with metals, which are effective in complex environments. The adsorbent attracts heavy metal ions to the surface and exchanges its ions with those of the pollutant ions, exerting an obvious adsorption effect. The performance of the adsorbent depends on many factors, including the adsorbent material, activated carbon, metal oxides, and minerals. Activated carbon is a specially treated carbon formed by heating organic raw materials (husks, coal, wood) in isolating air to reduce the components on the carbon. The heat-treated carbon is reacted with gas, which corrodes the surface and forms micropores. Activated carbon has a crystal structure and an internal pore structure. It combines with heavy metal ions not only through physical van der Waals forces but also by chemical bonding between its surface functional groups and metal ions. The Pb-adsorption capacity of 0.1 g activated carbon (7.23 mg g^{-1}) [20] is neither high nor sufficiently stable. The adsorption of Pb by activated carbon depends on the oxygen-containing functional groups on the carbon surface and is highly sensitive to pH. In nature, metal oxides are ubiquitous and readily undergo ion exchanges with inorganic ions. For example, Fe_2O_3 , MnO_2 and TiO_2 can adsorb heavy metal ions. Dong et al. [21] extracted MnO_2 and Fe–Mn oxides from lake water using hydroxylamine hydrochloride and sodium bisulfite, respectively. Both oxides effectively adsorbed Pb, Cd and Cu in aqueous solution. The Fe–Mn oxides preferentially adsorbed to Pb, with a maximum adsorption capacity of $27.5 \text{ } \mu\text{mol g}^{-1}$. The selectivity of Fe–Mn oxide decreased in the order $\text{Pb} > \text{Co} > \text{Cd} > \text{Cu}$. Natural clay, which mainly consists of silicate minerals such as magnesium and aluminum, performs the function of repairing and purifying the environment. Clay is an ideal material for treating heavy metal ions owing to its high porosity, large specific surface area and strong polarity, all of which enhance the metal-ion adsorption. Clay crystals host oxygen atoms on their surfaces and form no hydrogen bonds in the crystal layer, allowing the direct entry of cations. Moreover, the irregular defects and special molecular structure of clay are favorable for adsorbing heavy metal ions. At present, the removal of heavy metal-ion pollutants by clay is still in the research stage, and few practical applications have been reported. Composite materials deliver excellent performances in various scenarios by combining the functionalities of their individual constituents [22–25]. Starting from $\text{Fe}_5\text{O}_4 \cdot 7\text{H}_2\text{O}$ and activated carbon, Wang [20] synthesized a nano-zero-valent iron composite with activated carbon loading (NZVI/AC) and ultra-low iron content. At 298.15 K and pH 6.0, the adsorption capacity of NZVI/AC for Pb was 59.35 mg g^{-1} . Sang [26] prepared Fe_3O_4 nanoparticle-coated porous BN microrods ($\text{p-BNMR@Fe}_3\text{O}_4$) by an in situ solvothermal method. The $\text{p-BNMR@Fe}_3\text{O}_4$ nanocomposite exhibited significant adsorption activity for Pb (II). At an initial Pb (II) concentration of 180 mg L^{-1} and a pH of 5.5, the maximum adsorption capacity reached 249.5 mg g^{-1} .

The papermaking industry produces an enormous amount of lignin each year, but lignin applications are limited and much of the lignin is wasted. The main industrial uses of lignosulfonate are concrete water reducers, binders of flotation and smelting ore powders, dispersants and binders for refractory materials, carbon-content reducers to improve the green strength of ceramics, and dispersants in coal–water slurries. Lignin applications are also being developed in academic institutions. Calcium lignosulfonate acts as a reactive surfactant that improves the contact between the reactants. Sodium lignosulfonate is used as an adsorbent for organic dye removal and as a eutectic solvent for extracting and improving lignin [27]. Nano-lignin enhances the mechanical properties of lignin during the polymerization process and provides a strong UV-absorption capacity in the film. As lignosulfonate contains a large number of functional groups, it can be combined with heavy metal ions. Jiang [13] et al. found that the sulfur and oxygen groups of lignosulfonate combine with heavy metal ions such as copper, lead and cadmium, thereby separating them

from aqueous solutions. Chitosan is biocompatible, lipid-lowering, antibacterial, non-toxic and possesses other properties that are desired in various industries. Chitosan is slightly soluble in water and soluble in weak acid. After dissolution, it becomes gelatinous and has a strong adsorption capacity by virtue of its polar groups (hydroxyl and amino groups), which have a water absorption capacity above 500%. Therefore, these groups are used as the components of various humectants. The $-NH_2$ ortho-position on chitosan is $-OH$, which can coordinate with divalent heavy metal ions. This group can be modified or loaded on other substances to form composite materials that adsorb heavy metal ions. Chitosan has broad application prospects in papermaking, textiles, agriculture, food processing and treatment of heavy metal ions [28–31].

In this study, a sodium lignosulfonate–chitosan (LS/CS) adsorbent for Pb^{2+} removal was synthesized from sodium lignosulfonate and chitosan, and the synthesis conditions were optimized by an orthogonal design. Sodium lignosulfonate enables the fabrication of low-cost adsorbents, and both sodium lignosulfonate and chitosan are easily obtained and biocompatible. Therefore, LS/CS adsorbent is the expected future trend of adsorbent developments.

2. Materials and Methods

2.1. Materials and Experimental Reagents

Acrylic acid ($C_3H_4O_2$, Analytical Reagent (AR)), chitosan ($(C_6H_{11}NO_4)_n$, AR), sodium lignosulfonate ($C_{20}H_{24}Na_2O_{10}S_2$, AR), potassium persulfate ($K_2S_2O_8$, AR), N,N-methylene bisacrylamide (NMBA, AR), potassium hydroxide (KOH, AR), ethanol (CH_3CH_2OH , AR) and lead nitrate ($Pb(NO_3)_2$, AR) were purchased from Shanghai Guoyao Group. Unless stated otherwise, the solvent in all processes was deionized water.

2.2. Material Preparation

Preparation of LS/CS Adsorbent

LS/CS adsorbent was synthesized by neutralizing acrylic acid, followed by free-radical reaction with sodium lignosulfonate and chitosan. For this purpose, 2.744 g of KOH was dissolved in 5 mL of water and neutralized with 5 mL of acrylic acid added through a dropper. To the resulting solution, LS, CS, potassium persulfate and NMBA were added in succession, along with 10 mL of water with stirring to dissolve. The mixture was placed in a sonicator and reacted at 70 °C for 1 h. The obtained product was washed with absolute ethanol, dried and ground to obtain the LS/CS adsorbent.

To maximize the adsorption performance of the adsorbent, the dosages of LS, CS, $K_2S_2O_8$ and NMBA in the synthesis were optimized. A full factorial experimental design with various levels of each factor requires numerous groups of experiments that consume manpower and time and increase the error in the experimental process. An orthogonal design experiment is a multi-factor, multi-level design method performed on representative groups selected from the full-factor experiment. The selected groups should be evenly dispersed, neat, and comparable. Orthogonal experimental design effectively reduces the number of experiments and is an efficient, fast and economical approach for optimizing the synthesis scheme. To find the best adsorbent, the LS, CS, $K_2S_2O_8$ and NMBA contents were optimized by Orthogonal Experiment Assistant II (V3.1) software. Table 1 shows the data of the orthogonal design experiment.

2.3. Characterization of Adsorbents

The Fourier transform infrared (FT-IR) spectra of the samples were measured by a Nicolet nexus 470 spectrometer (Nicolet, USA) in the wavenumber range 400–4000 cm^{-1} . For these measurements, the sample mass was thoroughly ground with dry KBr (mass ratio 1:100). The sample microstructures were studied by emission scanning electron microscopy (FE-SEM) JSM-7800F (JEOL Co., Ltd., Mitaka, Japan). The dried samples were gold-coated and imaged at an acceleration voltage of 10.0 kV. The thermal gravimetric analysis (TGA) of the samples was evaluated by a 449 C integrated thermal analyzer

(Netzsch, Germany). During the TGA measurements, the samples were heated from 20 to 800 °C at 58 °C min^{−1} in a nitrogen environment. The Zeta (ζ) potentials were measured by a Nano ZS90 potential analyzer (Malvern, UK) at room temperature (20 °C). The Pb²⁺ contents before and after adsorption were measured by the flame method using a TAS-986 atomic absorption spectrophotometer (Beijing General Instrument Co., Ltd., Beijing, China). The wavelength was 283.3 nm, the combustion gas was 0.09 MPa acetylene flowing at 1.5 L min^{−1} and the combustion height was 6 mm.

Table 1. Orthogonal experimental data.

Factor	C ₂₀ H ₂₄ Na ₂ O ₁₀ S ₂ (g)	(C ₆ H ₁₁ NO ₄) _n (g)	K ₂ S ₂ O ₈ (g)	NMBA (g)
1	0.1	0.1	0.07	0.0085
2	0.1	0.2	0.09	0.0115
3	0.1	0.3	0.11	0.0145
4	0.2	0.1	0.09	0.0145
5	0.2	0.2	0.11	0.0085
6	0.2	0.3	0.07	0.0115
7	0.3	0.1	0.11	0.0115
8	0.3	0.2	0.07	0.0145
9	0.3	0.3	0.09	0.0085

2.4. Adsorption of Pb²⁺

All adsorption experiments were carried out in 50 mL salt solution (salt solution is formed by Pb(NO₃)₂ dissolving in water). During the experiments, the pH of the solution was adjusted with 0.1 mM HCl and 0.1 mM NaOH. The parameters of the kinetic experiment were set as follows: adsorption time = 5–240 min, initial concentration of heavy metal ions = 100 mg L^{−1}, LC/CS adsorbent dosage = 0.01 g, pH = 7.0, temperature = 20 °C. The parameters in the adsorption isotherm model were set as follows: initial concentration of heavy metal ions = 100–900 mg L^{−1}, amount of LC/CS adsorbent = 0.01 g, pH = 7.0, temperature = 20 °C. The parameters of adsorption thermodynamics were as follows: initial concentration of heavy metal ion = 100 mg L^{−1}, amount of LC/CS adsorbent = 0.01 g, pH = 7.0, temperature = 20–60 °C. The pH effect on the adsorption was obtained by varying the pH from 1.0 to 7.0. This experiment was performed in a solution of heavy metal ions (100 mg L^{−1}) with an LC/CS adsorbent dosage of 0.01 g at 20 °C. Finally, the effect of adsorbent dosage on the adsorption was investigated by varying the amount of LS/CS adsorbent from 0.01 to 0.07 g. The heavy-metal ion concentration, pH, and temperature were set to 100 mg L^{−1}, 7.0 and 20 °C, respectively. The residual concentrations of Pb²⁺ were determined by a TAS-986 atomic absorption spectrophotometer. The adsorption capacity Q_e at (equilibrium (mg g^{−1})) was calculated as

$$Q_e = \frac{(C_e - C_0)V}{M}, \quad (1)$$

where C_e and C_0 are the equilibrium and initial concentrations, respectively (both in mg L^{−1}), V (L) is the volume of the system and M (g) is the mass of the adsorbent.

3. Results and Discussion

3.1. Results of the Orthogonal Experiment

The synthesis was optimized for the adsorption capacity of Pb²⁺ by an orthogonal experimental design. The results of the orthogonal experiment are listed in Table 2.

In the orthogonal experimental results, changing the level of a factor with a high extremum exerts a greater effect on the experimental results than changing a factor with a low extremum. The factor with the maximum extremum is the most important factor. The influence of the factors on the adsorption decreased in the order K₂S₂O₈ > (C₆H₁₁NO₄)_n > C₂₀H₂₄Na₂O₁₀S₂ > NMBA. The orthogonal experiment does not consider the interactions between factors, so summing the experimental results of each factor at each level deter-

mines the best plan. As clarified in Supplementary Materials Figure S1, the best value is the value that maximizes the sum of the experimental results of each factor at each level. The best levels of the factors were thus determined as follows: $C_{20}H_{24}Na_2O_{10}S_2 = 0.3$ g, $(C_6H_{11}NO_4)_n = 0.3$ g, $K_2S_2O_8 = 0.07$ g and NMBA = 0.0115 g. By synthesizing the factors at their best levels, we could maximize the adsorption performance of the adsorbent. The adsorption capacity of LS/CS adsorbent for Pb^{2+} was 345 mg g^{-1} , obtained by measurement and calculation (the detailed results of this experiment are listed in Supplementary Materials Table S1).

Table 2. Results of the orthogonal experiment.

Factor	$C_{20}H_{24}Na_2O_{10}S_2$ (g)	$(C_6H_{11}NO_4)_n$ (g)	$K_2S_2O_8$ (g)	NMBA (g)	Q_e-Pb^{2+} (mg g^{-1})
1	0.1	0.1	0.07	0.0085	241
2	0.1	0.2	0.09	0.0115	185
3	0.1	0.3	0.11	0.0145	330
4	0.2	0.1	0.09	0.0145	161
5	0.2	0.2	0.11	0.0085	210
6	0.2	0.3	0.07	0.0115	325
7	0.3	0.1	0.11	0.0115	289
8	0.3	0.2	0.07	0.0145	286
9	0.3	0.3	0.09	0.0085	232
k_1	252	230	284	227	
k_2	232	227	193	266	
k_3	269	295	276	259	
R	37	65	91	29	

k_i —The sum of the experimental results at level i of each factor; R —The extremum of the data.

3.2. Characterization of the LS/CS Adsorbent

The LS/CS microstructure Figure 1A reveals a large number of small pore structures distributed over the surface. The pore depth differed from the SEM color depth, and the pore size was approximately $1.0\text{ }\mu\text{m}$. After adsorption, the pores in the LS/CS microstructure disappeared and were replaced by a sheet structure Figure 1B. The energy-dispersive X ray spectroscopy (EDS) spectra (colored panels in Figure 1) confirmed a large amount of Pb on the surface of LS/CS after adsorption, suggesting that the sheet structure was formed by Pb adhesion.

Figure 2 shows the FT-IR spectra of sodium lignosulfonate, the LS/CS adsorbent before adsorption, chitosan and the adsorbent after Pb^{2+} adsorption. The absorption peaks at 3400 , 1100 , and 589 cm^{-1} in the spectrum of sodium lignosulfonate were attributed to O–H tensile vibrations, vibrations of fatty ether, and vibrations of the sulfonic acid group, respectively. In the chitosan spectrum, the O–H stretching vibration peak appeared at 3430 cm^{-1} , and the peaks at 2890 and 1590 cm^{-1} were assigned to vibrations of the amino group. Comparing the infrared absorption spectra of sodium lignosulfonate and chitosan, the peaks in the LS/CS spectrum were assigned as follows: an O–H vibration absorption peak at 3450 cm^{-1} , a fatty ether vibration peak at 1108 cm^{-1} , amino vibration peaks at 2893 cm^{-1} and 1585 cm^{-1} and a sulfonic group at 590 cm^{-1} . LS/CS exhibited the characteristic absorption peaks of both sodium lignosulfonate and chitosan, confirming that LS/CS was successfully synthesized from these two constituents. After the adsorption of metal ions, the infrared absorption peaks of O–H, N–H, C–O–C and C = C in the LS/CS adsorbent shifted to low energies, and their intensities were diminished. Combining the FT-IR results with the images in Figure 1, one observes that when Pb adsorbed to LS/CS, it affected the functional groups on the surface, leading to changes in their electron clouds and hence in their absorption peaks.

Figure 1. SEM images of LS/CS before (A) and after (B) adsorption, and EDS images after adsorption (colored panels at bottom).

Figure 2. FT-IR spectra of sodium lignosulfonate (a), LS/CS adsorbent (b), chitosan (c) and adsorbent after adsorption of Pb²⁺ (d).

Figure 3 shows the thermogravimetry curves of chitosan, sodium lignosulfonate and the LS/CS adsorbents and their differentials. During the heating process, chitosan lost 5% of its weight by water evaporation at 100 °C. The weight loss was maximized at 210 °C, when the external small molecules were decomposed. High-temperature thermal decomposition continued until 500 °C, and the weight remained at 5%. No obvious boundary appeared between the dehydration stage and the low-temperature decomposition stage of the LS/CS adsorbent, because the first two stages of sodium lignosulfonate were staggered with those of chitosan; consequently, the two phases were merged into one large phase. The weight loss of the LS/CS adsorbents continued beyond 500 °C, indicating that the molecules in the adsorbent decomposed at higher temperatures after adding the sodium lignosulfonate. This result further proves that the LS/LC adsorbent was a compound of sodium lignosulfonate and chitosan.

Figure 3. Thermogravimetric diagrams of chitosan (left), sodium lignosulfonate (center) and the LS/CS adsorbent (right).

3.3. Adsorption Properties of the LS/CS Adsorbent

Figure 4A shows the effect of adsorbent dosage on the adsorption performance of the LS/CS adsorbent. When the adsorbent dosage increased from 0.01 to 0.15 g, the adsorption capacity for metal ions increased, but at dosages of 0.02 g and higher, the adsorption capacity showed a steady decline. At low dosage (0.01–0.15 g), increasing the amount of adsorbent increased the number of adsorption sites and hence the adsorption capacity. However, at dosages exceeding 0.15 g, an increasing number of adsorption sites were left, and the average adsorption capacity of adsorbent decreased accordingly.

Figure 4B shows the effect of pH on the adsorption capacity of the LS/CS adsorbent. The inset plots the Zeta potential of the adsorbent as a function of pH. The pH of the zero potential was 4.1. When the pH exceeded 4.0, the surface of the LS/CS adsorbent was negatively charged and attracted heavy metal ions. Increasing the pH increased the negative charge and hence the adsorption capacity. In contrast, the adsorbent surface was positively charged at pH below 4.0 and repelled heavy metal ions. The smaller the pH, the greater the rejection and the smaller the adsorption capacity.

Figure 4. Effect of adsorbent dose (A) and pH (B) on the adsorption performance of the LS/CS adsorbent.

Figure 5A,B plots the linear fittings of the data to the pseudo-first-order and pseudo-second-order models for Pb^{2+} adsorption to LC/CS. It is seen from Figure 5A that the adsorption capacity increased over time until the adsorption equilibrium was reached. While the adsorption capacity increased, the rate first increased and then decreased; this trend was related to the surface adsorption sites on LS/CS and their interaction with heavy metal ions. This relationship was explored by dynamic modeling.

Figure 5. Linear fitting of pseudo-first-order (A), pseudo-second-order (B) models for Pb^{2+} adsorption by LC/CS and the change of adsorption capacity with time (C).

The pseudo-first-order kinetics are given by

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

and the pseudo-second-order kinetics are described by

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (3)$$

The standardized standard deviation (ΔQ_e) is computed as

$$\Delta Q_e(\%) = 100 \sqrt{\sum \frac{[(Q_{e,\text{exp}} - Q_e) / Q_{e,\text{exp}}]^2}{N - 1}} \quad (4)$$

In these expressions, q_t (mg g^{-1}) is the adsorption capacity of the adsorbent at adsorption time t (min), and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants of the pseudo-first- and pseudo-second-order kinetics, respectively.

As shown in Figure 5A,B, the adsorption process can be roughly divided into three stages. During the first stage, metal ions are carried by convection–diffusion from the solution to the outer surface of the LS/CS adsorbent. During the second stage, the attached metal ions enter the micropores of the LS/CS adsorbent and then diffuse to the inner surface of the adsorbent. During the last stage, the metal ions affix to the adsorption sites on the LS/CS surface. The adsorption data of the heavy metal ions on the LS/CS adsorbent were fitted by the above kinetic models, and the fitting parameters are recorded in Table 3. The experimental data were better described by the pseudo-second-order kinetics (correlation coefficient R^2 closer to 1.0) than by the pseudo-first-order kinetics,

indicating that the pseudo-second-order kinetics described the actual process well. The actual adsorption process is a multi-process adsorption, consistent with the results of intraparticle diffusion [19–22].

Table 3. Linear fitting data of pseudo-first-order and pseudo-second-order models.

$q_{e,exp}$ (mg g ^{−1})	Pseudo First Order	Pseudo Second Order
345.356	$q_e = 581.412$	$q_e = 363.737$
	$k_1 = 0.060$	$k_2 = 0.00122$
	$R^2 = 0.717$	$R^2 = 0.999$
	$\Delta Q_e = 13.69$	$\Delta Q_e = 1.09$

Figure 6 plots the adsorption capacity of the LS/LC adsorbent for Pb²⁺ as a function of initial concentration. The adsorption capacity initially increased and then plateaued. The adsorption process exhibited equilibrium-like trends. As the initial concentration increased, the adsorption equilibrium moved in the direction of increasing adsorption capacity. As the number of adsorption sites was fixed, the adsorption capacity eventually saturated. To determine the adsorption model of the LS/CS adsorbent for heavy metal ions, we investigated two isotherm models.

Figure 6. Linear adjustments of the Langmuir (A), Freundlich (B) isotherms for Pb²⁺ on the LS/CS adsorbent and the change of adsorption capacity with initial concentration (C).

The Langmuir isotherm is given by

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{m,L}} + \frac{1}{K_L Q_{m,L}} \quad (5)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

The Freundlich isotherm is expressed as

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

The standardized standard deviation (ΔQ_e) is calculated as

$$\Delta Q_e(\%) = 100 \sqrt{\sum \frac{[(Q_{e,\text{exp}} - Q_e)/Q_{e,\text{exp}}]^2}{N-1}} \quad (8)$$

Here, Q_m , (mg g^{-1}) is the maximum adsorption capacity according to the Langmuir theory, K_L (L mg^{-1}) is the Langmuir correlation coefficient, C_e (mg L^{-1}) is the concentration of Pb^{2+} at adsorption equilibrium, R_L indicates the affinity of the adsorbent for the adsorbed substance, C_0 (mg L^{-1}) is the highest initial concentration of Pb^{2+} and K_F (L g^{-1}) is the Freundlich correlation coefficient.

Table 4 shows the fitting results of the Langmuir and Freundlich isotherms. The Langmuir isotherm yielded a larger R^2 and smaller ΔQ_e than the Freundlich isotherm, revealing that the Langmuir process more closely matched the actual adsorption process. Langmuir theory assumes a uniform surface of the adsorbent, meaning that the adsorption heat and areal coverage are unrelated, and there is no interactivity between the adsorbates. Therefore, the adsorption process of the LS/CS adsorbent was inferred to be similar to monolayer adsorption [23–25].

Table 4. Isothermal parameters of the adjusted nonlinear Langmuir and Freundlich fittings.

	Langmuir	Freundlich
Actual adsorption		524.95 mg g^{-1}
	$Q_m = 517.8 \text{ mg g}^{-1}$	$k_F = 301.6 \text{ mg g}^{-1}$
	$K_L = 0.202 \text{ L mg}^{-1}$	$n_F = 12.34$
	$R^2 = 0.993$	$R^2 = 0.831$
	$\Delta Q_e = 1.34\%$	$\Delta Q_e = 25.6\%$
	$R_L = 0.005$	

3.4. Adsorption Thermodynamics

It can be seen from Figure 7 that the adsorption capacity of ions increases with the increase of adsorption temperature. In order to study thermodynamics, the data obtained by fitting with the following formula are shown in Figure 7. The corresponding thermodynamic parameters, Gibbs free energy ΔG^0 , entropy change ΔS^0 and enthalpy change ΔH^0 are shown in Table 5.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

$$\ln(Q_e/C_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

where C_e (mg L^{-1}) is the equilibrium ion concentration, Q_e (mg g^{-1}) is the equilibrium adsorption capacity, R is the universal gas constant, and T (K) is the thermodynamic temperature.

Figure 7. Thermodynamic fitting of LC/CS adsorption (A) and effect of temperature on LC/CS adsorption (B).

Table 5. Adsorption thermodynamic parameters.

Thermodynamic Parameters	ΔH^0 (KJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG^0 (KJ mol ⁻¹)				
			293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
Pb ²⁺	10.41	49.86	-4.21	-4.71	-5.21	-5.71	-6.21

It can be seen from Table 5 that ΔG^0 is negative and decreases with the increase in temperature, indicating that the adsorption process is a spontaneous process, and the increase in temperature is conducive to the adsorption, which is consistent with the trend of Q_e-T . The positive value of ΔH^0 indicates that the adsorption process is accompanied by an endothermic process. The thermodynamic curve fitting shows that the adsorption process of the five ions adsorbed by LC/CS is accompanied by a confused spontaneous endothermic reaction.

3.5. Adsorption Mechanism

To reveal the adsorption mechanism of Pb²⁺ on LS/CS, the adsorption behavior of Pb²⁺ on LS/CS was analyzed by combining the above experimental results with the various characterization results (SEM observations, FT-IR spectra, and Zeta potentials). When the LS/CS was added to the solution, the Zeta potentials revealed a negative charge on the LS/CS surface that attracted the positively charged lead ions. Meanwhile, the SEM-EDS observations revealed a surface layer on the LS/CS, which was presumed as positively charged Pb. From the kinetics and isotherm analyses, the dominant adsorption mechanism of Pb²⁺ to the LS/CS adsorbent was inferred as single-molecular-layer chemical adsorption. The absorption peaks of -NH₂, -OH, C-O-C and C=C changed significantly after the Pb adsorption. The adsorption process likely involves the formation of a Pb- π structure between Pb²⁺ and aromatic functional groups on LS/CS [8], and the formations of Pb-O and Pb-N structures with hydroxyl [6] and amino groups [7], respectively. Electrostatic interaction between Pb²⁺ and the LS/CS surface also contributes to the adsorption process. The adsorption mechanism is shown in Figure 8.

Figure 8. Adsorption mechanism of Pb²⁺ on the LS/CS adsorbent.

4. Conclusions

The synthesis of sodium lignosulfonate/chitosan (LS/CS) was optimized by an orthogonal design, and the adsorption characteristics and mechanism of LS/CS for Pb were studied. The FT-IR, TGA, SEM, and Zeta potentials showed a porous, negatively charged structure of LS/CS with multi-functional groups. The adsorption performance of LS/CS was controlled by many factors and was especially sensitive to pH. The adsorption capacity of LS/CS for Pb (100 mg L⁻¹) was 345 mg g⁻¹ at a pH of 7.0, an adsorbent dosage of 0.01 g and a reaction time of 120 min. The adsorption process of Pb on LS/CS accorded with pseudo-second-order kinetics and the Langmuir isotherm model, revealing that the lead

ions attached by monolayer chemical adsorption. The thermodynamic results show that the adsorption process is a spontaneous endothermic reaction. The changes of the surface functional groups measured by FT-IR, the surface charge measured by the Zeta potential and the isotherm and kinetics results demonstrated electrostatic attraction and metal chelation between Pb^{2+} and LS/CS. In summary, LS/CS is a new and efficient adsorbent for Pb^{2+} removal from water.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2071-1050/13/5/2997/s1>, Figure S1: Sum of the experimental results of the three factors at each level, Table S1: Adsorption capacity of LC/CS for Pb^{2+} .

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References

- Chen, J.; Zhu, J.; Wang, N.; Feng, J.; Yan, W. Hydrophilic polythiophene/ SiO_2 composite for adsorption engineering: Green synthesis in aqueous medium and its synergistic and specific adsorption for heavy metals from wastewater. *Chem. Eng. J.* **2019**, *360*, 1486–1497. [CrossRef]
- Dao, T.H.; Vu, T.Q.M.; Nguyen, N.T.; Pham, T.T.; Nguyen, T.L.; Yusa, S.I.; Pham, T.D. Adsorption Characteristics of Synthesized Polyelectrolytes onto Alumina Nanoparticles and their Application in Antibiotic Removal. *Langmuir* **2020**, *36*, 13001–13011. [CrossRef]
- Pham, T.D.; Pham, T.T.; Phan, M.N.; Ngo, T.M.V.; Dang, V.D.; Vu, C.M. Adsorption characteristics of anionic surfactant onto laterite soil with differently charged surfaces and application for cationic dye removal. *J. Mol. Liq.* **2020**, *301*, 112456. [CrossRef]
- Chen, Q.; Zheng, J.; Wen, L.; Yang, C.; Zhang, L. A multi-functional-group modified cellulose for enhanced heavy metal cadmium adsorption: Performance and quantum chemical mechanism. *Chemosphere* **2019**, *224*, 509–518. [CrossRef] [PubMed]
- Kuang, Y.; Gao, Y.; Zhang, J.; Zhao, J.; Luo, S.; Zhang, D.; Lu, C.; Sun, Y. Effect of initial pH on the sludge fermentation performance enhanced by aged refuse at low temperature of 10 °C. *Environ. Sci. Pollut. Res.* **2020**, *27*, 31468–31476. [CrossRef] [PubMed]
- Xu, X.Y.; Ouyang, X.K.; Yang, L.Y. Adsorption of Pb(II) from aqueous solutions using crosslinked carboxylated chitosan/carboxylated nanocellulose hydrogel beads. *J. Mol. Liq.* **2021**, *322*, 114523. [CrossRef]
- Shi, S.; Xu, C.; Dong, Q.; Wang, Y.; Zhu, S.; Zhang, X.; Chow, Y.T.; Wang, X.; Zhu, L.; Zhang, G.; et al. High saturation magnetization $\text{MnO}_2/\text{PDA}/\text{Fe}_3\text{O}_4$ fibers for efficient Pb(II) adsorption and rapid magnetic separation. *Appl. Surf. Sci.* **2021**, *541*, 148379. [CrossRef]
- Wu, F.; Chen, L.; Hu, P.; Wang, Y.; Deng, J.; Mi, B. Industrial alkali lignin-derived biochar as highly efficient and low-cost adsorption material for Pb(II) from aquatic environment. *Bioresour. Technol.* **2021**, *322*, 124539. [CrossRef] [PubMed]
- Wu, D.-Q.; Zhu, J.; Han, H.; Zhang, J.-Z.; Wu, F.-F.; Qin, X.-H.; Yu, J.-Y. Synthesis and characterization of arginine-NIPAAm hybrid hydrogel as wound dressing: In vitro and in vivo study. *Acta Biomater.* **2018**, *65*, 305–316. [CrossRef]
- Wu, J.; Wang, T.; Wang, J.; Zhang, Y.; Pan, W.-P. A novel modified method for the efficient removal of Pb and Cd from wastewater by biochar: Enhanced the ion exchange and precipitation capacity. *Sci. Total. Environ.* **2021**, *754*, 142150. [CrossRef] [PubMed]
- Du, X.; Zhang, D.; Ma, X.; Qiao, W.; Wang, Z.; Hao, X.; Guan, G. Electrochemical redox induced rapid uptake/release of Pb(II) ions with high selectivity using a novel porous electroactive HZSM-5@PANI/PSS composite film. *Electrochim. Acta* **2018**, *282*, 384–394. [CrossRef]
- Antić-Mladenović, S.; Frohne, T.; Kresović, M.; Stärk, H.J.; Tomić, Z.; Ličina, V.; Rinklebe, J. Biogeochemistry of Ni and Pb in a periodically flooded arable soil: Fractionation and redox-induced (im)mobilization. *J. Environ. Manag.* **2017**, *186*, 141–150. [CrossRef]
- Jiang, C.L.; Wang, X.H.; Wang, G.H.; Hao, C.; Li, X.; Li, T.H. Adsorption performance of a polysaccharide composite hydrogel based on crosslinked glucan/chitosan for heavy metal ions. *Compos. Part B.* **2019**, *169*, 45–54. [CrossRef]

14. Godiya, C.B.; Liang, M.; Sayed, S.M.; Li, D.; Lu, X. Novel alginate/polyethyleneimine hydrogel adsorbent for cascaded removal and utilization of Cu²⁺ and Pb²⁺ ions. *J. Environ. Manag.* **2019**, *232*, 829–841. [[CrossRef](#)] [[PubMed](#)]
15. Ma, J.; Luo, J.; Liu, Y.; Wei, Y.; Cai, T.; Yu, X.; Liu, H.; Liu, C.; Crittenden, J.C. Pb(II), Cu(II) and Cd(II) removal using a humic substance-based double network hydrogel in individual and multicomponent systems. *J. Mater. Chem. A* **2018**, *6*, 20110–20120. [[CrossRef](#)]
16. Sun, J.; Li, M.; Zhang, Z.; Guo, J. Unravelling the adsorption disparity mechanism of heavy-metal ions on the biomass-derived hierarchically porous carbon. *Appl. Surf. Sci.* **2019**, *471*, 615–620. [[CrossRef](#)]
17. Wang, J.; Zhang, W.; Wei, J. Fabrication of poly(β -cyclodextrin)-conjugated magnetic graphene oxide by surface-initiated RAFT polymerization for synergetic adsorption of heavy metal ions and organic pollutants. *J. Mater. Chem. A* **2018**, *7*, 2055–2065. [[CrossRef](#)]
18. Pham, T.D.; Tran, T.T.; Le, V.A.; Pham, T.T.; Dao, T.H.; Le, T.S. Adsorption characteristics of molecular oxytetracycline onto alumina particles: The role of surface modification with an anionic surfactant. *J. Mol. Liq.* **2019**, *287*, 110900. [[CrossRef](#)]
19. Pham, T.D.; Bui, T.T.; Truong, T.T.T.; Hoang, T.H.; Le, T.S.; Duong, V.D.; Yamaguchi, A.; Kobayashi, M.; Adachi, Y. Adsorption characteristics of beta-lactam cefixime onto nanosilica fabricated from rice HUSK with surface modification by polyelectrolyte. *J. Mol. Liq.* **2020**, *298*, 111981. [[CrossRef](#)]
20. Liu, X.; Lai, D.; Wang, Y. Performance of Pb(II) removal by an activated carbon supported nanoscale zero-valent iron composite at ultralow iron content. *J. Hazard. Mater.* **2019**, *361*, 37–48. [[CrossRef](#)]
21. Dong, D.M.; Liu, L.; Hua, X.Y.; Lu, Y.Z. Comparison of lead, cadmium, copper and cobalt adsorption onto metal oxides and organic materials in natural surface coatings. *Microchem. J.* **2007**, *85*, 270–275. [[CrossRef](#)]
22. Wu, Y.; Qiu, X.; Cao, S.; Chen, J.; Shi, X.; Du, Y.; Deng, H. Adsorption of natural composite sandwich-like nanofibrous mats for heavy metals in aquatic environment. *J. Colloid Interface Sci.* **2019**, *539*, 533–544. [[CrossRef](#)]
23. Veselská, V.; Šillerová, H.; Göttlicher, J.; Micháľková, Z.; Siddique, J.A.; Číhalová, S.; Chrástný, V.; Steininger, R.; Mangold, S.; Komárek, M. The role of soil components in synthetic mixtures during the adsorption and speciation changes of Cr(VI): Conjunction of the modeling approach with spectroscopic and isotopic investigations. *Environ. Int.* **2019**, *127*, 848–857. [[CrossRef](#)] [[PubMed](#)]
24. Zheng, L.; Zhu, C.; Dang, Z.; Zhang, H.; Yi, X.; Liu, C. Preparation of cellulose derived from corn stalk and its application for cadmium ion adsorption from aqueous solution. *Carbohydr. Polym.* **2012**, *90*, 1008–1015. [[CrossRef](#)] [[PubMed](#)]
25. Zhang, W.; Zhang, Y.; Gutha, Y.; Jiao, X. Adsorption of Pb(II) ions from aqueous environment using eco-friendly chitosan schiff's base@Fe₃O₄ (CSB@Fe₃O₄) as an adsorbent; kinetics, isotherm and thermodynamic studies. *Int. J. Biol. Macromol.* **2017**, *105*, 422–430.
26. Sang, Y.; Gu, Q.; Sun, T.; Li, F.; Liang, C. Filtration by a novel nanofiber membrane and alumina adsorption to remove copper(II) from groundwater. *J. Hazard. Mater.* **2008**, *153*, 860–866. [[CrossRef](#)]
27. Xie, A.; Dai, J.; Chen, X.; Ma, P.; He, J.; Li, C.; Zhou, Z.; Yan, Y. Ultrahigh adsorption of typical antibiotics onto novel hierarchical porous carbons derived from renewable lignin via halloysite nanotubes-template and in-situ activation. *Chem. Eng. J.* **2016**, *304*, 609–620. [[CrossRef](#)]
28. Kandile, N.G.; Mohamed, H.M. Chitosan nanoparticle hydrogel based sebacoyl moiety with remarkable capability for metal ion removal from aqueous systems. *Int. J. Biol. Macromol.* **2019**, *122*, 578–586. [[CrossRef](#)]
29. Wang, J.; Zhang, L.; Zhang, T.; Du, T.; Li, T.; Yue, T.; Li, Z.; Wang, J. Selective removal of heavy metal ions in aqueous solutions by sulfide-selector intercalated layered double hydroxide adsorbent. *J. Mater. Sci. Technol.* **2019**, *35*, 1809–1816. [[CrossRef](#)]
30. Pu, S.; Hou, Y.; Yan, C.; Ma, H.; Huang, H.; Shi, Q.; Mandal, S.; Diao, Z.; Chu, W. In Situ Coprecipitation Formed Highly Water-Dispersible Magnetic Chitosan Nanopowder for Removal of Heavy Metals and Its Adsorption Mechanism. *ACS Sustain. Chem. Eng.* **2018**, *6*, 16754–16765. [[CrossRef](#)]
31. Tang, S.; Yang, J.; Lin, L.; Peng, K.; Chen, Y.; Jin, S.; Yao, W. Construction of physically crosslinked chitosan/sodium alginate/calcium ion double-network hydrogel and its application to heavy metal ions removal. *Chem. Eng. J.* **2020**, *393*, 124728. [[CrossRef](#)]