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Novel polyethyleneimine functionalized chitosan-lignin composite sponge with nanowall-network structures for fast and efficient removal of Hg(II) ions from aqueous solution

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2. Experimental

2.1. Materials and Characterization

Lignin (industrial grade, floccule) was purchased from commercial sources and used as received (Zhejiang Golden-Shell Pharmaceutical Co. Ltd., Zhejiang, China). Chitosan (CS, analytical grade, with a deacetylation degree of 95%, a vicosity of 100-200 mpa.s) was purchased from Macklin. Polyethylenimine [PEI, Mw = 70000 Da, 50 wt% aqueous solution, branched polymer $(–NHCH_2CH_2–)_x[–N(CH_2CH_2NH_2)–CH_2CH_2–]_y$] and Poly (vinyl alcohol) (PVA, analytical grade, the degree of alcoholysis was 89.0 mol % and a vicosity of 100-200 mpa.s) were purchased from Aladdin. Glutaraldehyde (GA, analytical grade, 50wt % in water) was bought from Adamas Reagent Co.,Ltd. (Tianjin China). $HgCl_2$, $Cd(NO_3)_2·4H_2O$, $Pb(NO_3)_2$ and $Cu(NO_3)_2·3H_2O$ were also used without any further purification (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). Ultrapure water (～18.25 MΩ/cm) was employed to prepare all the solutions.

PEI-CS-L sponge was lyophilized by a lyophilizer (LGJ-10E, Sihuan, Beijing). The mechanical properties of PEI-CS-L sponges were performed on a universal testing machine (C43-104, MTS) with a constant cross-head speed of 2 mm/min, the maximum strain was set at 60% and the compression test was repeated for 3 times for each sample. The surface morphology and structure of samples were determined with a scanning electron microscope (SEM, SUPRA55VP, Germany)) at an accelerating voltage of 10 kV and equipped with an energy dispersive X-ray spectroscopy to confirm the existence of heavy metal ions on the surface of samples at an accelerating voltage of 20 kV .The changes of functional groups on material before and after heavy metal ions adsorption were characterized by a FT-IR spectra (FTIR) analysis with a Fourier-transform infrared spectroscopy (Nicolet iS50) at a resolution of 4 cm^{-1} using the KBr disk method in the range of 400−4000 cm^{-1}. The surface elemental composition of PEI-CS-L sponge before and after adsorption were carried out on a X-ray photoelectron spectrometer (XPS; ESCALAB 250Xi, Thermo Fisher Scientific, USA).The operating condition is Al Kα X-ray working at 150 W, 1486.6 eV, and 500 um. The XPS curve fitting of elements was accomplished using XPS Peak 4.1. Thermal stability analysis (TGA) was conducted on a STA 449F3 thermo-gravimetric analyzer (NETZSCH Instrument Co. Ltd., Germany), samples were heated from room temperature to 700 °C at a rate of 10 °C / min in a nitrogen atmosphere.

2.2 Preparation

2.2.1 Preparation of Lignin Suspension

Lignin suspension was prepared according to the protocol developed in our previous work. 10 g of flocculent lignin was dispersed in 500 mL ultrapure water, and then the mixed suspension was homogenized at 15000 rpm for 2 h by an inline Ultra-Turrax system, and 1.96 wt% lignin suspension was obtained for later use.

2.2.2 Preparation of PEI-CS-L Sponge

PEI-CS-L sponge adsorbent was synthesized by cross-linking and subsequent lyophilization. In detail, 2% light yellow viscous chitosan solution was obtained by adding a certain amount of chitosan powder to 2% glacial acetic acid solution. After that 50 mL of the above solution and the same volume of the lignin suspension were mixed with 20 mL poly (vinyl alcohol) solution and homogenized for 10 min at 20000 rpm, then slowly added polyethylenimine (50%) of different masses as expected and continued to homogenize at the same speed for 30 min. After that, the mixture was transferred to the round bottom flask and mechanically stirred for 4 hours at 25 °C to obtain a milky homogeneous viscous mixture. Next, glutaraldehyde solution (2.5%) was added by a microsyringe at a set volume, and was mechanically stirred in a water bath with constant temperature. Following that, uniform yellow-brown sol was obtained after 6 hours, and the mixture was lyophilized. The samples were repeatedly washed after lyophilizing with deionized water and soaked in 0.5 M NaOH solution for 12 h, and then lyophilized again. The obtained sample was used for subsequent heavy metal ions adsorption experiments.

2.3 Adsorption Studies

The process of adsorption experiment was as follows: took 25 mg PEI-CS-L sponge and 25 mL heavy metal ions solution and mixed them evenly in 100 mL stopper conical flasks. Heavy metal ions solution was prepared by dilution of a standard substance with a concentration of 1000 mg/L single element solution. After that, the evenly mixed suspension was oscillated in a thermostatic shaker bath (THZ-98A) at a speed of 150 rpm for a certain time. The difference between the initial concentration of heavy metal ions and the concentration of heavy metal ions in the solution after adsorption can be used to calculate the adsorption capacity of the adsorbent for heavy metal ions. The equilibrium adsorption capacity (q_e, mg/g) and removal efficiency (%) of PEI-CS-L sponge were calculated according to the following Eqs 1-2:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

where C_0 (mg/L) is the initial concentration of heavy metal ions in the solution, C_e (mg/L) is the concentration of heavy metal ions in the solution after the adsorption reaches equilibrium, V (L) is the volume of the solution, and m (g) is the amount of adsorbent material, respectively.

For the adsorption experiment affected by the solution pH, to prevent the precipitation of Hg(II), 0.1 M HNO_3 and 1 M NaOH solutions were used to adjust the initial pH of Hg(II) ions solution to 1.5-5.5. The sample of 25 mg PEI-CS-L sponge and the mixture of 25 mL, 664.1 mg/L Hg(II) ions solution were oscillated at 150 rpm at 30 ℃ for 6 h until the equilibrium to be established. Then, Eq 1 was used to calculate the equilibrium adsorption capacity of adsorbent to Hg(II) ions at different pH values, so as to obtain the optimal adsorption pH.

The effects of adsorption time and sorption kinetics test: 25 mL of Hg (II) ions solution with an initial concentration of 664.1 mg/L was taken and adjusted to the optimal pH conditions with 0.1 M HNO_3 and 1 M NaOH solutions. A 25 mg PEI-CS-L sponge was mixed with the Hg(II) ions solution, and the mixture was oscillated at a constant temperature of 30 ℃ at 150 rpm, and the supernatant fluid Hg(II) ions concentration was sampled, separated, and measured at a certain time point. The adsorption capacity of Hg(II) ions at each specific time can be calculated by Eq 1. Then the adsorption kinetics can be calculated by using the curve of adsorption capacity and time.

The adsorption kinetics of heavy metal ions in water by adsorbent materials generally has pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The pseudo-first-order kinetic model based on adsorption capacity assumes that the adsorbate reaches the surface of the adsorbent and is controlled by diffusion. There is only one binding site on the surface of the adsorbent. The pseudo-second-order kinetic model is based on the assumption that the adsorption rate is controlled by chemical adsorption, including electron transfer and sharing between the adsorbate and the adsorbent, which has two binding sites on the adsorbent surface. Intra-particle diffusion is generally divided into three steps: ion diffusion to the surface of the adsorbent, intra particle diffusion, and adsorption and desorption between the active sites and the adsorbate. In order to determine the adsorption kinetics mechanism controlling the adsorption process of Hg(II) ions by PEI-CS-L sponge, this study calculated and evaluated the kinetic models of pseudo-first, second-order and intra-particle diffusion. The expressions of different models are as follows.

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

$$q_t = k_i t^{\frac{1}{2}} + c \qquad (5)$$

where q_e (mg/g) is the adsorption capacities on PEI-CS-L sponge at equilibrium, q_t (mg/g) is the adsorption capacities on PEI-CS-L sponge at a certain time t, and k_1 (min^{-1}), k_2 (g / (mg min)) and k_i (mg/g $min^{-0.5}$) are the adsorption rate constants of the pseudo-first-order kinetic, pseudo-second-order and intra-particle diffusion models, [35] respectively. In addition, c is the intercept related to the boundary thickness information.

The effects of initial concentration and sorption isotherm test: took 25 mL of Hg(II) ions solutions with different initial concentrations (1-1000 mg/L), and adjusted to the optimal pH value with 0.1 M HNO_3 and 1 M NaOH solutions. Then, 25 mg PEI-CS-L sponge was mixed with different concentrations of Hg(II) ions solution, and the mixture was adsorbed at a constant temperature of 30 ℃ at 150 rpm for 6 h. The adsorption capacity of PEI-CS-L sponge to Hg(II) ions solutions with different concentrations can be calculated by Eq 1. Then the adsorption isotherm can be calculated by using the relation curve between the adsorption capacity of PEI-CS-L sponge and the initial concentration of Hg(II) ions.

The adsorption isotherm models can be used to calculate the theoretical adsorption capacity and describe the adsorption behavior of adsorbed materials on heavy metal ions. The common adsorption isotherm models include Langmuir, Freundlich, and Redlich-Peterson. The Langmuir adsorption isotherm model is commonly used for monolayer adsorption, where most of the adsorption sites have the same affinity for the adsorbate, while the Freundlich adsorption isotherm model is used to describe heterogeneous chemical adsorption process with uneven surface energy. The Redlich-Peterson adsorption isotherm model is a combination of Langmuir model and Freundlich model. In order to better understand the adsorption process, Langmuir and Freundlich, the two most commonly used models, were introduced in this study to calculate the adsorption isotherm and the adsorption equilibrium point of heavy metal ions. The model expressions are as follows:

$$\frac{c_e}{q_e}=\frac{1}{bq_m}+\frac{c_e}{q_m} \tag{6}$$

$$\log q_e=\log k+\frac{1}{n}\log c_e \tag{7}$$

where k is the Freundlich constant, 1/n is the constant describing the adsorption density, q_m (mg/g) is the maximum saturation adsorption capacity of adsorbent, c_e (mg/g) is the equilibrium concentration of Hg(II) ions, and q_e (mg/g) is the equilibrium adsorption capacity of Hg(II) ions.

Hg(II) adsorption thermodynamic test: A 25 mg PEI-CS-L sponge was placed in a 25 mL initial concentration solution of 664.1 mg/L Hg(II) ions at a pH of 5.5 with a temperature adjustment range of 20-40 °C. After adsorption for 6h, the supernatant was separated from the adsorbent and the residual Hg(II) concentration was analyzed.

The thermodynamic parameters, including the Gibbs free-energy change (ΔG, kJ·mol^{-1}), enthalpy change (ΔH, kJ·mol^{-1}) and entropy change (ΔS, kJ·mol^{-1}·K^{-1}) were employed to explore the effect of temperature on Hg(II) ions adsorption onto the PEI-CS-L sponge. The detailed parameters obtained from the thermodynamic equations are as follows.

$$\Delta G=-RT\ln K_a \tag{8}$$

$$K_a = \frac{C_{Ae}}{C_e} \tag{9}$$

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

where K_a is the distribution coefficient, C_{Ae} (mg/L) is the concentration of Hg(II) ions adsorbed on PEI-CS-L sponge, R (8.314 J·mol^{-1}·K^{-1}) is the gas constant, T (K) is the adsorption temperature, ΔG (kJ/mol) is the standard Gibbs free energy change, ΔH (kJ/mol)is the standard enthalpy change, ΔS (J/(mol·K)) is the standard entropy change.

To evaluate the selectivity of PEI-CS-L sponge for heavy metal ions, we also investigated the adsorption capacity of PEI-CS-L sponge for heavy metal ions such as Hg(II), Cd(II), Cu(II) and Pb(II) ions. Under the condition of 30℃ and pH 5.5, 25 mg PEI-CS-L sponge was used to adsorb 25 mL mixed heavy metal ions solution with the following concentration for competitive adsorption experiment (Table S1). The concentration of Hg(II) or other heavy metal ions in the supernatant was determined by filtration after 6 h.

The adsorbent was separated from the mixture after the adsorption process, Then the Hg(II) concentration was analyzed via ICP-OES (ICP-6300, Thermo Electron Corp, US), and the concentrations of the other heavy metal ions were measured by ICP (VISTA-PRO, Varian, USA). All adsorption experiments were averaged three times.

Table S1

Parameters for selective adsorption experiments carried out in single- and multi-component heavy metal solutions (pH$_0$: the initial pH of solution; C$_0$: the initial concentration of metal ions in solution (mg/L)).

Single-component	Hg(II)	Cu(II)	Pb(II)	Cd(II)
pH_0	5.50	5.34	5.72	5.47
C_0	664.1	559.4	572.4	606.1
Sample dosage: 25 mg/25 mL; Temperature: 30 °C; Contact time: 6 h				

Multi-component	Hg(II)	Cu(II)	Pb(II)	Cd(II)
pH_0	5.50	5.50	5.50	5.50
C_0	505.5	479.5	407.2	489.5
Sample dosage: 25 mg/25 mL; Temperature: 30 °C; Contact time: 6 h				

3. Results and discussion

3.4. Effect of Contact Time and Kinetic Studies

To better understand the essence of the adsorption process, three kinetic models are used to fit the test results. Based on the comparison between experimental and theoretical calculations, the linear regression correlation coefficient is obtained. The adsorption of Hg(II) ions by PEI-CS-L sponge is more satisfied with the pseudo-second-order kinetic model (R^2=0.99992), and the fitted Q_f is very close to the experimental value (663.5mg/g). The fitting results of each adsorption model are shown in Table S2, suggesting that chemisorption is the main rate control step of Hg(II) ions on PEI-CS-L sponge. Hard-soft acid-base (HSAB) theory holds that Hg(II) ions are soft acids and are more likely to react with soft bases, such as amine/imine groups.

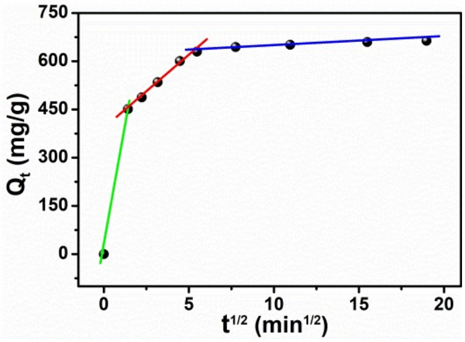

Fig. S1. Intra-particle diffusion model for Hg(II) ions on PEI-CS-L. Adsorption experiments—C_0: 1-1000 mg/L, sample dosage: 25 mg/25 mL, temperature: 30 °C, pH: 5.5, and contact time: 1-360 min.

Table S2

Kinetic model parameters for Hg(II) ions adsorption on PEI-CS-L sponge.

Q_e (mg/g)	Pseudo first-order			Pseudo second-order			Intra-particle diffusion	
	k_1 (L/min)	$Q_{e,cal}$ (mg/g)	R_1	k_2(g/(mg.min))	$Q_{e,cal}$ (mg/g)	R_2	$k_{i,1}$	$k_{i,2}$
663.5	0.51362	620.39	0.93192	0.00158	664.1	0.99992	596.1	0.97

3.5 Effect of Initial Hg(II) Concentration and Sorption Isotherm

To give deep insights into the adsorption behavior of Hg(II) ions, the experimental data were fitted using Langmuir and Freundlich isotherm models. The theoretical parameters obtained by calculation are presented in Table S3. Compared with the Freundlich model, the Langmuir model fits better (correlation coefficient R^2 = 0.99892) and the derived theoretical maximum adsorption value (q_m) is 686.94 mg/g, closely matching the experimental value of 663.5 mg/g, which indicates that the adsorption of Hg(II) ions on PEI-CS-L sponge is monolayer adsorption.

Table 3

Isotherm model parameters for Hg(II) ions adsorption on PEI-CS-L sponge.

Langmuir			Freundlich		
q_m (mg/g)	b	R^2	n	k	R^2
686.94	0.04793	0.99892	0.019	896.94	0.96547

3.6 Thermodynamic Studies

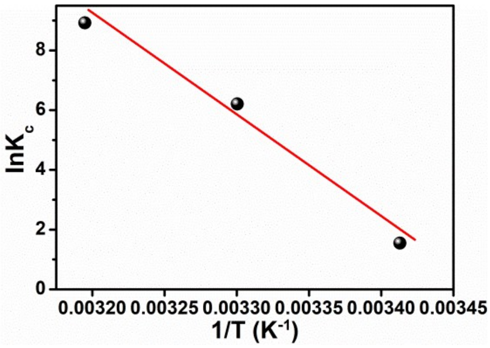

Fig. S2. Adsorption thermodynamics for Hg(II) ions on PEI-CS-L sponge: plot of lnKC versus 1/T. Adsorption experiments—C_0: 1-1000 mg/L, sample dosage: 25 mg/25 mL, temperature: 20, 30, 40 °C, pH: 5.5, and contact time: 360 min.

Table S4

Thermodynamic parameters for the adsorption of Hg(II) ions.

T (K)	ΔG ($kJ\cdot mol^{-1}$)	ΔH ($kJ\cdot mol^{-1}$)	ΔS ($kJ\cdot mol^{-1}\cdot K^{-1}$)
293	-1.36		
303	-5.21		
313	-12.04	451.3	1274

3.9. Desorption and Reusability

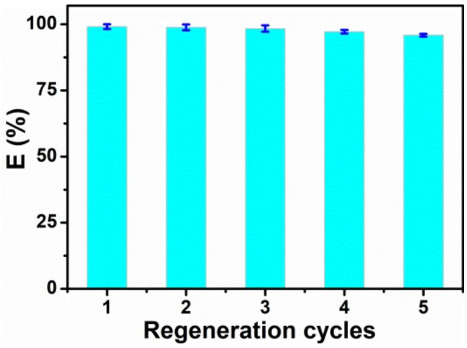

Fig. S3. The adsorption capacity of PEI-CS-L sponge on Hg(II) ions during regeneration cycles. Adsorption conditions: C_0: 664.1 mg/L, sample dose: 25 mg/25 mL, temperature: 30 °C, pH: 5.5, contact time: 6 h, and desorption time: 1 h.