Fabrication of Lignin-based Magnetic Adsorbent via Thiol-ene Click Reaction for the Effective Removal of Pb(II)

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Abstract

The effective and selective removal of heavy metal ions from sewage is a major challenge, and of great significance to the treatment and recovery of metal waste. Herein, a novel magnetic lignin-based adsorbent L@MNP was synthesized by thiol-ene click reaction under UV light irradiation. Multiple characterization techniques containing FT-IR, XRD, elemental analysis, VSM, SEM and TEM confirmed the formed nano-morphology and structure of L@MNP. Effects of pH, contact time, initial metal concentration and temperature on the batch adsorption of Pb(II) by L@MNP were investigated. Due to the existence of sulfur and oxygen containing sites, the maximum adsorption capacity of L@MNP for Pb(II) could reach 97.38 mg/g, while the adsorption equilibrium was achieved within 30 min. Adsorption kinetics and isotherms were well described by the pseudo-second-order model and Langmuir model, respectively, suggesting a chemical and monolayer adsorption process. In addition, L@MNP showed a high adsorption selectivity ($k_{Pb} = 0.903$) toward Pb(II) in the presence of other co-existing metal ions. Experimental results also revealed that L@MNP displayed structural stability, easy recovery under external magnetic field, and acceptable recyclability after the fifth cycle. Considering its facile preparation, low cost and high adsorption efficiency, the developed L@MNP adsorbent demonstrated great potential in removing heavy metal ions from wastewater.

Introduction

Pollution of sewage containing heavy metal ions has been an urgent problem facing the world [1–2], due to their high biological toxicity and bioaccumulation. As one of the most toxic heavy metal pollutants in wastewater, lead (Pb) can easily accumulate in human body through the food chain, causing severe damages to organs and tissues even at low concentrations [3–4]. To date, a variety of technologies for removing Pb(II) from wastewater have been developed [5], including coagulation-flocculation, adsorption, membrane separation [6], ion exchange and electrochemical precipitation [7]. The adsorption method stands out from many of those technologies due to its economic performance, high efficiency and simple operation [8]. Despite these advantages, the conventional adsorbents still need to be improved in the actual application, which puts forward specific requirements for improving the recycling efficiency and avoiding secondary pollution after discarding [9].

Magnetic adsorbents have been recently utilized in the application field of wastewater purification, due to their outstanding superiority of being readily removed after adsorption under an external magnetic field [10]. Normally, magnetic nanoparticles are used as magnetic cores, which could be easily coated with polymeric component to enhance their physicochemical stability and dispersion property [11]. Although different polymers [12] such as polyacrylamide, polyacrylate and polystyrene have been introduced onto magnetic cores surface as shell layers for heavy metal removal, these fossil-based chemicals suffer from high energy consumption and non-degradability. Very recently, owing to the increasing requirements of sustainable development and continuous environmental awareness [13–14], the seek for low-cost and renewable magnetic composites with high removal capacity have become a challenge.

Lignin is the second most abundant biopolymer and the main renewable aromatic resource on the earth [15–16]. Nevertheless, lignin has been long-term generated as a byproduct from pulping industry and mainly used in low-value applications like incineration [17–18]. The abundant hydroxyl, methoxy and phenyl groups in lignin structure [19], as well as its own low cost, environmental friendliness and biocompatibility [20], have made it an ideal candidate for the preparation of biodegradable composites [21]. Based on the advantages mentioned above, some lignin-based magnetic adsorbents have been successfully synthesized and applied for removing lead pollutants from wastewater [22–23]. In spite of the developed biobased magnetic adsorbents have overcome the low dispersibility and instability in heavy metal adsorption process, a facile preparation of lignin-based magnetic adsorbent with high adsorption efficiency, high adsorption selectivity, fast separation rate and easy recovery from system is still interesting for wastewater purification.

In this study, we reported a novel nanocomposite L@MNP by modifying alkenyl lignin onto sulfhydryl magnetic Fe_3O_4 nanoparticles through thiol-ene click reaction. Because of the unique characteristics of thiol-ene click reaction, the alkenyl group could effectively and selectively react with the thiol group, which might enable a controllable architecture [24–25]. In addition, the generated thioether groups were expected to provide more adsorption sites for Pb(II) adsorption. The structure and morphology of the L@MNP were comprehensively characterized, and the adsorption performance of Pb(II) ions was investigated under different pH, contact time, Pb(II) initial concentration, temperature and co-existing ions, allowing the insights into adsorption kinetics, isotherms and thermodynamics. Besides, the adsorption mechanism of L@MNP on Pb(II) was also explored.

Experimental Section

Materials and chemicals

Lignin was obtained from bamboo feedstock based on acetic acid treatment, and the total content of hydroxyl group (-OH) was determined to be 2.9 mmol/g through a quantitative ^{31}P NMR spectroscopy. Magnetic Fe_3O_4 nanoparticles (Fe_3O_4 MNPs) with average particle size about 30 nm were supplied by Shanghai Aladdin Corporation (China). 3-Bromopropene (99%), sodium hydroxide (NaOH , $\geq 96\%$), tetrahydrofuran (THF, $\geq 99\%$), ethanol ($\geq 99.7\%$), tetraethyl orthosilicate (TEOS, $\text{SiO}_2 \geq 28.4\%$), 3-mercaptopropyltrimethoxysilane (MPTS, 95%), 2,2-bis(hydroxymethyl)propionic acid (DMPA, 99%), and ammonium hydroxide (25%~28%), were supplied by Shanghai Adamas Corporation (China). All reagents were of AR grade and used as received without further purification. Metal ions solutions were obtained from lead nitrate ($\text{Pb}(\text{NO}_3)_2$, 99%), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99%), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%) with deionized water.

Synthesis of sulfhydryl magnetic nanoparticles (SMNP)

1. 2.4 g Fe_3O_4 MNPs was dispersed in 800 mL ethanol solution with sonication over 20 min, while 8 mL ammonium hydroxide was added and proceed with sonication over 30 min. Then, 8 mL TEOS was slowly added and continuously stirred at 25 °C for 8 h. The silicon-coated SiO_2 @MNPs was collected with a magnet, washed with ethanol and deionized water several times and dried at at 70 °C over 12 h.
2. 1.8 g SiO_2 @MNPs was dispersed in 600 mL of ethanol under sonication for 20 min, then 6 mL MPTS was added into the solution and stirred for 12 h. The product sulfhydryl magnetic nanoparticles (SMNP) were washed with ethanol and deionized water several times, and collected after drying at 70 °C for 12 h.

Synthesis of lignin-based magnetic nanoparticles (L@MNP)

Alkenyl lignin (2.6 mmol/g alkenyl group) was prepared according to our previous work [26]. For the synthesis of L@MNP: 0.14 g AL (0.37 mmol alkenyl group) was dissolved in 10 mL THF solution, then DMPA (96 mg) and SMNP (0.8 g, 0.243 mmol thiol group) were added to the solution, and the mixture was irradiated under a Hg lamp (365 nm, 2 Sun) within a certain time (30 min, 60 min, 90 min). The product was washed with THF and ethanol several times, which was subsequently freezing dried to give L@MNP as a brown powder.

Characterization.

The content of hydroxyl group of lignin was analyzed by ^{31}P NMR spectra using 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane as a phosphorylating reagent on a Bruker AVANCE III HD 400 MHz NMR spectrometer. The PerkinElmer-2400 analyzer was used to measure the element contents of the obtained samples. Functional groups of samples were characterized by the attenuated total reflection (ATR) mode with a resolution of 4 cm^{-1} , enabling measurements ranging from $4000 - 400\text{ cm}^{-1}$ by fourier transform infrared spectroscopy (FT-IR) on a Nicolet iS50 instrument. The surface and microstructures of SMNP and L@MNP were characterized using a Hitachi S3400N scanning electron microscope (SEM) and a JEOL JEM2100F transmission electron microscope (TEM). The surface element of prepared samples was also evaluated on the basis of X-ray photoelectron spectroscopy (AXIS-ULTRA DLD, Shimadzu/KRATOS). A VSM7307 vibrating sample magnetometer (VSM, Lakeshore Corporation) was applied to investigate the magnetic properties of the prepared composite. The crystalline phases of materials were analyzed with a Bruker D8 Advance diffractometer over an angular range of 10° - 90° using X-ray diffraction method.

Adsorption measurements

Batch experiments were carried out to investigate the Pb(II) adsorption capacity on L@MNP, and the specific operation was as follows: 10 mg adsorbent was added to a 50 mL flask containing 25 mL Pb(II) aqueous solution at a certain concentration, and the flask was placed in a constant temperature oscillator, setting at a rotation speed of 200 r/min. The adsorbent after sufficient adsorption was separated by a $0.22\text{ }\mu\text{m}$ membrane, and the Pb(II) concentration of residual solution was determined by

an inductively coupled plasma atomic emission spectroscopy instrument (ICP, Optima 8000) from Perkin Elmer Corp. (US). The adsorption capacity of L@MNP toward heavy metal ions was calculated using Eq. 1 [27]:

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

where q_e (mg/g) is the adsorption amount of metal ions on L@MNP at equilibrium, C_0 (mg/L) and C_e (mg/L) the initial concentration and the equilibrium concentration of metal ions, respectively; V (L) the volume of solution, and m (g) the dosage of the adsorbent. All adsorption amounts were the average of two experiments, and the error was less than 5%.

The relative selectivity of L@MNP towards Pb(II), Cu(II), Cd(II), Ni(II) and Zn(II) ions in mixed solution was investigated. Each ion concentration in the mixed solution is the same ($C_0 = 200$ mg/L). The distribution coefficient (k) value of each ion was assessed using Eq. 2:

$$k = \frac{q_x}{q'} \quad (2)$$

where q_x and q' stand for some ion adsorption amount on L@MNP, and the total other ions adsorption amount in solution, respectively.

The pH of initial metal ion solution was adjusted between 2.0 and 6.0 by 0.1 M HCl and 0.1 M NaOH solution. The initial concentration of Pb(II) was 200 mg/L and the suspensions were shaken for 3 h at 298 K. Adsorption kinetic study was conducted at pH 5.0 at 298 K for a Pb(II) concentration of 200 mg/L, with varying shaking times between 1-180 min. The adsorption isotherm was developed during varying initial Pb(II) concentrations between 25 and 750 mg/L. To evaluate the influence of temperature for adsorption, four different temperatures (15, 25, 35, and 45 °C) were studied at pH 5.0.

0.1 M HCl solution was used as an eluting agent for adsorption-desorption experimental study. The adsorbent L@MNP was placed in 0.1 M HCl solution, shaking at 200 r/min for 3 hr, and then with a magnet to separation from the solution. Next, the adsorbent was washed many times by HCl and deionized water, and dried to a constant weight at 70 °C. After above procedure, L@MNP was placed for the next adsorption-desorption cycle.

Results And Discussion

Preparation and Characterizations of L@MNP

As presented in Scheme 1, lignin-based magnetic adsorbent (L@MNP) was fabricated from sulfhydryl-functionalized SMNP and alkenyl lignin via thiol-ene click reaction under UV light (365 nm) irradiation [28]. It was expected that the lignin layer coated on L@MNP surface would enhance the dispersibility and

stability of magnetic core, and simultaneously facilitate its adsorption performance due to the generated thioether bonds (C-S) as adsorbing sites [29].

Fourier transform infrared (FT-IR) spectroscopy was conducted to verify the successful synthesis of L@MNP, as illustrated in Fig. 1a. Two bands at 3381 and 538 cm^{-1} were corresponded to O-H and Fe-O groups of Fe_3O_4 MNPs sample, respectively [30]. For SMNP sample, a new peak at 985 cm^{-1} assigned to Si-O asymmetric vibration could be observed, implying the silicon layer had been successfully coated on Fe_3O_4 surface [31]. The characteristic peaks of L@MNP at 1597, 1503 and 1227 cm^{-1} were ascribed to aromatic ring's skeletal vibration, demonstrating the presence of lignin layer [32]. Meanwhile, the appearance of thioether bond (C-S) at 1128 cm^{-1} further confirmed the successful crosslinking between lignin and magnetic nanoparticles [33]. In addition, the reaction process was monitored by FT-IR spectra (Fig. S1). At different UV light irradiation intervals (0–90 min), the peak intensity of C-S bond at 1128 cm^{-1} gradually increased and tended to be stable over 60 min, which revealed a complete transformation of alkenyl group into thioether bond. The elemental analysis was investigated to study the changing contents of C, H and S elements in Fe_3O_4 MNPs, SMNP and L@MNP during the reaction process (Table S1). After modification with sulfhydryl groups, the sulfur content of SMNP significantly increased to 0.973%. Meanwhile, the carbon content of L@MNP (4.96%) was higher than that of SMNP (1.67%) after the incorporation of lignin, confirming the successful introduction of lignin component. Moreover, the XRD patterns (Fig. 1b) appearing at 30.0° (220), 35.6° (311), 43.2° (400), 53.9° (422), 57.1° (511) and 62.8° (440) corresponding to typical crystalline Fe_3O_4 [34] were observed for Fe_3O_4 MNPs, SMNP and L@MNP samples, respectively, indicating the magnetic cores remained unchanged regardless any modification process.

More features of morphology were further characterized by TEM and SEM (Fig. 2). Upon comparison of the SEM images of SMNP (Fig. 2a) and L@MNP (Fig. 2b), a high similarity in their morphologies was discovered, which confirmed that both SMNP and L@MNP showed the uniform spherical morphology. Due to the coating of SiO_2 and lignin layers, L@MNP owned a bigger particle size (about 37 nm) than the unmodified MNPs (about 30 nm). The TEM image (Fig. 2c) of SMNP demonstrated that the magnetic nanoparticles exhibited a core-shell structure. Additionally, such core-shell structure was maintained for L@MNP (Fig. 2d) with the lignin layer modification onto SMNP surface [35]. The difference caused by lignin distribution between SMNP and L@MNP were also supported by the XPS analysis. As displayed in Table S2, the carbon distribution on SMNP (25.60%) and L@MNP (44.63%) measured by XPS study were obviously higher than that of SMNP (1.67%) and L@MNP (4.96%) from elemental analysis, indicating the lignin component mainly distributed as shell layer on the surface of magnetic Fe_3O_4 core [22].

The magnetic measurement results of Fe_3O_4 MNPs, SMNP and L@MNP were displayed in Fig. S2. There was no hysteresis loop in magnetization curves of SMNP and L@MNP as well as both of the remanence and coercivity closed to zero, which indicated SMNP and L@MNP were superparamagnetic in nature. The magnetization curves showed that the saturation magnetization of both SMNP (54.46 emu/g) and L@MNP (51.00 emu/g) sharply decreased compared to Fe_3O_4 MNPs (84.13 emu/g), due to the

modification of non-magnetic silicon and lignin layers. It is worth mentioning that the saturation magnetization of L@MNP is superior than many reported magnetic adsorbents [29, 36], which enables it a quick recovery (within 15 s) from the aqueous system using an external magnet.

Adsorption studies

Effect of pH

Effect of solution pH on adsorption performance of L@MNP was studied, and the results were shown in Fig. 3a. As the pH value rising from 2.0 to 6.0, the adsorption capacity of L@MNP for Pb(II) increased from 7.25 to 66.25 mg/g. In the L@MNP structure, both sulphur- and oxygen-containing groups could serve as active sites for chelating Pb(II) ions. When $\text{pH} < 5.0$, H_3O^+ species was dominant in solution, and thus only a small amount of cationic Pb(II) ions could be adsorbed since the mutually exclusive force between the protonated surface of L@MNP and Pb(II) cations. On the other hand, as $\text{pH} > 5.0$, the H_3O^+ concentration reduced and Pb(II) ions were easily coordinated by adsorbent, which resulted in the rising adsorption capacity of L@MNP [37]. In the case of lead, $\text{Pb}(\text{OH})_2$ precipitation began to form at $\text{pH} > 6.0$ [38]. Therefore, the solution pH value was set at 5.0 for further adsorption experiments.

Effect of adsorption time

To assess the adsorption process of Pb(II) on L@MNP, effect of contact time was investigated with the initial Pb(II) concentration set as 200 mg/L at 25 °C. As illustrated in Fig. 3b, the Pb(II) adsorption capacity of L@MNP sharply increased at the initial stage and reached equilibrium ($q_e = 64.25 \text{ mg/g}$) within 30 min. This rapid adsorption of Pb(II) by L@MNP could be mainly attributed to its well dispersion property within the crosslinked core-shell structure, which was beneficial for ions transportation and provided sufficient binding sites to capture Pb(II).

The obtained kinetics data was fitted by the pseudo-first-order model (Eq. 3), pseudo-second-order model (Eq. 4) and intraparticle diffusion model (Eq. 5) to evaluate the relationship between adsorption rate and capturing mechanism, respectively [39], and the fitting results were presented in Fig. 3c-d:

$\log (q_e - q_t) = \log q_e - \frac{1}{2.303} k_1 t$	(3)
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	(4)
$q_t = k_p t^{0.5} + C$	(5)

where q_e (mg/g) and q_t (mg/g) are the Pb(II) adsorption capacity at equilibrium time and time t , respectively, k_1 (1/min) the pseudo-first-order adsorption kinetic constant, k_2 [g/(mg·min)] the pseudo-second-order adsorption kinetic constant, k_p [g/(mg·min^{0.5})] the intraparticle diffusion rate constant, and C a constant.

Table 1
Kinetic adsorption parameters for Pb(II) adsorption on L@MNP

Pseudo-first-order model					
q_e (mg/g)	k_1 (1/min)			R^2	
25.87	0.02871			0.7805	
Pseudo-second-order model					
q_e (mg/g)	k_2 [g/(mg·min)]			R^2	
63.13	0.00414			0.9987	
Intraparticle diffusion model					
k_{p1} [g/(mg·min ^{0.5})]	R_1^2	k_{p2}	R_2^2	k_{p3}	R_3^2
		[g/(mg·min ^{0.5})]		[g/(mg·min ^{0.5})]	
15.8078	0.9518	9.0273	0.9877	0.4351	0.9794

As displayed in Table 1, the fitting results exhibited that the coefficient ($R^2 = 0.9987$) of pseudo-second-order kinetic model was higher than that of pseudo-first-order kinetic model ($R^2 = 0.7805$). In addition, the theoretical adsorption capacity (63.13 mg/g) derived by the pseudo-second-order kinetic model was much closer to the experimental value (62.25 mg/g), which indicated that the pseudo-second-order kinetic model could well describe the adsorption process. These observations verified that the chemical adsorption played a major role during the adsorption process [40].

The fitting results of intraparticle diffusion model showed that there were three stages in the diffusion of Pb(II) onto adsorbent. Thus, three intraparticle constants (k_{p1} , k_{p2} and k_{p3}) were used to express the diffusion rates of these three stages. It could be found from the fitting data in Table 1 that the order of diffusion rate followed an order as $k_{p1}>k_{p2}>k_{p3}$. Evidently, the first stage was dominated by rapid surface diffusion in initial adsorption process ($k_{p1} = 15.8078$), where a large number of Pb(II) ions were rapidly chelated onto L@MNP surface [41]. When the surface sites of adsorbent reached saturation, Pb(II) ions began to diffuse into the pores of adsorbent and attached to inner surface during the second stage. At the same time, there existed resistance when Pb(II) diffused into adsorbent pores, which led to the decrease of diffusion rate constant ($k_{p2} = 9.0273$) [42]. Subsequently, the third stage presented the

adsorption equilibrium stage. As diffusion continued, active sites on the inner surface of adsorbent for the most part had reached adsorption equilibrium, which led to the minimum diffusion rate constant ($k_{p3} = 0.4351$) in three stages [43]. In addition, since the fitting line did not pass through zero point, it seemed that boundary diffusion and external diffusion would also effect the Pb(II) adsorption process on L@MNP.

Adsorption isotherms

Adsorption isotherm of L@MNP for Pb(II) was studied at various initial Pb(II) concentrations (25–750 mg/L), pH 5.0, and at 25 °C. As displayed in Fig. 4a, adsorption capacity of L@MNP increased along with the ascending initial Pb(II) concentration, which illustrated that high solution concentration was beneficial for the adsorption performance of L@MNP. Adsorption behavior of L@MNP was analyzed using the Langmuir model (Eq. 6) [44] and Freundlich model (Eq. 7) [45], respectively:

$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \quad (6)$
$q_e = K_F C_e^{1/n} \quad (7)$

where q_e (mg/g) is the adsorption capacity at equilibrium, $q_{\max}$ (mg/g) the maximum adsorption capacity of L@MNP, C_e (mg/L) the solution concentration at adsorption equilibrium, K_L (L/mg) the Langmuir model constant, K_F (mg/g) the Freundlich model constant, and $1/n$ the Freundlich adsorption coefficient.

The fitting curves and parameters of the Langmuir and Freundlich models were shown in Fig. 4a and Table 2, respectively. These fitting findings indicated that the Pb(II) adsorption by L@MNP well followed the Langmuir model with a high fitting coefficient ($R^2 = 0.9928$), demonstrating a monolayer adsorption process [46]. In addition, $q_{\max}$ was calculated to be 97.38 mg/g, which was not only obviously higher than that of the raw lignin ($q_{\max} = 12.00$ mg/g), but also surpassed many reported adsorbents (Table 3).

Table 2
Fitting parameters of the Langmuir and
Freundlich models for Pb(II)

Langmuir isotherm model		
$Q_{\max}$ (mg/g)	K_L (1/min)	R^2
97.38	0.00678	0.9928
Freundlich isotherm model		
K_F	$1/n$	R^2
5.6791	0.4130	0.9244

Table 3
Adsorption capacities of different adsorbents reported for Pb(II)

Adsorbents	Condition		$q_{\max}$ (mg/g)	Ref
	pH	Temperature (K)		
lignin	_a	330	9.00	[47]
1-Aza-18-crown-6 functionalized lignin-based adsorbent (AFL)	6.0	298	91.4	[48]
Lignin xanthate resin	5.0	303	63.90	[49]
N-Acetyl-L-cysteine-functionalized lignin (CFL)	6.0	288	58.80	[26]
Hiol-functionalized cellulose nanofiber membrane	4.0	rt ^b	22.00	[50]
Magnetized activated carbons (MAC)	5.0	298	253.20	[51]
Lignin derivate magnetic hydrogel microspheres	5.0	298	33.00	[52]
Magnesium oxide cores with silica coated nano- magnetite (MTM)	_a	298	85.10	[53]
L@MNP	5.0	298	97.38	this study
raw lignin	5.0	298	12.00	this study
^a Not available. ^b Room temperature.				

Adsorption thermodynamics.

Adsorption thermodynamics were further investigated to explore the energy changes and feasibility of Pb(II) adsorption on L@MNP, as temperatures ranging from 25 to 45 °C. Correspondingly, the thermodynamic parameters including Gibbs free energy change (ΔG^0 , kJ/mol), enthalpy change (ΔH^0 , kJ/mol), and entropy change [ΔS^0 , J/(mol·K)] could be calculated based on Eq. 8–10 [54]:

$\Delta G^0 = -RT \ln k_d$	(8)
$\ln k_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	(9)
$k_d = \frac{q_e}{C_e}$	(10)

where R [8.314 J/(mol·K)] stands for the universal gas constant, and k_d the distribution coefficient.

The linear function of $\ln k_d$ versus $1/T$ was fitted based on the equilibrium adsorption data at different adsorption temperatures (Fig. 4b), and the thermodynamic parameters were shown in Table 4. Negative values of ΔG^0 at all tested temperatures implied that the adsorption process occurred spontaneously [55]. Meanwhile, the ΔG^0 values decreased gradually with the increase of temperature, indicating that the force in adsorption driving was positively correlated with the spontaneous degree range [56]. Positive value of ΔH^0 proved that adsorption was endothermic in nature. Additionally, the positive value of ΔS^0 suggested an increasing freedom degree at solid-liquid interface [57].

Table 4

Parameters of thermodynamic about adsorption for Pb(II) on L@MNP

Adsorbent	ΔH^0 (kJ/mol)	ΔS^0 [J/(K·mol)]	ΔG^0 (kJ/mol)			
			298 K	308 K	318 K	328 K
L@MNP	6.36	46.80	-7.12	-7.58	-8.05	-8.52

Adsorption selectivity

It is impossible to have only a single heavy metal in actual sewage. Thus, different co-existing substances including Cu(II), Cd(II), Ni(II) and Zn(II) ions were tested herein for possible competitive effect on the adsorption of Pb(II) by L@MNP with pH 5.0 at 25 °C. As presented in Fig. 4c, adsorption capacities of L@MNP toward various heavy metal ions were found to follow the order of Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). Despite suffering electrostatic repulsion among various cations [58], L@MNP still showed an excellent selectivity toward Pb(II) over other competitive metal ions. Convectively, the affinity and selectivity of L@MNP to various metal cations could be distinguished via comparing the distribution coefficient (k). As listed in Table 5, the high-relative k (0.903) for Pb(II) encourages L@MNP to be an

excellent selective adsorbent for Pb(II) adsorption. On the basis of the Pearson’s hard/soft acid/base (HSAB) theory, Pb(II) has been classified as a more softer acid than other metal ions due to its higher water binding energy and larger radius of hydrated ions. Thus, the S/O containing functional groups serving as soft bases in L@MNP could feasibly chelate the soft metal Pb(II) [59], which resulted in a remarkable selectivity for Pb(II) capture.

Table 5
Adsorption selectivity paraments of L@MNP for metal ions

Adsorbent	Selective coefficient <i>k</i>				
	<i>k</i> (Pb)	<i>k</i> (Cd)	<i>k</i> (Cu)	<i>k</i> (Ni)	<i>k</i> (Zn)
L@MNP	0.903	0.381	0.135	0.061	0.080

Adsorption recyclability

The recyclability characteristics of an adsorbent are critical in practical application. Under the suitable adsorption conditions (pH 5.0, *T* = 25 °C and contact time 3 h), the Pb(II) loaded L@MNP could be desorbed by rinsing with 0.1 M HCl solvent to evaluate its reusability performance. As shown in Fig. 4d, the adsorption efficiency remained 62.86% after 5 adsorption-desorption cycles. Besides, the desorption efficiency of L@MNP was found over 95.27%. Thus, the acceptable regeneration performance of L@MNP would favor a recyclable utilization in wastewater treatment.

Adsorption mechanism

For the purpose of proving the adsorption mechanism between adsorbent and metal ion pollutants, the L@MNP sample before and after Pb(II) adsorption was detected by XPS spectra (Fig. 5a-c). In Fig. 5a, the high-resolution XPS spectrum showed three characteristic peaks of Pb 4f^{3/2}, Pb 4f^{5/2} Pb 4f^{7/2} at 436.3, 414.4 and 139.5 eV, respectively, which indicated that Pb(II) was adsorbed onto L@MNP surface in an ionic state [60]. Figure 5b-c presented the obvious shifts of the O 1s and S 2p peaks, which proved that both O and S containing groups contributed to the adsorption process. Particularly, three O 1s peaks at 532.8, 530.8, and 529.7 eV attributed to Si-O, C-O and Fe-O groups moved to 532.9, 531.5 and 530.1 eV after Pb(II) adsorbed onto L@MNP surface, respectively [61]. Meanwhile, two S 2p peaks at 164.8 and 162.9 eV ascribed to C-S and -SH groups of L@MNP shifted to 167.9 and 163.5 eV for L@MNP-Pb(II), confirming the coordination behavior also occurred between sulfur containing groups and Pb(II) [62]. These observations could be explained as follows: after Pb(II) adsorption, O and S atoms shared lone pair electrons with the adsorbed Pb(II), which made them shifted to higher binding energy with the decreased electron density [34]. Based on the above findings, the Pb(II) complexation with functional groups involved in the primary interaction mechanism between L@MNP and Pb(II) ions.

Conclusion

In summary, we have demonstrated a novel lignin-based magnetic adsorbent L@MNP synthesized through thiol-ene click reaction. Structural and morphological characterizations had been comprehensively investigated to gain a detailed insight into L@MNP. The Pb(II) adsorption on L@MNP well followed the pseudo-second-order kinetic model and the Langmuir isothermal model, yielding a rapid adsorption equilibrium (within 30 min) and a relative high $q_{\max}$ of 97.38 mg/g. Thermodynamic adsorption investigation indicated a spontaneous and exothermic process. In addition, L@MNP exhibited excellent selectivity and acceptable reusability for Pb(II) adsorption with fast recovery behavior. We anticipate that the present findings would offer a novel strategy in the development of lignin-based adsorbent material for wastewater treatment.

Declarations

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/XXXXXXX>

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Conflict of interest

The authors declare that they have not any financial/commercial conflicts of interest.

References

1. Bolisetty S, Peydayesh M, Mezzenga R (2019) Sustainable technologies for water purification from heavy metals: review and analysis. *Chem Soc Rev* 48(2):463–487
2. Zhang R, Chen T, Zhang Y, Hou YH, Chang QR (2020) Health risk assessment of heavy metals in agricultural soils and identification of main influencing factors in a typical industrial park in northwest China. *Chemosphere* 252:126591
3. Renu K, Chakraborty R, Myakala H, Koti R, Famurewa AC, Madhyastha H, Vellingiri B, George A, Valsala Gopalakrishnan A (2021) Molecular mechanism of heavy metals (Lead, Chromium, Arsenic, Mercury, Nickel and Cadmium) - induced hepatotoxicity - A review. *Chemosphere* 271:129735
4. Verma J, Kumari S, Dhasmana A (2020) Toxic effect of Lead on earth's life. *Int J Innov Res Technol* 7(1):672–676
5. Hasanpour M, Hatami M (2020) Application of three dimensional porous aerogels as adsorbent for removal of heavy metal ions from water/wastewater: A review study. *Adv Colloid Interface Sci*

6. Zhang LP, Liu Z, Zhou XL, Zhang C, Cai QW, Xie R, Ju XJ, Wang W, Faraj Y, Chu LY (2020) Novel composite membranes for simultaneous catalytic degradation of organic contaminants and adsorption of heavy metal ions. *Sep Purif Technol* 237:116364
7. Mao ML, Yan TT, Shen JJ, Zhang JP, Zhang DS (2021) Capacitive Removal of Heavy Metal Ions from Wastewater via an Electro-Adsorption and Electro-Reaction Coupling Process. *Environ Sci Technol* 55(5):3333–3340
8. Femina Carolin C, Senthil Kumar P, Saravanan A, Janet Joshiba G, Naushad M (2017) Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J Environ Chem Eng* 5(3):2782–2799
9. Chai WS, Cheun JY, Senthil Kumar P, Mubashir M, Majeed Z, Banat F, Ho SH, Show PL (2021) A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. *J Clean Prod* 296:126589
10. Gao FF (2019) An Overview of Surface-Functionalized Magnetic Nanoparticles: Preparation and Application for Wastewater Treatment. *ChemistrySelect* 4(22):6805–6811
11. Chenab KK, Sohrabi B, Jafari A, Ramakrishna S (2020) Water treatment: functional nanomaterials and applications from adsorption to photodegradation. *Mater Today Chem* 16:100262
12. Almomani F, Bhosale R, Khraisheh M, Kumar A, Almomani T (2020) Heavy metal ions removal from industrial wastewater using magnetic nanoparticles (MNP). *Appl Surf Sci* 506:144924
13. Lin XQ, Liu Y, Zheng XJ, Qureshi N (2021) High-efficient cellulosic butanol production from deep eutectic solvent pretreated corn stover without detoxification. *Ind Crop Prod* 162:113258
14. Liu HY, Du HS, Zheng T, Liu K, Ji XX, Xu T, Zhang XY, Si CL (2021) Cellulose based composite foams and aerogels for advanced energy storage devices. *Chem Eng J* 426:130817
15. Wu Y, Qian Y, Lou HM, Yang DJ, Qiu XQ (2019) Enhancing the Broad-Spectrum Adsorption of Lignin through Methoxyl Activation, Grafting Modification, and Reverse Self-Assembly. *ACS Sustainable Chem Eng* 7(19):15966–15973
16. Xu JY, Li CY, Dai L, Xu CL, Zhong YD, Yu FX, Si CL (2020) Biomass Fractionation and Lignin Fractionation towards Lignin Valorization. *ChemSusChem* 13(17):4284–4295
17. Gao WJ, Fatehi P (2019) Lignin for polymer and nanoparticle production: Current status and challenges. *Can J Chem Eng* 97(11):2827–2842
18. Supanchaiyamat N, Jetsrisuparb K, Knijnenburg JTN, Tsang DCW, Hunt AJ (2019) Lignin materials for adsorption: Current trend, perspectives and opportunities. *Bioresour Technol* 272:570–581
19. Ralph J, Lapierre C, Boerjan W (2019) Lignin structure and its engineering. *Curr Opin Biotechnol* 56:240–249
20. Wang JY, Qian Y, Li LB, Qiu XQ (2020) Atomic Force Microscopy and Molecular Dynamics Simulations for Study of Lignin Solution Self-Assembly Mechanisms in Organic-Aqueous Solvent Mixtures. *ChemSusChem* 13(17):4420–4427

21. Liu YL, Jin C, Yang ZZ, Wu GM, Liu GF, Kong ZW (2021) Recent advances in lignin-based porous materials for pollutants removal from wastewater. *Int J Biol Macromol* 187:880–891
22. Zhou X, Jin C, Liu GF, Wu GM, Huo SP, Kong ZW (2021) Functionalized lignin-based magnetic adsorbents with tunable structure for the efficient and selective removal of Pb(II) from aqueous solution. *Chem Eng J* 420:130409
23. Zhang YC, Ni SZ, Wang XJ, Zhang WH, Lagerquist L, Qin MH, Willför S, Xu CL, Fatehi P (2019) Ultrafast adsorption of heavy metal ions onto functionalized lignin-based hybrid magnetic nanoparticles. *Chem Eng J* 372:82–91
24. Jin C, Zhang XY, Xin JN, Liu GF, Wu GM, Kong ZW, Zhang JW (2017) Clickable Synthesis of 1,2,4-Triazole Modified Lignin-Based Adsorbent for the Selective Removal of Cd(II). *ACS Sustainable Chem Eng* 5(5):4086–4093
25. Yap PL, Kabiri S, Tran DNH, Losic D (2019) Multifunctional Binding Chemistry on Modified Graphene Composite for Selective and Highly Efficient Adsorption of Mercury. *ACS Appl Mater Interfaces* 11(6):6350–6362
26. Jin C, Zhang XY, Xin JN, Liu GF, Chen J, Wu GM, Liu T, Zhang JW, Kong ZW (2018) Thiol-Ene Synthesis of Cysteine-Functionalized Lignin for the Enhanced Adsorption of Cu(II) and Pb(II). *Ind Eng Chem Res* 57(23):7872–7880
27. Huang YJ, Zhao WC, Zhang X, Peng H, Gong YF (2019) Thiol-ene synthesis of thioether/carboxyl-functionalized polymers for selective adsorption of silver (I) ions. *Chem Eng J* 375:121935
28. Wang X, Guo HX, Lu ZH, Liu X, Luo XF, Li SJ, Liu SX, Li J, Wu YZ, Chen ZJ (2021) Lignin Nanoparticles: Promising Sustainable Building Blocks of Photoluminescent and Haze Films for Improving Efficiency of Solar Cells. *ACS Appl Mater Interfaces* 13(28):33536–33545
29. He HF, Meng XY, Yue QY, Yin WY, Gao Y, Fang P, Shen L (2021) Thiol-ene click chemistry synthesis of a novel magnetic mesoporous silica/chitosan composite for selective Hg(II) capture and high catalytic activity of spent Hg(II) adsorbent. *Chem Eng J* 405:126743
30. Yap PL, Auyoong YL, Hassan K, Farivar F, Tran DNH, Ma J, Losic D (2020) Multithiol functionalized graphene bio-sponge via photoinitiated thiol-ene click chemistry for efficient heavy metal ions adsorption. *Chem Eng J* 395:124965
31. Guo XY, Mao FF, Wang WJ, Yang Y, Bai ZM (2015) Sulfhydryl-Modified Fe₃O₄@SiO₂ Core/Shell Nanocomposite: Synthesis and Toxicity Assessment in Vitro. *ACS Appl Mater Interfaces* 7(27):14983–14991
32. Nasir ANM, Yahaya N, Zain NNM, Lim V, Kamaruzaman S, Saad B, Nishiyama N, Yoshida N, Hirota Y (2019) Thiol-functionalized magnetic carbon nanotubes for magnetic micro-solid phase extraction of sulfonamide antibiotics from milks and commercial chicken meat products. *Food Chem* 276:458–466
33. Deng A, Yuan J, Qi CZ, Gao Y, Hollow SiO₂ microspheres with thiol-rich surfaces: The scalable templated fabrication and their application for toxic metal ions adsorption. *Mater Chem Phys* 243: 122625

34. Hao Y, Gao Y, Gao LY, He YL, Niu YY, Hussain S, Gao RX, Pfefferle LD, Shahid M, Wang SC (2021) Amphiphilic core–shell magnetic adsorbents for efficient removal and detection of phthalate esters. *Chem Eng J* 423:129817
35. Liu X, Guan JN, Lai GH, Xu Q, Bai XB, Wang ZM, Cui SP (2020) Stimuli-responsive adsorption behavior toward heavy metal ions based on comb polymer functionalized magnetic nanoparticles. *J Clean Prod* 253:119915
36. Cheng DK, Dai XH, Chen L, Cui YH, Qiang CW, Sun Q, Dai JD (2019) Thiol–Yne Click Synthesis of Polyamide–Amine Dendritic Magnetic Halloysite Nanotubes for the Efficient Removal of Pb(II). *ACS Sustainable Chem Eng* 8(2):771–781
37. Shahraki S, Delarami HS, Khosravi F, Nejat R (2020) Improving the adsorption potential of chitosan for heavy metal ions using aromatic ring-rich derivatives. *J Colloid Interface Sci* 576:79–89
38. Wang HC, Wang ZW, Yue RR, Gao F, Ren RL, Wei JF, Wang XL, Kong ZY (2020) Rapid preparation of adsorbent based on mussel inspired chemistry and simultaneous removal of heavy metal ions in water. *Chem Eng J* 383:123107
39. Duan ZH, Zhang WH, Lu MH, Shao ZW, Huang WL, Li J, Li YN, Mo JC, Li YT, Chen CY (2020) Magnetic Fe₃O₄/activated carbon for combined adsorption and Fenton oxidation of 4-chlorophenol. *Carbon* 167:351–363
40. Mu RH, Liu B, Chen X, Wang N, Yang J (2020) Adsorption of Cu(II) and Co(II) from aqueous solution using lignosulfonate/chitosan adsorbent. *Int J Biol Macromol* 163:120–127
41. Jiang CL, Wang XH, Hou BX, Hao C, Li X, Wu JB (2020) Construction of a Lignosulfonate-Lysine Hydrogel for the Adsorption of Heavy Metal Ions. *J Agric Food Chem* 68(10):3050–3060
42. Wu ZJ, Huang WX, Shan XY, Li ZL (2020) Preparation of a porous graphene oxide/alkali lignin aerogel composite and its adsorption properties for methylene blue. *Int J Biol Macromol* 143:325–333
43. Li AY, Deng H, Jiang YH, Ye CH, Yu BG, Zhou XL, Ma AY (2020) Superefficient Removal of Heavy Metals from Wastewater by Mg-Loaded Biochars: Adsorption Characteristics and Removal Mechanisms. *Langmuir* 36(31):9160–9174
44. Dai L, Li YT, Liu R, Si CL, Ni YC (2019) Green mussel-inspired lignin magnetic nanoparticles with high adsorptive capacity and environmental friendliness for chromium(III) removal. *Int J Biol Macromol* 132:478–486
45. Zhou XF, Jia ZR, Feng AL, Qu SL, Wang XN, Liu XH, Wang BB, Wu GL (2020) Synthesis of porous carbon embedded with NiCo/CoNiO₂ hybrids composites for excellent electromagnetic wave absorption performance. *J Colloid Interface Sci* 575:130–139
46. Bugarčić M, Lopičić Z, Šoštarić T, Marinković A, Rusmirovic JD, Milošević D, Milivojević M (2021) Vermiculite enriched by Fe(III) oxides as a novel adsorbent for toxic metals removal. *J Environ Chem Eng* 9(5):106020
47. Demirbas A (2004) Adsorption of lead and cadmium ions in aqueous solutions onto modified lignin from alkali glycerol delignification. *J Hazard Mater* 109(1–3):221–226

48. Jin C, Liu GF, Wu GM, Huo SP, Liu ZS, Kong ZW (2020) Facile fabrication of crown ether functionalized lignin-based biosorbent for the selective removal of Pb(II). *Ind Crop Prod* 155:112829
49. Li ZL, Kong Y, Ge Y (2015) Synthesis of porous lignin xanthate resin for Pb²⁺ removal from aqueous solution. *Chem Eng J* 270:229–234
50. Choi HY, Bae JH, Hasegawa Y, An S, Kim IS, Lee H, Kim M (2020) Thiol-functionalized cellulose nanofiber membranes for the effective adsorption of heavy metal ions in water. *Carbohydr Polym* 234:115881
51. Zhang Z, Wang T, Zhang HX, Liu YH, Xing BS (2021) Adsorption of Pb(II) and Cd(II) by magnetic activated carbon and its mechanism. *Sci Total Environ* 757:143910
52. Meng Y, Li CX, Liu XQ, Lu J, Cheng Y, Xiao LP, Wang HS (2019) Preparation of magnetic hydrogel microspheres of lignin derivate for application in water. *Sci Total Environ* 685:847–855
53. Nagarajah R, Wong KT, Lee G, Chu KH, Yoon Y, Kim NC, Jang M (2017) Synthesis of a unique nanostructured magnesium oxide coated magnetite cluster composite and its application for the removal of selected heavy metals. *Sep Purif Technol* 174:290–300
54. Liu Y, Qian P, Yu Y, Yu B, Wang YL, Ye SF, Chen YF (2018) Preparation and characterization of a novel hybrid chelating material for effective adsorption of Cu(II) and Pb(II). *J Environ Sci* 67:224–236
55. Wang QJ, Zhang Y, Wangjin XX, Wang YL, Meng GH, Chen YH (2020) The adsorption behavior of metals in aqueous solution by microplastics effected by UV radiation. *J Environ Sci* 87:272–280
56. Wang HC, Wang ZW, Yue RR, Gao F, Ren RL, Wei JF, Wang XL, Kong ZY (2020) Functional group-rich hyperbranched magnetic material for simultaneous efficient removal of heavy metal ions from aqueous solution. *J Hazard Mater* 384:121288
57. Mahmoudi E, Azizkhani S, Mohammad AW, Ng LY, Benamor A, Ang WL, Ba-Abbad M (2020) Simultaneous removal of Congo red and cadmium(II) from aqueous solutions using graphene oxide-silica composite as a multifunctional adsorbent. *J Environ Sci* 98:151–160
58. Liu CK, Bai RB, San Ly Q (2008) Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: behaviors and mechanisms. *Water Res* 42(6–7):1511–1522
59. Bo SF, Luo JM, An QD, Xiao ZY, Wang HS, Cai WJ, Zhai SR, Li ZC (2020) Efficiently selective adsorption of Pb(II) with functionalized alginate-based adsorbent in batch/column systems: Mechanism and application simulation. *J Clean Prod* 250:119585
60. Pan JW, Gao BY, Wang SY, Guo KY, Xu X, Yue QY (2020) Waste-to-resources: Green preparation of magnetic biogas residues-based biochar for effective heavy metal removals. *Sci Total Environ* 737:140283
61. Zhao JJ, Luan LP, Li ZW, Duan ZF, Li YF, Zheng SB, Xue ZX, Xu WL, Niu YZ (2020) The adsorption property and mechanism for Hg(II) and Ag(I) by Schiff base functionalized magnetic Fe₃O₄ from aqueous solution. *J Alloy Compd* 825:154051
62. Yan MF, Huang WX, Li ZL (2019) Chitosan cross-linked graphene oxide/lignosulfonate composite aerogel for enhanced adsorption of methylene blue in water. *Int J Biol Macromol* 136:927–935

Figures

Figure 1

(a) FT-IR spectra of Fe₃O₄ MNPs, SMNP and L@MNP; (b) XRD patterns of Fe₃O₄ MNPs, SMNP, and L@MNP

Figure 2

SEM images of (a) SMNP, (b) L@MNP and TEM images of (c) SMNP, (d) L@MNP

Figure 3

Effect of (a) pH, and (b) contact time on Pb(II) adsorption on L@MNP; Adsorption kinetics of Pb(II) on L@MNP by (c) pseudo-first-order and pseudo-second-order models, and (d) intraparticle diffusion model

Figure 4

(a) Equilibrium data and fitting curves for Pb(II) adsorption on L@MNP; (b) Plot of $1/T$ versus $\ln k_d$ of L@MNP; (c) Adsorption selectivity of L@MNP for co-existing metal ions; (d) Adsorption-desorption cycles of L@MNP for Pb(II) recovery (pH 5.0, dosage 10 mg/25 mL, 200 mg/L Pb(II) solution, 25 °C, and 180 min)

Figure 5

(a) XPS survey spectra, (b) O 1s and (c) S 2p of L@MNP before and after Pb(II) adsorption

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