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Carboxylate functionalized wool fibers for removal of Cu(II) and Pb(II) from aqueous solution

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ABSTRACT

Carboxylate groups were introduced onto wool fibers (Wool-g-COOH) by graft copolymerization with acrylic acid by initiation of potassium permanganate and oxalic acid redox system aiming at the removal of Cu(II) and Pb(II) ions from aqueous solutions. FT-IR results showed successful grafting. Batch adsorption experiments were carried out to investigate its adsorption capability to Cu(II) and Pb(II) ions. The results showed that the adsorption equilibrium could be obtained at 40 min for Cu (II) and at 60 min for Pb(II). Kinetic studies showed that the experimental data for adsorbing both Cu(II) and Pb(II) ions onto Wool-g-COOH were fitted well with pseudo-second-order kinetics. The equilibrium data could be better described by the Langmuir isotherm model than the Freundlich isotherm model for adsorbing both Cu(II) and Pb(II) ions onto Wool-g-COOH. The adsorption capacity for Cu (II) and Pb(II) ions was 66.67 and 204.1 mg/g calculated by Langmuir adsorption model, respectively. The adsorption process was favorable for adsorption of both Cu(II) and Pb(II) is cut from here]–> ions onto Wool-g-COOH. The Wool-g-COOH showed good regeneration property and reusability. The relative adsorption capacity for Cu(II) and Pb(II) ions still remained at 60.5 and 83.8%, respectively, after six times of recycling. The current study showed that Wool-g-COOH is a promising adsorbent for removing Cu(II) and Pb(II) ions from contaminated aqueous solutions.

Keywords: Wool fiber; Adsorbent; Carboxylate; Graft copolymerization; Adsorption; Copper; Lead

1. Introduction

Removal of heavy metal ions from municipal and industrial wastewater is of increasing importance. Copper (Cu) is a necessary element for human beings; however, when excess amount of Cu(II) is uptaken by the human body, it will cause serious health problems such as hair loss, kidney damage, anemia, nausea, hypoglycemia, and even death [1]. The main sources of Cu(II) ions are industrial wastewater effluents from metal cleaning and plating baths, pulp, paper, paperboard and wood preservative-employing mills,

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fertilizer industry, etc. [2]. World health organization (WHO) recommends the concentration of Cu(II) in drinking water should be below 1.5 mg/L [3]. Lead (Pb) is one of the 10 most hazardous contaminants in the world. The main way of Pb(II) discharge into the environment and water is through exhaust gasses from automobile and effluents from battery manufacturing, paper and pulp industries, etc. [4]. Pb(II) causes breakdown of the biosynthesis of hemoglobin, kidney damage, abortion, and moreover brain damage in children [5]. The concentration of Pb(II) in drinking water should be lower than 0.01 mg/L as recommended by the WHO [6].

For removing heavy metal ions from water, several methods have been reviewed in the literature [7] such as, chemical precipitation, ion exchange, membrane separation and adsorption. The adsorption approach is widely considered to be more effective and economical. Various adsorbents have been developed for the removal of Cu(II) and Pb(II) ions from aqueous solutions, including inorganic materials such as activated carbon [8], expanded perlite [9], MnO_2 [10], Fe_3O_4 [11], and natural polymers such as chitosan [12,13], cellulose [14], collagen [15], and biological wastes [16]. However, the development of effective and economic adsorbents is still increasingly needed.

Wool fiber is an abundant renewable natural polymer [17–19]. It is reported that around 9 tons of wool fibers are disposed yearly as waste due to their low quality and difficulty in processing [20]. In contrast to many synthetic polymer adsorbents, wool fibers, composed of α-keratin, are water insoluble while showing better hydrophilic properties [21]. Moreover, keratin is a major structural fibrous protein with better mechanical and chemical stabilities than most of the natural polymers. The application of wool fibers for the removal of heavy metal ions is equivalent to the use of one waste for the cleanup of another.

Because of the carboxylate, hydroxyl, and amino groups existing on their surfaces, wool fibers have the ability to bind metal ions. Sun et al. investigated the adsorption process of Cu(II) on wool fibers [22]. Balkaya et al. studied the adsorption characteristic of Cr(VI) on wool fibers [23]. To increase the adsorption capacity of metal ions, additional functional groups should be introduced onto the surface of wool fibers [21,24,25]. In textile industries, graft polymerization with vinyl monomers, such as methyl methacrylate [26], ethyl methacrylate [27], ethyl acrylate [28], benzyl methacrylate [29], and acrylic acid [30], has been developed to improve the properties of wool fibers. The introduction of poly(acrylic acid) imparts adsorbents with sufficient carboxylate groups, and thus improves their adsorption efficiency [31,32]. This work aims at preparing a wool fiber-based adsorbent by graft copolymerization with acrylic acid (AA) for effective removal of Cu(II) and Pb(II) ions from aqueous solutions. Adsorption of Cu(II) and Pb(II) ions is investigated in batch while varying the initial pH and initial concentration of metal ions, and contact time.

2. Experimental

2.1. Materials

Wool fibers were collected from leather making process and degreased by acetone and dried at 40℃ till constant weight. $Cu(NO_3)_2$, $Pb(NO_3)_2$, and the other materials were all analytically pure and used directly without further treatment.

2.2. Preparation of polyacrylic acid-grafted wool fibers

1.0 g of wool was treated with 50 mL of 1% sodium hydroxide at 50℃ for 10 min. The residual alkali was washed thoroughly with distilled water until the pH was close to neutral. The treated wool fibers were then soaked in 50-mL distilled water in a 250-mL conical flask. The redox initiator system which consists of 10 mL of 0.2 mol/L potassium permanganate and 10 mL of 0.4 mol/L oxalic acid was added and vigorously shaken for 5 min. Five milliliter of monomeric acrylic acid (AA) was added and the reaction was conducted at 25℃ for 1 h with continuous shaking. To terminate the reaction, 10 mL of 1% hydroquinone solution was added. Then, the poly (acrylic acid) homopolymers were extracted by distilled water. The grafted wool fibers were then dried to constant weight at 40℃ and designated as Wool-g-COOH. The graft yield was calculated according to the following Eq. (1):

$$\text{Graft yield } \% = \frac{W_0 - W}{W} \times 100\% \qquad (1)$$

where W and W_0 are the weights of wool fiber before and after graft polymerization, respectively. Graft yield was found to be 80.0%.

2.3. Batch adsorption experiments

Adsorption processes were carried out in a HZS-H thermostatic water bath shaker (Donglian Electronic, China). Briefly, 0.1 g of adsorbent was placed in a flask containing 100 mL of the metal ion solution. The initial pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. The contents were shaken at 25˚C with 200 rpm for a predetermined period of time and then were centrifuged. The concentration of metal ions in the supernatant was measured by a 2100 DV inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer, USA). The amount of the adsorption was calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e) \times V}{W} \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentration of metal ions in solution (mg/L), respectively. V is the volume of the solution (L) and W is the amount of the adsorbent used (g).

Kinetic studies were conducted at 25˚C using 300 mL of metal ion solution at pH 4.0. Samples were withdrawn at regular intervals and the concentration of metal ions was determined to plot the amount adsorbed vs. time. The isotherm experiments were performed at 25˚C using different concentrations of metal ions at pH 4.0 for 60 min.

2.4. Desorption and recycling experiments

Desorption experiments were carried out with 0.2 M of oxalic acid solution. 0.1 g of the metal ion adsorbed adsorbent was agitated with 200 mL of 0.2 M oxalic acid solution at 40˚C for 24 h. The solution was removed by centrifugation. The recovered adsorbent was reused for metal ion adsorption to evaluate its reusability.

2.5. Characterization

Characterization of the graft wool fiber was compared with the native wool fiber. FT-IR spectra of the Wool-g-COOH adsorbent before and after adsorption were recorded by a Nicolet IS10 Fourier transform infrared spectrometer (Thermo Scientific, USA). The morphology of the surface of adsorbent before and after adsorption was analyzed by a JSM-F7500 Scanning electron microscope (SEM) (Japan Electron Optical Laboratory Co., Ltd, Japan). All the samples were coated with gold ions before analysis.

3. Results and discussion

3.1. Characterization

The FT-IR spectra of natural wool fiber, Wool-g-COOH, before and after ion adsorption experiments are shown in Fig. 1. The bands at 1,627, 1,523, and 1,392 cm^{-1} are characteristic of the stretching vibration of –C=O (amide I), bending vibration of –N–H (amide II), and stretching vibration of –C–N of amide (amide III), respectively [24]. After graft copolymerization with acrylic acid, a weak band appeared at 1,718 cm^{-1} that corresponds to the stretching vibration of –C=O of carboxylic acid (Fig. 1(b)) [33]. It indicates that poly (acrylic acid) has been successfully grafted onto the wool fibers. The band at 1,627 cm^{-1} for Wool-g-COOH was shifted to a higher wave number (Fig. 1(c) and (d)), when Cu(II) or Pb(II) ions are absorbed by modified wool fibers.

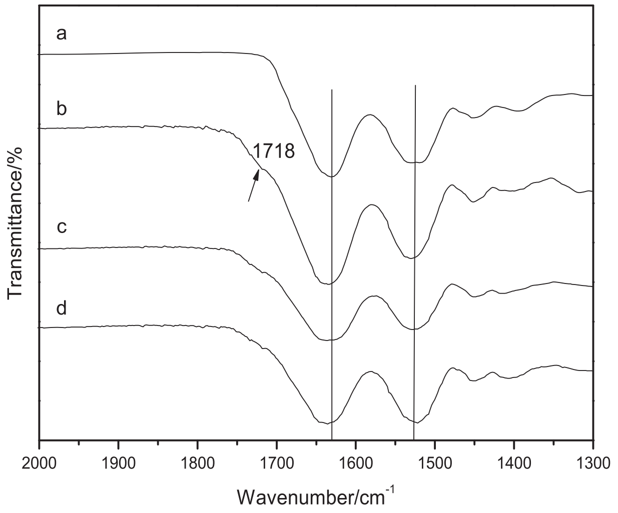

Fig. 1. The FT-IR spectra of native wool fiber and Wool-g-COOH before and after adsorption. (a) Native wool, (b) Wool-g-COOH, (c) Wool-g-COOH after adsorbing Cu(II), and (d) Wool-g-COOH after adsorbing Pb(II).

SEM-EDS profiles give the information about the elements on the surface of materials. The element on the surface of Wool-g-COOH contains C, N, O, S, and a small amount of Ca and Al (Fig. 2(a)). After adsorption, Cu and Pb were observed on the surface of the adsorbent (Fig. 2(b) and(c)) which illustrated that the metal ions were absorbed by the Wool-g-COOH.

3.2. Batch adsorption

3.2.1. Effect of pH on the removal of Cu(II) and Pb(II) ions

The adsorption of Cu(II) and Pb(II) ions on Wool-g-COOH was studied by varying the initial pH of the solution from 1.5 to 5.0. All experiments were conducted at 25˚C with the initial concentration of 100 mg/L metal ions for 60 min. The uptake of the ions increased with increasing pH value (Fig. 3). For

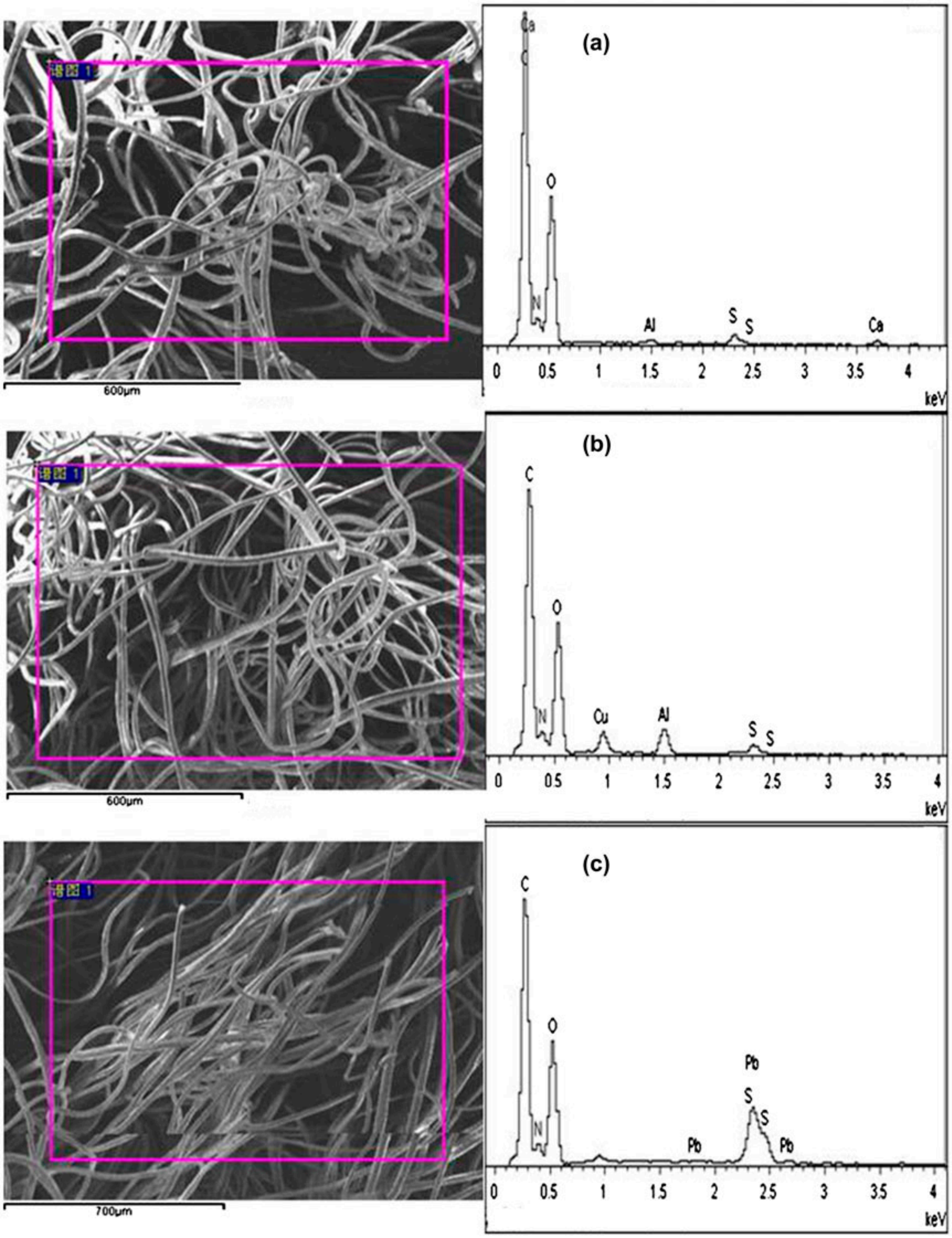

Fig. 2. The SEM-EDS spectra of Wool-g-COOH fibers. (a) Native wool fiber, (b) Wool-g-COOH after absorbing Cu(II), and (c) Wool-g-COOH after absorbing Pb(II).

adsorption of Cu(II), when pH was below 2.0, the uptake of Cu(II) was lower than 1.5 mg/g but sharply increased to 22.6 mg/g as the initial pH was raised to 3.0. The uptake of Cu(II) reached 46.3 mg/g when the initial pH was at pH 4.6. For adsorption of Pb(II), the uptake was below 2.0 mg/g when the initial pH was below 2.0. The uptake increased to 88.7 mg/g when the initial pH was at 3.0, and then the uptake was relatively constant at this level at higher pH values. When the initial pH is below 3.0, the carboxylate groups on Wool-g-COOH are protonated and the metal ions have to compete with the protons, thus the uptake amount is low. At higher pH, carboxylate groups would be deprotonated and the surface of Wool-g-COOH became more negatively charged, which would increase its binding ability to the positively charged metal ions [34].

3.2.2. Effect of contact time

The effect of contact time on the adsorption of Cu (II) and Pb(II) ions onto Wool-g-COOH was investigated at 25°C and pH 4.0 with the initial concentration of 100 mg/L metal ions. The results are shown in Fig. 4. It is clear that the adsorption rate of metal ions by Wool-g-COOH was high during the first 30 min, then slowed down slightly and reached equilibrium at around 40 min for Cu(II) and 60 min for Pb(II). Many active sites were available for adsorption at the early stage; however, after a number of active sites were occupied by the metal ions, the adsorption process becomes difficult to continue [35]. The adsorption capacity at equilibrium is 62.52 mg/g for Cu(II) and 106.25 mg/g for Pb(II). The adsorption capacity in the sequence of Cu(II) < Pb(II) may due to the disparity in their cationic radii [36], and similar results were reported by Zou et al. [37]. To ensure the adsorption process reaches equilibrium, the contact time of the subsequent experiments was all set at 60 min.

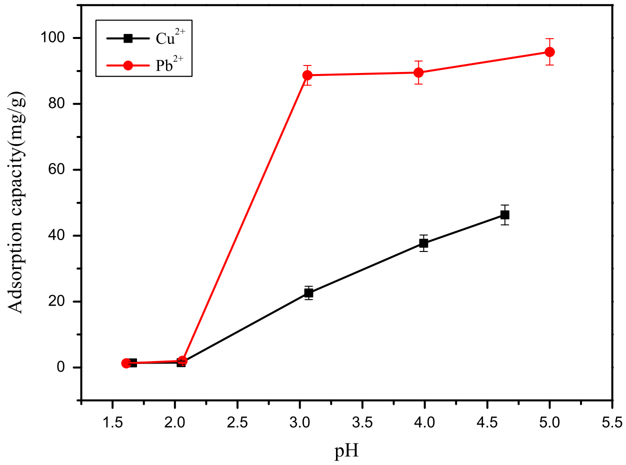

Fig. 3. Effect of pH on the adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH.

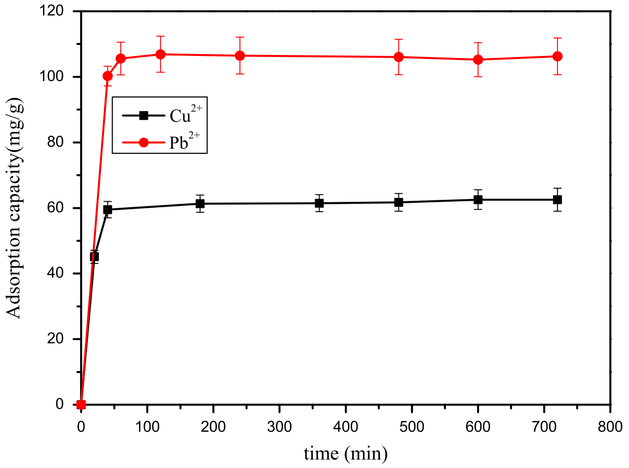

Fig. 4. Effect of contact time on the adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH.

3.2.3. Effect of initial concentration of metal ions

The effect of initial concentration of metal ions for adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH was investigated by varying the concentration from 50 to 550 mg/L for 60 min. All experiments were conducted at 25°C and pH 4.0. The results (Fig. 5) showed that the uptake amount of metal ions on Wool-g-COOH increased with increasing initial concentration of metal ions. When the initial concentration of Cu(II) ions increased from 50 to 550 mg/L, the amount of adsorption increased almost linearly from 35.65 to 79.51 mg/g. When the initial concentration of Pb(II) increased from 50 to 250 mg/L, the amount of adsorption increased sharply from 91.21 to 182.23 mg/g, then the adsorbed

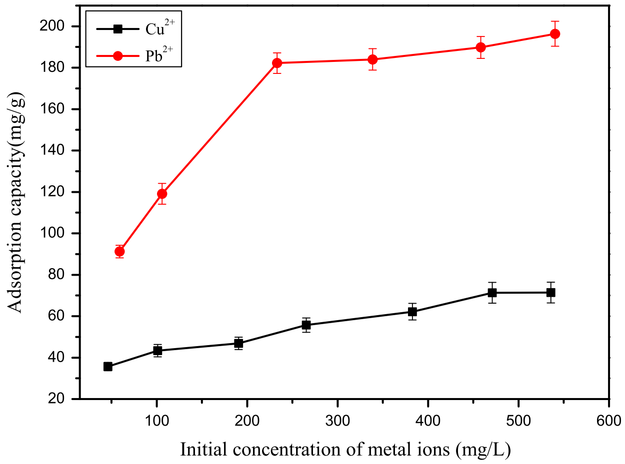

Fig. 5. Effect of initial concentration of metal ions on the adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH.

Table 1
Parameters of adsorption kinetics

	Pseudo-first-order model			Pseudo-second-order model		
Metals	k_1	q_e	R^2	k_2	q_e	R^2
Cu(II)	7.236	63.69	0.8502	0.0027	62.89	0.9999
Pb(II)	1.968	106.38	0.5454	0.0260	105.93	0.9999

amount increased slowly with increasing initial concentration, reaching upto 196.39 mg/g when the initial concentration of Pb(II) ions was at 550 mg/L.

3.3. Adsorption kinetics

Adsorption kinetics plays an essential role in understanding the mechanism of adsorption process. The adsorption data obtained at 25℃ were evaluated according to the pseudo-first-order [38,39] and pseudo-second-order [40,41], which can be described by Eqs. (3) and (4), respectively.

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where k_1 and k_2 are the adsorption rate constants of pseudo-first-order equation (min^{-1}) and pseudo-second-order equation (g/mg/min). q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t (min), respectively.

The kinetics parameters are listed in Table 1. The correlation coefficients (R^2) of pseudo-second-order kinetics for adsorbing both Cu(II) and Pb(II) ions are

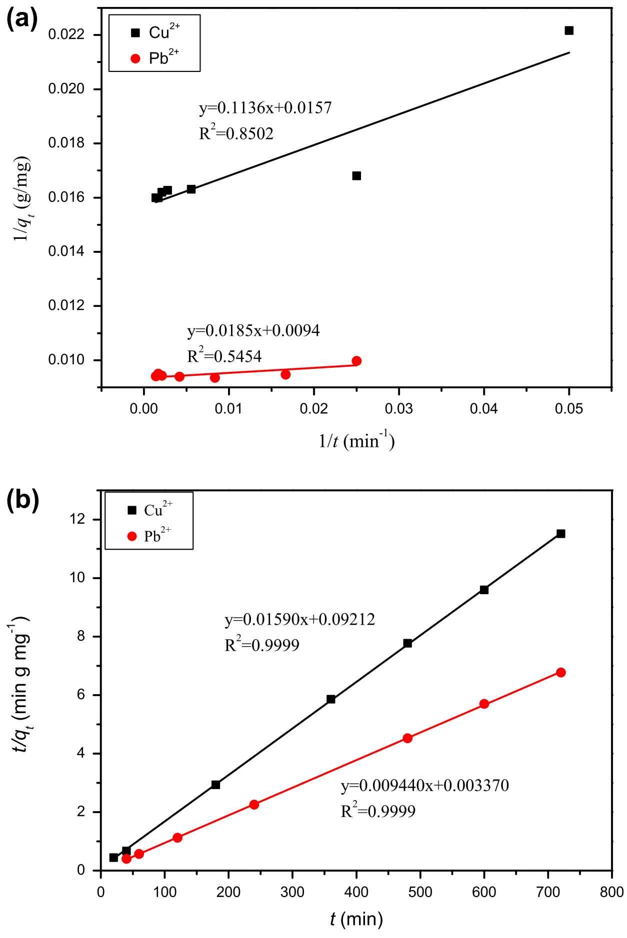

Fig. 6. The adsorption kinetic models of adsorption of Cu (II) and Pb(II) onto Wool-g-COOH. (a) Pseudo-first-order model and (b) Pseudo-second-order model.

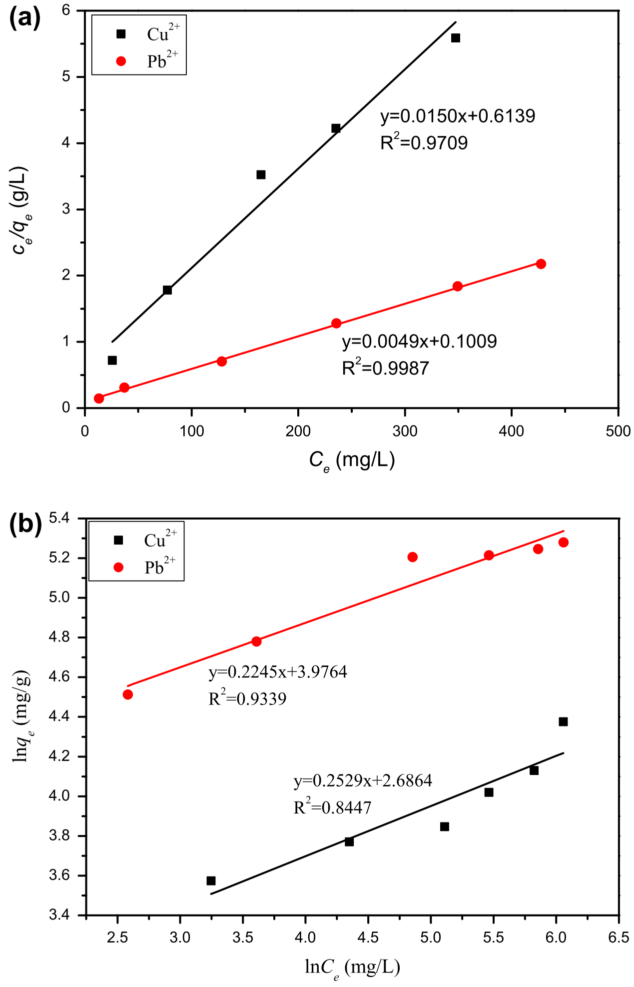

Fig. 7. The plots of adsorption isotherms: (a) Langmuir isotherm and (b) Freundlich isotherm.

Table 2
Parameters of adsorption isotherm

	Langmuir isotherm			Freundlich isotherm		
Metals	k_L(L/mg)	q_m(mg/g)	R^2	k_F(L/mg)	n	R^2
Cu(II)	0.02440	66.67	0.9709	53.32	4.454	0.8447
Pb(II)	0.04856	204.1	0.9987	14.68	3.954	0.9339

Table 3
Adsorption capacity of Cu(II) and Pb(II) by different adsorbents

Metal ions	Adsorbent	Adsorption capacity (mg/g)	References
Cu(II)	Wool-g-COOH	66.67	This work
	EDTA functionalized Fe_3O_4	46.27	[11]
	Untreated *B. Subtilis*	29.62	[46]
	Expanded perlite	8.62	[9]
	Peanut hull	21.25	[47]
Pb(II)	Wool-g-COOH	204.1	This work
	Raw maize stover	19.65	[48]
	Maize stover treated with HNO_3	27.10	[48]
	Litchi pericarp	163.93	[49]
	Data pits	30.70	[50]
	Chitosan bead	79.20	[35]
	β-MnO_2	16.72	[10]

at 0.9999, which is larger than the pseudo-first-order kinetic model. Furthermore, the amounts adsorbed at equilibrium calculated from the pseudo-second-order plots (Fig. 6(b)) were 62.89 and 105.93 mg/g for the adsorption of Cu(II) and Pb(II) ions, respectively, which were close to the experimental values of 62.52 and 106.25 mg/g. The adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH fitted well with a pseudo-second-order kinetic model indicating that the chemical adsorption process is dominant [40,41].

3.4. Adsorption isotherms

Adsorption isotherms reflect the relation of metal ions between solid phase (adsorbent) and aqueous phase which provides important parameters and better understanding on the adsorption mechanism. Langmuir model [42] and Freundlich model [43] were applied to investigate the adsorption isotherms and are shown in Eqs. (5) and (6):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{5}$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n} \tag{6}$$

where K_L is the Langmuir constant (L/mg), q_m is the maximum adsorption capacity formed monolayer on the adsorbent (mg/g). K_F (L/mg) and n are the Freundlich constants which are related to the adsorption capacity of the adsorbent and the intensity of adsorption, respectively.

The adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH fitted better to the Langmuir isotherm

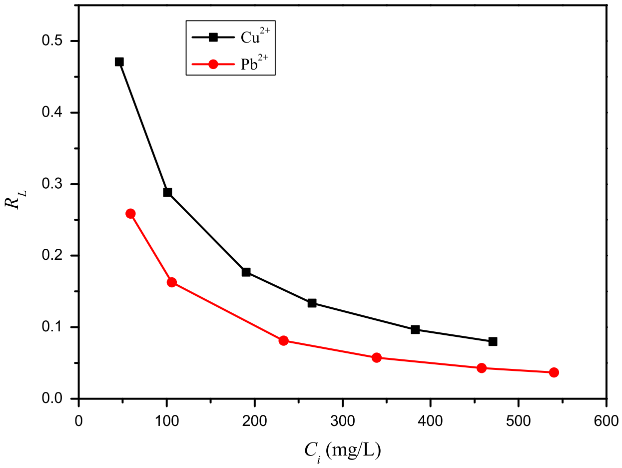

Fig. 8. The value of R_L at different concentrations of metal ions.

Table 4
The adsorption capacity on the cycle of adsorption-desorption

	Cu(II)		Pb(II)	
Adsorption time	Adsorption capacity (mg/g)	Relative rate of adsorption (%)	Adsorption capacity (mg/g)	Relative rate of adsorption (%)
1	37.68	100	89.51	100
2	33.95	90.1	85.81	95.8
3	28.81	76.4	81.25	90.8
4	27.47	72.9	79.52	88.8
5	25.04	66.4	77.41	86.5
6	22.80	60.5	75.04	83.8

model than the Freundlich isotherm model (Fig. 7). The adsorption capacity calculated using non-linear regression analysis was 66.67 and 204.1 mg/g for adsorption of Cu(II) and Pb(II) ions, respectively (Table 2), which implies that the adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH was monolayer and the surface of adsorbent was homogeneous. The adsorbed metal ions have no relation with each other on the surface of adsorbent and the adsorption equilibrium was dynamic [44]. Different adsorbents from the literature were compared in terms of adsorption capacity of Cu(II) and Pb(II) ions as shown in Table 3. The results illustrated that Wool-g-COOH is a more effective adsorbent for the removal of Cu(II) and Pb (II) ions from aqueous solutions.

A dimensionless parameter R_L [45] can predict if an adsorption system is favorable or not, which is defined in Eq. (7):

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

When the value of R_L is between 0 and 1, the adsorption process is favorable.

Fig. 8 showed that all the values of R_L were between 0 and 1, which suggest the adsorption process of Cu(II) and Pb(II) ions onto Wool-g-COOH was favorable.

3.5. Regeneration and reusability investigation

The regeneration ability is an important property of an adsorbent. As illustrated in Fig. 3, poor adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH was found when the pH was lower than 2.0, which implied that the adsorbed ions can be desorbed by an acid. The desorption of Cu(II) and Pb(II) ions onto Wool-g-COOH was performed with 0.2 M of oxalic acid solution and the degree of desorption was found to be 92.4%. The reusability of the Wool-g-COOH was evaluated in six cycles of adsorption/desorption processes. The results of adsorption capacity and the relative rate of adsorption for each time are shown in Table 4. For adsorption of Cu(II) onto Wool-g-COOH, the adsorption capacity decreased from 37.68 mg/g in the first adsorption to 22.80 mg/g in the sixth adsorption. For adsorption of Pb(II) onto Wool-g-COOH, the adsorption capacity decreased from 89.51 mg/g in the first adsorption to 75.04 mg/g in the sixth adsorption. It indicated that carboxylate functionalized wool fiber used for adsorption of Cu(II) and Pb(II) ions could be regenerated easily and showed effective reusability.

4. Conclusions

The following conclusions could be drawn according to the results obtained for the adsorption of Cu(II) and Pb(II) ions onto Wool-g-COOH:

Carboxylate groups can be introduced onto wool fiber by grafting copolymerization with acrylic acid. The obtained Wool-g-COOH can be used for the removal of Cu(II) and Pb(II) ions from aqueous solutions.

Kinetic studies showed that the experimental data for adsorbing both Cu(II) and Pb(II) ions onto Wool-g-COOH fitted well with a pseudo-second-order model. Chemical adsorption was the rate-limiting step of adsorption process.

For adsorption of both Cu(II) and Pb(II) ions onto Wool-g-COOH, the equilibrium data could be better described by the Langmuir isotherm model than the Freundlich isotherm model. In accordance with the Langmuir equation, the monolayer adsorption capacity of Wool-g-COOH was found to be 66.67 and 204.1 mg/g for Cu(II) and Pb(II) ions, respectively. The adsorption process is favorable.

The Wool-g-COOH showed good regeneration property and reusability. After recycling for six times, the adsorption capacity for Cu(II) and Pb(II) ions still remained at 60.5 and 83.8%, respectively.

Acknowledgments

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