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Studies on adsorption behavior of Pb(II) onto a thiourea-modified chitosan resin with Pb(II) as template

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ABSTRACT

In order to find an effective absorbent material based on chitosan which has good adsorption selectivity for heavy metals, we prepared thiourea-modified chitosan resin with Pb(II) as template (TMCR template). TMCR template was synthesized by using O-carboxymethylated chitosan to absorb Pb(II) ions first and then being cross-linked with a polymeric Schiff's base of thiourea/glutaraldehyde. The effects of parameters such as pH, contact time, initial concentration and temperature on the adsorption of TMCR template were studied. The result showed the maximum uptake of Pb(II) was found to be 2.02 mmol/g at pH 6.0, 25 °C. Adsorption experiments showed the TMCR template had high selectivity for Pb(II) in solution containing binary mixtures with Cu(II), Zn(II), Cd(II) and Ni(II). The experimental data also indicated that the adsorption process was exothermic spontaneous and fit well with Lagergren's pseudo-second-order model in comparison to pseudo-first-order kinetic.

1. Introduction

Water contamination by heavy metal ions is a serious environmental problem; hence, selective and quantitative separation of metal ions from waste water has drawn more and more attention in recent years. Chelating polymer resins have attracted attention as the metal selective adsorbents in the field of wastewater treatment (Senkal & Yavuz, 2007). Resins from modified chitosan have proved to be highly efficient at removing metal ions from dilute solutions (Chassary, Vincent, & Guibal, 2004; Guibal, 2004).

Because cross-linkers like glutaraldehyde (Dzul Erosa, Saucedo Medina, Navarro Mendoza, Avila Rodriguez, & Guibal, 2001; Ruiz, Sastre, & Guibal, 2000; Webster, Halling, & Grant, 2007) and epichlorohydrin (Coelho, Laus, Mangrich, de Fávere, & Laranjeira, 2007) would weaken the adsorption efficiency of chitosan, the insertion of cross-linking agent with functional groups into chitosan becomes an effective way to get resins with good adsorption capacity. Thiourea has been proved to be a good material to modify chitosan and improve its adsorption ability for many heavy metals (Birinci, Gülfen, & AydIn, 2009; Donia, Atia, & Elwakeel, 2007; Guibal, Vincent, & Mendoza, 2000; Zhou, Wang, Liu, & Huang, 2009). In former studies, we have synthesized thiourea-modified chitosan resin using O-carboxymethylated chitosan to cross-link a polymeric Schiff's base derived from thiourea and glutaraldehyde and investigated the resin's adsorption behavior. Recently, we attempt not only to enhance the adsorption ability, but also to improve the selectivity of chitosan. In that case, the thiourea-modified chitosan resin with Pb(II) as template was synthesized. The adsorption behavior of TMCR template was examined and the adsorption mechanism of TMCR template for Pb(II) in nitric solution was studied.

2. Experimental

2.1. Materials

Chitosan with 80 mesh, 96% degree of deacetylation and average-molecular weight of 6.36×10^5 was purchased from Qingdao Baicheng Biochemical Corp. (China). Thiourea, nitric acid and all the other reagents were analytical grade and distilled water used to prepare all the solution. Standard solution of Pb(II) (1000 mg/L) for ICP-OES was obtained from Beijing NCS Analytical Instruments Co. Ltd.

2.2. Preparation of TMCR template

(i) O-carboxymethylated chitosan was prepared following the method of Zhu, Chan-Park, Dai, and Li (2005). 3.0 g of O-carboxymethylated chitosan was dissolved in 50 mL distilled water and then was added to a 500 mL beaker flask containing 300 mL of Lead acetate solution (initial concentration 0.02 mol/L, pH 5.7). The beaker was shaken for 24 h at 150 rpm,

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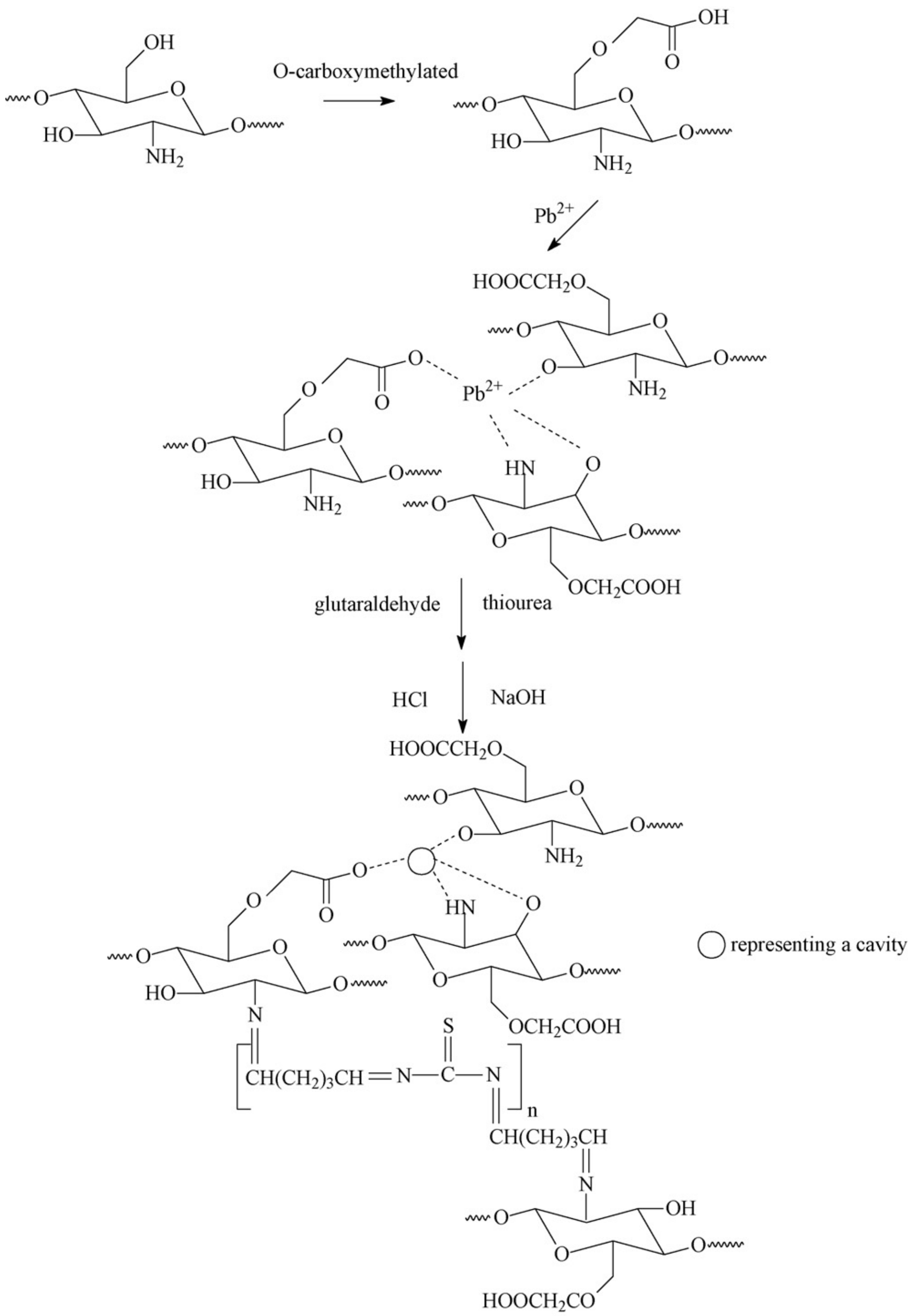

Scheme 1. Proposed procedure of synthesis of TMCR template.

25 °C. The pH of the mixture in beaker was adjusted to 6.2 by 0.1 mol/L NaOH solution and the product was filtered under reduced pressure. The filtrate was washed with distilled water until no Pb(II) ions was detected by Na_2S and then washed with ethanol and ether in turn, dried in vacuum.

(ii) 3.0 g of thiourea was dissolved in 50 mL distilled water. A 17.1 mL of (50%) glutaraldehyde solution was added to thiourea solution in a round flask. The mixture was heated on a water bath for 3 h at 50 °C. After completion of the reaction, 1.96 g of product got from step (i) was dissolved in 30 mL distilled water, and the solution was then added to the mixture of the flask and heated for 8 h at 70 °C. The resin was formed and washed with distilled water until pH 7.0. Subsequently the resin was put into a beaker containing 100 mL 0.1 mol/L HCl and stirred for 2 h at 25 °C, filtered. This process was repeated until no lead ions were detected in solution. The obtained resin was treated with 0.1 mol/L NaOH for 5 h and then washed several times with distilled water, acetone in turn. The TMCR template was obtained after dried at 60 °C for 5 h.

The preparation process was presented in Scheme 1.

2.3. Characterization of TMCR template

FTIR spectra were used to identify the structure of the TMCR template. The sample was prepared by mixing 1 mg of material with

100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Magne-Avatar 360 equipment.

2.4. Effect of pH

Uptake experiments were performed at controlled pH (1.0–7.0) and 25 °C by shaking 0.1 g of dry TMCR template with 100 mL (1×10^{-2} mol/L) lead nitrate solution for 12 h at 200 rpm. The desired pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH. After filtration, the concentration of Pb(II) in aqueous solutions was analyzed using inductively coupled plasma (ICP-OES, Thermo-Fisher).

2.5. Binary metallic system

The selective separation of Pb(II) from binary mixtures with Cu(II), Zn(II), Cd(II) and Ni(II) (the initial concentration of each metal ion was 1×10^{-2} mol/L) was carried at pH 6.0 with the same other adsorption conditions as those in Section 2.4. After adsorption equilibrium, the concentration of each metal ion in the solution was measured by ICP-OES.

2.6. Kinetics

Kinetic studies were conducted by placing 0.1 g TMCR template in a flask containing 100 mL (1×10^{-2} M) metal ion solution at pH 6.0. The contents of the flask were agitated on a shaker at 200 rpm, 25 °C. Samples of 5 mL solution were withdrawn at scheduled time intervals and analyzed for Pb(II) concentration. The concentration of Pb(II) in the aqueous solution was calculated after correction of volume.

2.7. Adsorption isotherms

0.1 g TMCR template was swelled in a series of 250 mL flasks containing 50 mL of distilled water for 1 h. In each flask, 50 mL of metal ion solution at desired concentration was added to the flask, and the pH value was 6.0. The flasks were shaken at 200 rpm while keeping the temperature at 25, 35, 45 and 55 °C for 12 h, respectively. Later on, the concentration was determined by ICP-OES and the metal ion uptake was calculated.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of chitosan, TMCR template before and after Pb(II) adsorption were recorded and presented in Fig. 1. Apparently, compared with chitosan, the spectrum of TMCR template displays new bands near 1100 and 1055 cm^{-1} corresponding to νC–O, one of the characteristics of O-carboxymethyl chitosan (Chen & Park, 2003). The bands near 1650 and 1556 cm^{-1} are assigned to νC–N of Schiff's base moiety and νC–N of thiourea moiety, respectively. Because of the overlapping of peaks of C=N, –COOH and $-COO^-$, the intensity of the broad peak around 1650 cm^{-1} became stronger. The band representative of thiourea appears at about 1400 cm^{-1}, which is assigned to >N–C=S group (Gavilan et al., 2009). Moreover, obvious changes in the spectra before and after Pb(II) sorption were observed. In the spectrum of Pb(II) adsorbed onto TMCR template, it was seen that a new peak around 1594 cm^{-1} appeared. Additionally, the broad peaks around 3330 cm^{-1}, corresponding to the stretching vibration of $-NH_2$ and –OH groups, narrowed significantly. The bands at 2921 cm^{-1} strengthened. The intensity of the band at 1361 cm^{-1} was substantially decreased after Pb(II) binding. This result confirms that sulfur groups were involved in metal binding.

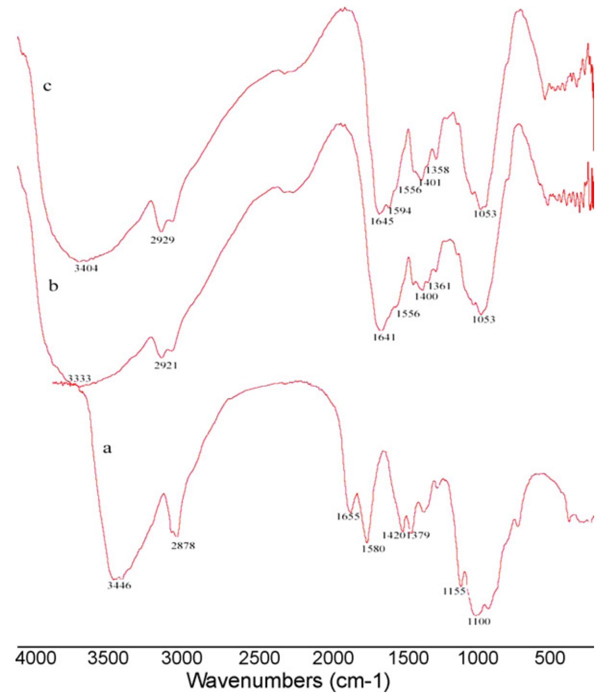

Fig. 1. IR-Spectra of chitosan (a), TMCR template before (b) and after (c) Pb(II) adsorption.

3.2. Effect of pH on the uptake of Pb(II)

As shown in Fig. 2, the adsorption of Pb(II) increased as pH value increased when pH <6.0. At lower pH, the decreased adsorption of Pb(II) may be attributed to the partial protonation of the active groups and the weaker electrostatic repulsion between the Pb(II) cations and protonated amino and carboxymethyl groups of TMCR template. With the increase of pH value, the adsorption process was mainly controlled by chelation mechanism and the adsorption capacity increased. The maximum adsorption for Pb(II) ions on TMCR template in nitric solution appears at the pH 6.0, which exhibits similar trend with TMCR. In addition, the uptake for Pb(II) ions of TMCR template was always greater than that of TMCR, which further indicated that the formation of three dimensional structure is favorable for Pb(II) adsorption. In the higher pH range, existing of counter ions might result in lower efficiency

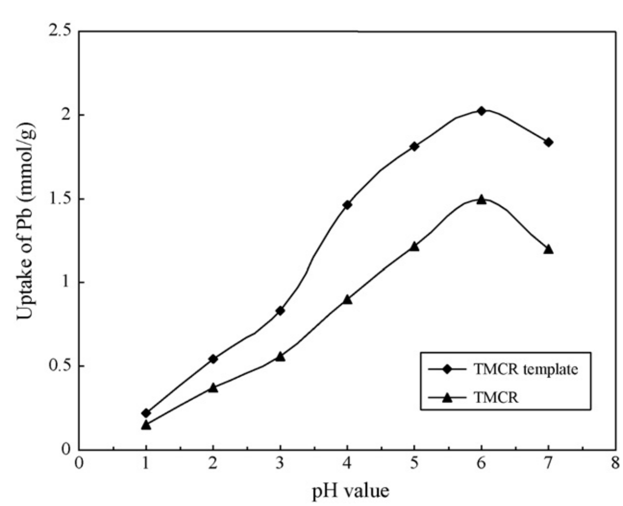

Fig. 2. Effect of pH on adsorption.

Table 1
Parameters of the pseudo-first-order and pseudo-second-order kinetic models for adsorption of Pb(II) by TMCR template.

Metal ion	Pseudo-first order			Pseudo-second order		
	k_1 (min^{-1})	q_e (mmol/g)	R^2	k_2 (g/mmolmin)	q_e (mmol/g)	R^2
Pb(II)	0.009	1.440	0.971	0.0086	2.305	0.995

of adsorption and also precipitation of Pb(II) ions could occur at higher pH.

3.3. Kinetic studies

As shown in Fig. 3, it can be observed that the adsorption of Pb(II) could achieve equilibrium within 6 h and the maximum adsorption capacity reached 2.02 mmol/g. The reaction kinetic parameters for the adsorption process were studied by batch method. The pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho & McKay, 2000) were applied for predicting the adsorption kinetic process in this study.

The Lagergren pseudo-first-order kinetic model is represented as:

$$\log(q_e - q_t) = \log \ q_e - (\frac{k_l}{2.303})t \quad (1)$$

where k_1 is the pseudo-first-order rate constant (h^{-1}) of adsorption, q_e and q_t (mmol/g) are the amounts of metal ion adsorbed at equilibrium and time t (h), respectively. The q_e and k_1 were calculated by plotting the log $(q_e - q_t)$ versus t.

The pseudo-second-order model can be written as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \left(\frac{1}{q_e}\right) t \quad (2)$$

where k_2 is the pseudo-second-order rate constant of adsorption (g/(mmol h^{-1})). The kinetic parameters for pseudo-second-order model are determined from the linear plots of (t/q_t) versus t.

The kinetic models for Pb(II) adsorption were shown in Figs. 4 and 5. The parameter values obtained from the application of kinetic models were presented in Table 1. According to Fig. 4, Fig. 5 and Table 1, although the first-order model provides a good fitting to the experimental data, the less relative errors and higher correlation coefficient of the second-order model indicated that the second-order model could better describe the adsorption of Pb(II) on TMCR template. This suggests that the rate-limiting step may be intra-particle diffusion. Moreover, compared to the experimental data in Fig. 3, the calculated q_e values from the pseudo-second-order equation are in good agreement with experimental

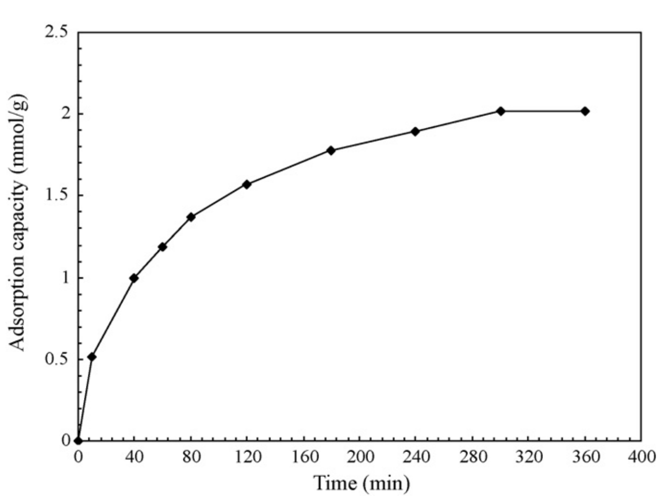

Fig. 3. Effect of adsorption time on the uptake of Pb(II) by TMCR template.

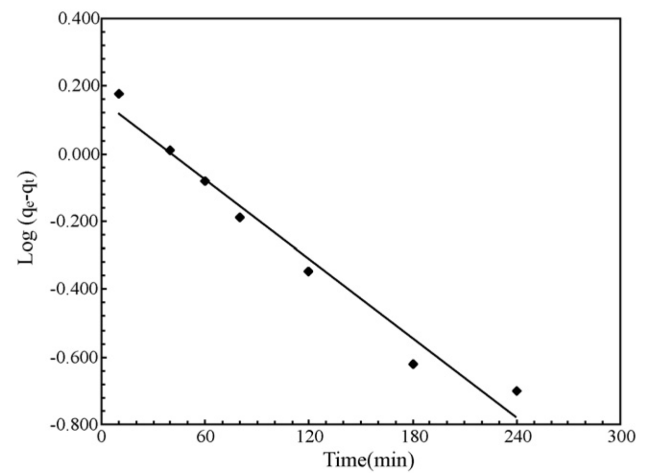

Fig. 4. Pseudo-first-order kinetic plots for the adsorption of Pb(II) onto TMCR template.

q_e value, demonstrating the validity of pseudo-second-order model.

3.4. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents, which are critical in optimizing the practical use of adsorbents. Fig. 6 shows the isotherms of adsorption of Pb(II) onto TMCR template. From the experimental data plotted, the adsorption capacity decreased with increasing temperature, which, indicated that the adsorption process was exothermic. To examine the relationship between sorption and aqueous concentration at equilibrium, the Langmuir and Freundlich isotherm models were used.

The Langmuir model is based on the assumption that all adsorption sites are equivalent and adsorption in an active site is independent of whether the adjacent sites are occupied or not.

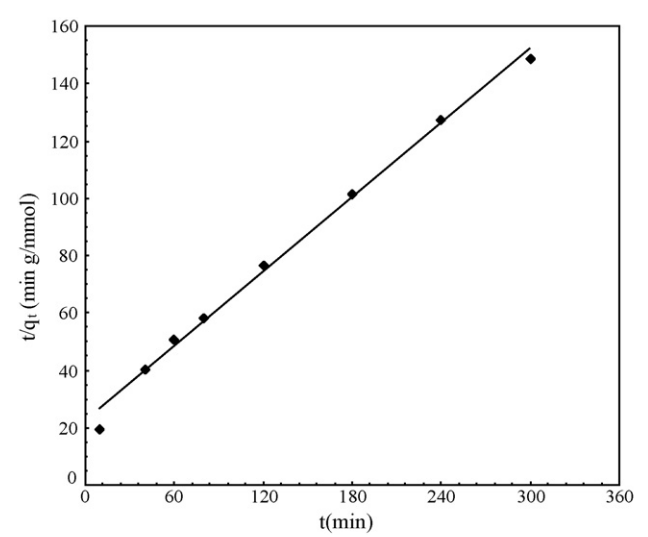

Fig. 5. Pseudo-second-order kinetic plots for the adsorption of Pb(II) onto TMCR template.

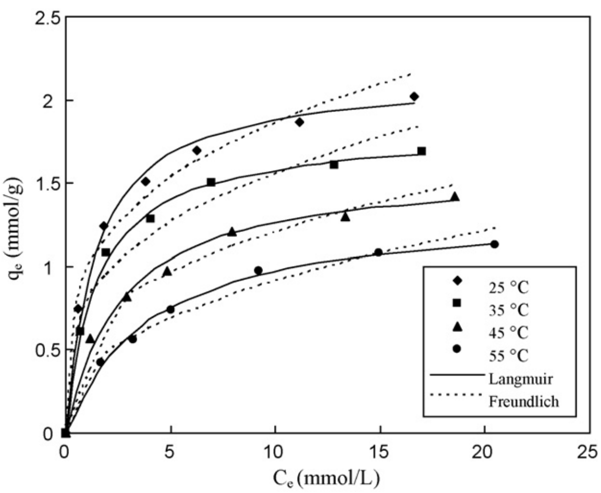

Fig. 6. Adsorption isotherms of Pb(II) by TMCR template.

The Langmuir equation (Langmuir, 1917) can be presented as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

In this model, q_e is the amount of Pb(II) adsorbed (mmol/g) at equilibrium; C_e is the concentration of Pb(II) at equilibrium; K_L represents the Langmuir constant (L/mmol) which relates to the affinity of binding sites and $q_{\max}$ is the theoretical saturation adsorption capacity of the monolayer (mmol/g). The values of K_L and $q_{\max}$ at different temperatures for adsorption of Pb(II) were reported in Table 2. It is seen that the value of $q_{\max}$ at 25 °C is consistent with that experimentally obtained, indicating that the adsorption process was mainly monolayer.

For Langmuir model, to determine if the sorption is favorable or not, a dimensionless separation factor is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L (L/mmol) is the Langmuir equilibrium constant and C_0 (mmol/L) is the initial concentration of metal ion. If $R_L > 1.0$, the isotherm is unsuitable; $R_L = 1.0$, the isotherm is linear; $0 < R_L < 1.0$, the isotherm is suitable; $R_L = 0$, the isotherm is irreversible. The values of R_L in this study lie in the range of 0.124 and 0.334, confirming the suitability of TMCR template for the adsorption of Pb(II).

The Freundlich model (Freundlich, 1906) is expressed as:

$$q_e = K_F C_e^{1/n} \quad (5)$$

In this model, K_F is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity. K_F and n can be calculated from the slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$.

Table 2
Parameters of Langmuir and Freundlich isotherms.

Temperature (°C)	Langmuir model		
	$q_{\max}$ (mmol/g)	K_L (L/mmol)	R^2
25	2.15	0.707	0.9978
35	1.82	0.663	0.9993
45	1.59	0.383	0.9962
55	1.37	0.244	0.9978

Temperature (°C)	Freundlich model		
	k_f	n	R^2
25	0.965	3.490	0.9629
35	0.772	3.254	0.9218
45	0.567	3.031	0.9815
55	0.357	2.444	0.9719

Table 3
Thermodynamic parameters for adsorption of Pb(II) on TMCR template at different temperatures.

Temperature (°C)	ΔG° (kJ/mol)	$T\Delta S^\circ$ (kJ/mol)
25	−28.82	−1.36
35	−28.78	−1.40
45	−28.73	−1.45
55	−28.68	−1.50

The model constants of both Langmuir and Freundlich along with correlation coefficient (R^2) values are listed in Table 2. The R^2 values indicate that the Langmuir model fit the experimental data better than the Freundlich model, which predicts the monolayer coverage of Pb(II) on TMCR template.

In addition, the obvious decrease in both values of $q_{\max}$ and K_L with elevated temperature indicates the exothermic property of the adsorption process. The values of K_L at different temperatures were treated according to van't Hoff equation (Tellinghuisen, 2006):

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

where ΔH° and ΔS° are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in Kelvin). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively.

Gibbs free energy of adsorption (ΔG°) was calculated from the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

The values of ΔH°, ΔS° and ΔG° were reported in Table 3. The negative values of ΔH° indicate the exothermic nature of adsorption process and the negative value of ΔG° confirms that the adsorption reaction is spontaneous. The observed decrease in negative values of ΔG° with increasing temperature implies that the adsorption becomes less favorable at higher temperature (Tahir & Rauf, 2003).

3.5. Binary metallic system

The uptake obtained for Pb(II) in the presence of Cu(II), Zn(II), Cd(II) and Ni(II) in solution was 1.56, 0.10, 0.24, 0.15 and 0.30 mmol/g, respectively. This data indicated that the TMCR template was effective in selective separation of Pb(II) from other metal ions in aqueous solution .

3.6. Desorption cycles

Pb(II)-loaded TMCR template were collected and washed with deionized water to remove any unabsorbed metal ions. Then batch desorption experiments were carried out using 2.0 M $H_2SO_4^-$ 0.5 M thiourea solution. The TMCR template after desorption was reused in adsorption experiment, and the process was repeated for five times. The elution efficiency was found to be >97% and the result showed that there were no obvious changes on adsorption capacity of TMCR template (<10%), which, indicated that the resin had good reusability.

4. Conclusions

In this study, the capacity of a thiourea-modified chitosan resin with Pb(II) as template to adsorb Pb(II) ions from aqueous medium was examined, including equilibrium and kinetic studies. The adsorption process could be best described by pseudo-second-order kinetic model. In addition, The adsorption for Pb(II) was exothermic and proceeded according to Langmuir isotherm. Compared to TMCR, the adsorption capacity and selectivity were improved evidently. It was also found that the TMCR template can be easily regenerated and efficiently reused.

Acknowledgements

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