Microwave Preparation and Properties of O-Crosslinked Maleic Acyl Chitosan Adsorbent for Pb^{2+} and Cu^{2+}

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ABSTRACT: A novel chitosan-based adsorbent (CCTM) was prepared by the reaction of epichlorohydrin O-crosslinked chitosan with maleic anhydride under microwave irradiation. The chemical structure of this polymer was characterized by infrared spectroscopy and X-ray diffraction analyses. The effects of various variables such as degree of substitution, adsorption time, initial metal ion concentration, solution pH, and temperature, on the adsorption of Pb^{2+} and Cu^{2+} by CCTM were investigated. The results demonstrate that the microwave irradiation can remarkably enhance the reaction. CCTM has higher adsorption capacity than chitosan. The maximum adsorption capacities for Pb^{2+} and Cu^{2+}, with initial concentrations of 0.02 mol L^{-1} at pH 5, are 246.3 and 132.5 mg g^{-1}, respectively. The adsorbent can be recycled. These results have important implications for the design of effective chitosan-based adsorbents in the removal of heavy metal ions from wastewaters. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2716–2723, 2012

Key words: modified chitosan; maleic anhydride; microwave irradiation; heavy metal ions; adsorption

INTRODUCTION

Contamination of water by heavy metals has been attracting great attention because of their toxicity toward human beings and the environment. Lead and copper are the widely used heavy metals and their ions present in industrial and municipal wastewaters. Even at extremely low concentrations, lead can cause brain damage in children.[1] The copper (ion) is one of the essential trace elements for the human body. However, the excessive intake of copper may result in vomit, cramps, convulsion, and even death.[2] Therefore, it is of great practical interest to explore ways to effectively remove these heavy metal ions from the wastewaters before their discharge.

Several technologies have been developed for the removal of heavy metal ions from the wastewaters, such as chemical precipitation, coagulation, membrane separation, ion exchange, electro deposition, and adsorption.[3,4] Of these, adsorption is considered an effective and extensively used method. Many biosorbents such as chitosan and modified chitosan have been used to remove heavy metal ions from the wastewaters.[4–6] Chitosan is a biocompatible polysaccharide obtained from deacetylation of chitin.

It can chemically or physically entrap various metal ions due to the presence of amine and hydroxyl groups that can serve as the chelating and reaction sites.[5,6] However, it is difficult to directly apply the raw chitosan for removal of metal ions because of its disadvantage such as swelling, solubility in acidic conditions, and unsatisfying mechanical property.[7] To overcome these problems, chitosan must be chemically modified with different crosslinking reagents such as glutaraldehyde and epichorohydrin.[7–9] However, the adsorption capacity of crosslinked chitosan would be largely reduced due to consumption of amino groups and hydroxyl groups after chemical modification.[10] Hence, the crosslinked chitosan must be further modified to improve the adsorption performance by grafting new functional groups.[11,12]

Recently, microwave chemistry has received much attention due to higher conversion, shorter reaction times, and lower energy consumption under microwave irradiation than those of conventional heating.[13–15] Therefore, microwave irradiation as a means of chemical reaction has been widely applied in various synthetic fields of chemistry such as organic synthesis, polymer synthesis, and so on.[14–17] In the previous work, we prepared a novel chitosan-based adsorbent (CCTE) by the reaction of epichlorohydrin O-crosslinked chitosan with EDTA dianhydride under microwave irradiation.[18] In this article, we will prepare another new chitosan-based adsorbent (CCTM) by the reaction of epichlorohydrin O-crosslinked chitosan with maleic anhydride under microwave irradiation. The objective of this study is to
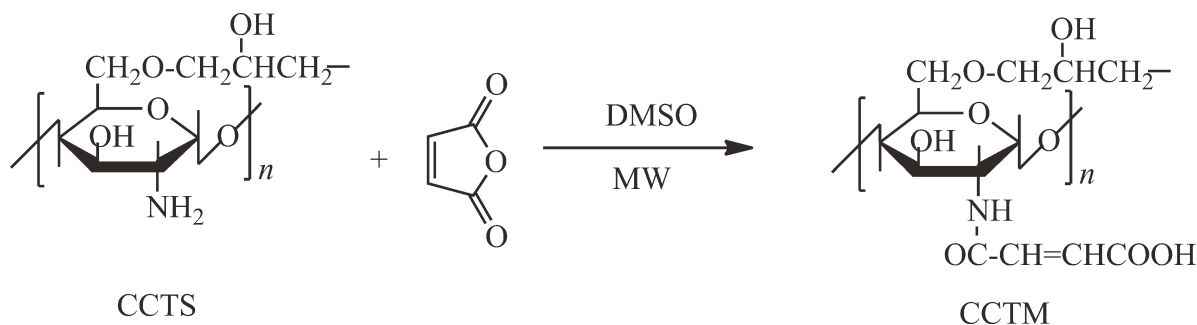
Figure 1 The reaction scheme for the preparation of CCTM.

prepare an efficient modified chitosan adsorbent for the removal of metal ions from wastewaters. The maleic anhydride is much cheaper than EDTA dianhydride and the carboxyl groups of maleic anhydride residues could significantly enhance the adsorption ability of the modified chitosan which are similar to those of EDTA dianhydride residues.[18] Therefore, this derivative of chitosan may be possible to show its promising application in effluents treatment.

MATERIALS AND METHODS

Materials and apparatus

Chitosan (degree of deacetylation: 85%, viscosity-average molar mass: 500,000) was purchased from Qingdao Lizhong chitin factory (Qingdao, China). The chosen metal salts, $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$, were analytical-grade reagents obtained from Guangzhou Chemical Reagent Co. (Guangzhou, China). All other reagents and solvents were used on analytical grade without further purification. All solutions were prepared with distilled deionized water.

A Galanz microwave oven (WP700L17) produced by Shunde Galanz Electric Appliance Factory, China, was employed and the temperature of microwave reaction system could be controlled in these studies after modification.[14,17] Measurements of solution pH were performed on a pH meter (PHS-25) produced by Shanghai Weiye Instrument company, China.

Preparation of CCTM

A schematic representation for the preparation of O-crosslinked maleic acyl chitosan (CCTM) is illustrated in Figure 1. The O-crosslinked chitosan (CCTS) was synthesized according to the procedure described by Ge and Huang.[18] Maleic anhydride (2 g) was dissolved in 60 mL of dimethyl sulfoxide. Then, CCTS (1.35 g) was added into the solution, and the mixture was agitated at 70°C under microwave irradiation for some time. The solid product was filtered and successively washed with water, ethanol, acetone, and dried in vacuum. Light yellow powder (CCTM) was obtained.

For purposes of comparison with the microwave method, the traditional heating method was also done. All other steps were the same as mentioned above except that the reaction was carried out in a thermostated water bath and the reaction time was 4 h.

Degree of substitution

Degree of substitution (DS) of the product was estimated from potentiometric titration.[19,20] Products were swelled in 0.1 mol L^{-1} hydrochloric acid (50 mL) in the presence of 0.1 mol L^{-1} sodium chloride and titrated with 0.1 mol L^{-1} sodium hydroxide. The alkalimetric curves were recorded on a PHS-25 pH meter.

Characterization

FTIR spectra of the solid products were recorded on a Fourier transform infrared spectrometer (Teser 27, Bruker, Germany) using KBr pellets. X-ray diffraction patterns (XRD) were determined with a diffractometer (D/max-IIIA, Rigaku, Japan).

Adsorption experiment

Aqueous solutions of metal ions were prepared from $Pb(NO_3)_2$ or $CuSO_4 \cdot 5H_2O$. About 0.1 g of chitosan or CCTM was added into a reagent bottle containing 25 mL of metal ion solution (0.02 mol L^{-1}). The pH of the solution was adjusted to the desired value (5 except the effect of pH) with 0.1 mol L^{-1} hydrochloric acid or an acetate buffer solution. The mixture was stirred at room temperature (about 303 K) for 8 h, and then the mixture was filtered. The concentrations of the metal ions in the original solution and in the filtrate were determined by the titration with 0.01 mol L^{-1} EDTA solution.[15] The amounts of adsorbed metal ions were calculated as follows:

$$q = (c_0 - c)VM/m \qquad (1)$$

where q is the adsorption capacity of adsorbent (mg g^{-1}), c_0 and c are the concentrations of metal ion before and after adsorption (mol L^{-1}), V is the volume of solution (mL), M is the molar mass of metal ion (g mol^{-1}), and m is the mass of adsorbent (g).

Adsorption kinetics was obtained by determining the adsorption capacity at different time intervals at pH 5.

Adsorption isotherms and effect of temperature

The isothermal studies were conducted by placing 0.1 g CCTM in a series of flasks containing 50 mL of metal ions at definite concentrations (0.005–0.025 mol L^{-1}) and pH 5. The flasks were agitated for 8 h at 303 K. After adsorption, the solution was filtered and the residual concentration of the metal ion was determined.

Effect of temperature was obtained by determining the adsorption capacity of CCTM at metal ion concentration of 0.025 mol L^{-1} and pH 5 at the definite temperature (288–338 K).

Desorption of metal ions and reuse of the adsorbent

CCTM adsorbed Cu^{2+} was agitated in 20 mL of 2.0 mol L^{-1} hydrochloric acid solution at room temperature for 8 h, and CCTM adsorbed Pb^{2+} was stirred in 20 mL of 1.0 mol L^{-1} thiourea and 2.0 mol L^{-1} hydrochloric acid mixture solution at room temperature for 8 h. Following filtration, the residual concentration of metal ion was determined. The CCTM after desorption was reused in adsorption experiment, and the process was repeated for five cycles. The desorption efficiency of metal ion and the retention rate of adsorption capacity were calculated and defined as

$$\text{Desorption efficiency} = \frac{\text{desorbed mount of metal ion}}{\text{adsorbed mount of metal ion}} \times 100\% \quad (2)$$

$$\text{Retention rate} = \frac{\text{adsorbed mount in the } i\text{th cycle}}{\text{adsorbed mount in the first cycle}} \times 100\% \quad (3)$$

RESULTS AND DISCUSSION

Characterization of chitosan and modified chitosan

Figure 2 displays FTIR spectra of chitosan, CCTS, and CCTM. The major peaks for chitosan can be assigned as follows: 3415 cm^{-1} (O—H and N—H stretch), 1662 and 1558 cm^{-1} (amide band), 1598 cm^{-1}(NH$_2$ bending), 1075 cm^{-1} (C—O stretch), and 900 cm^{-1} (pyranoid ring stretch).[21] The spectrum for CCTS however shows a few major changes. The C—O stretch at 1075 cm^{-1} shifts to 1066 cm^{-1} and the peak intensity increases significantly. These indicate that the epichlorohydrin in CCTS is crosslinked at the OH groups of chitosan. The disappearance of
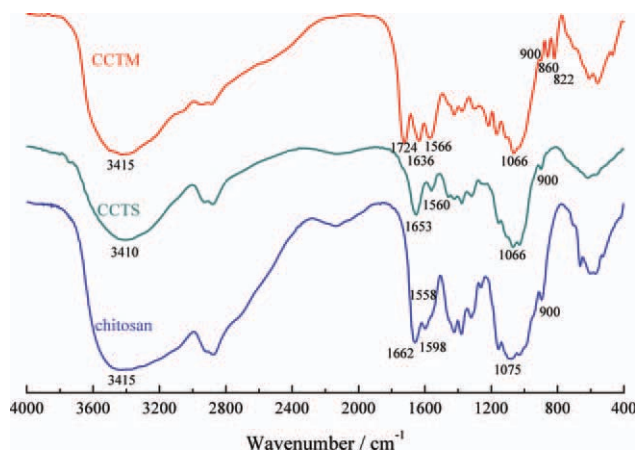

Figure 2 FTIR spectra of chitosan, CCTS, and CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the peak at 1598 cm^{-1} may be attributed to the fact that O-crosslinked structure of chitosan hinders the NH$_2$ bending. By comparing the spectrum of CCTM with CCTS, a new and strong peak at 1724 cm^{-1} appears in CCTM and it can be assigned to the stretching vibration of C=O in the carboxyl groups of reacted maleic anhydride.[22] The new peaks at 860 and 822 cm^{-1} correspond to the out-of-plane bending vibration of C—H from the olefin group of reacted maleic anhydride. The peak at 1636 cm^{-1} may be related to the C=O stretch of amide groups and C=C stretch of maleic groups.[23] Furthermore, the peak at 1566 cm^{-1} (amide II) is greatly enhanced. The above analyses clearly indicate that the amino groups of CCTS are involved in the reaction with maleic anhydride.

The change of chitosan structure before and after chemical modification was investigated by means of powder XRD. Figure 3 depicts XRD patterns of chitosan and CCTM. The XRD pattern of chitosan represents the distinct crystalline peaks at $2\theta = 10°$ and $20°$.This is because plenty of hydroxyl and amino groups of the chitosan structure could form stronger intermolecular and intramolecular hydrogen bonds. In addition, the structure of chitosan molecules has certain regularity. As a result, chitosan molecules could form crystalline regions very easily.[24] However, as regards CCTM, the characteristic peaks at $2\theta = 10°$ and $20°$ disappear, and a weak and wide peak at $2\theta = 27°$ appears. The decrease in crystallinity of CCTM should be attributed to the deformation of the strong hydrogen bond in original chitosan due to the substitution of hydroxyl and amino groups by epichlorohydrin and maleic acyl groups. This implies that the modified chitosan is substantially more amorphous than chitosan. This might be very favorable for improving the adsorption capacities of CCTM for metal ions.
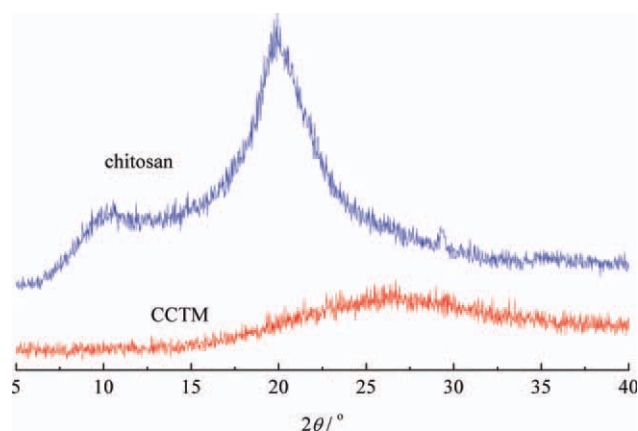
Figure 3 XRD patterns of chitosan and CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of the substitution degree

The relationship between DS and the reaction time is given in Table I. The DS value is increased with microwave reaction time. Under the traditional heating conditions, the DS value of 0.4 is achieved after 240 min reaction time. With the use of microwave radiation, however, the same DS value is reached after about 20 min reaction time. Therefore, the microwave reaction is about 12 times faster than the traditional.

The adsorption capacities of Pb^{2+} and Cu^{2+} on CCTM are also shown in Table I. The adsorption capacity increases with the increase of the microwave time or DS. This is because more carboxyl groups in CCTM form more coordination sites to chelate with metal ions. Several studies have also reported that the introduction of carboxyl groups into chitosan backbone gives rise to enhancement of adsorption capacity toward metal ions.[18,25] However, the adsorption capacity increases indistinctively beyond the DS value 0.445 or after microwave time 25 min. Therefore, the optimum microwave time is 25 min and the microwave product of this time will be only discussed in the following sections.

From Table I, it can be seen that the adsorption capacity of the (25 min) microwave product is higher than that of the traditional. This is because the microwave product has higher DS value than the traditional. In addition, the adsorption capacities of raw chitosan and CCTE are given in Table I. Evidently, the adsorption capacity of Pb^{2+} on the microwave product is significantly improved and that of Cu^{2+} is slightly increased in comparison with chitosan. Furthermore, CCTM has comparable capacities for Pb^{2+} and Cu^{2+} with CCTE. Therefore, the CCTM prepared by the microwave method should be an effective and low-cost modified chitosan adsorbent for heavy metals.

Effect of pH

Figure 4 exhibits the relationship between the pH value of metal ion solution and the adsorption capacity of CCTM for Pb^{2+} and Cu^{2+}. The experiments were conducted in the pH ranges of 2.0–6.0. The influences of pH>6.0 were not studied to avoid the formation of precipitate. From Figure 4, it can be observed that the pH value of the solution affects the adsorption performance of this adsorbent. The adsorption uptake of CCTM for metal ions increases with the increase of the pH value till a maximum value at pH 5, and then decreases with further increase of pH. A similar effect of pH on the modified chitosan adsorbent was also observed.[18] Low pH favors the protonation of NH_2 and COO^- groups in CCTM and the protonated groups are difficult to form complexes with metal ions. Therefore, the metal uptake increases as pH increases. However, when the pH increases too higher, the hydrolysis of metal ion might lead to reduction in the adsorption capacity. Thus, it can be concluded that the adsorption capacity of CCTM for metal ions has a maximum value at pH 5.

Adsorption kinetics

Adsorption kinetics is an important parameter for the evaluation of a good sorbent. The adsorption capacity of CCTM for Pb^{2+} and Cu^{2+} as a function of time is shown in Figure 5. It can be seen from Figure 5 that metal ions uptake on CCTM is a fast process. The amount of adsorption increases rapidly in the first 40 min, contributing to 75% or 86% of the ultimate adsorption amount for Pb^{2+} or Cu^{2+}, and

TABLE I
Adsorption Capacity (q_e) and DS of CCTM

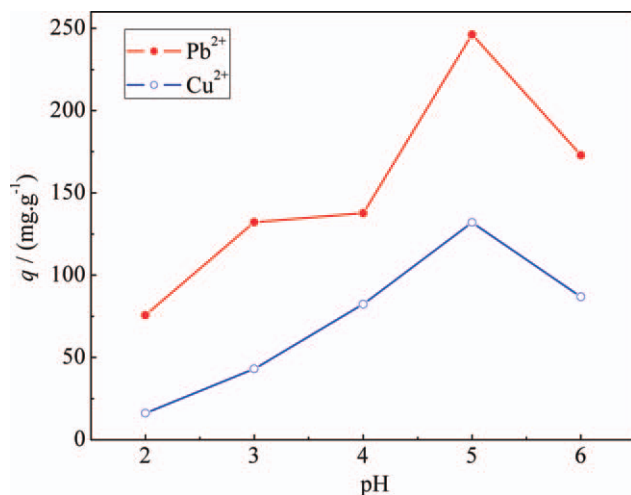| Method	Microwave				Traditional	CCTE[a]	Chitosan
Reaction time (min)	5	15	25	35	240		
DS	0.224	0.356	0.445	0.549	0.400	0.417	
q_e (mg g^{-1})							
Pb^{2+}	116.4	179.0	246.3	259.9	194.9	265.2	77.0
Cu^{2+}	61.91	95.30	132.5	148.3	98.70	135.4	125.1

[a] Calculated from Ge et al.[18]

Figure 4 Effect of pH on adsorption of Pb^{2+} and Cu^{2+} by CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

then augments gradually. Under our experimental conditions, the adsorption equilibrium was achieved within about 3 h for Pb^{2+} or about 1.5 h for Cu^{2+}. Hence, the adsorption of CCTM for Pb^{2+} is slower than for Cu^{2+}.

In order to examine the kinetic mechanism controlling the adsorption of Pb^{2+} and Cu^{2+} on CCTM, the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were used to interpret the experimental data.[26] The linear form of pseudo-first-order equation is represented by

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where k_1 is the pseudo-first-order adsorption rate constant (min^{-1}), q_t is the amount adsorbed at time t (min), and q_e denotes the amount adsorbed at equilibrium, both in units of mg g^{-1}. The values of k_1 and q_e (namely q_e^{cal}) are calculated from the slope and intercept of the plot of $\ln(q_e^{exp} - q_t)$ versus t, and q_e^{exp} is the experimental value of q_e. The linear form of pseudo-second-order equation may be described by

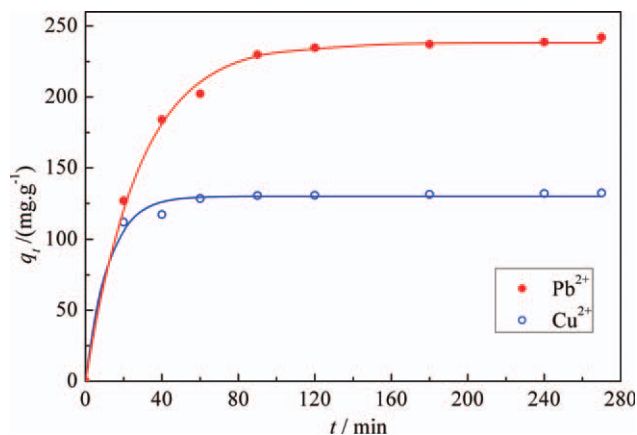$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

Figure 5 Adsorption kinetics of Pb^{2+} and Cu^{2+} onto CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where k_2 is the adsorption rate constant of pseudo-second-order (g mg^{-1} min^{-1}). The values of k_2 and q_e can be obtained from the linear plot of t/q_t versus t. The intraparticle diffusion kinetics model may be formulated as

$$q_t = k_i t^{1/2} + C \tag{6}$$

where k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$) and C is a constant (mg g^{-1}). The values of k_i and C are obtained by the linear fitness of q_t against $t^{1/2}$.

The linear fit results of the parameters and the correlation coefficients (R^2) for three kinetics models are listed in Table II. The validity of each model could be checked by the R^2 values. It can be seen clearly from Table II that the adsorption of Pb^{2+} and Cu^{2+} on CCTM perfectly fit pseudo-second-order model rather than other ones. Furthermore, the experimental and theoretical values of q_e (obtained from pseudo-second-order model) are closely similar, confirming the validity of that model to the adsorption system under consideration. These indicate that the adsorption of Pb^{2+} and Cu^{2+} on CCTM mainly is chemical adsorption.[27]

In many cases, the pseudo-second-order kinetic model could give the better results on the adsorption of Cr and Cu ions on chitosan,[28] Cu, Cd, and Ni ions on chemically modified chitosan.[29]

TABLE II
Parameters of Kinetic Models of Ions Adsorption onto CCTM

	Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion		
Ion	q_e^{exp} (mg g^{-1})[a]	q_e^{cal} (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	k_i (mg g^{-1} min$^{-1/2}$)	C (mg g^{-1})	R^2
Pb^{2+}	246.3	113.4	0.01317	0.863	256.7	2.524×10^{-4}	0.999	13.13	65.39	0.775
Cu^{2+}	132.5	34.04	0.02088	0.881	134.4	1.914×10^{-3}	1.000	6.022	56.27	0.567

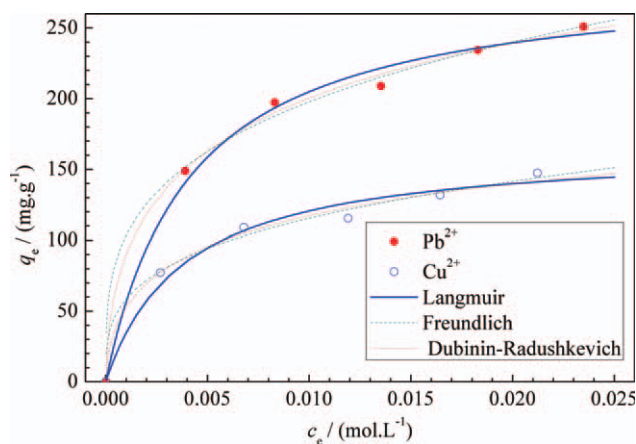[a] The experimental values from Table I.

Figure 6 Adsorption isotherms of Pb^{2+} and Cu^{2+} on CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Adsorption equilibria of Pb^{2+} and Cu^{2+}

Adsorption isotherm is critical to evaluate the sorption capacity of CCTM as well as understand the adsorbate–adsorbent interactions. Figure 6 shows the adsorption amount of Pb^{2+} and Cu^{2+} on the CCTM at different equilibrium concentrations. Langmuir, Freundlich, and Dubinin-Radushkevich models were employed to explain the experimental data.[8]

The Langmuir and Freundlich isotherms are expressed respectively as

$$q_e = \frac{q_m b c_e}{1 + b c_e} \tag{7}$$

$$q_e = K_F c_e^{b_F} \tag{8}$$

and their linear forms can be represented as

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b} \tag{9}$$

$$\ln q_e = b_F \ln c_e + \ln K_F \tag{10}$$

where q_e is the equilibrium amount of metal ion adsorbed (mg g^{-1}), c_e is the equilibrium concentration of metal ion (mol L^{-1}), q_m is the maximum adsorption capacity of metal ion (mg g^{-1}), b is the Langmuir adsorption equilibrium constant (mol L^{-1}), K_F is a constant representing the sorption capacity (mg g^{-1}), and b_F is a constant depicting the

sorption intensity. The Langmuir constants, q_m and b, can be calculated from the linear fit of c_e/q_e versus c_e. The Freundlich constants, K_F and b_F, can be obtained from the linear fit of $\ln q_e$ versus $\ln c_e$.

The linear form of the Dubinin-Radushkevich (D–R) isotherm is expressed as

$$\ln q_e = K\varepsilon^2 + \ln q_{DR} \tag{11}$$

$$\varepsilon = RT\ln(1 + 1/c_e) \tag{12}$$

where q_{DR} is the maximum adsorption capacity of metal ions (mg g^{-1}), K is the Dubinin-Radushkevich constant (mol^2 kJ^{-2}), ε is Polanyi potential (kJ mol^{-1}), R is the gas constant (J K^{-1} mol^{-1}), T is the absolute temperature (K), q_e and c_e are the same as mentioned above. The K and q_{DR} values can be obtained from the linear plot of $\ln q_e$ against ε^2. The Dubinin-Radushkevich constant K can be used to evaluate the mean energy of adsorption by

$$E = (-2K)^{-1/2} \tag{13}$$

where E is the mean adsorption energy (kJ mol^{-1}).

As can be seen from the isotherms in Figure 6 and the R^2 values in Table III, the Langmuir model shows better fit compared to the Freundlich and Dubinin-Radushkevich models. The maximum adsorption capacities (q_m) of Pb^{2+} and Cu^{2+} from the Langmuir isotherm equation are 288.1 and 166.4 mg g^{-1}, respectively. However, the Langmuir adsorption equilibrium constant (b) of Pb^{2+} is smaller than that of Cu^{2+}. Because the Langmuir equation is derived from the assumption of monolayer coverage, the better fitting results of the sorption hint that the sorption should mainly be monolayer. The mean adsorption energies of both Pb^{2+} and Cu^{2+} obtained from Dubinin-Radushkevich model are greater than 8 kJ mol^{-1}. These reveal that the sorption should be dominated by the chemical process.[30]

Effect of temperature

The effect of temperature on the adsorption of Pb^{2+} and Cu^{2+} by CCTM is indicated in Figure 7. The ion uptake decreases with increasing temperature. The thermodynamic parameters of the adsorption

TABLE III
Langmuir, Freundlich, and Dubinin-Radushkevich Isotherms Constants for Pb^{2+} and Cu^{2+} on CCTM

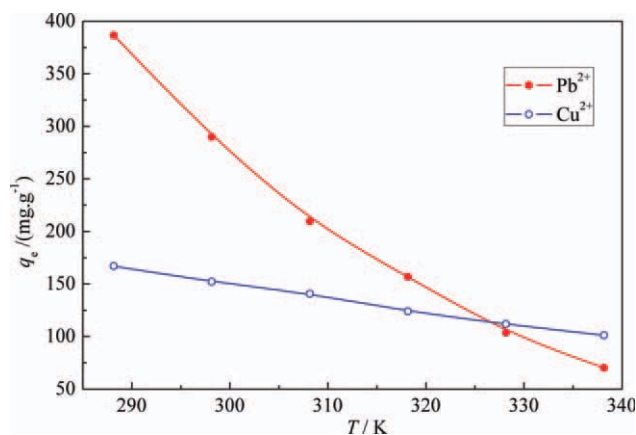| Ion	Langmuir isotherm			Freundlich isotherm			Dubinin-Radushkevich isotherm			
	q_m (mg g^{-1})	b (L mol^{-1})	R^2	K_F (mg g^{-1})	b_F	R^2	q_{DR} (mg g^{-1})	K (kJ^{-2} mol^2)	E (kJ mol^{-1})	R^2
Pb^{2+}	288.1	247.0	0.993	719.2	0.2803	0.977	382.2	−0.004769	10.24	0.981
Cu^{2+}	166.4	263.8	0.982	446.6	0.2937	0.972	222.4	−0.004727	10.29	0.971

Figure 7 Effect of temperature on ions adsorption of CCTM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

process are obtained from experiments at various temperatures using the following equations.[31]

$$\ln\left(\frac{q_e}{c_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

where ΔS is the entropy change, R the molar gas constant, ΔH the enthalpy change, ΔG the change of Gibbs function, T the absolute temperature, and q_e and c_e are the same as indicated above. The ΔS and ΔH values can be calculated from the linear fit of $\ln(q_e/c_e)$ versus $1/T$.

The thermodynamic parameters are summarized in Table IV. The values of ΔS for the adsorption of Pb^{2+} and Cu^{2+} are -65.36 and 5.951 J K^{-1} mol^{-1}, respectively. The positive or negative value of ΔS shows the increasing or decreasing randomness at

the solid/liquid interface during the sorption of ion onto CCTM. The negative values of ΔH and ΔG for the adsorption of Pb^{2+} and Cu^{2+} indicate the exothermicity and spontaneousity of the adsorption process. It is noteworthy that the absolute values of ΔH are close to the common reaction enthalpy (40 kJ mol^{-1}). This means that the adsorption process should be predominantly chemical. This result is in agreement with the sorption kinetic and isotherm analyses described previously.

Desorption and regeneration

One of the important features of adsorbents is their regeneration. The regeneration of CCTM for the adsorption of Pb^{2+} and Cu^{2+} was also studied. The retention rate of capacity and desorption efficiency are shown in Table V. From Table V, it can be concluded that CCTM had higher desorption efficiency and retention rate of capacity. By the fifth cycle, the desorption efficiency and the retention rate of capacity remained above 91% and 96%, respectively. These results indicate that CCTM should be used for the removal and collection of Pb^{2+} and Cu^{2+} from wastewaters.

CONCLUSIONS

Under microwave irradiation, a novel chitosan adsorbent (CCTM) was successfully prepared by the reaction of epichlorohydrin O-crosslinked chitosan with maleic anhydride. The chemical structure of this biosorbent was confirmed by FTIR and XRD. The experimental results indicate that the microwave reaction is about 12 times faster than the traditional. The optimum microwave time and DS value are 25 min and 0.445, respectively. The adsorbent has

TABLE IV
Thermodynamic Parameters for Adsorption of Pb^{2+} and Cu^{2+} on CCTM

Ion	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	R^2	ΔG (kJ mol^{-1})					
				288 K	298 K	308 K	318 K	328 K	338 K
Pb^{2+}	-29.67	-65.36	0.991	-10.19	-9.539	-8.886	-8.232	-7.578	-6.925
Cu^{2+}	-9.995	5.951	0.995	-11.77	-11.83	-11.89	-11.95	-12.01	-12.07

TABLE V
The Retention Rate of Capacity and Desorption Efficiency of Pb^{2+} and Cu^{2+} on CCTM after Five Cycles

Cycle	1	2	3	4	5
Retention rate of capacity (%)					
Pb^{2+}	100	98.70	98.21	96.83	96.71
Cu^{2+}	100	98.03	97.27	96.97	97.20
Desorption efficiency (%)					
Pb^{2+}	92.07	93.21	92.13	91.47	91.30
Cu^{2+}	94.96	94.73	95.19	94.89	94.29

comparably good adsorption performance for Pb^{2+} and Cu^{2+} with CCTE. The adsorption of CCTM is dependent on adsorption time, initial metal ion concentration, solution pH, and temperature. The maximum adsorption of metal ions is at pH 5. Kinetic studies indicate that the adsorption process is perfectly fit pseudo-second-order equation. The adsorption isotherm agrees well with the Langmuir model. Thermodynamic studies reveal that the adsorption is exothermic and spontaneous chemical process. The adsorbed Pb^{2+} and Cu^{2+} could be desorbed efficiently and CCTM is recyclable. Therefore, the adsorbent is promising for application in the removal of Pb^{2+} and Cu^{2+} from wastewaters.

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