

Novel Porous Chitosan Resin for the Removal of Cd(II) from Aqueous Solutions

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A novel chitosan derivative, porous tetraethylenepentamine-type chitosan resin, was chemically modified by chloromethyloxirane and tetraethylenepentamine. The uptake behaviour of resin towards Cd(II) was studied in aqueous medium, where the maximum adsorption capacity of the resin was 125.1 mg/g at pH 8.0 at room temperature. Kinetic studies referred that the uptake reaction is pseudo second order. The uptake reaction is a monolayer and found to be endothermic. Interference of other cations and anions in Cd(II) adsorption was found to be significant. The resin was regenerated effectively (desorption ratio $\approx 98\%$) using a mixture of 2 M NaCl and 0.5 M and can be regenerated many times as well as stable performance in adsorption of Cd(II).

Key Words: Chitosan, Resin, Cadmium, Removal.

INTRODUCTION

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems¹. These contaminants must be removed from wastewaters before discharge, as they are considered persistent, bioaccumulative and toxic². Cadmium is a heavy metal with obvious chronic toxicity and is most sensitive to genital system³. The processes currently used to remove these pollutants from water are chemical precipitation, oxidation-reduction, electrochemical deposition, filtering, ion exchange and adsorption. Adsorption is the most employed process because of its low cost and acceptable efficiency⁴.

Recently, much attention has been paid to utilize chitosan in wastewater treatment⁵. Chitosan, poly D-glucosamine, is the deacetylated form of chitin that has a large number of amino groups which are responsible for the high adsorption property of metal⁶. However the good solubility of chitosan in acid solution limits its application in water treatment. Therefore, it was developed a number of acid-stable chitosan derivatives according to the need for structural design, such as high-capacity chitosan-based chelating resin for on-line collection of transition and rare-earth metals^{7,8}.

For this purpose, we have developed a novel structure of chitosan resin employing chelating agent with amino group incorporated on chemically modified. This modified chitosan can then be lead into porous structure by stirring in atoleine with PEG-2000 and Span-80 without specific processing technique. The ultimate goal of this paper is the development

of new porous chitosan resin and the study on removal behaviour of cadmium using this resin. Thermodynamic as well as kinetic properties of the removal process will be also be clarified.

EXPERIMENTAL

Chitosan (Shanghai Jilan Co. Ltd., China) with deacetylation degree of 85 %, ethyleneglycol diglycidylether and tetra-ethylenepentamine were purchased from Sigma Chemicals. All other reagents used for the synthesis of the chelating resin were of analytical reagent grade. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as a source of Cr(II). The wastewater samples were acquired from a local electroplating industry located in Yancheng city, Jiangsu Province, China. The characteristics of electroplating wastewater were: colour, colourless; pH 11.0; TDS, 50.0 mg/L; TSS, 5530 mg/L; cadmium, 1500 mg/L; cyanide, 3200 mg/L; sulfate, 1890 mg/L; carbonate, 50.0 mg/L.

Porous tetra-ethylenepentamine-type chitosan resin:

The porous tetra-ethylenepentamine-type chitosan resin was synthesized as follows. The cross-linked chitosan was synthesized as shown in Fig. 1 (mechanism 1). Chitosan (10 g) was suspended in 60 mL of water-ethanol (1:1 v/v), then benzaldehyde (40 g) was added to the chitosan suspension. The mixture was stirred at room temperature for 12 h to protected amino groups of chitosan as Schiff base. After the reaction, the product was filtered and washed each three times with ethanol and water to remove unreacted benzaldehyde. The chitosan derivative protected the amino groups by benzaldehyde

The porous tetra-ethylenepentamine-type chitosan resin morphology is observed in Fig. 3. It can be seen that the resin surface has porous structure obviously. The modified chitosan could be lead into porous structure by stirring in atoleine with PEG-2000 and Span-80 without specific processing technique, which indicates that it is likely to has high adsorption capacity and the sorption process could be fast.

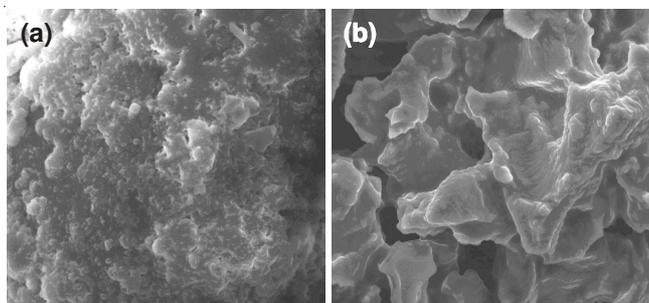


Fig. 3. SEM images of porous tetra-ethylenepentamine-type chitosan (a) augment 1200 \times , (b) augment 3000 \times

Effect of pH: A pH effect test is performed to determine the pH of adsorption at which maximum uptake of metal occurs. The pH from 2 to 10 was adjusted initially with either hydrochloric acid or sodium hydroxide (0.1 M). The removal increased from 90.5 to 100 % with increase of pH from 6 to 8 and thereafter a slight decline in removal was observed with increase in pH (Fig. 4). The optimum pH for the removal of Cd(II) was found to be 8. This could be attributed to Cd(OH)⁺ species which exist⁹ at pH 7.0-8.6. It is well known that hydroxyl metal complexes adsorb with a higher affinity than the completely hydrated metals because the formation of an OH group on the metal reduced the free energy requirement for adsorption.

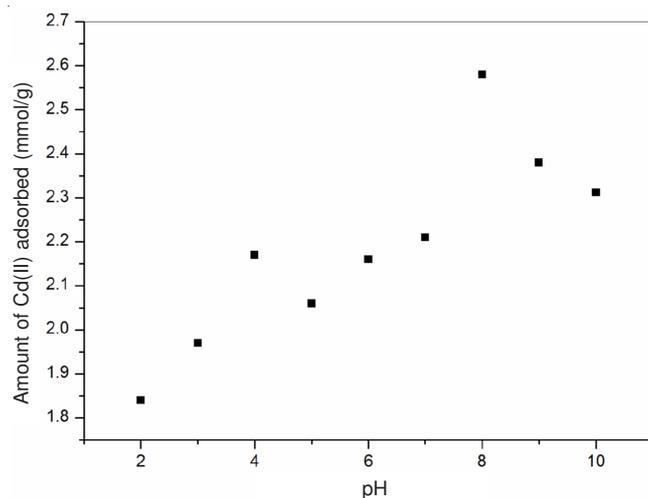


Fig. 4. Effect of pH on Cd(II) adsorption at 30 °C and the initial concentration of Cd²⁺ is 5 \times 10⁻³ M

Sorption kinetics: Fig. 5 shows the change in the Cd(II) adsorption by the resins as a function of time at initial concentration of 5 \times 10⁻³ M, pH 8 and different temperatures. The kinetics of removal of cadmium indicated rapid binding of cadmium by the resin during the first few minutes followed

by a slow increase until a state of equilibrium is reached. These observations were in agreement with the work reported earlier with the other metal ion-biomaterial systems⁹. The data in Fig. 5 were treated according to pseudo second-order kinetic model expressed as¹⁰:

$$\frac{t}{q_t} = \frac{1}{k' q_e^2} + \frac{t}{q_e} \quad (1)$$

where k' is the pseudo second-order rate constant of adsorption (g mmol⁻¹ min⁻¹) and q_e and q_t are the amounts of metal ion adsorbed (mmol/g) at equilibrium and at time t , respectively. Linear plots of t/q_t versus t are shown in the insert of Fig. 5. The results obtained for the model are also furnished in Table-1. It is evident from the table that the prepared adsorbent followed pseudo second-order kinetics for the concentration range studied.

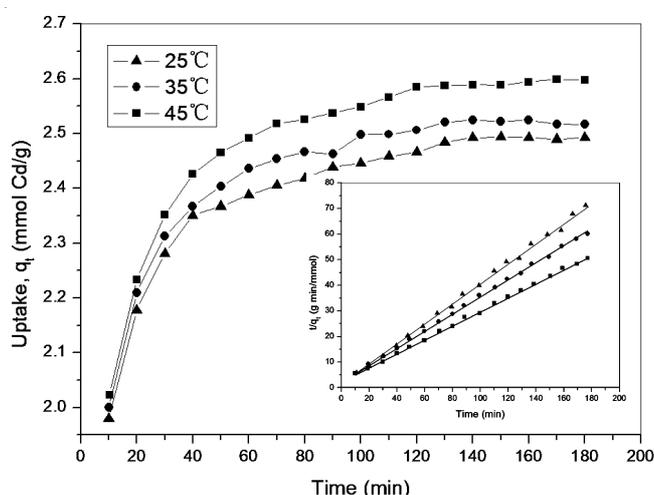


Fig. 5. Effect of time on Cd(II) adsorption at different temperatures and the insert is the pseudo second-order kinetics of Cd(II) adsorption by the resin.

TABLE-1
PSEUDO SECOND-ORDER SORPTION
KINETICS OF Cd(II) BY RESIN

Temp. (°C)	q_e (mmol/g)	k' (g/mmol min)	R^2
25	2.847	0.027	0.988
35	2.913	0.021	0.993
45	3.025	0.018	0.996

Sorption equilibrium: Fig. 6 shows the adsorption isotherms of Cd(II) at different temperatures and pH 8. The adsorption data in Fig. 6 were treated according to the following Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (2)$$

where C_e is the equilibrium concentration of the adsorbate (mmol/L), q_e is the adsorbed value of adsorbate at equilibrium concentration (mmol/g), Q_{\max} is the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives a straight line with slope and intercept equal to $1/Q_{\max}$ and $1/K_L Q_{\max}$, respectively. The values of K_L and Q_{\max} at different temperatures for adsorption of Cd(II) were

obtained from the insert of Fig. 6 and reported in Table-2. It is seen that the adsorption process is mainly monolayer at all temperatures.

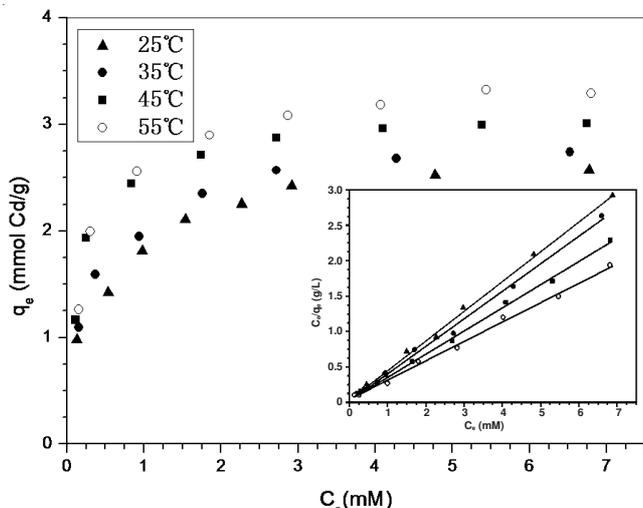


Fig. 6. Adsorption isotherms for Cd(II) at different temperatures and the insert is the Langmuir isotherms for adsorption of Cd(II) by the resin

TABLE-2
LANGMUIR AND THERMODYNAMIC PARAMETERS
FOR ADSORPTION OF Cd(II)

Temp. (°C)	Langmuir parameters			Thermodynamic parameters			
	Q_{max} (mmol/g)	K_L (L/mmol)	R^2	ΔH° (KJ/mol)	ΔS° (KJ/mol)	ΔG° (KJ/mol)	$T\Delta S^\circ$ (KJ/mol)
25	2.57	1.28	0.992	25.52	144.92	-17.68	43.20
35	2.75	1.84	0.991			-19.13	44.65
45	3.03	2.37	0.996			-20.58	46.10
55	3.36	3.03	0.993			-22.03	47.55

It is also seen that as the temperature increases the value of K_L increases. To obtain the thermodynamic parameters of the adsorption reaction, the values of K_L at different temperatures were processed according to the following van't Hoff equation¹¹:

$$\ln K_L = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

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 (K). 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. The values of ΔH° and ΔS° were calculated from Fig. 7 and reported in Table-2. The positive value of ΔH° indicate the endothermic nature of adsorption process. The positive value of ΔS° may be related to the increased randomness due to the liberation of water of hydration during the adsorption of Cd(II). The Gibbs free energy of adsorption ΔG° was calculated from the following relation and given in Table- 2.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

The negative values of ΔG° obtained indicate that the adsorption reaction is spontaneous. The data given in Table-2 also show an increase in the values of $T\Delta S^\circ$ with increasing temperature and $|T\Delta S^\circ| > |\Delta H^\circ|$. This indicates that the adsorption

process is dominated by entropic rather than the enthalpic changes¹².

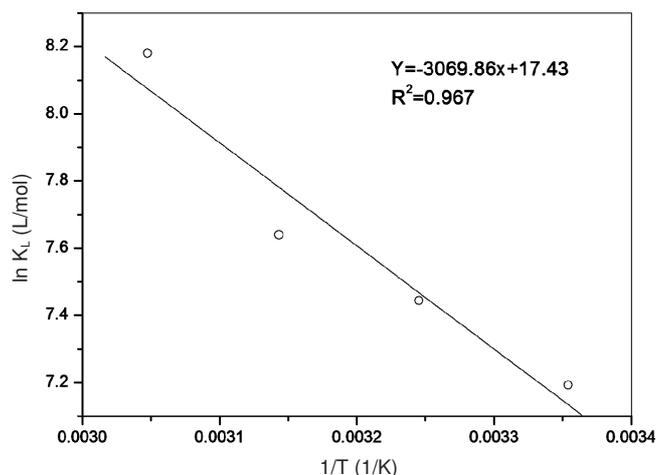


Fig. 7. van't Hoff plots for the adsorption for Cd(II) on the studied resin

Removal of Cd(II) from electroplating wastewater and desorption studies: Removal of Cd(II) from real electroplating wastewater using the porous tetra-ethylenepentamine-type chitosan resin was studied. Firstly, the wastewater should be diluted to a valid working range, otherwise, it was difficult to observe the removal of Cd(II) by the resin. The result shows that at 10 times dilution the resin could remove 85 % Cd(II) at a high adsorbent dose of 15 g/L with the experiment. With further increase in dilutions, the porous tetra-ethylenepentamine-type chitosan resin could attain almost complete removal but at a higher adsorbent dose.

The maximum adsorption capacity of porous tetra-ethylenepentamine-type chitosan resin was 125.1 mg Cd(II)/g resin, which was obtained from sorption equilibrium studies. For the real electroplating wastewater, the concentration of Cd(II) 1500 mg/L, theoretically need porous tetra-ethylenepentamine-type chitosan resin 11.99 g to achieve 100 % of Cd(II) removed, however, the experimental value was 76 %. It was obviously that the interference of other cations and anions such as Cl^- , CN^- , Pb^{2+} , Hg^{2+} , etc. in Cd adsorption was significant. These factors need further studies.

Desorption studies were carried out with solutions of 2 M NaCl and 0.5 M NaOH. The resin was regenerated effectively (desorption ratio $\approx 98\%$) using a mixture of 2 M NaCl and 0.5 M NaOH. After regeneration, the colour, size and adsorption capacity of the chitosan resin did not change significantly. The adsorbent/desorption cycles were repeated for 10 cycles using 0.1 g of the adsorbent and the results obtained are furnished in Fig. 8. Cd(II) adsorption remained unaltered up to six cycles and thereafter there was a steady decline in adsorption. Thus, porous tetra-ethylenepentamine-type chitosan resin can be regenerated many times and stable performance in adsorption of Cd(II).

Conclusion

A novel porous tetra-ethylenepentamine-type chitosan resin was prepared. The uptake behaviour of resin towards Cd(II) was studied in aqueous medium. Kinetic studies referred that the uptake reaction is pseudo second order. The uptake

reaction is a monolayer and found to be endothermic. Interference of other cations and anions in Cd(II) adsorption was found to be significant. The resin was regenerated effectively (desorption ratio $\approx 98\%$) using a mixture of 2 M NaCl and 0.5 M and can be regenerated many times as well as stable performance in adsorption of Cd(II).

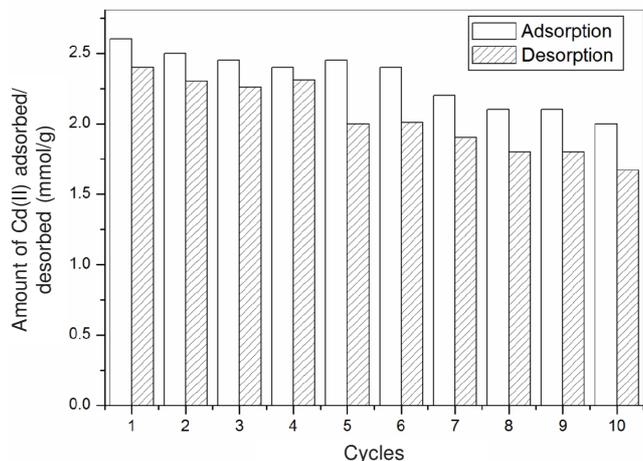


Fig. 8. Amount of Cd(II) adsorption and desorption with 10 cycles

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