

Preparation and Coordination Behavior of Cellulose Beads Derivative Modified by 1,5-Diaminoethyl-3-Hydroxy-1,5-Diazacycloheptane

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ABSTRACT: Cellulose derivative (MPCN) modified by 1,5-diaminoethyl-3-hydroxy-1,5-diazacycloheptane (DADN) was prepared and characterized by scanning electron microscopy and elemental, and infrared analysis. MPCN and its Cu^{2+} , Pb^{2+} complexes were characterized by thermogravimetric and differential thermal analysis. The coordination adsorption behavior of MPCN with divalent copper and lead ions was determined. The effects of temperature, initial pH value, and the concentration of MPCN ligand to the equilibrium adsorption were discussed. The optimum pH range of the coordination adsorption of MPCN with Cu^{2+} and Pb^{2+} is 5–6. The rate constants of the coordination reaction were found. At 323 K, the rate constant is 1.0×10^{-3} and $7.0 \times 10^{-4} \text{ s}^{-1}$ for Cu^{2+} and Pb^{2+} , respectively. The thermodynamic parameters of the coordination reaction were obtained based on the experiment data of the adsorption isotherms. The coordination reaction was performed spontaneously from the data of ΔG , as follows: -21.65 and -19.41 kJ/mol and ΔS , 87.06 and 67.92 J/mol K for Cu^{2+} and Pb^{2+} , respectively. The coordination ratio of DADN coordination group immobilized on cellulose beads with either metal ion is about 1 : 2 from the plot of the relation of $\lg D$ versus $\lg L$ and the capacity of saturation adsorption. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1278–1285, 1999

Key words: cellulose derivative; polyamine compound; coordination adsorption; Cu^{2+} ; Pb^{2+}

INTRODUCTION

Cellulose is the most abundant natural polymer. Cellulose can be modified by grafting, crosslinking, etherification, and esterification. A large number of commercially important products have been derived from cellulose.^{1,2} Cellulose derivatives have been used for enrichment and separation metal ions,^{3–5} protein,⁶ and dyes.⁷ Teshirogi and Ohtomo⁸ prepared powder cellulose ion ex-

change adsorbents by the reaction of *N,N'*-bis(2-chloroethyl)piperazine or *N,N'*-bis(2-hydroxyethyl) piperazine with cellulose modified by epichlorohydrin and studied adsorption capacity for bovin serum albumin by column chromatography. Krizanova et al.⁹ reported that cellulose derivative was used as a hydrophobic carrier in affinity chromatography for routine isolation of calmodulin, albumin, and insulin.

In affinity chromatography, some soft acids (such as divalent copper, lead, or mercury) were used as an alternative, which interact with some soft bases (such as functional groups containing nitrogen or sulfur).¹⁰ So it is interesting that the studying cellulose derivatives modified by specific ligands interacts with transition metal ions.

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Our work is to prepare a new macroporous spherical-shaped cellulose ligand, which was synthesized by the reaction of the porous cellulose beads containing active epoxy groups with 1,5-diaminoethyl-3-hydroxy-1,5-diazacycloheptane-tetra-hydrobromide, and examine coordination adsorption behavior of the ligand for divalent copper and lead from aqueous solutions of metal nitrate. The influences on temperature, initial pH value, concentration of metal ion solution, and concentration of ligand were discussed.

EXPERIMENTAL

Materials and Chemicals

Degreasing cotton was supplied by Jiaozuo Sarifary Materials Factory of Henan Province. Carbon disulfide, chlorobenzene, calcium carbonate, epichlorohydrin, copper nitrate, and lead nitrate were supplied by Shanghai Chemical Reagent Co. They are laboratory grade chemicals.

Preparation of Cellulose Beads

The cellulose xanthate viscose was prepared by the reaction of 5 g alkalid-treated and aged cotton cellulose with 3 mL carbon disulfide at room temperature. This xanthate viscose, 45 mL of 6% (w/v) sodium hydroxide aqueous solution and 4.5 g of calcium carbonate (300 mesh) were mixed under stirring. The mixture was added into the solution containing 0.5 g of potassium oleate and 250 mL of chlorobenzene with stirring, and then the reaction temperature was slowly raised to 80°C and remained there for 0.5 h. When the reaction temperature was raised to 90°C, the coagulated and regenerated cellulose beads were formed. After cooling, filtrating, and washing with heat water, the cellulose beads obtained were suspended in HCl–NaCl–CaCO₃ solution to remove calcium carbonate. The macroporous spheric-shaped cellulose was obtained by filtrating and washing with distilled water; per 10 mL wet beads, it has about 0.5 g dring beads.

Preparation of Active Cellulose Beads¹¹

2 g of dried macroporous cellulose beads (80–100 mesh) were swelled by 40 mL of 2N NaOH aqueous solution, and then 12 mL of epichlorohydrin and 0.5 mL of Tween-20 were added. The mixture was shaken at room temperature for 20 h and then filtrated and washed with acetone and dis-

tilled water, respectively. After extracting with acetone in a Soxhlet apparatus for 8 h to remove the low polymer of epichlorohydrin, the residue was dried at 70°C, and white macroporous spheric-shaped cellulose activated by epichlorohydrin (MPCE) was collected, and the active epoxy groups were determined by epoxide ring opening with 0.1N hydrochloric acid solution and titrating with 0.1N standard solution of sodium hydroxide. MPCE contains 0.76 mmol epoxy group per gram.

Synthesis of 1,5-Diaminoethyl-3-Hydroxy-1,5-Diazacycloheptane-Tetra-Hydrobromide

Synthesis of 1,5-diaminoethyl-3-hydroxy-1,5-diazacycloheptane (DADN)–tetra-hydrobromide was synthesized referring to the literature.¹²

Yield, 53%. Anal calcd (%) for C₉H₂₆N₄OBr₄: C, 20.55; H, 4.99; N, 10.65. Found (%): C, 20.51; H, 5.01; N, 10.54. FAB-MS: *m/z* 202 (RI: 70, M–4HBr).

Macroporous Cellulose Beads Modified by DADN

2.0 g of dried macroporous cellulose beads activated by epichlorohydrin were swelled by 30 mL of 30% (v/v) 1,4-dioxane aqueous solution, then 0.5 g (0.95 mmol) of DADN · 4HBr and 0.6 g (5.7 mmol) of Na₂CO₃ were added. The reaction bottle was shaken at 50°C for 20 h under nitrogen ambience. After cooling and filtrating, the residue was washed with acetone and distilled water, respectively, and extracted with acetone in Soxhlet apparatus for 4 h and then dried at 80°C. The white macroporous cellulose beads derivative (MPCN) modified by DADN was obtained.

ANALYSIS AND CHARACTERIZATION

Element Analysis

Element analysis was obtained by 1106 elemental auto analysis apparatus (Carlo-Erba, Italy) MPCN: N (%), 1.28; per gram MPCN immobilized: 0.229 mmol DADN residue group.

Determination of Cu and Pb Ions

Determination of divalent copper and lead was carried out by a 180-80 atomic absorption spectrometer (AAS) (Hitachi, Japan).

Infrared Spectra

The infrared (IR) spectra of macroporous cellulose beads (MPCE) and its derivative (MPCN) modi-

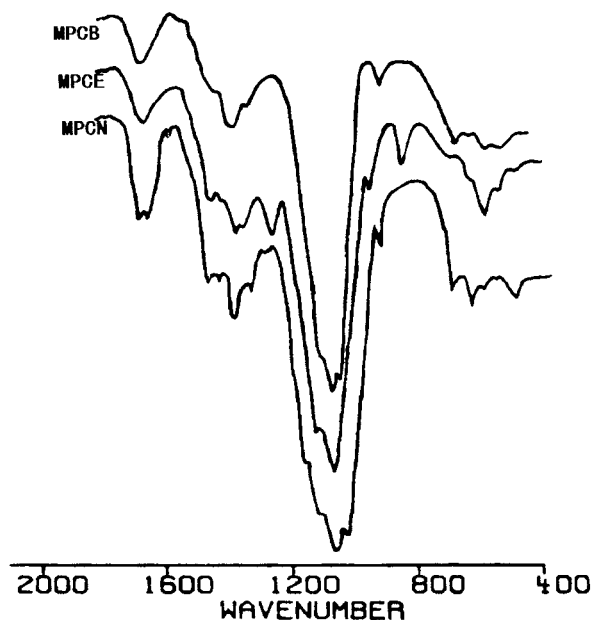


Figure 1 IR of MPCB, MPCE and MPCN (2000–400 cm^{-1}).

fied by DADN were determined on a Nicolet 170 SX Fourier transform infrared FTIR spectrometer by KBr technique.

Scanning Electron Microscopy

Scanning electron micrographs (SEM) were measured for the structure of cellulose beads surface by a X-650 SEM (Hitachi, Japan). The cellulose beads were coated with gold.

Thermogravimetric and Differential Thermal Analysis

Thermogravimetry (TG) and the differential thermal analysis (DTA) were determined by a STA 409 thermal analyzer (Netzsch, Germany). The TG and DTA curves were run in nitrogen ambience (80 mL/min), and at a heating rate of $15^\circ\text{C}/\text{min}$ from 40 to 700°C . Calcined alumina was taken as the reference material.

Coordination Adsorption Experiment

The coordination adsorption of MPCN for Cu^{2+} and Pb^{2+} was carried out. 0.02 g (W) MPCN was placed in a closed flask, 10 mL (V) 2×10^{-3} mmol/mL (C_i , initial concentration) of copper or lead nitrate aqueous solution was added. A series of such flask were shaken at a constant speed of 150 times for 2 h. Aliquots of the solution were

analyzed for determining metal ionic concentration of the solution at equilibrium adsorption (C_e , free metal ionic concentration at equilibrium) by AAS. The capacity of equilibrium adsorption (Q_e) of MPCN for metal ion was calculated as follows:

$$Q_e = (C_i - C_e)V/W \text{ (mmol/g)} \quad (1)$$

RESULTS AND DISCUSSION

Characterization of MPCN Ligand

IR Characterization

IR spectra (2000–400 cm^{-1}) of MPCB, MPCE, and MPCN were shown in Figure 1. Figure 1

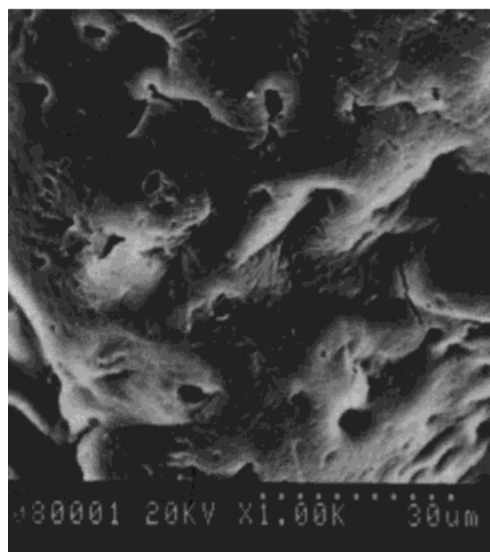
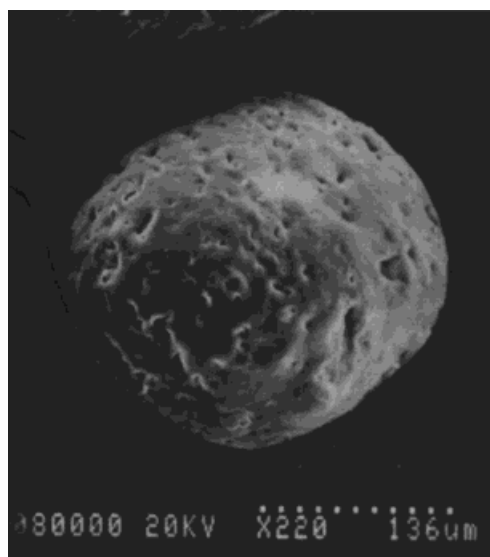
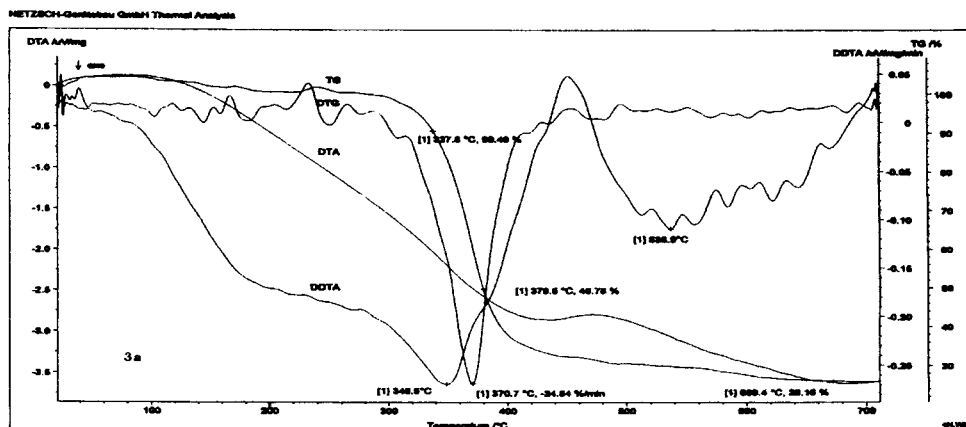
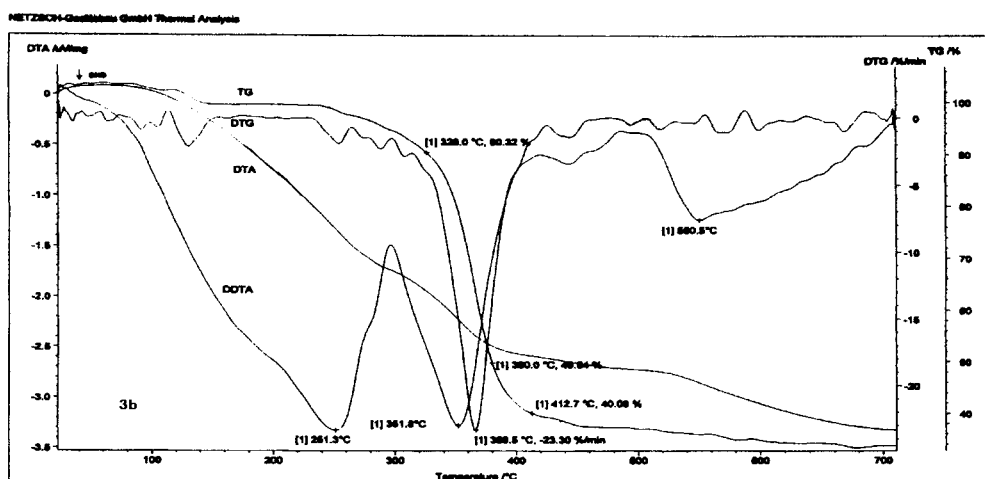


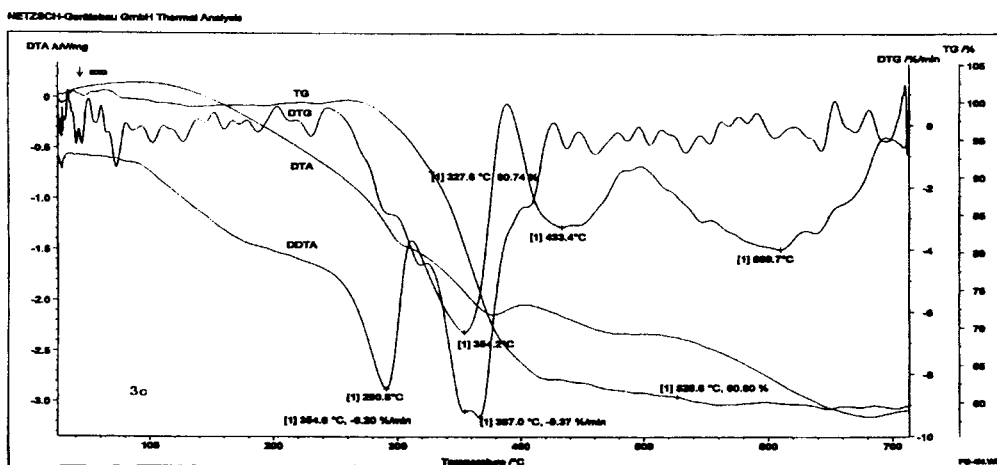
Figure 2 SEM of the cellulose beads modified by DADN.



(a)



(b)



(c)

Figure 3 TG and DTA analysis of (a) MPCN, (b) MPCN-Cu, and (c) MPCN-Pb.

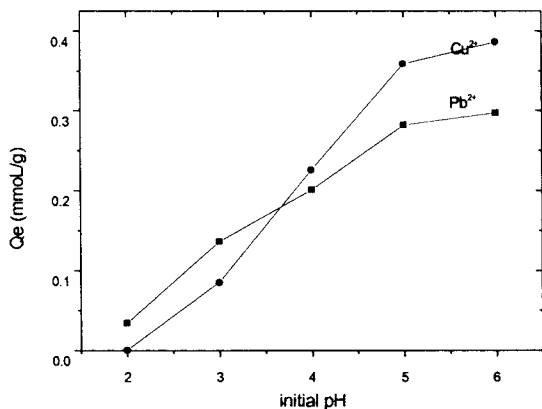


Figure 4 Effect of initial pH for Q_e (50°C, 2 h).

shows that characteristic bands of epoxy group presented at 1254, 928, and 851 cm^{-1} in IR of MPCN, but these bands disappeared in IR of MPCN. N—H bending vibration of MPCN is at 1654 cm^{-1} . The intensity of the band is close to O—H bending vibration at 1637 cm^{-1} .

SEM Characterization

Scanning electron micrographs of the surface morphology of the cellulose beads modified by DADN are presented in Figure 2. Figure 2 shows that the cellulose derivative has a spherical shape and the surface of cellulose beads has abundant porous structure. The porosity of cellulose beads was formed by washing regenerated cellulose beads with acid to remove CaCO_3 .

TG and DTA Characterization

TG, DTG, DTA, and DDTA curves of MPCN, MPCN—Cu, and MPCN—Pb were presented in Figure 3(a)–(c), respectively. DTG curves of MPCN, MPCN—Cu, and MPCN—Pb show that there isn't weight loss until 310, 242, and 273°C, respectively. The temperature of starting weight loss of MPCN complexes is lower than that of MPCN ligand. DTG curves also indicate that the temperature of the fastest decomposition rate is at 370.7, 366.5, and 367.0 for MPCN, MPCN—Cu, and MPCN—Pb, respectively. This implied that the temperature of the fastest decomposition rate of MPCN and its complexes is close.

The DDTA curve of MPCN [Fig. 3(a)] shows two exothermic peaks at 348.5 and 536.9°C, respectively. Figure 3(b) and 3(c) show three exothermic peaks at 251.3, 351.8, and 550.5°C for MPCN—Cu, and 290.8, 354.2, and 609.7°C for

MPCN—Pb; respectively. The exothermic process between 250 to 355°C can be due to the dehydration, decomposition, and rearrangement of the products. The exothermic process of the higher temperature is due to the cross-bridging, aromatic cyclization of charred residue.^{13,14}

Coordination Behavior of MPCN Ligand for Metal Ions

Effect of Initial PH Value

The initial pH value of metal nitrate aqueous solution can be adjusted to desirable level by using 0.01N HNO_3 aqueous solution. In different initial pH value solution, the coordination adsorption of MPCN was determined for divalent Cu and Pb ions. The experimental data obtained were plotted Figure 4.

In selective pH value range, the adsorption capacity is increased by increasing the initial pH value of either metal nitrate solution. But in pH 2–3 range, the adsorption capacity is very low for both metal ions. It is obvious that this related to property of accepting proton by nitrogen atom in MPCN ligand in the different pH values. Higher pH value of metal salt solution will result in the hydrolysis of metal salt.¹⁵

Effect of Solution Temperature

In the temperature range of 30–60°C, coordination adsorption for divalent copper and lead ions were determined. The data obtained are listed Table I. In the Table I, D is distribution ratio, $D = Q_e/C_e$, and Q_e and C_e are adsorption capacity and the concentration of free metal ion at the equilibrium adsorption, respectively.

The data of Table I shows that the distribution coefficient (D) for Cu^{2+} and Pb^{2+} increased with increasing temperature of solution, which indicated that the coordination adsorption process was an endothermal procedure and could be regarded as chemical adsorption.

Table I Effect of Solution Temperature

t (°C)	30	40	50	60
$1/T(10^{-3}/\text{K})$	3.195	3.096	3.003	3.300
$D(\text{Cu}^{2+})$	235.3	258.7	280.0	296.2
$D(\text{Pb}^{2+})$	191.1	197.3	202.0	208.9

0.02 g MPCN, pH 5, 2 h.

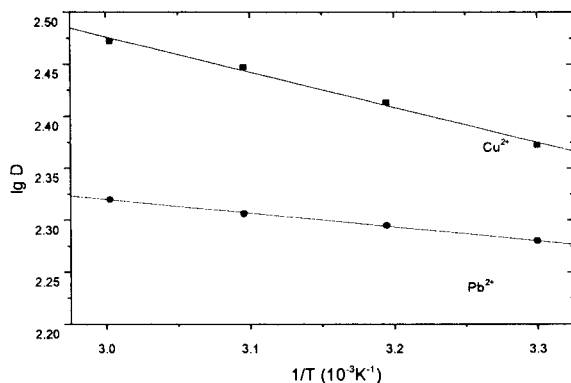


Figure 5 Effect of temperature for distribution ratio.

Thermodynamic Parameters

Based on the data of Table I, $\lg D$ versus $1/T$ were plotted in Figure 5. From Figure 5, it can be obtained that the linear slope is -0.338×10^3 and -0.132×10^3 , and the correlation coefficient (r) is 0.997 and 0.998 for divalent copper and lead, respectively. According to $\lg D = -\Delta H/2.303RT + C$, ΔH can be found as follows: for Cu^{2+} , $\Delta H = 6.47$ (kJ/mol); for Pb^{2+} , $\Delta H = 2.53$ (kJ/mol).

Based on the equation $\Delta G = -RT \ln K_e$ (K_e is the equilibrium constant of coordination reaction), it was found from the slopes of Fig. 8 that $\ln K_e$ equals 3.501 and 3.139 for Cu^{2+} and Pb^{2+} , respectively. At a temperature of 323 K, ΔG was found as follows: for Cu^{2+} , $\Delta G = -21.65$ (kJ/mol); for Pb^{2+} , $\Delta G = -19.41$ (kJ/mol). Based on the equation $\Delta G = \Delta H - T\Delta S$ and ΔG and ΔH values, the following ΔS can be found: for Cu^{2+} , $\Delta S = 87.06$ (J/mol K); for Pb^{2+} , $\Delta S = 67.92$ (J/mol K). The data of ΔG and ΔS indicated that the coordination reaction of MPCN for divalent copper and lead was performed spontaneously in the experimental conditions.

Coordination Adsorption Isotherms^{16,17}

Keeping constant the concentration of the metal ion (2 mmol/L) and changing the concentration of

Table II Effect of MPCN Concentration

MPCN (g/L)	1.0	2.0	3.0	4.0
Cu²⁺:				
<i>C_e</i> (mmol/L)	1.634	1.282	0.994	0.750
<i>Q_e</i> (mmol/g)	0.366	0.359	0.355	0.313
Pb²⁺:				
<i>C_e</i> (mmol/L)	1.702	1.424	1.198	0.952
<i>Q_e</i> (mmol/g)	0.298	0.288	0.267	0.262

PH 5, 2 h.

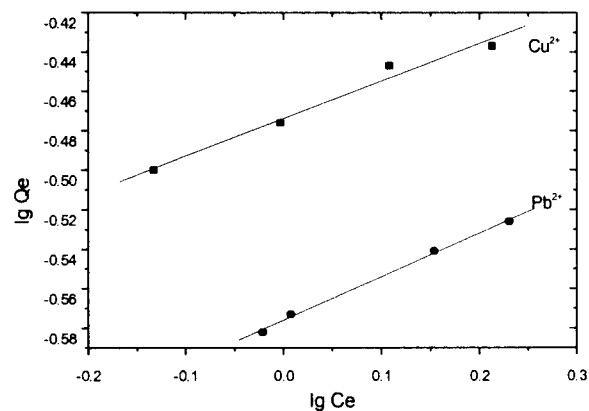


Figure 6 Linearized Freundlich isotherms.

MPCN ligand from 1.0 to 4.0 g/L, the concentration of free metal ion of the reaction solution was determined. The adsorption capacity (Q_e) can be calculated from C_e and the concentration of MPCN ligand at equilibrium adsorption. The data obtained were listed Table II.

The data of Table II indicated that the adsorption capacity decreased with an increase in the concentration of MPCN ligand. The adsorption capacity of MPCN for divalent copper ion was slightly higher than for the lead ion. According to the Freundlich isotherms equation,

$$Q_e = K_F C_e^{1/n} \quad (2)$$

Equation (2) can be rearranged to the linear form, as follows:

$$\lg Q_e = 1/n \lg C_e + \lg K_F \quad (3)$$

In eq. (3), n and K_F are Freundlich constants. $\lg Q_e$ versus $\lg C_e$ are plotted in Figure 6.

Figure 6 indicates that the correlation coefficients (r) of Cu^{2+} and Pb^{2+} were 0.988 and 0.998, respectively. It showed that the coordinate adsorption isotherms of MPCN ligand for divalent copper and lead ions were the adsorption of Freundlich model. The Freundlich parameters (K_F and n) can be obtained from Figure 6 for Cu^{2+} , $K_F = 0.337$, $n = 5.26$; and for Pb^{2+} , $K_F = 0.266$, $n = 4.55$.

The Freundlich parameter n value is about 5 for both metal ions. It showed that the coordinate adsorption of MPCN ligand for divalent copper and lead ions was easy.^{18,19} The empirical formulas obtained from Freundlich parameters K_F and

Table III Effect of Reaction Time

t (min)	5	15	30	60
Cu ²⁺ :				
Qt (mmol/g)	0.116	0.216	0.312	0.350
Qt/Q_e	0.323	0.601	0.853	0.974
Pb ²⁺ :				
Qt (mmol/g)	0.081	0.148	0.210	0.266
Qt/Q_e	0.281	0.513	0.728	0.924

n were found as follows: for Cu²⁺, $Q_e = 0.377 Ce^{0.19}$; for Pb²⁺, $Q_e = 0.266 Ce^{0.22}$.

Rate Constant of Coordinated Adsorption

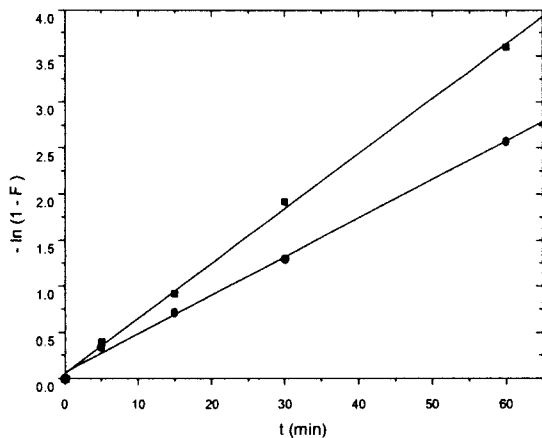
Keeping constant the concentration of the metal ion (2 mmol/L) and the concentration of MPCN ligand (2 g/L), aliquots of the free metal ion of the reaction solution were analyzed at different reaction times. The experimental data obtained are listed in Table III.

In the Table III, Qt and Q_e are the adsorption capacity (mmol/g) at reaction time (t) and the equilibrium adsorption, respectively. According to Davankov,²⁰ reporting the equation,

$$-\ln(1 - F) = K_T t \quad (4)$$

In eq. (4), $F = Qt/Q_e$, where t is reaction time (minute), and K_T is rate constant of the coordination adsorption at temperature T . Based upon the data of Table III and the above equation, $-\ln(1 - F)$ versus t were plotted Figure 7.

From Figure 7, it can be obtained that the corresponding correlation coefficients (r) are

**Figure 7** The relation of $-\ln(1 - F)$ versus time.

0.999 and 0.998 for Cu²⁺ and Pb²⁺, respectively. Based on the linear slope and the equation $-\ln(1 - F) = K_T \cdot t$, at 323 K, the adsorption rate constant of MPCN ligand for divalent metal ions can be obtained; for Cu²⁺, it is $K_{323} = 1.0 \times 10^{-3} s^{-1}$, and for Pb²⁺, $K_{323} = 7.0 \times 10^{-4} s^{-1}$.

Coordination Ratio of Ligand with Metal Ion¹⁹

The equation of the coordination reaction of MPCN ligand (L) with metal ion (M) can be shown in the follows:



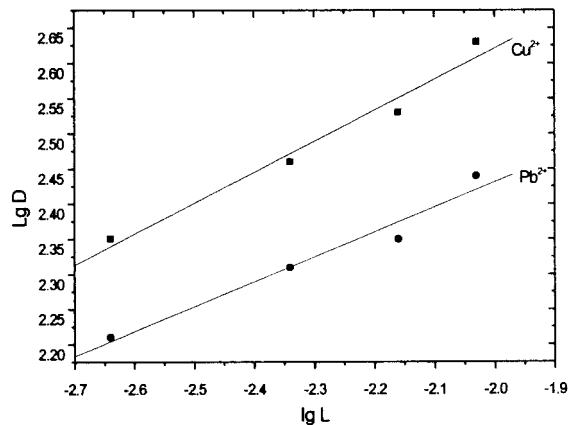
In eq. (5), a is coordination ratio. At the equilibrium of coordination adsorption, the equilibrium constant Ke was given as follows:

$$Ke = [LaM]/[L]^a[Cu^{2+}] = D/[L]^a \quad (6)$$

Equation (6) was rearranged as follows:

$$\lg D = \lg Ke + a \lg [L] \quad (7)$$

In eq. (7), L is the mmol number of DADN coordination group immobilized in MPCN ligand, and a is the coordination ratio. Based on experiment data and elemental analysis of MPCN ligand (N: 1.28%), $\lg D$ versus $\lg L$ were plotted in Figure 8. a was obtained from the linear slope of Figure 8. For Cu²⁺, $a = 0.44$ (correlation coefficient: r 0.988) and for Pb²⁺, $a = 0.35$ (correlation coefficient: r 0.981). It showed that the coordination ratio of DADN coordination group immobilized in the MPCN ligand with either metal ion was close to 1 : 2.

**Figure 8** The relation $\lg D$ versus $\lg L$.

When the concentration of MPCN ligand was constant and the concentration of the metal ion was increased to three times (8 mmol/L), the concentration of free metal ion was determined at saturation adsorption. The capacity of saturation adsorption is 0.414 and 0.408 mmol/g for divalent copper and lead, respectively. It showed that the coordination ratio of DADN coordination group immobilized on cellulose beads with either metal ion was about 1 : 2.

CONCLUSIONS

Cellulose derivative (MPCN) modified by 1,5-diaminoethyl-3-hydroxy-1,5-diazacycloheptane (DADN) was prepared. MPCN was characterized by SEM, elemental and IR analysis. MPCN and its Cu^{2+} and Pb^{2+} complexes were determined by TG and DTA. The coordination reaction of MPCN for Cu^{2+} and Pb^{2+} is performed spontaneously based on the thermodynamic parameters and Freundlich constants. The coordination ratio of DADN ligand group immobilized on cellulose beads with Cu^{2+} or Pb^{2+} was about 1 : 2.

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REFERENCES

- Mishra, M. K. *J Makromol Sci Rev Macromol Chem Phys C*, 1982–83, 22(3), 471.
- Bhattacharyya, B. N.; Maldas, D. *Prog Polym Sci* 1984, 10, 171.
- Rocha, J. C.; Tosano, I. A. S.; Burba, P. *Talanta*, 1997, 44(1), 69.
- Da Silva, L. R. D.; Peixoto, C. R. M.; Gushikem, Y. *Sep Sci Technol* 1996, 31(8), 1045.
- Lamb, J. D.; Nazarenko, A. Y. *Separ Sci Technol* 1997, 32(17), 2749.
- Zhu, B. R.; Shi, Z. Q.; He, B. L. *Ion Exchange Adsorp (Chinese)* 1996, 12(6), 522.
- Hebeish, A.; Waly, A.; Abdel-Mohdy, F. A.; Aly, A. S. *J Appl Polym Sci* 1997, 66(4), 1029.
- Teshirogi, T.; Ohtomo, T. *Seni Gakkaishi* 1986, 42(2), T-119.
- Krizanova, O.; Zubor, V.; Gemeiner, P.; Zorad, S. *Gen Physiol Biophys* 1986, 5(2), 201.
- Ramirez-Vick, J. E.; Garcia, A. A. *Separ Purifica Methods*, 1996–97, 25(2), 85.
- Zhu, B. R.; Shi, Z. Q.; He, B. L. *Ion Exchange Adsorp (Chinese)* 1997, 13(1), 43.
- Liu, Y.; Xue, G. P.; Wu, C. T. *Chin J Chem* 1998, 16(5), 448.
- Tian, C. M.; Guo, H. Z.; Zhang, H. Y.; Xu, J. Z.; Shi, J. R. *Thermochim Acta* 1995, 253, 243.
- Mitra, B. C.; Basak, R. K.; Sarkar, M. *J Appl Polym Sci* 1998, 67, 1093.
- Johns, M. M.; Marshall, W. E.; Toles, C. A. *J Chem Technol Biotechnol* 1998, 71, 131.
- Ahamad, A. H. A.; Ribhi, E. B. *J Chem Technol Biotechnol* 1997, 69, 27.
- Juang, R. S.; Tseng, R. L.; Wu, F. C.; Lee, S. H. *J Chem Technol Biotechnol* 1997, 70, 391.
- Lafuma, F.; Audebert, R.; Quivoron, C. Y. P. *Inorg Chim Acta* 1982, 66, 167.
- Huang, W. P.; Si, Z. H.; Li, C. X.; He, B. L. *Ion Exchange Adsorp (Chinese)* 1997, 13(3), 307.
- Davankov, V. A.; Zolotarev, Y. A. *J Chromatogr* 1978, 155, 285, 303.