The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in aqueous medium

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A B S T R A C T

The chemically crosslinked metal-complexed chitosans were synthesized by using the ion-imprinting method from a chitosan with four metals (Cu(II), Zn(II), Ni(II) and Pb(II)) as templates and glutaraldehyde as a crosslinker. The influences of adsorption conditions, including molar ratios of crosslinker/chitosan and pH changes, were studied. They were used to investigate for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in an aqueous medium. They were demonstrated the comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in the orders of the adsorbed amounts with templates: $Cu(II) \sim Pb(II) > Zn(II) \sim Ni(II)$, $Zn(II) > Cu(II) \sim Pb(II) > Ni(II)$, $Ni(II) > Pb(II) > Zn(II) > Cu(II)$ and $Pb(II) \sim Cu(II) > Zn(II) > Ni(II)$, respectively. In addition, the dynamical study showed to be well followed the second-order kinetic equation in the adsorption process. At the same time, the equilibrium adsorption data were fitted in three adsorption isotherm models, namely, Langmuir, Freundlich, and Dubinin–Radushkevich to show very good fits in the Langmuir isotherm equation for the monolayer adsorption process. The most important aspect of the chemically crosslinked metal-complexed chitosans with glutaraldehyde demonstrated to afford a higher adsorption capacity, and a more efficient adsorption toward metals in an aqueous medium.

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1. Introduction

Environmental pollution caused by toxic metals is one of the most pressing problems in the world. The potential sources of metal ions from industrial wastewaters include fertilizers, metal fabrications, paints, pigments, batteries, and the like. These would endanger public health and the environment if discharged improperly. Many technologies such as chemical precipitation, membrane separation, advanced oxidation process, electrochemical technique, biological treatment, adsorption procedure, and the like have been widely used to remove toxic metals from industrial effluents [1–6]. Among all treatments that are proposed, adsorption is recognized as an effective and economic method for the removal of pollutants from wastewaters [7,8]. Chitosan, poly(β-1,4)2-amino-2-deoxy-D-glucopyranose, has been one of the most popular adsorbents for the removal of metal ions, dyes and proteins from an aqueous solution and has been widely used in waste treatment applications [9–16]. Further physical and chemical modifications of chitosan have been developed to improve its chemical stability in acid media, resistance to biochemical and microbiolog-

ical degradation, and selectivity and capacity for the adsorption of metals [17–28]. Although the crosslinking method may enhance the resistance of chitosan against acids and chemicals, it can reduce the adsorption capacity of chitosan to remove toxic metals. This may be attributed to the extent of crosslinking and the decrease of amount of amino group, which is expected to play a great part in the adsorption process. To overcome the problem of decreasing adsorption capacity of heavy metals on the chemically crosslinked chitosan, the ion-imprinting method, similar to that of molecularly imprinted polymers, was developed to prepare metal complexed chitosans. This method uses a metal as template, then crosslinks with a crosslinker, and removes a metal ion [22,29–33]. In the ion-imprinting process, its recognition is based on the specificity of the ligand, on the coordination geometry, the coordination number, the charge and the size of metal ion. They might be higher in the selectivity and the adsorption capacity of metals and could be quite stable in an acid media.

In this study, the chemically crosslinked metal-complexed chitosans were synthesized by using the ion-imprinting method from a chitosan with four metals as templates and glutaraldehyde as a crosslinker. They were used for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in an aqueous solution. The reaction conditions for the preparation of the chemically crosslinked metal-complexed chitosans and the influences of adsorption conditions, including molar ratios of crosslinker/chitosan and pH changes, were

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investigated. The adsorption isotherms, the adsorption kinetics and the adsorption efficiencies were studied to gain a good comparison.

2. Experimental

2.1. Chemicals

Chitosan with a deacetylation percentage of approximately 75% as defined by FTIR method was purchased from Sigma–Aldrich Co., USA, with the average molecular weight of 690,000 as measured by viscometric method. Glutaraldehyde (GLA) of 50% purity was purchased from Acros Organics, Belgium. Cupric chloride, zinc chloride, nickel chloride and lead acetate purchased from Wako Co., Japan, were analytical-reagent grade. All the reagents were used without further purification or treatment.

2.2. Preparation of the crosslinked metal-complexed chitosans

A 0.2 M sodium hydroxide solution was added dropwise to a 100-mL solution of acetic acid (1%, v/v) containing chitosan (8.8 mmol) and a metal ion (8.8 mmol) with vigorous stirring to obtain a gelatinous metal-complexed chitosan at around pH 5.5. The isolated gel was added to a 100-mL aqueous solution of glutaraldehyde (44.0 mmol) and the mixture was stirred for 1 h at room temperature. The precipitate was filtrated and washed intensively with distilled water to remove any unreacted glutaraldehyde. Subsequently, the precipitate was stirred with a 1.2 M hydrochloric acid solution to remove a metal ion by monitoring with an atomic absorption spectrophotometer and subsequently with a 1% (v/v) acetic acid to remove non-crosslinking chitosan. Finally, it was washed with 0.2 M sodium hydroxide solution, distilled water, and acetone. The precipitate was dried on vacuum oven for 8 h. The resulting material was grounded and sieved to collect particles with a diameter between 250 μm and 500 μm for this study.

The Fourier transform infrared spectra (FTIR) were measured on a PerkinElmer Spectrum One FTIR spectrometer. The energy-dispersive X-ray spectra (EDS) were determined on an Oxford EDS INCA 350 spectrometer. The mean pore diameters were obtained using a mercury intrusion porosimeter, Scientek STK019348.

2.3. Adsorption experiments

2.3.1. Kinetics of adsorption of copper(II) ion

The three crosslinked Cu(II)-complexed chitosans prepared with 5.0, 10.0 and 15.0 molar ratios of CHO/NH$_2$ were studied to determine the adsorption of Cu(II) ion by adding 10 mg of each kind of particles into 100 mL of 15 mg/L cupric chloride solution at pH 5.0 while stirring at room temperature. Then 10 mL aliquots of these solutions at intervals of 1 h were filtrated and their concentrations of Cu(II) ion were measured on a Hitachi 170-30 atomic absorption spectrophotometer at 324.8 nm. The adsorption capacity (Q_e) was calculated by the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 is the initial concentration of Cu(II) ion (mg/L), C_e is the final concentration of Cu(II) ion (mg/L), V is the volume of Cu(II) ion solution (L) and W is the weight of the crosslinked Cu(II)-complexed chitosan (g) used.

2.3.2. pH effect for adsorption of copper(II) ion

The crosslinked Cu(II)-complexed chitosan prepared with 10.0 molar ratios of CHO/NH$_2$ was investigated to determine the pH effects of its adsorption of copper(II) ion by adding 10 mg of its particle into 100 mL of 10 mg/L cupric chloride solutions. These were adjusted to pH from 1.0 to 5.0 with 1.0 M hydrochloric acid solution or 1.0 M sodium hydroxide solution while stirring at room temperature. Then 10 mL aliquots of these solutions at intervals of 1 h were filtrated and their concentrations of Cu(II) ion were determined by an atomic absorption spectrophotometer. The adsorption capacity (Q_e) was calculated by Eq. (1).

2.4. Adsorption isotherms

The isothermal studies were carried out with 10 mg of the crosslinked metal-complexed chitosans prepared from four metal ions of Cu(II), Zn(II), Ni(II) and Pb(II) ions with 10.0 molar ratio of CHO/NH$_2$ in 100 mL of initial concentration of copper(II), zinc(II), nickel(II) or lead(II) ions, respectively, in the range of 0–15 mg/L at pH 5.0 and with stirring for 4 h at room temperature. Their solutions were filtrated and the concentrations of copper(II), zinc(II), nickel(II) or lead(II) ions were measured by an atomic absorption spectrophotometer at 324.8 nm, 213.9 nm, 232.0 nm or 217.0 nm, respectively. The amounts of metal ions adsorption were calculated based on the differences of the concentration in an aqueous solution (100 mL) before and after adsorption and the weight of the crosslinked metal-complexed chitosan particles (0.010 g) according to Eq. (1).

2.5. Desorption studies

After having adsorbed each metal ion of Cu(II), Zn(II), Ni(II) or Pb(II) ions, four crosslinked metal-complexed chitosans were conducted by using 10 mg of each kind of particles in each 100 mL of three different concentrations of EDTA solutions, 1.00 mM, 0.50 mM, and 0.25 mM, respectively, under stirring for 8 h at room temperature. The solutions were filtrated and the concentrations of copper(II), zinc(II), nickel(II) or lead(II) ions were measured by an atomic absorption spectrophotometer.

3. Results and discussion

3.1. Preparation and characterization

In the ion-imprinting process, chitosan was first chelated with a template of metal ion, followed by being chemically crosslinked with a crosslinker (e.g. glutaraldehyde via Schiff's base linkage). Finally, a metal ion was removed to obtain the crosslinked metal-complexed chitosans as shown in Fig. 1. They were found to be insoluble in acid and alkaline media as well as distilled water. This was similar to the crosslinked chitosan without metals as templates, but better than native chitosan. It is well known that the high hydrophilicity of chitosan with the primary amino group makes it easily soluble in dilute organic acids and yields a hydrogel in water. Therefore, the crosslinking treatments of chitosan with or without metals as templates should reinforce the chemical stability in organic acidic media, making them more useful for the removal of chemical pollutants from wastewaters in acidic medium.

The Fourier transform infrared spectra of four glutaraldehyde-crosslinked metal-complexed chitosans prepared from a 10.0 molar ratio of CHO/NH$_2$ with Cu(II), Zn(II), Ni(II) and Pb(II) ions as templates were shown in Fig. 2. They indicated to have a absorption peak for imine C=N and amide C=O stretching vibrations at 1650 cm^{-1} and another absorption peak for amide N–H bending vibration at 1560 cm^{-1} [34]. It was clear that the absorbance ratios of A_{1650}/A_{1560} for the glutaraldehyde-crosslinked metal-complexed chitosans were become to be higher than that of the native chitosan,
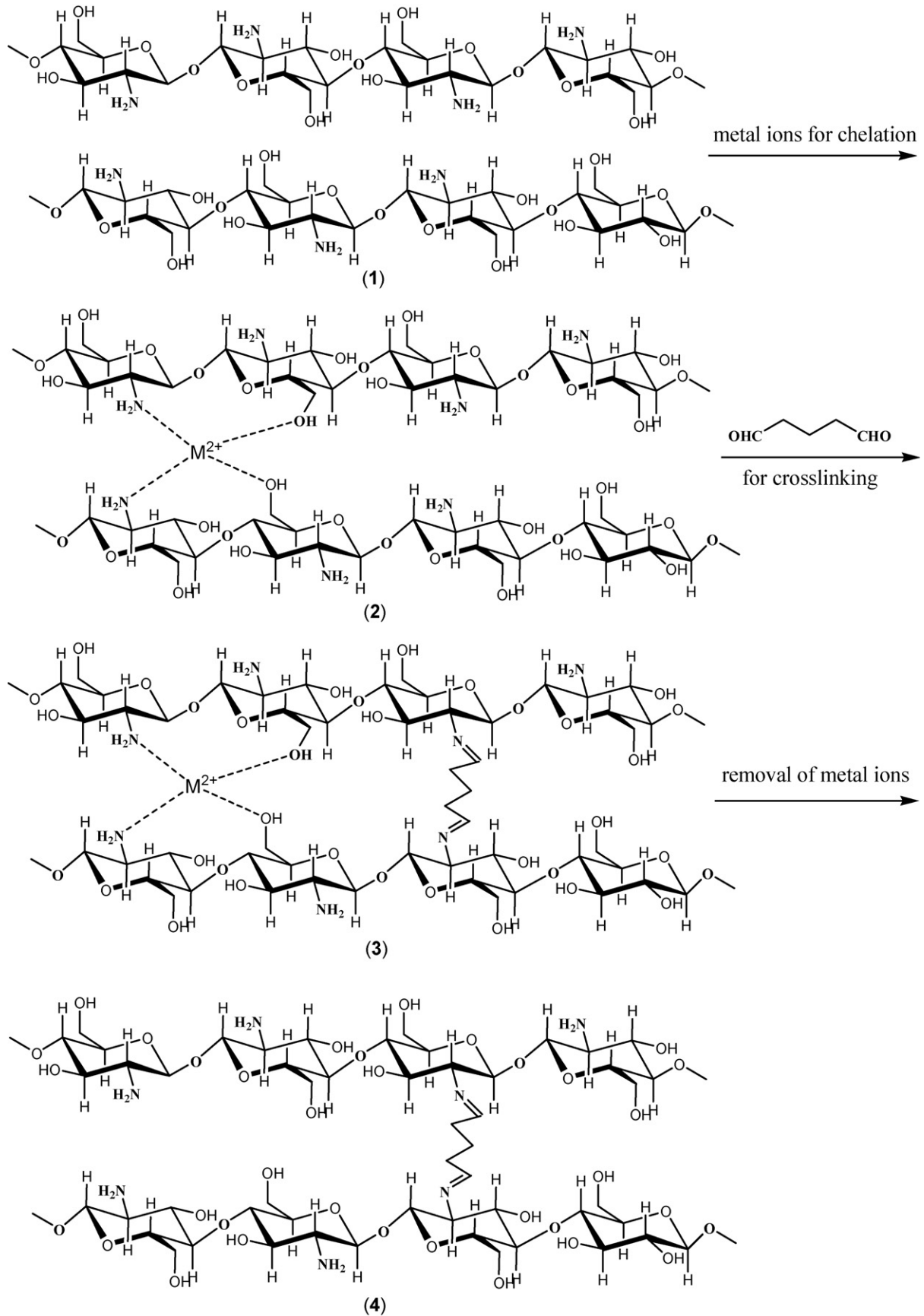
Fig. 1. Schematic representation for preparation process of the crosslinked metal-complexed chitosans with glutaraldehyde.
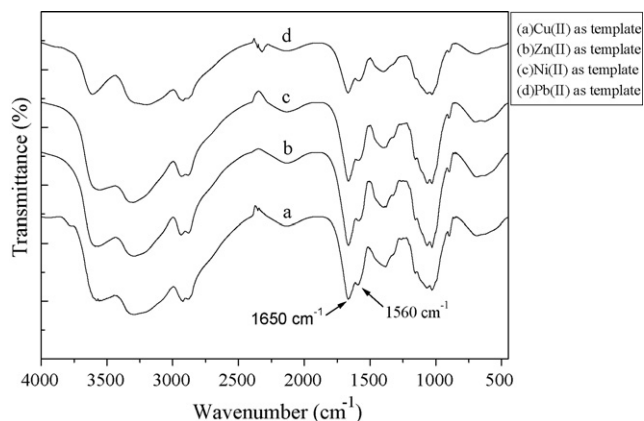
Fig. 2. FTIR spectra of the glutaraldehyde-crosslinked chitosans with (a) Cu(II), (b) Zn(II), (c) Ni(II) and (d) Pb(II) ions as templates.

as increasing the degrees of crosslinking via the formation of Schiff's base linkage. They were found that the degrees of crosslinking for four glutaraldehyde-crosslinked metal-complexed chitosans with Cu(II), Zn(II), Ni(II) and Pb(II) ions as templates in 6.8, 9.5, 8.1 and 4.9%, respectively, were smaller than the glutaraldehyde-crosslinked chitosan without metal template in 12.6%. This might be caused by losing some free amino groups for the formation of chelation of metal ion with amino and hydroxyl groups of chitosan in the ion-imprinting process (Fig. 1). The mean pore diameters of the four crosslinked metal-complexed chitosans by using the mercury intrusion porosimetry were found the following orders: Pb(II) ion as template (114.88 μm) > Cu(II) ion as template (65.56 μm) ∼ Ni(II) ion as template (64.59 μm) ∼ Zn(II) ion as template (44.97 μm). It might be attributed to the diameters of metal ions in the orders: Pb(II) ion > Cu(II) ion ∼ Ni(II) ion ∼ Zn(II) ion. The energy-dispersive X-ray spectrometer (EDS) was utilized for element analysis of the adsorbed metal chitosans. As shown in Fig. 3, the EDS spectra taken from top view of samples were confirmed that the metals were indeed adsorbed on the glutaraldehyde-crosslinked metal-complexed chitosans. The weight percents of the imprinted amounts for four metals: Cu, Zn, Ni and Pb, were 3.3 wt.%, 1.3 wt.%, 3.6 wt.% and 10.5 wt.%, respectively, on the glutaraldehyde-crosslinked chitosans with Cu(II), Zn(II), Ni(II) and Pb(II) ions as templates. The results were corresponded well to the adsorbed amounts.

3.2. Adsorption kinetics and effect of molar ratios of CHO/NH₂

The adsorption of copper(II) on three crosslinked Cu(II)-complexed chitosans were studied on the variation of concentrations of Cu(II) ion (mg/L) in an aqueous Cu(II) ion solution at pH 5.0 with times ranging from 1 h to 6 h, as shown in Fig. 4. The rapid initial rates of adsorption of Cu(II) ion on three crosslinked Cu(II)-complexed chitosans prepared with molar ratios of 5.0, 10.0 and 15.0 were seen to increase markedly during the first hour and to gradually approach the limiting adsorption after 4 h. Both of the adsorption capacities of Cu(II) ion on 5.0 and 10.0 molar ratios of CHO/NH₂ were found to be almost same, but to be higher than that on the 15.0 molar ratio of CHO/NH₂ (Fig. 5). That was due to an increase in the formation of chemical bonds at adsorption sites as large excess amount of crosslinker. At the same time, the kinetics for the adsorptions of Zn(II), Ni(II), and Pb(II) ions on the crosslinked Zn(II)-, Ni(II)-, and Pb(II)-complexed chitosans, respectively, were as same as those of Cu(II) ion on the crosslinked Cu(II)-complexed chitosan. Therefore, the crosslinked metal-complexed chitosans prepared from a 10.0 molar
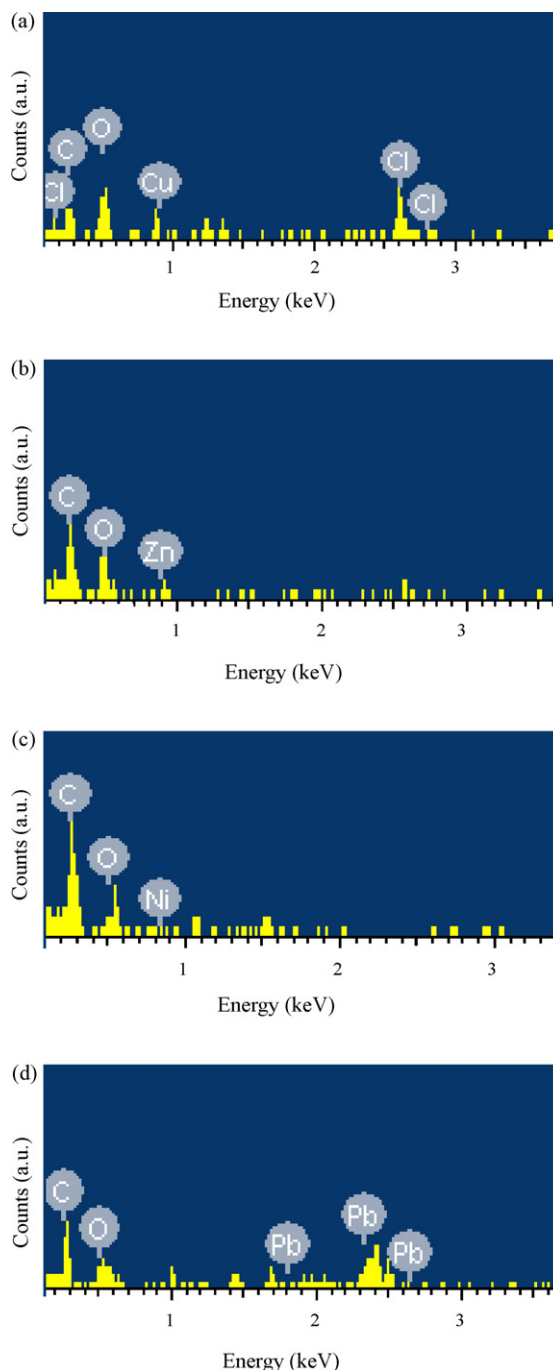

Fig. 3. EDS spectra for the metal-adsorbed glutaraldehyde-crosslinked chitosans: (a) CuCl₂ on Cu(II) ion as template, (b) ZnCl₂ on Zn(II) ion as template, (c) NiCl₂ on Ni(II) ion as template and (d) Pb(CH₃CO₂)₂ on Pb(II) ion as template.

ratio of CHO/chitosan with 2 h of crosslinking were used for this study.

The dynamical experimental data at pH 5.0 were applied to the first order kinetics according to the following equation:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{2}$$

where Q_e and Q_t are the amount of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant of first-order adsorption (min⁻¹) [34]. They did not fit well with low correlation coefficients from 0.8182 to 0.8732 (and Table 1).
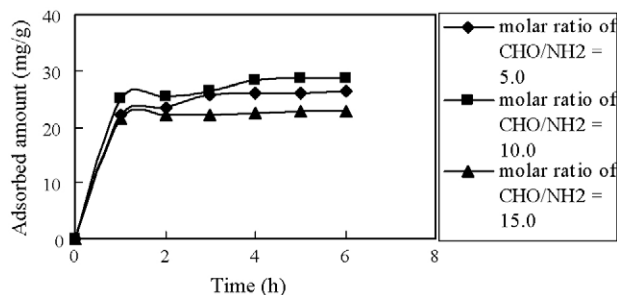
Fig. 4. Kinetics for adsorption of Cu(II) ion on the glutaraldehyde-crosslinked Cu(II)-complexed chitosans prepared from different molar ratios of CHO/NH$_2$.
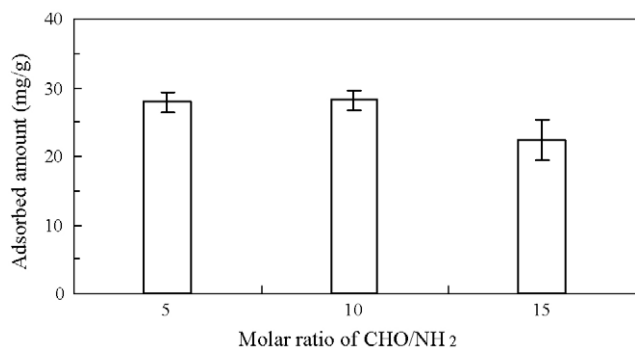

Fig. 5. Adsorption of Cu(II) ion on the glutaraldehyde-crosslinked Cu(II)-complexed chitosans prepared from different molar ratios of CHO/NH$_2$.

But they were subjected to the second order kinetics represented by the following equation:

$$\frac{t}{Q_t} = \frac{1}{(k_2 Q_e^2)} + \frac{t}{Q_e} \tag{3}$$

where Q_e and Q_t are the amount of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at time t, respectively, and k_2 is the rate constant of second-order adsorption (g/(mg min)) [34]. They could be a good agreement with the dynamical experimental data with high correlation coefficients from 0.9967 to 0.9997 (Table 1). It was more likely to reflect that the rat-determining step might be chemical adsorption and the adsorption behavior might involve the valency forces through sharing electrons between metal ions and adsorbents [35].

3.3. Influence of pH

It is not possible to carry out the adsorption of Cu(II), Zn(II), Ni(II) and Pb(II) ions at pH > 6, >8, >8 and >8, respectively, due to precipitation of the metals as the hydroxides. The adsorption of copper(II)

Table 1
Kinetic parameters for Cu(II) ion on the glutaraldehyde-crosslinked Cu(II)-complexed chitosans prepared from different molar ratios of CHO/NH$_2$

	Molar ratio of CHO/NH$_2$		
	5.0	10.0	15.0
First-order kinetics			
k_1 ($\times 10^{-2}$ min^{-1})	1.10	1.50	0.93
R_1	0.8732	0.8551	0.8182
Second-order kinetics			
k_2 ($\times 10^{-3}$ g/(mg min))	2.38	1.88	8.48
R_2	0.9989	0.9967	0.9997

Note: R_1 and R_2 are the correlation coefficients of first- and second-order kinetic equation plots.
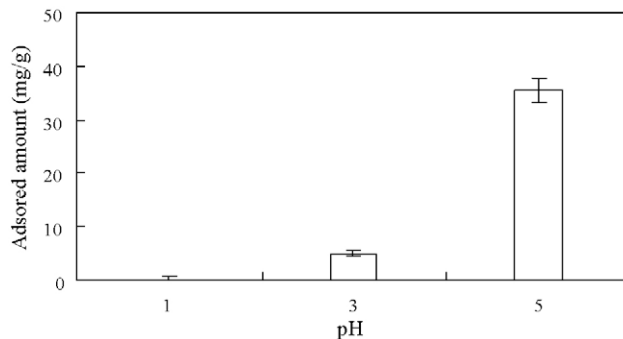

Fig. 6. Adsorption of Cu(II) ion on the glutaraldehyde-crosslinked Cu(II)-complexed chitosan in different pHs.

ion on the crosslinked Cu(II)-complexed chitosan prepared from a 10.0 molar ratio of CHO/NH$_2$ in an aqueous Cu(II) ion solution at pH from 1.0 to 5.0 for 4 h were shown in Fig. 6. The adsorption of Cu(II) ions from an aqueous medium was remarkably influenced by the pH of aqueous solution. The adsorbed amount of Cu(II) ion was largely increased from 0.10 mg/g to 35.51 mg/g as pH from 1.0 to 5.0 (Fig. 6). In addition, the adsorbed amounts of other three metals (Zn(II), Ni(II) and Pb(II)) on the crosslinked Zn(II)-, Ni(II)- and Pb(II)-complexed chitosans, respectively, had the following results: pH 1 < 3 < 5 < 7. The pH values were monitored before and after the adsorption of four metals with only pH differences from 0.1 to 0.3. The adsorption capacity of metal ion revealed to be lower at low pH due to the electrostatic repulsion between the metal cation and the protonated amino group. As pH value was increased, the amino group was free from the protonation for the adsorption behavior in the chelation mechanism of metal ions.

3.4. Adsorption isotherms

The equilibrium adsorption data of Cu(II), Zn(II), Ni(II) or Pb(II) ions on the crosslinked metal-complexed chitosans with Cu(II), Zn(II), Ni(II) or Pb(II) ions as templates, respectively, in initial concentrations of metal ions with the range of 0–15 mg/L at pH 5.0 for 4 h at room temperature were subjected to three different adsorption isotherms, namely, Langmuir, Freundlich, and Dubinin–Radushkevich isotherms.

The isotherm fitting procedures showed that the equilibrium adsorption data of Cu(II), Zn(II), Ni(II) or Pb(II) ions gave very good fits with high correlation coefficients from 0.9626 to 0.9984 (Fig. 7 and Table 2) according the Langmuir isotherm equation
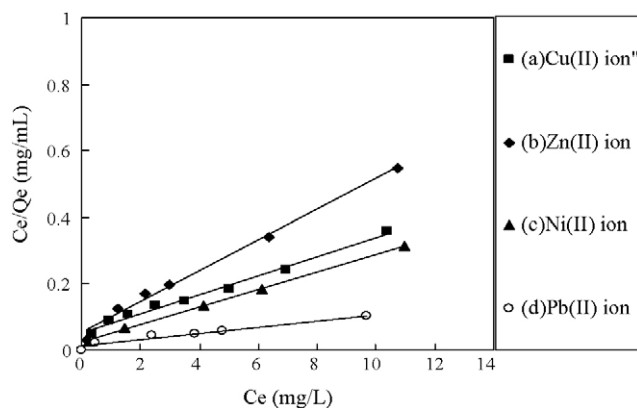

Fig. 7. Adsorption isotherms of (a) Cu(II), (b) Zn(II), (c) Ni(II) or (d) Pb(II) ions on the glutaraldehyde-crosslinked chitosans with Cu(II), Zn(II), Ni(II) or Pb(II) as templates, respectively, linearized according to Langmuir equation.

Table 2
Langmuir, Freundlich, and Dubinin–Radushkevich isotherm constants for metal ion on the glutaraldehyde-crosslinked metal-complexed chitosans

Parameter	Adsorption of Cu(II) ion	Adsorption of Zn(II) ion	Adsorption of Ni(II) ion	Adsorption of Pb(II) ion
Langmuir isotherm				
Q_m (mg/g) (S.D.)	33.00 (2.26)	15.08 (0.29)	37.88 (0.23)	105.26 (0.01)
b (L/mg) (S.D.)	0.75 (0.04)	3.73 (1.10)	1.13 (0.01)	0.78 (0.01)
R_3	0.9677	0.9898	0.9987	0.9569
Freundlich isotherm				
K_F (mg/g) (S.D.)	10.61 (1.03)	8.87 (0.54)	35.55 (0.89)	28.02 (0.89)
b_F (S.D.)	0.38 (0.06)	0.06 (0.03)	0.13 (0.08)	0.42 (0.01)
R_4	0.9476	0.8052	0.9401	0.8370
Dubinin–Radushkevich isotherm				
Q_{DR} (mg/g) (S.D.)	15.31 (0.52)	8.86 (0.30)	38.63 (0.38)	115.70 (0.28)
K (kJ^2/mol^2) (S.D.)	−0.0047 (0.0007)	−0.0040 (0.0028)	−0.0014 (0.0004)	−0.0038 (0.0001)
E (kJ/mol) (S.D.)	10.35 (0.91)	12.48 (4.72)	11.96 (4.92)	11.40 (0.08)
R_5	0.9506	0.8694	0.9532	0.9453

Note: Adsorptions of Cu(II), Zn(II), Ni(II) or Pb(II) ions are conducted on the glutaraldehyde-crosslinked chitosans with Cu(II), Zn(II), Ni(II) or Pb(II) as templates, respectively. R_3, R_4 and R_5 are the correlation coefficients of Langmuir, Freundlich and Dubinin–Radushkevich isotherm plots, respectively. S.D. in the parentheses is the standard deviation.

for monolayer adsorption on to a surface with a finite number of identical sites. It represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{(Q_m b)} \qquad (4)$$

where C_e is the equilibrium concentration of metal ions (mg/L), Q_e is the amount of metal ions adsorbed (mg/g), Q_m is the maximum adsorption capacity of metal ions (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mg) [35,36]. The Langmuir adsorption equilibrium constants (b) were found to be from 0.41 L/mg to 8.84 L/mg.

The equilibrium adsorption data were applied to the Freundlich isotherm equation for multilayer adsorption isotherm on heterogeneous surfaces, as described by the following equation:

$$\ln Q_e = b_F \ln C_e + \ln K_F \qquad (5)$$

where C_e is the equilibrium concentration of metal ions (mg/L), Q_e is the amount of metal ions adsorbed (mg/g), K_F is the maximum adsorption capacity of metal ions (mg/g), and b_F is the adsorption intensity [35,36]. As can be seen, the experimental data did not fit well in the Freundlich isotherm equation with low correlation coefficients from 0.8052 to 0.9476 (Table 2).

In order to distinguish between physical and chemical adsorption, the equilibrium adsorption data of Cu(II), Zn(II), Ni(II) or Pb(II) ions were subjected to the Dubinin–Radushkevich isotherm equation, given by the following equation:

$$\ln Q_e = K\varepsilon^2 + \ln Q_{DR} \qquad (6)$$

where Q_e is the amount of metal ions adsorbed (mg/g), Q_{DR} is the maximum adsorption capacity of metal ions (mg/g), K is the Dubinin–Radushkevich constant (kJ^2/mol^2) and ε is Polanyi potential given as Eq. (7).

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \qquad (7)$$

where C_e is the equilibrium concentration of metal ions (mg/L), R is the gas constant in J/K mol, and T is the temperate in Kelvin [26]. The Dubinin–Radushkevich constant can give the valuable information regarding the mean energy of adsorption by the following equation.

$$E = (-2K)^{-1/2} \qquad (8)$$

where E is the mean adsorption energy (kJ/mol), and K is the Dubinin–Radushkevich constant (kJ^2/mol^2). The Dubinin–Radushkevich adsorption capacities (Q_{DR}) of the four metal ions were similar to the Q_m of the Langmuir adsorption (Table 2). Therefore, the adsorption isotherms revealed to fit well

with the Langmuir isotherm equation for the monolayer adsorption process. The Langmuir monolayer adsorption capacities (Q_m, mg/g) of four metal ions were as follows: Pb(II) (105.70) > Ni(II) (37.88) ~ Cu(II) (33.00) > Zn(II) (15.08). In addition, the mean adsorption energy (E) from the Dubinin–Radushkevich isotherm is involved the transfer of free energy of one mole of solute from infinity (in solution) to the surface of adsorbent. The adsorption behavior might be predicted the physical adsorption in the range of 1–8 kJ/mol of the mean adsorption energies (E), and the chemical adsorption in more than 8 kJ/mol of the mean adsorption energies (E) [28,37]. The mean adsorption energies (E) of these four metals from 10.35 kJ/mol to 12.48 kJ/mol reflected that the adsorptions were predominant on the chemisorption process.

3.5. Comparative adsorptions

The four kinds of the glutaraldehyde-crosslinked metal-complexed chitosan prepared by the ion-imprinting method 10.0 molar ratio of CHO/NH$_2$ were used as absorbents to compare the adsorption of four metal ions in 50 mg/L aqueous solutions of metal ions at pH 5.0 for 4 h. The adsorbed amount (mg/g) of Cu(II) ion indicated in the orders as follows: Cu(II) as template (35.51) ~ Pb(II) as template (35.42) > Zn(II) as template (29.33) ~ Ni(II) as template (28.96) (Fig. 8). The adsorbed amount of Cu(II) ion showed the need to be increased from 26% to 55% as compared with the glutaraldehyde-crosslinked chitosan prepared with 10.0 molar ratio of CHO/NH$_2$. In the adsorption of Zn(II) ion, they revealed the adsorbed amount (mg/g) as follows: Zn(II) as template (15.97) > Cu(II) as template (14.22) ~ Pb(II) as template (14.06) > Ni(II) as template (11.60) (Fig. 8). The adsorbed
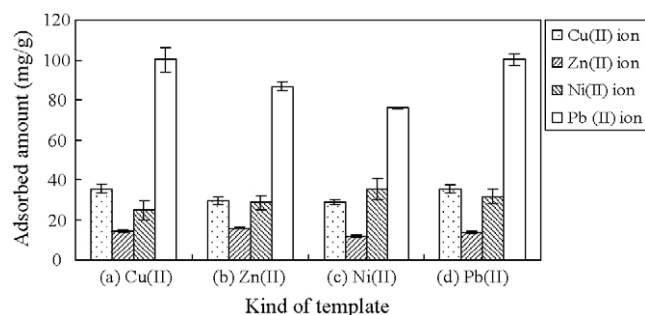

Fig. 8. Adsorption of Cu(II), Zn(II), Ni(II) and Pb(II) ions on the glutaraldehyde-crosslinked chitosans with (a) Cu(II), (b) Zn(II), (c) Ni(II) or (d) Pb(II) ions as templates, respectively, in 50 mg/L aqueous solution of metal ions at pH 5.0 for 4 h.

amounts of Zn(II) ion were increased from 3% to 42% as compared to the glutaraldehyde-crosslinked chitosan prepared with 10.0 molar ratio of CHO/NH_2. In the study of adsorption of Ni(II) ion, the adsorption orders showed as follows: Ni(II) as template (35.38 mg/g) > Pb(II) as template (31.67 mg/g) > Zn(II) as template (28.67 mg/g) > Cu(II) as template (24.75 mg/g) (Fig. 8). The adsorbed amounts of Ni(II) ion were found to have increased from 13% to 61% as compared to the glutaraldehyde-crosslinked chitosan prepared with 10.0 molar ratio of CHO/NH_2. The orders of the adsorbed amount of Pb(II) ion were as follows: Pb(II) as template (100.12 mg/g) ∼ Cu(II) as template (100.09 mg/g) > Zn(II) as template (86.76 mg/g) > Ni(II) as template (75.74 mg/g) (Fig. 8). The adsorbed amounts of Pb(II) ion were increased from 7% to 42% as compared to the glutaraldehyde-crosslinked chitosan prepared with 10.0 molar ratio of CHO/NH_2. But the adsorbed amount of Pb(II) ion on the crosslinked metal-complexed chitosans with four metal ions as templates showed to have the highest than the adsorption amounts of other three metal ions (Cu(II), Zn(II), and Ni(II)). This might be due to larger in the size and less in the hardness of Pb(II) ion than other three metal ions [31]. Recently, Birlik reported that the adsorbed amounts of Cu(II), Zn(II), and Ni(II) ions were conducted in the low initial concentrations of 20 mg/L metal ions to get 0.528 mg/g, 0.004 mg/g and 0.232 mg/g on the Cu(II) single imprinted chitosan–succinate and 22.39 mg/g, 0.243 mg/g and 0.012 mg/g on the Cu(II)/sol–gel double imprinted chitosan–succinate, respectively [33]. But Ge's report was performed in the high initial concentrations of Cu(II) (5083 mg/L) and Ni(II) (4695 mg/L) ions to obtain the adsorbed amounts of Cu(II) and Ni(II) ions in 163.93 ∼ 149.95 and 133.81 ∼ 136.16 mg/g, respectively, on the crosslinked chitosan with Cu(II) as template [38]. At the same time, Wang's reports were conducted in the high initial concentrations of Cu(II) (1270 mg/L), Zn(II) (1307 mg/L) and Pb(II) (4144 mg/L) ions to get the adsorbed amounts of Cu(II), Zn(II) and Pb(II) in 136.67 ∼ 155.48, 1.76 ∼ 0.45 and 25.48 ∼ 43.51 mg/g on the crosslinked carboxymethyl-chitosan resins with Cu(II) as template and about 117, 16, 321 on the crosslinked N-succinyl-chitosan resins with Pb(II) as template, respectively [39,40]. It was apparent that the adsorption capacity could be increased while the initial concentration was raised. However, the crosslinked N-succinyl-chitosan resin was not suitable to utilize in a low pH aqueous solution, pH < 3.0, due to dissolving in aqueous solution with high polarity of carboxylic acid groups in its N-succinyl-chitosan. In this study, the absorbed amounts of four metal ions were carried out in the low initial concentrations of 50 mg/L metal ions. In addition, the crosslinked metal-complexed chitosans could be utilized in a low pH aqueous solution, even at pH 1.0. Therefore, the crosslinked metal-complexed chitosans with glutaraldehyde for adsorptions of metal ions showed to be significantly dependent on the kinds of metal ions as templates and the metal species.

3.6. Desorption and reuse

After having adsorbed each metal ion of Cu(II), Zn(II), Ni(II) or Pb(II) ions, respectively, the four crosslinked metal-complexed chitosans were investigated through desorption studies in three different concentrations of EDTA solutions, 0.25 mM, 0.50 mM, and 1.00 mM, respectively, under stirring for 8 h at room temperature. As shown in Fig. 9, the desorption of the four crosslinked metal-complexed chitosans was shown to be significantly dependent on kinds of metals, and concentrations of EDTA solution. The desorption percentage of Cu(II) ion on Cu(II) as template was larger than those of Pb(II) ion on Pb(II) as template, Zn(II) ion on Zn(II) as template and Ni(II) ion on Ni(II) as template. This was likely attributed to the fact that the larger in the stability constant of Cu(II) ion with EDTA than other three metal ions caused the higher in its desorption
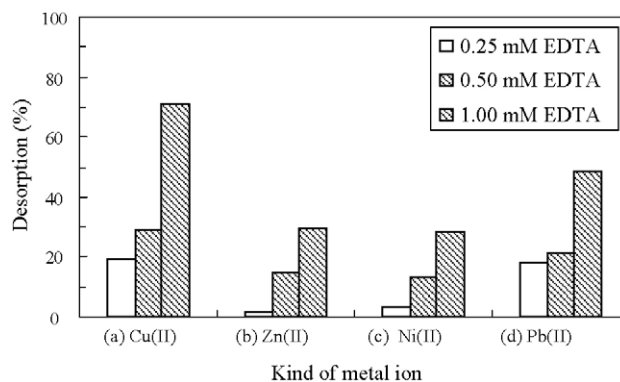

Fig. 9. Desorption of Cu(II), Zn(II), Ni(II) or Pb(II) ions from Cu(II), Zn(II), Ni(II) or Pb(II) ions adsorbed on the glutaraldehyde-crosslinked chitosans with (a) Cu(II), (b) Zn(II), (c) Ni(II) or (d) Pb(II) ions as templates, respectively, in different concentrations of EDTA.
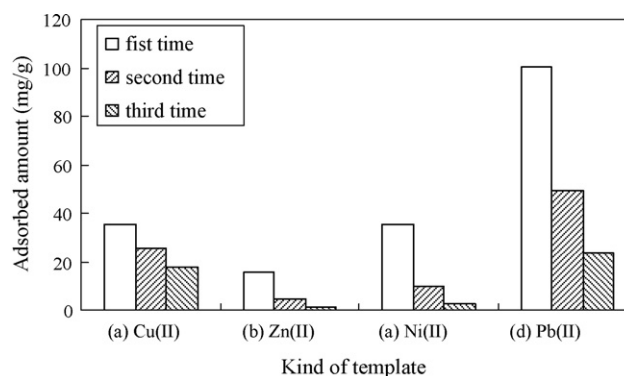

Fig. 10. Reuse data for the adsorption of meta ions on the glutaraldehyde-crosslinked metal-complexed chitosans: (a) Cu(II) on Cu(II) template, (b) Zn(II) on Zn(II) template, (c) Ni(II) on Ni(II) template and (d) Pb(II) on Pb(II) template.

[41]. They were tried to reuse the adsorptions of Cu(II), Zn(II), Ni(II) or Pb(II) ions for three times in Fig. 10. They were found that the adsorbed amount of Pb(II) ion on Pb(II) as template was higher than other metals at the third time. Therefore, the crosslinked metal-complexed chitosan could be generated and reused again for the adsorptions of metals.

4. Conclusion

The chemically crosslinked metal-complexed chitosans were synthesized by using the ion-imprinting method from chitosan with four metals as templates and glutaraldehyde as a crosslinker. They were used to investigate for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in an aqueous medium. The adsorption amounts of the crosslinked metal-complexed chitosans for metal ions were significantly dependent on the molar ratio of chitosan/crosslinker, the pH in the solution and the metal species. They were demonstrated that the comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions followed in the orders of the adsorbed amounts with templates: Cu(II) ∼ Pb(II) > Zn(II) ∼ Ni(II), Zn(II) > Cu(II) ∼ Pb(II) > Ni(II), Ni(II) > Pb(II) > Zn(II) > Cu(II) and Pb(II) ∼ Cu(II) > Zn(II) > Ni(II), respectively. The adsorbed amount of Pb(II) ion on the crosslinked metal-complexed chitosans with four metal ions as templates showed to have the highest than those of other three metal ions (Cu(II), Zn(II), and NI(II)). In addition, the dynamical study showed to be well followed the second-order kinetic equation in the adsorption process. At the same time, the equilibrium adsorption studies were fitted

in three adsorption isotherm models, namely, Langmuir, Freundlich, and Dubinin–Radushkevich to show very good fits in the Langmuir isotherm equation for the monolayer adsorption process. The mean adsorption energies of the four metals from the Dubinin–Radushkevich isotherm reflected that the adsorptions might be predominant on the chemisorption process. Therefore, the chemically crosslinked metal-complexed chitosans with glutaraldehyde with glutaraldehyde were demonstrated to afford higher adsorption capacity, and better adsorption efficiency of adsorbents toward metals in an aqueous medium.

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