

Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin

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Abstract

The crosslinked chitosans synthesized by the homogeneous reaction of chitosan in aqueous acetic acid solution with epichlorohydrin were used to investigate the adsorptions of three metals of Cu(II), Zn(II), and Pb(II) ions in an aqueous solution. The crosslinked chitosan characterized by ¹³CNMR, SEM, and elemental analysis, and the effects of pH and anion on the adsorption capacity were carried out. The dynamical study demonstrated that the adsorption process was followed the second-order kinetic equation. The results obtained from the equilibrium isotherms adsorption studies of three metals of Cu(II), Zn(II), and Pb(II) ions by being analyzed in three adsorption models, namely, Langmuir, Freundlich, and Dubinin-Radushkevich isotherm equations, indicated to be well fitted to the Langmuir isotherm equation under the concentration range studied, by comparing the linear correlation coefficients. The order of the adsorption capacity (Q_m) for three metal ions was as follows: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. This technique for syntheses of the crosslinked chitosans with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution showed that the adsorptions of three metal ions in aqueous solution were followed the monolayer coverage of the adsorbents through physical adsorption phenomena.

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1. Introduction

Chitosan, poly(β -1,4)-2-amino-2-deoxy-D-glucopyranose, is prepared from chitin, a natural biopolymer extracted from crustacean shells by partially deacetylating its acetamido groups, generally more than 60%, with a strong alkaline solution. Since both chitin and chitosan exist with some unique properties like biodegradability, biocompatibility and bioactivity, they have a variety of potential applications in biomedical products, cosmetics and food processing, metal chelating agents, and the like [1].

At present, the presence of heavy metal ions in the environment has received extensive attention due to increased discharge, toxicity in the environment, and other adverse effects which heavy metal ions have on receiving waters. The potential sources of heavy metal ions from industrial wastewaters include fertilizer, metal fabrication, paints, pigments, batteries, and the like. These would endanger public health and the environment if

discharged improperly. Many methods such as ion exchange, precipitation, adsorption, membrane processes, and the like have been used for removal of toxic metal ions [2–7]. In particular, adsorption is recognized as an effective and economic method for removal of pollutants from wastewaters. Activated carbon is one of the most widely used adsorbent [8,9]. However, because it is expensive, low-cost biosorbents have been considerable attention in drastically reducing the cost of an adsorption system. In particular, chitin and chitosan, two low-cost natural materials, have been used for adsorption of metal ions, dyes and proteins [10–14]. Comparing the two, chitosan is more efficient than chitin in terms of adsorption capacity due to the presence of a large number of free amino groups on chitosan chain for its adsorption [15–17]. However, unlike chitin, chitosan is soluble in dilute organic acids, such as acetic acid, formic acid, and the like. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in acid media and in its resistance to biochemical and microbiological degradation [18–28]. Although the crosslinking method may reduce the adsorption capacity of chitosan, it can enhance the resistance of chitosan against acids and chemicals.

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Most importantly, this study considered the adsorption characteristics of copper(II), lead(II) and zinc(II) ions on chitosan crosslinked with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution. The reaction conditions for preparation of chitosan crosslinked with epichlorohydrin and the influences of adsorption conditions such as molar ratios of crosslinker/chitosan, pH changes and anion effects were investigated. The adsorption isotherms of copper(II), zinc(II) and lead(II) ions on chitosan crosslinked with epichlorohydrin were studied to gain a good comparison, accordingly.

2. Experimental

2.1. Chemicals

Chitosan with a deacetylation percentage of approximately 75% as defined by elemental analysis and FTIR methods was purchased from Aldrich. Epichlorohydrin (ECH) of 99.6% purity was purchased from Tedia. Cupric sulfate, cupric chloride, zinc sulfate, and lead nitrate purchased from Wako were analytical-reagent grade.

2.2. Preparation and characterization

The solution of chitosan was prepared with 0.5 g of chitosan dissolved into 5.0 mL of acetic acid (5%, v/v) and added with 45 mL of distilled water. Its pH was adjusted from 3.0 to 11.0 with 1.0 M of sodium hydroxide solution. Epichlorohydrin solution was added, and the mixture was stirred for 24 h at room temperature. Then 50 mL of 1.0 M sodium hydroxide solution was added into the mixture to form the precipitate. The precipitate was filtered and washed intensively with distilled water to remove any unreacted epichlorohydrin. Subsequently, it was dried on vacuum oven for 12 h. The resulting material was grounded and sieved to collect particles with a diameter from 250 to 500 μm for this study.

The CN analyses of the particles were determined on a Heraeus CHN-O-Rapid Analyzer. Solid-state ^{13}C nuclear magnetic resonance spectra of the materials were measured on a Bruker Avance 400 NMR spectrometer. The SEM photomicrographs of the particles were taken using a Hitachi S-3000N scanning electron microscopy.

2.3. Solubility

The epichlorohydrin-crosslinked chitosan particles prepared using the molar ratios of ECH/chitosan from 0.1 to 3.0 were tested with regard to their solubility in each 10 mL of 5% acetic acid (v/v), distilled water and 1.0 M sodium hydroxide solution by adding 0.1 g of each kind of particles into each solution for a period of 24 h with stirring.

2.4. Adsorption experiments

2.4.1. pH effects

The epichlorohydrin-crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 3.0 were investi-

gated to determine the pH effects of their adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solutions. These were adjusted to pH 3.0 and 6.0 with 1.0 M hydrochloric acid solution, and then by stirring for 4 h at room temperature. Their solutions were filtered 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 Eq. (1):

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o is the initial concentration of Cu(II) ion (ppm), C_e is the final concentration of Cu(II) ion (ppm), V is the volume of Cu(II) ion solution (mL) and W is the weight of the ECH-crosslinked chitosan (g) used.

2.4.2. Kinetics of adsorption

The five epichlorohydrin-crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 3.0 and the chitosan were studied to determine adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solution at pH 6.0 while stirring at room temperature. Then 10 mL aliquots of these solutions at intervals of 25 min were filtered and their concentrations of Cu(II) ion were measured by atomic absorption spectrophotometer. The adsorption capacity was calculated by Eq. (1).

2.4.3. Anion effects for the adsorption of copper(II) ion

The epichlorohydrin-crosslinked chitosan materials prepared with 0.1 to 3.0 molar ratios of ECH/chitosan were evaluated to determine the anion effects of their adsorption of copper(II) ion by adding 10 mg of each kind of particles into 100 mL of 10 ppm cupric sulfate solutions or 100 mL of 10 ppm cupric chloride solutions at pH 6.0 and then by stirring for 4 h at room temperature. The adsorption capacity (Q_e) was calculated by Eq. (1).

2.5. Adsorption isotherms

The isothermal studies were conducted with 10 mg of the epichlorohydrin-crosslinked chitosan (molar ratio of ECH/chitosan = 0.5/1.0) in 100 mL of initial concentration of copper(II), lead(II) or zinc(II) ions in the range of 0–15 ppm at pH 6.0 and with stirring for 4 h at room temperature. Their solutions were filtered and the concentrations of Cu(II), Pb(II) or Zn(II) ions were measured on a Hitachi 170-30 atomic absorption spectrophotometer at 324.8, 217.0 or 213.9 nm, respectively. The amounts of copper(II), lead(II) or zinc(II) ions adsorption were calculated by Eq. (1).

3. Results and discussion

3.1. Preparation and characterization

Some reported that there was heterogeneous reaction between chitosan bead and epichlorohydrin performed in alkaline

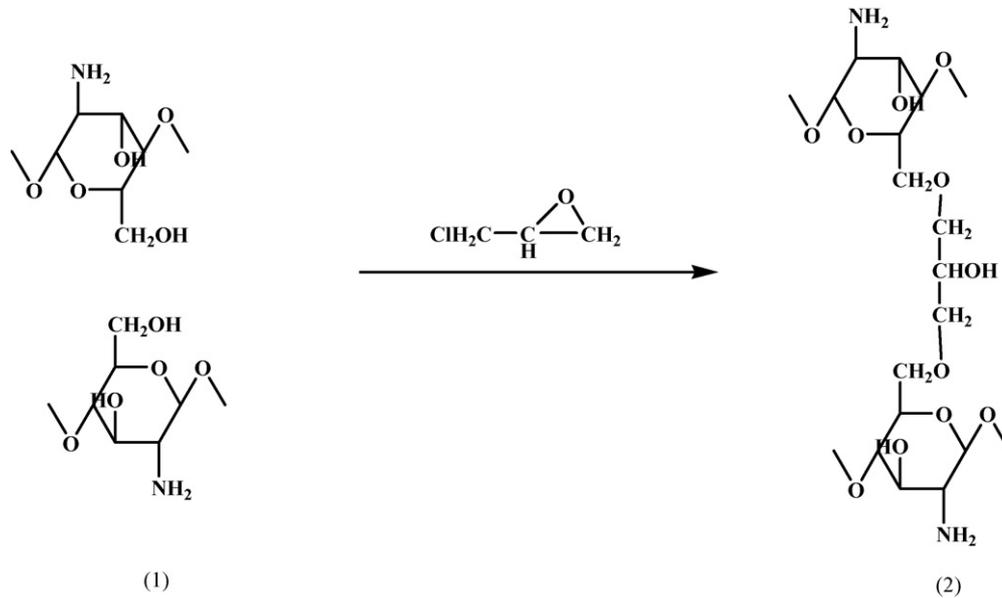


Fig. 1. Schematic representation for the crosslinking reaction of chitosan with epichlorohydrin.

medium (pH 10.0) at between 40 and 50 °C for 2 h [21,24,26]. But the homogeneous reaction of chitosan being dissolved in aqueous acetic acid with treatment of epichlorohydrin was worth investigating because the aqueous acetic acid solution of chitosan should be precipitated while adding alkaline solution of epichlorohydrin. The reaction of chitosan (1) with epichlorohydrin in an acidic condition might be crosslinked at hydroxyl groups to form the epichlorohydrin crosslinked chitosan product (2), as shown in Fig. 1 [21]. Therefore, in the present case, the pHs and molar ratios of epichlorohy-

drin to chitosan conditions established were appropriated for the crosslinking reaction between chitosan and epichlorohydrin in the homogeneous reaction. The solid-state ^{13}C NMR of ECH–chitosan appeared to have three peaks at 61.6, 85.0 and 97.6 ppm due to exiting of $-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O}-$ linkage between two chitosan molecules in comparison with chitosan (Fig. 2). The C/N ratios of epichlorohydrin crosslinked chitosans prepared from 3.0 to 11.0 pH in elemental analysis showed to be larger at high pH (≥ 7.0), as shown in Fig. 3. Therefore, the homogeneous reaction of the aqueous acetic acid

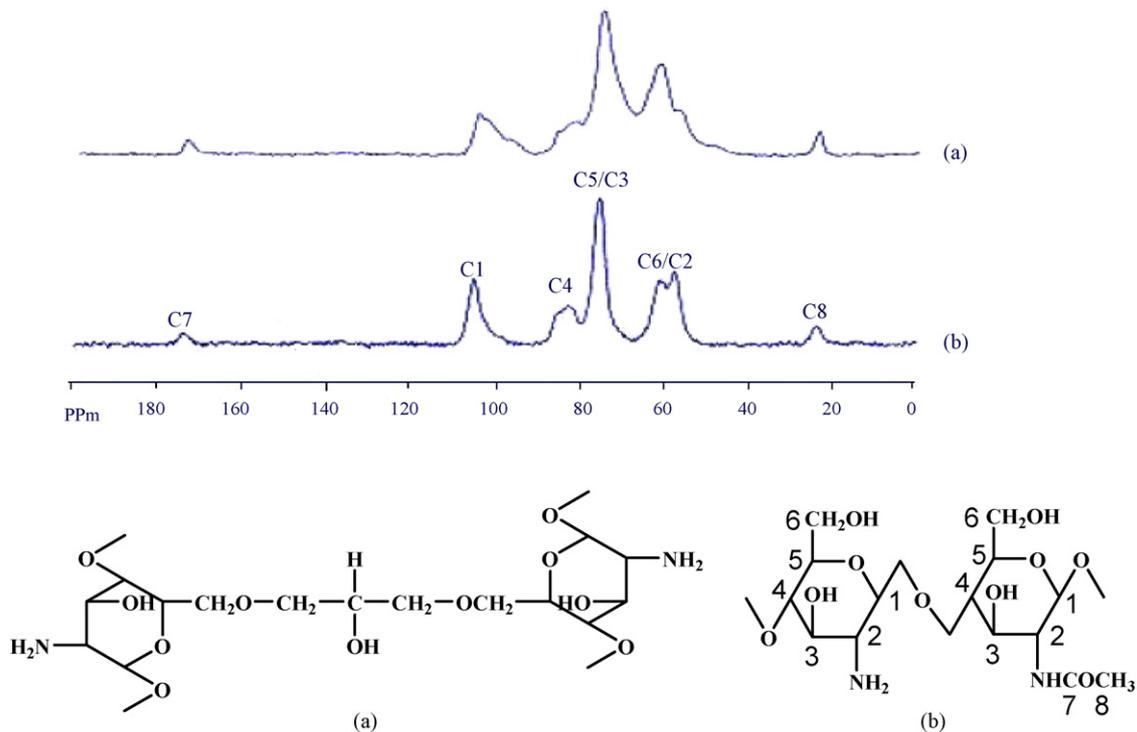


Fig. 2. Solid-state ^{13}C NMR of the epichlorohydrin-crosslinked chitosan (a) and the chitosan with a partial acetylation (b).

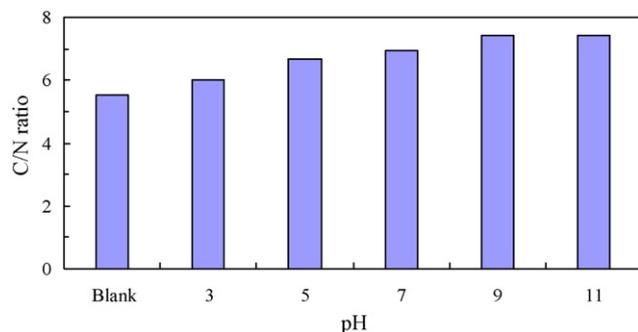


Fig. 3. C/N ratios of the epichlorohydrin–chitosans prepared at different pHs.

solution of chitosan with epichlorohydrin could be conducted to afford better crosslinking at pH 7.0 due to the precipitation of chitosan from a homogeneous reaction solution at pH > 7.

3.2. Solubility and surface morphology

After crosslinking with different molar ratios of ECH/chitosan ranging from 0.1 to 3.0, the crosslinked chitosans were found to be insoluble in acid and alkaline media as well as distilled water in comparison with native chitosan. It has been well known that the high hydrophilicity of chitosan with the primary amino group makes it easily soluble in dilute organic acids to yield a hydrogel in water. Therefore, the crosslinking treatment of chitosan reinforces its chemical stability in organic acidic media, making it useful for the removal of chemical pollutants from wastewaters in acidic solution. The scanning electron microscopies of chitosan and epichlorohydrin crosslinked chitosan prepared from different molar ratios of epichlorohydrin/chitosan were shown in Fig. 4. It was found that the surfaces of the crosslinked chitosans prepared with more molar ratios of epichlorohydrin/chitosan were noted to have much asperity and to be more coarsely grained.

3.3. Kinetics and effects of molar ratios of ECH/chitosan, pH and anions

The kinetics for the adsorption of copper(II) on epichlorohydrin crosslinked chitosan was studied in an aqueous Cu^{2+} solution at pH 6.0 on five epichlorohydrin crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 3.0 at pH 7.0, and chitosan with times ranging from 0 to 300 min, as shown in Fig. 5. The relatively rapid initial rates of adsorption of copper(II) ion on four epichlorohydrin crosslinked chitosan materials prepared with molar ratios of ECH/chitosan from 0.1 to 1.0, and on chitosan were seen to increase markedly during the first 20 min and to gradually approach the limiting adsorption after 240 min. But there was a slow initial rate in an epichlorohydrin crosslinked chitosan materials prepared with 3.0 molar ratios of ECH/chitosan. At the same time, the kinetics for the adsorptions of Zn(II) and Pb(II) ions were as same as those of Cu(II) ion.

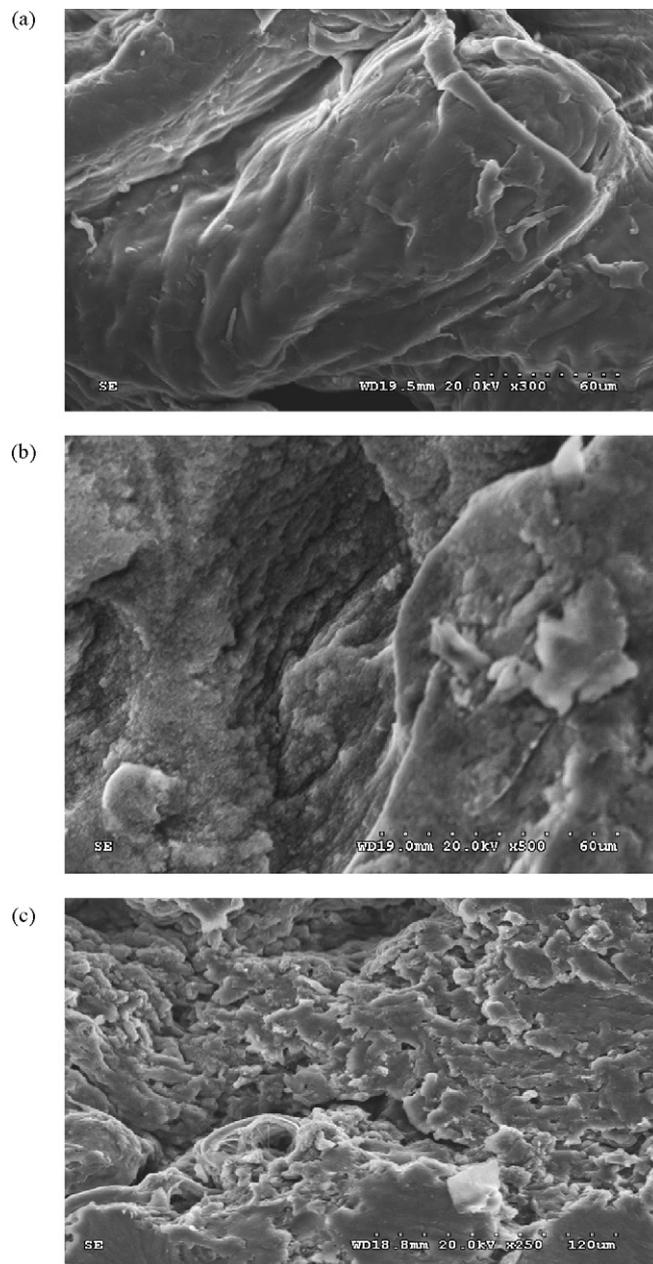


Fig. 4. SEM photomicrographs of (a) chitosan, (b) molar ratio of ECH/chitosan (0.5/1.0), and (c) molar ratio of epichlorohydrin/chitosan (3.0/1.0).

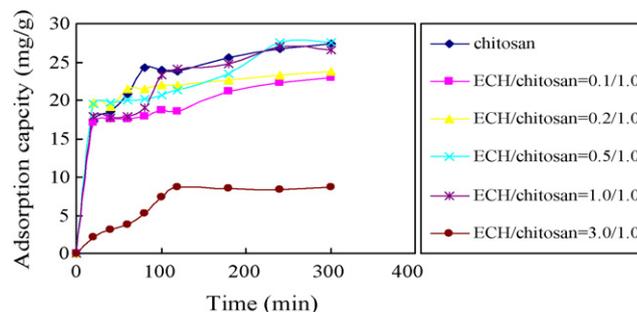


Fig. 5. Kinetics on adsorption of Cu(II) ion on the epichlorohydrin-crosslinked chitosans prepared from different molar ratios of epichlorohydrin and chitosan at pH 7.

Table 1
Kinetic parameters on the epichlorohydrin-crosslinked chitosans prepared from 0.5 molar ratios of ECH/chitosan

Metal ions	Cu(II) ion	Zn(II) ion	Pb(II) ion
First-order kinetics			
k_1 ($\times 10^{-2}$ min $^{-1}$)	0.41	0.94	0.95
R^2	0.8829	0.9505	0.8870
Second-order kinetics			
k_2 ($\times 10^{-3}$ g/mg min)	3.87	5.34	2.41
R^2	0.9908	0.9991	0.9985

Note: R^2 is the correlation coefficient.

Table 2
Langmuir, Freundlich, and Dubinin-Radushkevich isotherms constants for Cu(II), Zn(II), and Pb(II) ions on the epichlorohydrin-crosslinked chitosan

Constants	Cu(II)	Zn(II)	Pb(II)
Langmuir isotherm			
Q_m (mg/g)	35.46 ± 0.95	10.21 ± 0.81	34.13 ± 0.93
b (mL/mg)	1.49 ± 0.32	0.56 ± 0.05	2.46 ± 0.25
R^2	0.9912	0.9978	0.9981
Freundlich isotherm			
K_F (mg/g)	15.00 ± 2.35	3.28 ± 0.09	20.27 ± 1.48
b_F	0.41 ± 0.07	0.76 ± 0.04	0.19 ± 0.01
R^2	0.9401	0.8620	0.8843
Dubinin-Radushkevich isotherm			
Q_{DR} (mg/g)	29.10 ± 3.01	7.78 ± 0.22	34.69 ± 0.54
K (kJ 2 /mol)	-0.0083 ± 0.0001	-0.0197 ± 0.0001	-0.0364 ± 0.0001
E (kJ/mol)	7.79 ± 0.03	5.05 ± 0.01	3.71 ± 0.001
R^2	0.8783	0.9204	0.8929

Note: R^2 is the correlation coefficient.

The dynamical experimental data were applied to the first- and the second-order equations, as shown in Table 1. Comparing the correction coefficients, the second-order kinetic equation could be a good fit with the dynamical experimental data. Therefore, it was more likely to reflect that the adsorption behavior might involve the valency forces through sharing electrons between metal ions and adsorbents [11,29–31].

The adsorption capacities of copper(II) ion on the five epichlorohydrin crosslinked chitosan materials and on the chitosan in an aqueous Cu^{2+} solution at pH 3.0 and 6.0 for 4 h were shown in Fig. 6. But all those materials were soluble at pH 1.0.

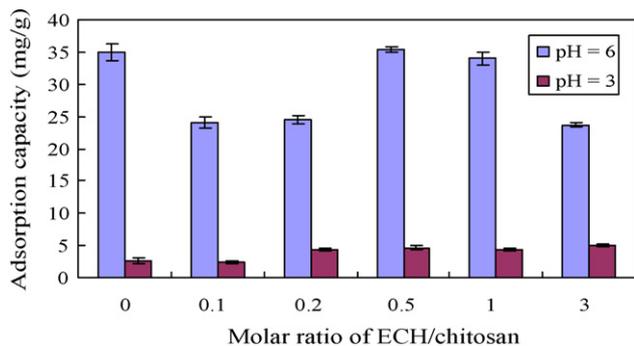


Fig. 6. Adsorption capacity of Cu^{2+} ion on the epichlorohydrin-crosslinked chitosans prepared from different molar ratios in aqueous solutions of different pHs.

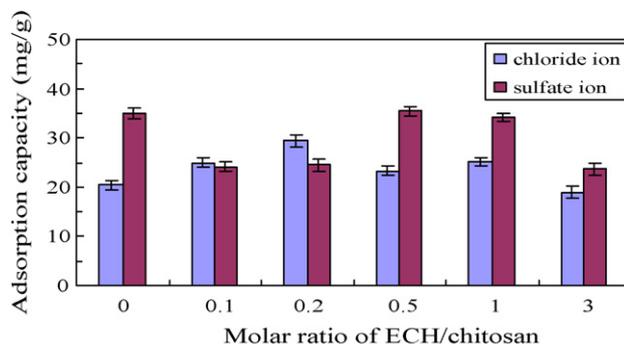


Fig. 7. Anion effects of adsorption capacity of Cu^{2+} ion on the epichlorohydrin-crosslinked chitosans prepared from different molar ratios in aqueous solutions of CuCl_2 and CuSO_4 .

All the five materials and the chitosan were found to have higher adsorption capacities at pH 6.0 than at pH 3.0. The adsorption capacities of Cu(II) ion revealed to be lower at low pH due to the electrostatic repulsion between the Cu(II) 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 heavy metal ions. At the same time, they were found to be the largest adsorption capacity of Cu^{2+} ion at pH 6.0, that is, 35.40 ± 0.41 mg/g, on the epichlorohydrin crosslinked chitosan materials prepared with 0.5 molar ratios of ECH/chitosan at pH 7.0. However, the adsorption capacities of copper(II) ion on those five epichlorohydrin crosslinked chitosan materials and on the chitosan in an aqueous Cu^{2+} solution of sulfate or chloride at pH 6.0 for 4 h showed to be larger in sulfate solution than in chloride solution (Fig. 7). Obviously sulfate with higher charge than chloride might be more effective in charge compensation and ionic binding [20,31]. At the same time, the epichlorohydrin crosslinked chitosan material prepared with 0.5 molar ratio of ECH/chitosan at pH 7.0 had the highest adsorption capacity of Cu^{2+} ion in sulfate solution.

3.4. Adsorption equilibria of copper(II), lead(II) and zinc(II)

The equilibrium adsorption data of copper(II), zinc(II), and lead(II) ions were subjected to three different adsorption isotherms, namely Langmuir, Freundlich, and Dubinin-Radushkevich isotherms.

The Langmuir isotherm equation, which is the most commonly used for monolayer adsorption on to a surface with a finite number of identical sites, is represented by the following Eq. (2):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (2)$$

where C_e is the equilibrium concentration of metal ions (ppm), 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 (mL/mg). Therefore, the plot of C_e/Q_e against C_e gives a straight line with a slope of $1/Q_m$ and an intercept of $1/(Q_m b)$.

The Freundlich isotherm equation, the most important multilayer adsorption isotherm for heterogeneous surfaces, is described by the following Eq. (3):

$$\ln Q_e = b_F \ln C_e + \ln K_F \quad (3)$$

where C_e is the equilibrium concentration of metal ions (ppm), 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. Freundlich constants, K_F and b_F , can be determined from a linear plot of $\ln Q_e$ versus $\ln C_e$.

The Dubinin-Radushkevich isotherm equation, which is more generally used to distinguish between physical and chemical adsorption, is given by the following Eq. (4):

$$\ln Q_e = K\varepsilon^2 + \ln Q_{DR} \quad (4)$$

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 (kJ²/mol) and ε is Polanyi potential given as the Eq. (5):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (5)$$

where R is the gas constant in J (K mol)⁻¹, T is the temperature in Kelvin and C_e is the equilibrium concentration of metal ions (ppm). Thus the plot of $\ln Q_e$ against ε^2 gives a straight line with a slope of K and an intercept of Q_{DR} . The Dubinin-Radushkevich constant can give the valuable information regarding the mean energy of adsorption by the following Eq. (6):

$$E = (-2K)^{-1/2} \quad (6)$$

where E is the mean adsorption energy (kJ/mol), and K is the Dubinin-Radushkevich constant.

The experimental equilibrium isotherms for adsorption of copper(II) ion on the epichlorohydrin crosslinked chitosan and on the chitosan without chemical modification were shown in Fig. 8. Their adsorption isotherms according to the Langmuir, the Freundlich, and the Dubinin-Radushkevich isotherm equations were shown in Fig. 9, and their isotherm constants were summarized in Table 2. Comparing their linear correlation coefficients listed in Table 2, it could be made the conclusion that the adsorption of copper(II) ion on the epichlorohydrin crosslinked

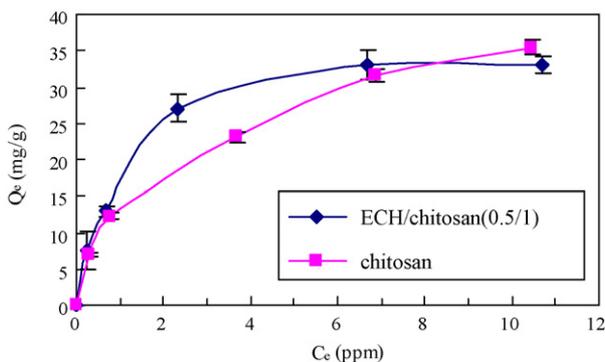


Fig. 8. Adsorption isotherms of copper(II) ion on the epichlorohydrin-crosslinked chitosan and chitosan.

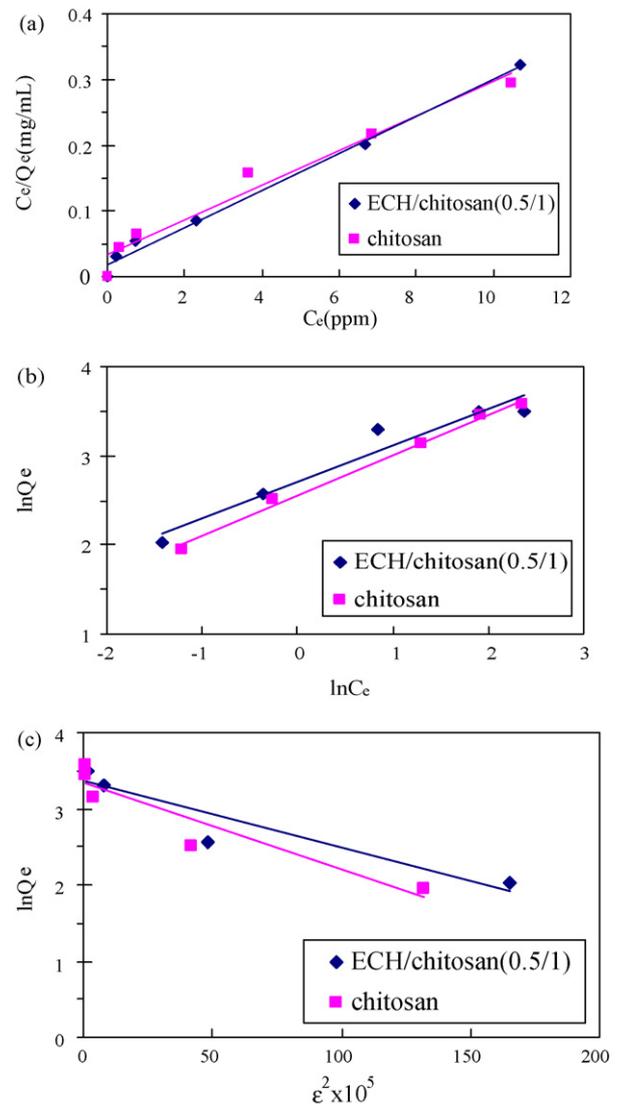


Fig. 9. Adsorption isotherms of copper(II) ion on the epichlorohydrin-crosslinked chitosan and chitosan, linearized according to (a) Langmuir, (b) Freundlich, and (c) Dubinin-Radushkevich equations.

chitosan was well followed as the Langmuir isotherm equation under the concentration range studied. In addition, the adsorptions of other two metals of zinc(II), and lead(II) ions on the epichlorohydrin crosslinked chitosan were still well followed as the Langmuir isotherm equation under the concentration range studied, summarized in Table 2. The orders of the adsorption capacities (Q_m , mg/g) from the Langmuir isotherm equation for three metal ions were as follows: Cu^{2+} (35.46 ± 0.95) > Pb^{2+} (34.13 ± 0.93) > Zn^{2+} (10.21 ± 0.81). The adsorption capacities of three metals from the Dubinin-Radushkevich isotherms based on Polanyi potential theory of solution were near to the Langmuir isotherms than the Freundlich isotherms. The mean adsorption energy (E) was 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 energy, and the chemical adsorption in more than 8 kJ/mol of the mean adsorption energy [32]. The values of the

mean energy of adsorption (E) for three metals from 3.71 to 7.79 kJ/mol revealed that their adsorptions were predominant on the physical adsorption process. Therefore, this technique for syntheses of the crosslinked chitosans with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution showed that the adsorptions of three metals of Cu(II), Zn(II), and Pb(II) ions in aqueous solution were followed the monolayer coverage of the adsorbents through physical adsorption phenomena.

According to the Langmuir isotherm equation, the maximum adsorption (Q_m) of Cu(II) ion on the epichlorohydrin crosslinked chitosan was a little smaller than that on chitosan, which were 35.46 ± 0.95 and 37.88 ± 1.08 mg/g, respectively. At the same time, the maximum adsorptions (Q_m) of Zn(II) ion on the epichlorohydrin crosslinked chitosan and on the chitosan, which were 10.21 ± 0.81 and 10.32 ± 0.72 mg/g, respectively, were nearly same. In general, the crosslinked treatment of chitosan with epichlorohydrin should have a reduced adsorption capacity of metal ions due to a decrease in the accessibility to the internal sites or block a number of adsorption sites [21]. Therefore, the crosslinked chitosan prepared by the homogeneous reaction of chitosan in aqueous acetic acid solution with epichlorohydrin in 0.5 molar ratio of ECH/chitosan demonstrated that the adsorptions (Q_m) of Cu(II), and Zn(II) ions were similar to chitosan, with only a little decrease (6.39% and 1.07%, respectively). But Ngah et al. reported that the adsorption (Q_m) of Cu(II) ion was decreased in 22.60% on the crosslinked chitosan prepared via the heterogeneous reaction between chitosan bead and epichlorohydrin in alkaline medium as compared with chitosan [21]. However, the maximum adsorption (Q_m) of Pb(II) ion on the epichlorohydrin crosslinked chitosan was found to be more than two times of chitosan, which were 34.13 ± 0.93 and 13.05 ± 2.13 mg/g, respectively.

4. Conclusion

The crosslinked chitosans synthesized by the homogeneous reaction of chitosan in aqueous acetic acid solution with epichlorohydrin had been used to investigate the adsorptions of three metals of Cu(II), Zn(II), and Pb(II) ions in aqueous solution. The crosslinked chitosan material prepared with 0.5 molar ratio of epichlorohydrin/chitosan at pH 7.0 showed to have the highest adsorption. The dynamical study demonstrated that the adsorption process was followed the second-order kinetic equation. The results obtained from the equilibrium isotherms adsorption studies of three metals of Cu(II), Zn(II), and Pb(II) ions by being analyzed in three adsorption models, namely, Langmuir, Freundlich, and Dubinin-Radushkevich isotherm equations, indicated to be well fitted to the Langmuir isotherm equation under the concentration range studied. The orders of the adsorption capacities (Q_m) from the Langmuir isotherm equation for three metal ions were as follows: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. The adsorption capacities of three metals from the Dubinin-Radushkevich isotherms were near to the Langmuir isotherms than the Freundlich isotherms. From the Dubinin-Radushkevich isotherm, the values of the mean energy of adsorption (E) for three metals revealed that their adsorptions

were predominant on the physical adsorption process. Therefore, this technique for syntheses of the crosslinked chitosans with epichlorohydrin via the homogeneous reaction in aqueous acetic acid solution showed that the adsorptions of three metals of Cu(II), Zn(II), and Pb(II) ions in aqueous solution were followed the monolayer coverage of the adsorbents through physical adsorption phenomena.

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