Adsorption of Cd(II), Pb(II), and Ag(I) in Aqueous Solution on Hollow Chitosan Microspheres

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ABSTRACT: Cross-linked chitosans synthesized by the inverse emulsion cross-link method were used to investigate adsorption of three metal ions [Cd(II), Pb(II), and Ag(I)] in an aqueous solution. The chitosan microsphere, was characterized by FTIR and SEM, and adsorption of Cd(II), Pb(II), and Ag(I) ions onto a cross-linked chitosan was examined through analysis of pH, agitation time, temperature, and initial concentration of the metal. The order of adsorption capacity for the three metal ions was $Cd^{2+} > Pb^{2+} > Ag^+$. This method showed that adsorption of the three metal ions in an aqueous solution followed the monolayer coverage of the adsorbents through physical adsorption phenomena and coordination because the amino ($-NH_2$) and/or hydroxy ($-OH$) groups on chitosan chains serve as coordination sites. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 733–739, 2010

Key words: hollow chitosan microsphere; noble metal; adsorption

INTRODUCTION

Chitosan [poly(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. Chitin, which generally comprises more than 60% of the crustacean shells, has unique properties, such as biodegradability, biocompatibility, and bioactivity. Chitosan has a variety of potential applications in, for example, biomedical products, cosmetics, food processing, and as metal chelating agents.[1] At present, the presence of heavy metal ions in the environment has received extensive attention as a result of increased discharges, environmental toxicity, and other adverse effects that heavy metal ions have on receiving waters. The potential sources of heavy metal ions in industrial wastewaters include fertilizer, metal fabrication, paints, pigments, and batteries. These would endanger public health and the environment if discharged improperly. Many methods, such as ion exchange, precipitation, adsorption, and membrane processes have been used for the removal of toxic metal ions.[2–7]

In particular, adsorption is recognized as an effective and economic method for removing pollutants from wastewaters. Activated carbon is one of the most widely used adsorbents.[8,9] However, because activated carbon is expensive, low-cost biosorbents have received considerable attention in attempts to reduce 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] Of the two, chitosan is more efficient than chitin in terms of adsorption capacity because of the presence of a large number of free amino groups for adsorption on the chitosan chain.[15–17] However, unlike chitin, chitosan is soluble in dilute organic acids, such as acetic acid. Therefore, various physical and chemical modifications have been developed to improve the chemical stability of chitosan in an acid media and in its resistance to biochemical and microbiological degradation.[18–28] Although the cross-linking method may reduce the adsorption capacity of chitosan, it can enhance the resistance of chitosan against acids and chemicals. The present investigation considered the adsorption characteristics of Cd(II), Pb(II), and Ag(I) ions on a hollow chitosan microsphere. The reaction conditions for preparation of the hollow chitosan microsphere and the influence of adsorption conditions, such as pH, agitation time, temperature, and concentration of the metals, was investigated. A comparison of the adsorption isotherms of Cd(II), Pb(II), and Ag(I) ions on the chitosan microsphere were also studied.

METHODOLOGY

Chemicals

Chitosan (molecular volume 750,000) was synthesized and the degree of deacetylation was 55%. Formaldehyde was obtained from Sigma-Aldrich Inc. All other materials used in the dissolution studies were of analytical reagent grade.

Preparation and characterization

A 250 mL three-necked boiling flask was equipped with a mechanical stirrer, a nitrogen inlet, and a Hirsch funnel. To the flask, 1.0 g of Chitosan (CS) was dissolved into 20 mL of 2% (v/v) aqueous acetic acid. Ten minutes later, 100 mL of liquid oil and 4 drops 1% PVA containing emulsifier (Span-20) were added by drops into the three-necked flask at 50°C. The suspension was stirred with a mechanical stirrer at 500 rpm for ∼60 min. The mixture was stirred vigorously in a nitrogen atmosphere until the water phase was uniformly dispersed. A certain amount of 3.7% formaldehyde was slowly added to the suspension and the mixture was stirred with a mechanical stirrer at 400 rpm for an additional 30 min at 50°C. Then 2 mL of 37% formaldehyde was added to the suspension and the mixture was stirred continuously in a nitrogen atmosphere for 30 min. Next OH^{-1} was added to the flask until the pH of the mixture reached 9.0–10.0; stirring continued for a further 15 min. Finally, the product mixture of products was filtered and washed first with acetone and then ethanol to remove unreacted chitosan and other impurities and then dried at room temperature.

Adsorption experiments

The adsorption of the metals was determined using batch procedures[20] where the chitosan quantities specified by the adsorption factorial design were placed in contact with 50 mL of aqueous solutions in 100-mL polyethylene flasks. The suspensions were agitated for a period of time sufficient to reach equilibrium.

pH effects

The pH of the hollow chitosan microspheres was adjusted to pH 1.0 and 9.0 with 1.0 M hydrochloric acid solution and 1.0 M NaOH solution, respectively, and then stirred for 2 h at room temperature. The solutions were filtered and the ion concentrations of Cd(II), Pb(II), and Ag(I) were measured on a Hitachi 170-30 atomic absorption spectrophotometer. The adsorption capacity (Q_e) was calculated by the following equation:

$$Q_e = (C_o - C_e)V/W, \tag{1}$$

where C_o is the initial concentration of Cd(II), C_e is the final concentration of Cd(II), V is the volume of Cd(II) solution (mL), and W is the weight of the chitosan microsphere (g).

Effect of initial concentration

The hollow chitosan microsphere was investigated to determine the initial concentration effects of the metal ions on adsorption of Cd(II), Pb(II), and Ag(I). Concentrations of Cd(II), Pb(II), and Ag(I) ion solutions were adjusted to be in the range of 0–1000 mg/L at pH 7.0, 5.0, 7.0 and then stirred for 2 h at room temperature. The solutions were filtered and ion concentrations were measured on a Hitachi 170-30 atomic absorption spectrophotometer. The adsorption capacity (Q_e) was calculated by eq. (1).

Effect of temperature

The effect of temperature of the hollow chitosan microsphere on Cd(II), Pb(II), and Ag(I) ion adsorption was investigated. Temperature of the three ion solutions was adjusted to be in the range of 20–45 °C at intervals of 5°C at pH 7.0, 5.0, 7.0, and the solutions were then stirred for 2 h at room temperature, filtered, and the ion concentrations of each solution measured on a Hitachi 170-30 atomic absorption spectrophotometer. The adsorption capacity (Q_e) was calculated by eq. (1).

Kinetics of adsorption

Ion adsorption of the hollow chitosan microsphere was studied by adding microspheres into a CdCl$_2$, PbCl$_2$, or AgNO$_3$ solution at pH 7, 5, 7 while stirring at room temperature. Then 10 mL aliquots of these solutions were filtered at intervals of 25 min and Cd(II), Pb(II), Ag(I) ion concentrations were measured with an atomic absorption spectrophotometer. The adsorption capacity was calculated by eq. (1).

Adsorption isotherms

Isothermal studies were conducted with 10 mg of the chitosan microsphere in 100 mL of an initial concentration of Cd(II), Pb(II), or Ag(I) ions in the range of 0–1000 ppm at pH 7.0, 5.0, 7.0 and stirring for 2 h at room temperature. Solutions were filtered and the ion concentrations of Cd(II), Pb(II) or Ag (I) were measured on a Hitachi 170-30 atomic absorption spectrophotometer at 544.8 nm, 283.3 nm, 328.1 nm, respectively. The amounts of Cd(II), Pb(II), or Ag(I) ion adsorption were calculated by eq. (1).
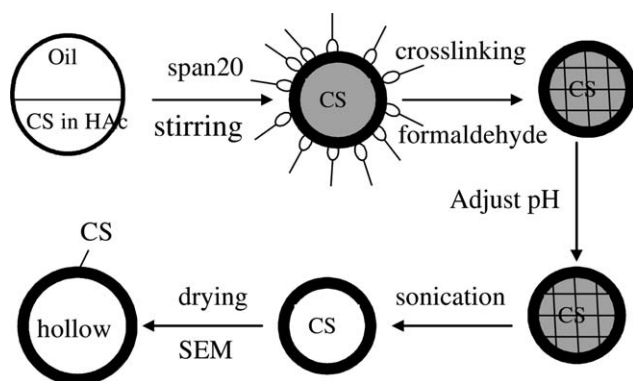
Figure 1 Schematic illustration for the preparation of chitosan microsphere.

RESULTS AND DISCUSSION

Preparation and characterization

The presence of CS in the microspheres has been confirmed by FTIR measurements. Curves a and b in Figure 2 are the FTIR spectra of the CS and CS microsphere. The FTIR spectra of the chitosan flakes and chitosan microspheres are shown in Figure 2(a,b). Usually, the major peaks of the chitosan flakes are located at ~ 3400 cm^{-1} for OH stretching vibration and 1650 cm^{-1} for NH stretching vibration. The bands observed at 1320 cm^{-1} and 1380 cm^{-1} are assigned to the CH$_3$ deformation and C—N bend. The broad band at 3433 cm^{-1} was —OH stretching, which overlapped the NH stretching in the same region. The shifts at 1660 and 1597 cm^{-1} were the bands of amide I and II, respectively. For the chitosan microspheres, a new peak at 1635 cm^{-1} was seen [Fig. 2(b)], which corresponded to stretching vibrations of the C=N bond. It indicated that the chitosan was cross-linked.

Solubility and surface morphology

The chitosan microspheres were found to be insoluble in acid and alkaline media as well as distilled water compared to 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 to yield a hydrogel in water. Therefore, the cross-linking 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 SEM images of the chitosan microspheres prepared under standard preparative conditions in Figure 3 show the CS microsphere and its enlarged surface structure. The microsphere is shown to be spherical with a diameter of $\sim$74 μm [Fig. 3(a)]. The chitosan microspheres were found to have a regular spherical geometry [Fig. 3(b)]. Further study indicated that the micro-

sphere contracts with drying and is swollen after being immersed in water, and this contracting and swelling could be repeated for a number of times. The average value 9/S.D. In addition, the size distribution of the composite microspheres was narrow. Figure 3(c) shows the broken CS spherical particle in which the contrast across the diameter reveals that the thickness of the shell wall is about 2 μm. A comparative analysis of SEM images [Fig. 3(c)] demonstrates that the particles are hollow. Chitosan microspheres are shown to exhibit a smooth surface morphology [Fig. 3(d)].

Effect of pH

Figure 4 shows the effect of pH on the adsorption of Cd(II), Pb(II), and Ag(I) ions by chitosan microsphere. The adsorption of Cd(II) increases with increasing pH of the solution. This could be explained by the fact that at a low pH (acidic solution), protonation of the amine groups in the beads easily occurs, which induces an electrostatic repulsion of Cd(II) ions. Competition then exists between protons and Cd(II) ions for adsorption sites and adsorption capacity decreases. At higher pH values, precipitation of Cd(II) hydroxide occurs simultaneously with the adsorption of Cd(II) ions. Hence, one needs to be careful in interpreting the adsorption capacity of the beads. pH 7 was chosen for the adsorption of Cd(II) ions to avoid the formation of Cd(II) hydroxide, which would affect adsorption. The adsorption capacities of Cd(II) ions on the cross-linked chitosan materials in an aqueous Cd^{2+} solution for 3 h at pH 3.0 and 7.0 are shown in Figure 5. This showed adsorption capacity to be lower at a low pH due to the electrostatic repulsion between the Cd(II) cation and the protonated amino group. When the pH value was increased, the amino group
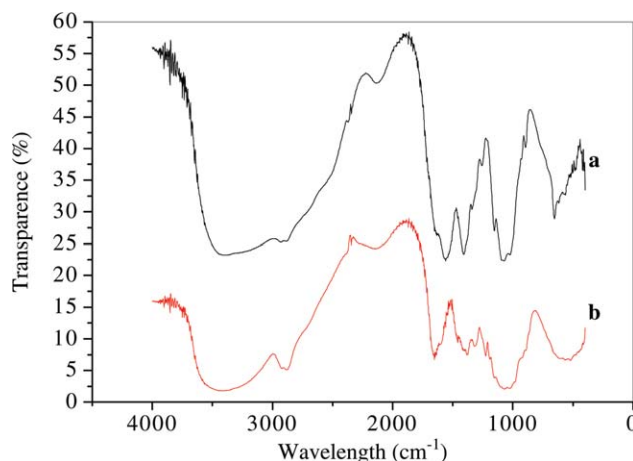

Figure 2 FTIR spectra of chitosan (a) and microsphere (b). [Color figure acn be viewed in the online issue, which is available at www.interscience.wiley.com.]
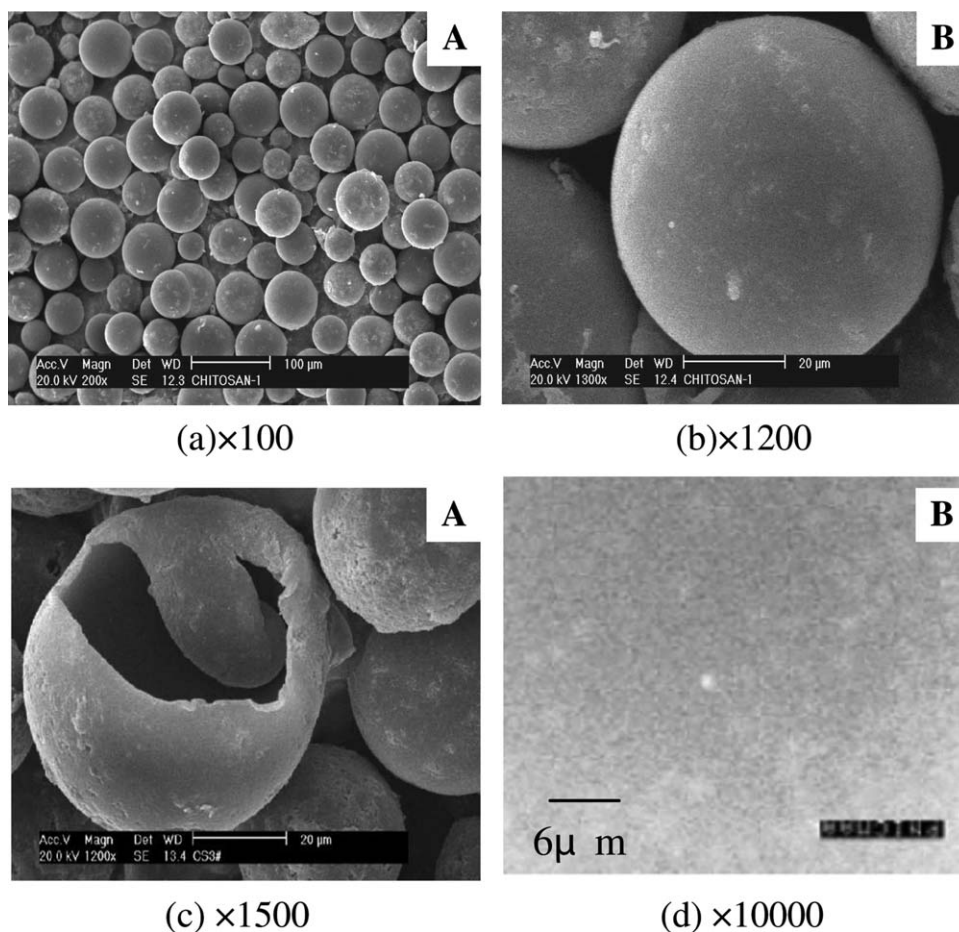
(a)×100

(b)×1200

(c) ×1500

(d) ×10000

Figure 3 SEM of the CS microsphere.

was freed from protonation for the adsorption behavior in the chelation mechanism of the heavy metal ions. At the same time, they were found to be the largest adsorption capacity of Cd^{2+} ion at pH 7.0 was 420 mg/g. However, the adsorption capacities

of Cd^{2+} ion on the chitosan microsphere was shown to be greater in a sulfate solution than in a chloride solution. Obviously sulfate, with a higher charge than chloride, might be more effective in charge compensation and ionic binding.[20,29] and the same
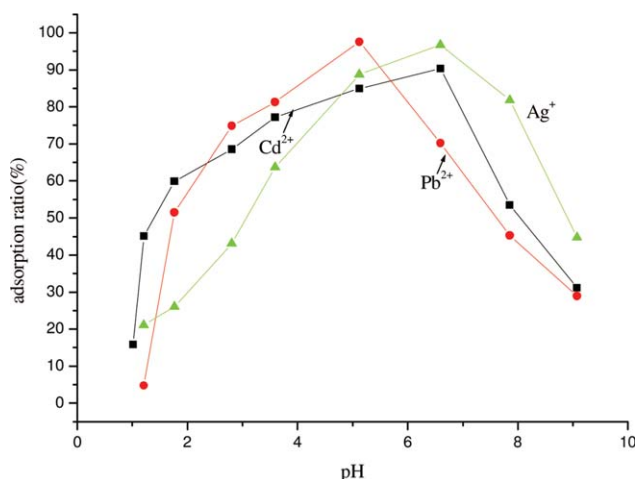

Figure 4 Effect of pH to the adsorption of metal ions. [Color figure acn be viewed in the online issue, which is available at www.interscience.wiley.com.]
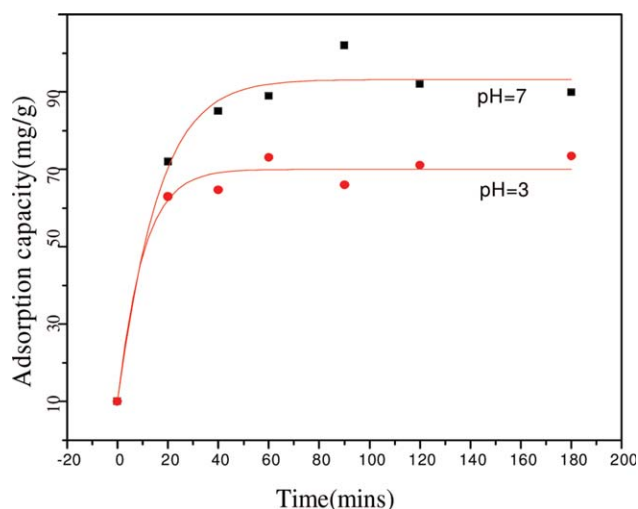

Figure 5 The time effect to the adsorption of Cd(II). [Color figure acn be viewed in the online issue, which is available at www.interscience.wiley.com.]
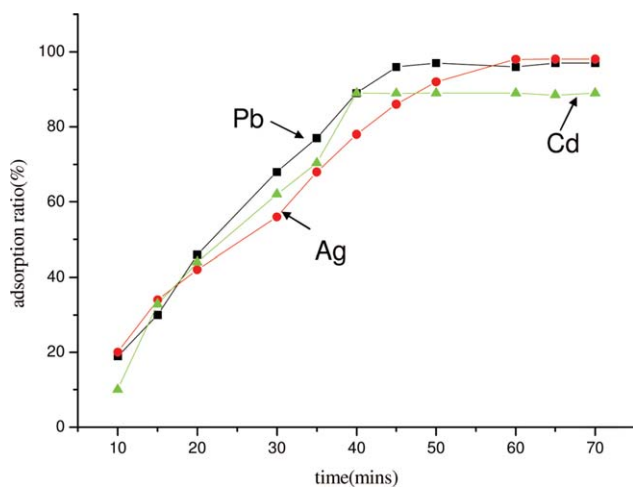
Figure 6 Effect of agitation time to the adsorption. [Color figure acn be viewed in the online issue, which is available at www.interscience.wiley.com.]

with Ag(I), and pH 5.0 was chosen for Pb(II) the adsorption of ions to avoid the formation of hydroxide and coordination which affects adsorption.

Effect of agitation time

The effect of agitation for on the adsorption of Cd(II), Pb(II), and Ag(I) on the hollow chitosan microsphere can be observed at the different times in Figure 6. The adsorption of Cd(II), Pb(II), and Ag(I) increases with increasing agitation time and attains equilibrium at about 40 min, 45 min, and 60 min with initial Cd(II), Pb(II), and Ag(I) ion concentrations of 1000 mg/L, 174 mg/L, and 40 mg/L, respectively. The adsorption remains constant after these times, implying that equilibrium, and hence optimum agitation time, has been reached.
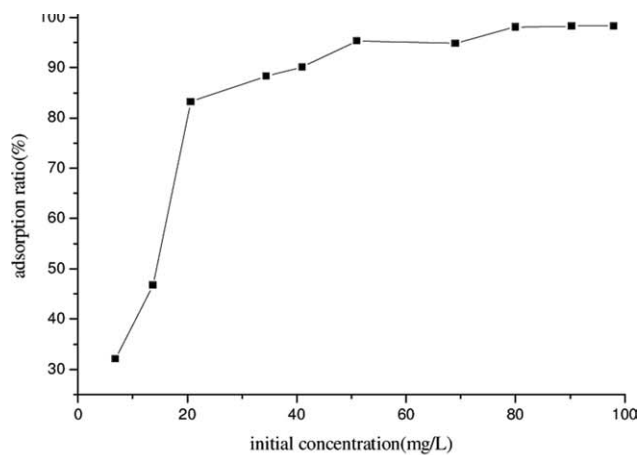
Effect of initial concentration

Figure 7 shows the effect of ion concentration on the adsorption of Cd(II), Pb(II), and Ag(I) by hollow chitosan microsphere. Adsorption increases with increasing ion concentration and attains equilibrium at an initial concentration of 1000 mg/L, 174 mg/L, and 40 mg/L for Cd(II), Pb(II), and Ag(I), respectively.
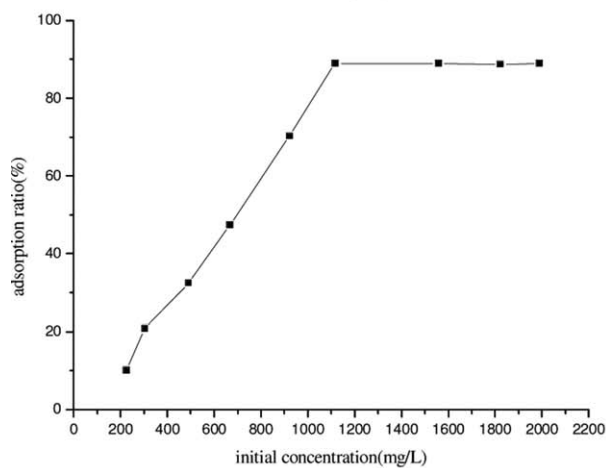
Effect of temperature

The optimum temperature for adsorption of Cd(II), Pb(II), and Ag(I) onto the hollow chitosan microsphere was investigated. Little effect from temperature was observed, although the optimum temperature was room temperature. Figure 7 shows the
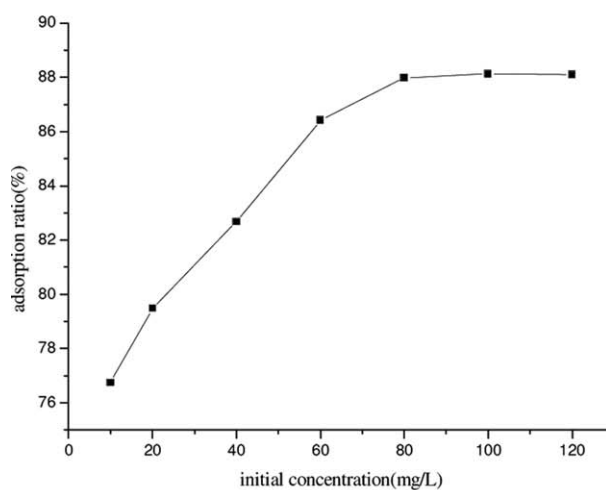
effect of temperature on the adsorption of Ag(I) by the hollow chitosan microsphere. Optimum adsorption of Ag(I) occurred at 30°C.

Figure 7 Effect of initial concentration [a, Pb(II); b, Cd(II); c, Ag(I)].
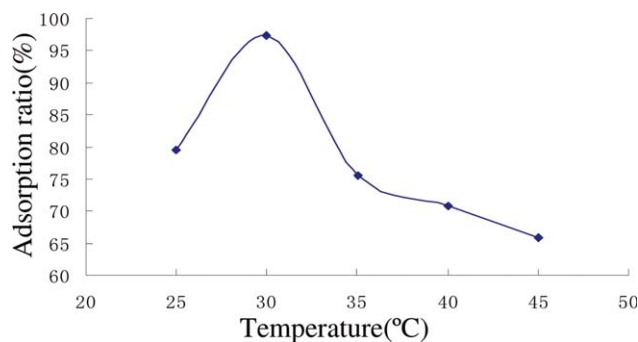
Figure 8 Effect of temperature of Ag(I). [Color figure acn be viewed in the online issue, which is available at www.interscience.wiley.com.]

Adsorption equilibria of Cd(II), Pb(II), and Ag(I)

The equilibrium adsorption data of Cd(II), Pb(II), and Ag(I) ions were subjected to three different adsorption isotherm analyzes, namely the Langmuir, Freundlich, and Dubinin–Radushkevich equations. The Langmuir isotherm equation, which is the most commonly used for monolayer adsorption onto a surface with a finite number of identical sites, is represented by the following:

$$C_e/Q_e = C_e/Q_m + 1/Q_m b, \tag{2}$$

where C_e is the equilibrium concentration of metal ions, 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). 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:

$$ln\ Q_e = b_F\ ln\ C_e + lnK_F, \tag{3}$$

where C_e is the equilibrium concentration of metal ions, 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 lnQ_e versus lnC_e. The Dubinin–Radushkevich isotherm equation, which is more

TABLE I
Langmuir Isotherms Constants for Cd(II), Pb(II), and Ag(I) Ions on the Hollow Chitosan Microsphere

Constants	Cd(II)	Pb(II)	Ag(I)
Langmuir isotherms			
Q_m (mg/g)	420 mg/g	283 mg/g	33mg/g
b (mL/mg)	0.0197	0. 0114	0.0126
R^2	0.9998	0.9979	0.9983

R^2 is the correlation coefficient.

generally used to distinguish between physical and chemical adsorption, is given by the following:

$$lnQ_e = K\varepsilon^2 + \ln Q_{DR}, \tag{4}$$

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 (kJ/mol), and ε is the Polanyi potential given as

$$\varepsilon = RT\ ln\ (1 + 1/Ce), \tag{5}$$

where R is the gas constant in kJ/mol^{-1}, T is the temperature in Kelvin, and C_e is the equilibrium concentration of metal ions. Thus, the plot of lnQ_e against ε gives a straight line with a slope of K and an intercept of Q_{DR}. The Dubinin–Radushkevich constant can provide valuable information regarding the mean energy of adsorption by:

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

where E is the mean adsorption energy (kJ/mol) and K is the Dubinin–Radushkevich constant. Experimental equilibrium isotherms for adsorption of Cd(II) ions on the cross-linked chitosan and their isotherm constants are summarized in Table I. Comparing their linear correlation coefficients leads to the conclusion that the adsorption of Cd(II) ion on the cross-linked chitosan. It was well followed as the Langmuir isotherm equation under the concentration range studied. In addition, the adsorptions of the metal ions of Pb(II) and Ag(I) on the cross-linked chitosan were still well followed as the Langmuir isotherm equation under the concentration range studied (Table II). The order of adsorption capacity

TABLE II
Result of Cd(II), Pb(II), and Ag(I) Adsorption in CS Microsphere

M (MClx salts)	Q_m (mg/g)	Microsphere size(μm) effect	General conditions	Adsorption ratio(%)
Cd(II)	420	Little effect	20°C, pH = 7.40 mins, 100 mg/0.1 L	89
Pb(II)	283	Little effect	20°C, pH = 4.8, 45 mins, 17.4 mg/0.1 L	98
Ag(I)	33	Little effect	30 °C, pH = 7.60 min	97.7

TABLE III
The Effect of Pb2+ to the Adsorption of Cd2+

The concentration of Cd2+ (mg/L) before adsorption	The concentration of Cd2+ (mg/L) after adsorption in the single metal system	The concentration of Cd2+ (mg/L) after adsorption (mg/L) in the Cd2+ --Pb2+ system
500	265	420
800	530	735
1500	1055	1495
2000	1585	1945
3000	1660	2105
4000	1965	2365

(Q_m, mg/g) from the Langmuir isotherm equation for the three metal ions was as follows: $Cd^{2+} > Pb^{2+} > Ag^+$. In general, the cross-linked chitosan should have a reduced adsorption capacity of metal ions because of a decrease in accessibility to internal sites or blocking of a number of adsorption sites. However, the maximum adsorption (Q_m) of Cd(II), Pb(II), and Ag(I) ions on the hollow chitosan microsphere (Table II) was found to be more than two times that of chitosan because of the increased surface area available for adsorption on the hollow chitosan microsphere. Ions are adsorbed not only on the surface of the microsphere but also in the interior.

Adsorption behavior in binary-metal systems

Comparing the concentration of Cd^{2+} (mg/L) after adsorption results in the single metal system and binary Cd^{2+}–Pb^{2+} system. In addition to competition, the heterogeneity and chemical fabric of chitosan may affect adsorption. The amino (mainly) and hydroxyl groups on chitosan were recognized as active binding sites for heavy metals. Table III shows the results of adsorption in binary-metal systems at the same initial concentration. There is a difference between the single metal system and in the Cd^{2+}–Pb^{2+} binary-metal system. It is evident that Pb^{2+} strongly affects the adsorption ratio of Cd^{2+} depending on Cd^{2+} concentration in the single metal system(This is likely due to consideration of competitive effect of two metals).

CONCLUSION

The hollow chitosan microsphere synthesized by the inverse emulsion cross-link method has been used to investigate the adsorption capacity of three metal ions, Cd(II), Pb(II), and Ag(I), in an aqueous solution. The hollow microsphere was shown to have the highest adsorption. Results of the concentration ranges of the three metal ions fit well in the Langmuir isotherm equation, which showed the order of adsorption capacity to be $Cd^{2+} > Pb^{2+} > Ag^+$.

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