Removal of Hg^{2+} from Aqueous Solution Using Alginate Gel Containing Chitosan

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ABSTRACT: Glutaraldehyde-crosslinked alginate gel containing chitosan (AGCC) used for the removal of Hg^{2+} ions from aqueous solutions. Three bead sizes were obtained and performed to study the uptake equilibrium and kinetics of Hg^{2+} by AGCC (ca. an hour). The adsorption capacity was found to be independent of adsorbent particle size indicating that sorption occurs in the whole AGCC bead. A high initial rate of Hg^{2+} uptake was followed by a slower uptake rate suggesting intraparticle diffusion as the rate-limiting step. The rate of Hg^{2+} uptake increases with decreasing AGCC bead size. AGCC also enhanced the rate and the capacity of Hg^{2+} adsorption. The maximum Hg^{2+} adsorption capacity of AGCC was found 667 mg/g, which is over 20 times higher than that of alginate bead. Our results reveal the well-distributed chitosan powders in the alginate gel bead and Hg^{2+} ions can reach inside the chitosan bead. It indicates the feasibility of using AGCC as metal adsorbent at low pH values, and allows the regeneration of adsorbent. Hg^{2+} ions adsorbed on AGCC bead were desorbed effectively about 95% by H_2SO_4 at the third cycle. The use of AGCC for the removal of Hg^{2+} ions from the waste streams appears to be promising. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2896–2905, 2007

Key words: biomaterials; gels; metal–polymer complexes; chitosan; mercury

INTRODUCTION

Mercury is one of the most toxic heavy metals.[1,2] Many areas in the world are contaminated by mercury, posing serious environmental problems.[3,4] Consequently, removal of mercury ions in water and wastewater is very important. Several techniques are available for this, including precipitation, ion exchange, and adsorption. Precipitation results in large volumes of mercury containing sludge, while ion exchange is effective only for wastes with low dissolved solids concentrations. Adsorbents can be designed that are specific to mercury and whose volume is much less than an amorphous sludge.[2] Bailey et al., Babel and Kurniawan reviewed several adsorbents and their applications for metal removal and found that chitosan was capable of adsorbing moderately high amounts of Hg^{2+}.[5,6]

Chitosan is a hydrophilic, natural cationic polymer formed by the N-deacetylation of chitin,[7] which is present in fungi, insects, and crustaceans. Chitosan has been known for its metal adsorption properties since 1970s,[7,8] and it has been shown to effectively remove metals such as silver,[8] cadmium,[9] arsenic,[10] gold,[11,12] vanadium,[13] copper,[14–16] nickel,[14,17] chromium,[14,18] and mercury[17,19] from aqueous solutions. It was reported that the maximum adsorption capacity of chitosan for Hg^{2+} was 815 mg/g.[17] However, the result of Hg^{2+} removal was different from that obtained in the latter study,[19] which indicated that an adsorption capacity of 430 mg of Hg^{2+}/g was achieved by chitosan. This difference occurs due to the fact that the latter study used chitosan, with particle size ranging from 1.25 to 2.5 mm (against 0.21–1 mm in the former study).[6] Because of the resistance to intraparticle mass transfer in raw chitosan, it is usually necessary to use very small particles to improve sorption kinetics. Nevertheless, small particles have proved to be inappropriate for use in column systems since they cause column clogging and serious hydrodynamic limitations. Using chitosan gel beads may be an alternative because it improves both diffusion properties and hydrodynamic behavior.[20,21] The adsorption capacity of chitosan gel bead for Hg^{2+} was reported to be 294 mg/g.[22] Merrifield et al. reported that the adsorption capacity of thiol-grafted chitosan gel beads for Hg^{2+} was 1600 mg/g, but the equilibrium time for Hg^{2+} adsorption on this adsorbent was as long as 1200 min.[2] Otherwise, Jeon et al. reported that the adsorption capacity of aminated chitosan bead for Hg^{2+} was 476 mg Hg^{2+}/g-dry mass, and it took only 100 min to reach the equilibrium of adsorption.[23] However, several chemical modifications are required for preparing these chitosan derivative adsorbents. Since the Hg^{2+} adsorption capacity of chitosn powder was reported to be 815 mg/g,[17]

immobilizing chitosan powder in a porous support material is a potential and economic means to produce an adsorbent with satisfactory kinetic and hydrodynamic properties, and high capacity for Hg^{2+} adsorption.

Alginate is a linear polysaccharides composed of (1 → 4)-linked residues of α-L-guluronic acid (G) and β-D-mannuronic acid (M). Alginate can be found in many algal species and certain bacteria.[24] This polyelectrolyte is soluble in water but precipitates in the form of a coacervate in the presence of multivalent metal ions like Ca^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+}.[25] Alginate is one of the most extensively investigated biopolymers for metal ion removal from dilute aqueous solutions.[26,27] The interaction of cationic metals with alginate has been attributed to metal complexation by the carboxylate functionalities of the polyuronic acid.[28,29] Alginate has been previously used as a support material for the immobilization of several enzymes and microbial cells.[30] The incorporation of humic acid into calcium alginate beads was demonstrated to be useful in metal recovery.[31] Several researches have shown that the Hg^{2+} sorption capacity of the alginate beads entrapped with fungus is higher than that of plain alginate beads.[4,32] However, the maximum Hg^{2+} sorption capacity of the fungus-immobilized alginate beads (172.41 mg/g) is not higher than that of other adsorbents.[2,22,23] The combination of alginate and chitosan had introduced the composite matrix in many applications,[33,34] including adsorbent for metal removal.[35] Takeshi Gotoh et al. used the water-soluble chitosan to prepare alginate-chitosan hybrid gel beads for the adsorption of Cu^{2+}, Co^{2+}, and Cd^{2+}.[35] By using a simple method, Huang et al. have immobilized the chitosan powders in the alginate pellets to produce the alginate/chitosan pellets to remove nickel ion and nickel cyanide complex from polluted water. However, he showed that the adsorption of Cu^{2+} ion by the alginate/chitosan pellets is not superior to that by alginate bead.[36]

Since chitosan is soluble in dilute mineral acids, except for sulfuric acid, it is thus necessary to stabilize it chemically for the recovery of metal ions in acidic solutions.[37] The treatment of glutaraldehyde crosslinking induces new linkages between the chitosan chains allowing the polymer to be highly resistant to dissolution even in harsh solutions such as hydrochloric molar solutions.[38] Glutaraldehyde has been used for cadmium recovery on chitosan beads.[39] In this study, chitosan powder was crosslinked with glutaraldehyde and its solubility was measured before and after crosslinking. The crosslinked chitosan was then homogeneously immobilized in alginate gel bead for the application of removing Hg^{2+} ions from aquatic systems. The morphology and porosity of the resulting alginate gel

containing chitosan (hereafter called: AGCC) were characterized by scanning electron microscopy (SEM) and porosimeter. The kinetics and equilibrium characteristics of Hg^{2+} adsorption on AGCC were studied in batch experiments. The adsorption of Hg^{2+} ion by AGCC was confirmed to be significantly superior to that by alginate bead. Among reported capacity results of adsorbents with feasible adsorptive kinetic property (adsorption equilibrium time = 100 min), the maximum uptake capacity (667 mg Hg^{2+}/g-dry mass) of AGCC was to be one of the highest capacities, up to now. Besides, the Hg^{2+}-loaded adsorbents were characterized by X-ray energy dispersion (EDS) analysis. The reusability of AGCC was evaluated by desorption studies.

EXPERIMENTAL

Materials

Chitosan flake produced from crab shell wastes was obtained from Kiotek Corp., Taiwan, without further purification. The chitosan flake was ground in a blender and then passed through a sieve stack consisting of no. 150 (0.106 mm) and no. 200 (0.075 mm) sieves. The chitosan powder (150/200 mesh) with particle size ranging from 0.075 to 0.106 mm was separated for this study. The degree of deacetylation of the powder is 92 mol %. The M_w of chitosan is 280,000, and the polydispersity index M_w/M_n is 2.8. Mercury nitrate was supplied by Merck as analytical-reagent grade. Sodium alginate, glutaraldehyde, calcium chloride (CaCl$_2$), sulfuric acid, and acetic acid were purchased from Sigma-Aldrich and used without further purification.

Chitosan crosslinking

Glutaraldehyde was used as crosslinking agent in this study. The crosslinking bath contained a 2.5 wt % glutaraldehyde solution. The ratio of glutaraldehyde to chitosan (crosslinking ratio CR: mol GA/mol NH) is 1 : 1. Crosslinking lasted for 24 h. The crosslinked chitosan particles were extensively rinsed with deionized water to remove any free glutaraldehyde.

Dissolution test of crosslinked chitosan

Chitosan and crosslinked chitosan were tested with regard to their solubility in 5% (v/v) acetic acid and deionized water by adding 0.1 g of chitosan and crosslinked chitosan in the dilute acid and deionized water for a period of 24 h with stirring.[40]

Preparation of alginate gel containing chitosan

AGCC($X : Y$) contains alginate and chitosan with a weight ratio of $X : Y$. The immobilization of the crosslinked chitosan via entrapment was carried out as follows: 5 g sodium alginate was dissolved in 250 mL of deionized water and mixed with 2 g chitosan powder for preparation of AGCC(5 : 2). The sodium alginate solution containing chitosan was then added drop by drop by means of a peristaltic pump with a tube diameter of 0.5 mm into a stirred 10% CaCl$_2$ solution, and the size of the droplets was controlled by applying a coaxial air stream.[36,41] By doing so, the water-soluble sodium alginate is converted into water insoluble calcium alginate beads.[31] The beads were washed with deionized water several times to remove CaCl$_2$ from the bead surface and stored at 4°C before use. AGCC(5 : 10) and the alginate bead were also produced by the same method.

SEM studies

The AGCC(5 : 10) with diameter of 2.7 mm was freeze-dried for SEM observation. The dried AGCC(5 : 10) was coated under vacuum with a thin layer of gold and examined by a Hitachi S-570 SEM.

Characterization of AGCC

The dry weights of alginate bead, AGCC(5 : 2), and AGCC(5 : 10) were determined by weighing the beads after drying in an oven at 70°C overnight. The water contents of the wet adsorbents were measured using a gravimetric method. The loss of weight during drying was found to be 95.11, 94.93, and 94.72% for alginate bead, AGCC(5 : 2), and AGCC(5 : 10), respectively. The porosity of AGCC(5 : 10) was measured by a mercury porosimeter (Micromeritics Autopore II 9200).

Equilibrium uptake experiments

Adsorption of Hg^{2+} ions from aqueous solutions was studied in batch systems using mercuric nitrate. Standard solution of Hg^{2+} was prepared at a concentration of 1000 mg/L. Batch equilibrium experiments were carried out using 1 g wet AGCC beads or alginate beads as adsorbents. A series of flasks containing 100 mL solution with various metal concentrations prepared from the standard solution and adsorbent were agitated in a rotary shaker at 200 rpm, 25°C for 24 h, which is sufficient for the metal ion uptake process to reach final equilibrium.[16] The loss of weight during drying was found to be 95.11, 94.93, and 94.72 for the alginate bead, AGCC(5 : 2), and AGCC(5 : 10), respectively. Therefore, the dosages of adsorbents in this equilibrium study were 0.0489 g-dry weight/100 mL, 0.0507 g-dry weight/100 mL, and 0.0528 g-dry

weight/100 mL for alginate bead, AGCC(5 : 2), and AGCC(5 : 10), respectively. The sorption experiments were conducted at a pH value close to 5 by adjusting with HCl or NaOH. After equilibrium, the solution in each flask was analyzed for metal content by a GBC Avanta Σ Atomic Absorption Spectrophotometer (AAS). Metal-free and adsorbent-free blanks were used as controls. Extent of the metal ion uptake by the adsorbent, based on dry weight, was determined by the following mass balance equation:

$$Q = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where Q and C_e are the adsorbent phase metal concentration and the solution phase metal concentration at equilibrium. C_0 is the initial metal concentration, V is the solution volume, and m is the dry mass of the adsorbent. In this equilibrium study, all the parameters were calculated based on the dry weight of adsorbent.

Scanning electron microscope and EDS analysis of metal distribution

The isothermal adsorption of Hg^{2+} ion by 2.7 mm AGCC(5 : 10) was conducted for the concentration (500 ppm) of the Hg^{2+} ion solution at pH 5. After 24 h, the AGCC(5 : 10) beads were separated from the Hg^{2+} ion solution. AGCC(5 : 10) beads were then washed several times with deionized water and air dried for several days at room temperature and stored for further observations. Examination of the beads by Hitachi S-2500 SEM was made after coating them with a thin layer of gold. The distribution of Hg^{2+} ions inside the Hg^{2+}-loaded beads was examined using the SEM with an attachment of X-ray energy dispersion (EDS) analyzer.[42]

Transient uptake experiments

Batch experiments for determination of the kinetics of Hg^{2+} adsorption on wet adsorbents were carried out using a continuously stirred 500-mL glass beaker.[16] A motor was used to drive a 4-blade impeller with a diameter of 6 cm. The following experimental conditions were kept constant for the kinetic experiments: volume of mercuric nitrate solution = 300 mL, temperature = 25°C, stirring speed = 200 rpm. 5.11 g wet alginate bead, 4.93 g wet AGCC(5 : 2), or 4.73 g wet AGCC(5 : 10) was added in 300 mL solution, respectively, to make the dosage of adsorbent = 0.25 g-dry weight/300 mL. The sorption experiment was conducted at a pH value close to 5 by adjusting with HCl or NaOH. The adsorbent particles in the solution were uniformly dispersed in the reactor. The initial metal concentration, $C(0)$, was varied to investigate its

effect on the adsorption kinetics. During the kinetic experiments, samples were withdrawn at fixed time intervals and analyzed for metal content as described above. By plotting $C(t)/C(0)$ against time (min), where $C(t)$ is the solution metal concentration and $C(0)$ is the initial metal concentration, the experimental results are demonstrated.

Desorption

Desorption of Hg^{2+} ions was achieved by using $1N$ H$_2$SO$_4$ as the desorbing agent. The AGCC(5 : 10) loaded with Hg^{2+} ion in the following conditions-initial concentration of Hg^{2+} ion: 500 mg/L, amount of AGCC(5 : 10): 1 g-wet weight (0.0528 g-dry weight); volume of adsorption medium: 100 mL; pH: 5; temperature: 25°C; and adsorption time: 24 h. Then, the AGCC(5 : 10) was placed in the desorption medium and stirred at a stirring rate of 200 rpm up to 24 h. The concentrations of Hg^{2+} ions in the aqueous phase were determined as mentioned earlier. The extent of desorption percents was calculated from the following expression[43]:

$$\text{desorption (\%)}$$
$$= \frac{\text{amount of Hg}^{2+} \text{ ions desorbed}}{\text{amount of Hg}^{2+} \text{ ion sabsorbed}} \times 100 \quad (2)$$

RESULTS AND DISCUSSIONS

Solubility test of chitosan and crosslinked chitosan

In this study, chitosan was found to be soluble in 5% (v/v) acetic acid and insoluble in deionized water. However, it was shown that after crosslinking, the crosslinked chitosan was found to be insoluble in 5% (v/v) acidic acid and deionized water. It is well-known that the high hydrophilicity of chitosan due to a primary amine group makes chitosan easily soluble in dilute acetic or formic acid solutions to yield a hydrogel in water. Thus, it is necessary to reinforce its chemical stability by a chemical crosslinking using glutaraldehyde.[44,45] The reaction of aldehyde functions with amine groups leads to the formation of imine functions and the insolubility of the polymer even at low pH.[46]

Properties of AGCC

AGCC, calcium alginate beads containing crosslinked chitosan powders, were prepared by the liquid curing method in the presence of Ca^{2+} ions. They are spherical in shape and their diameters are within a narrow range around 1.8, 2.7, and 3.6 mm diameter, respectively. Both crosslinked chitosan powders and calcium alginate beads were shown to be very stable at low pH.[4,25,32] The operational stability of the adsorbent under specified solution conditions is also a very important parameter in the Hg^{2+} adsorption. Besides, to allow regeneration by acids, the sorbent materials have to be insoluble at low pH values.

By using a mercury porosimeter, the porosity of AGCC(5 : 10) was found to be 0.59. Figure 1 presents SEM photographs of AGCC(5 : 10) with diameter of 2.7 mm. The beads are highly porous, which agrees with the porosity data. The scanning electron micrograph of AGCC(5 : 10) also reveals a uniform chitosan distribution in the bead. This is an important criterion for the proper adsorption of Hg^{2+} ions
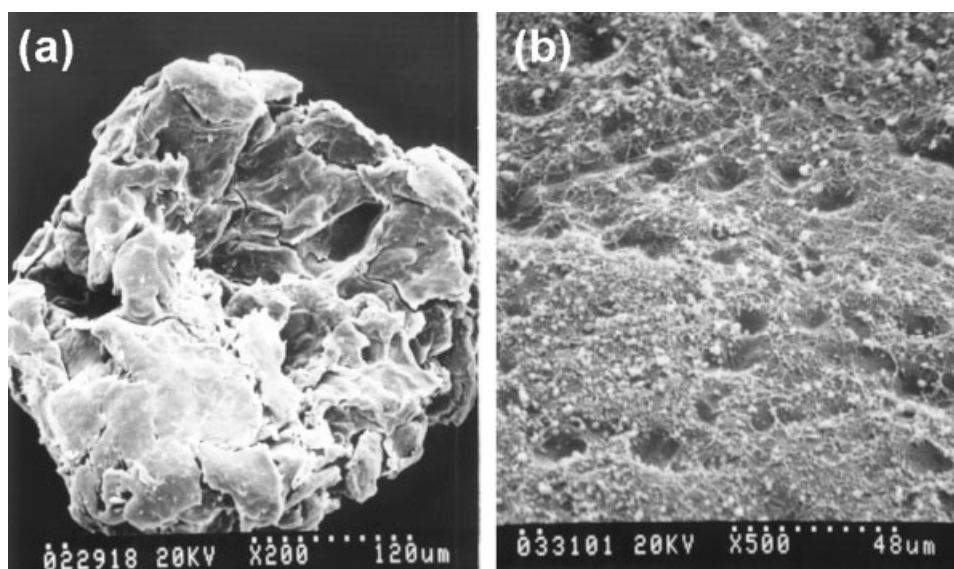

Figure 1 The scanning electron micrographs of AGCC(5 : 10) with diameter of 2.7 mm: (a) surface ($\times$200); (b) surface ($\times$500).
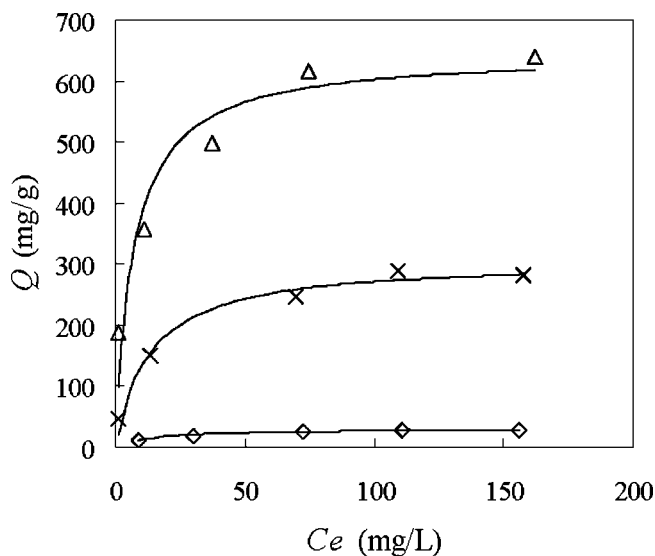
Figure 2 Adsorption isotherms of Hg^{2+} ions on adsorbents with diameter of 2.7 mm: alginate bead ($\diamond$), AGCC(5 : 2) ($\times$), and AGCC(5 : 10) ($\triangle$) (the solid curves are calculated by the Langmuir equation).

Figure 3 Adsorption isotherms of Hg^{2+} ions on AGCC (5 : 10) with diameter of 1.8 mm ($\square$) and 2.7 mm ($\triangle$) (the solid curves are calculated by the Langmuir equation).

on AGCC(5 : 10). Thus, immobilization of chitosan in the alginate beads could provide advantages over the chitosan powder. Besides, it was demonstrated that the chitosan and alginate could be homogeneous mixed using this preparation method.

Adsorption isotherms

The adsorptive capacity of alginate bead and AGCC for Hg^{2+} removal was determined through adsorption isotherm studies whose parameters were calculated based on the dry weight of adsorbent. Figures 2 and 3 show the relationship between the quantities of Hg^{2+} adsorbed per unit dry mass adsorbent (Q) and the equilibrium concentration (C_e) in terms of chitosan content and particle size of the adsorbent, respectively. All of the isotherms showed similar behavior which can be described by using the Langmuir adsorption equation as:

$$\frac{C_e}{Q} = \frac{C_e}{Q_{max}} + \frac{1}{(Q_{max})K_s} \quad (3)$$

where Q_{max}, the maximum adsorption capacity at monolayer coverage, and K_s is the Langmuir adsorption equilibrium constant (mL/mg) which is a measure of the energy of adsorption.

The plots of the experimental Q and C_e values as specific sorption (C_e/Q) against the equilibrium concentration (C_e) for adsorption of Hg^{2+} on adsorbents are shown in Figures 4 and 5. These isotherms are linear over the entire concentration range studied and the correlation coefficients are extremely high ($R^2 > 0.99$), implying strongly that the sorptions of
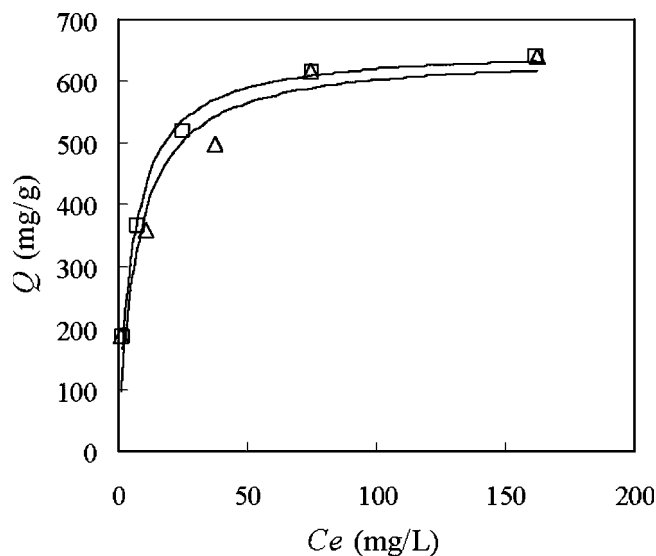
Hg^{2+} closely follow the Langmuir model of sorption for monolayer adsorption onto a surface containing finite number of identical sites.[15,32] Linearized plots of (C_e/Q) versus (C_e) give Q_{max} and K_s values and are summarized in Table I.

Unlike the adsorption of alginate/chitosan pellets for Cu^{2+},[36] the adsorption capacity of AGCC for Hg^{2+} significantly increased with its chitosan content (Fig. 2). This might be due to the difference between the Hg^{2+} adsorption capacity of chitosan and that of alginate. The maximum adsorption capacity of chitosan for Hg^{2+} is 815 mg/g,[17] while that of alginate
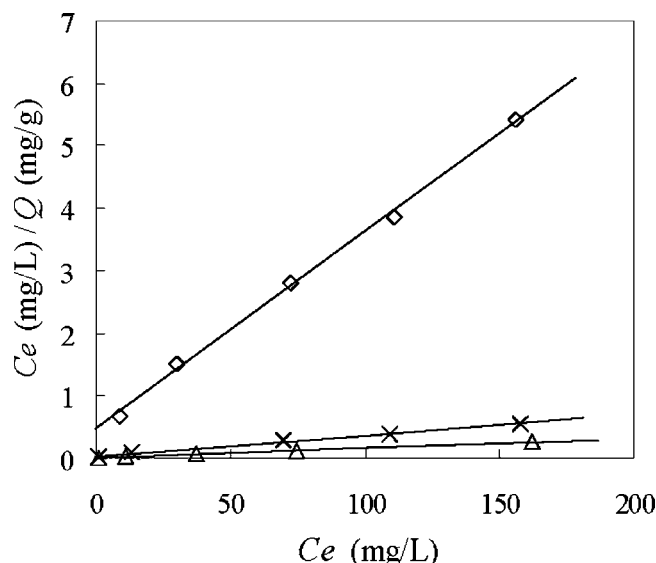

Figure 4 Langmuir isotherms of Hg^{2+} ions on adsorbents with diameter of 2.7 mm: alginate bead ($\diamond$), AGCC(5 : 2) ($\times$), and AGCC(5 : 10) ($\triangle$).
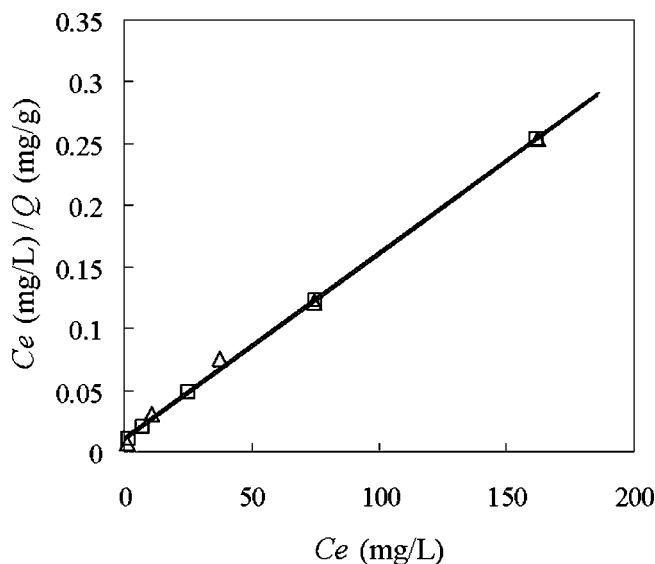
Figure 5 Langmuir isotherms of Hg^{2+} ions on AGCC(5 : 10) with diameter of 1.8 mm (□) and 2.7 mm (△).

bead for Hg^{2+} is only 32 mg/g (Table I). Hence, the chitosan may play an important role in the adsorption of Hg^{2+} ions. Although crosslinking did somewhat reduce the adsorption capacity of the chitosan, but this loss of capacity may be necessary to ensure stability of the polymer.[5] Moreover, it was reported that the heterogeneous crosslinking of chitosan flakes resulted in a significant decrease in sorption capacities for large particle sizes, whatever the characteristics of the chitosan samples, while for small particle sizes the sorption capacities were comparable for raw and crosslinked materials.[20] The computed maximum monolayer capacity Q_{max} of Hg^{2+} on the AGCC(5 : 10) has large value, ranging from 662 to 667 mg/g, which is over 20 times higher than that of plain alginate bead (Table I). The Hg^{2+} adsorption by chitosan was reported to increase with decreasing its particle size.[6,17,19] Therefore, in AGCC, small particle size (0.075–0.106 mm) of the immobilized chitosan might result in enhancing its Hg^{2+} adsorption capacity. However, the high adsorption capacity of AGCC might be attributable in part to the high porosity of alginate bead so that all the activated sites of chitosan become accessible to the Hg^{2+} ions. In general, chitosan is more responsible for Hg^{2+} adsorption and alginate is more responsible for supporting structure in this bead system.

The size of sorbent particles has been shown to be a key parameter in the control of sorption performances of several metal ions on chitosan. However, the influence of this experimental parameter depends on the chemistry of the metal ion and the characteristics of the sorbent.[37] Therefore, different results about the influence of the size of chitosan

particles on metal adsorption have been demonstrated.[6,13,15,37] It was reported that the particle size of chitosan in flaked or powdered forms influences Hg^{2+} sorption performance, and these results can be explained by the surface limitations for chitosan particles.[6] In this study, the Hg^{2+} sorption capacity was found to be independent of the size of AGCC gel beads (Fig. 3, Table I). It means that sorption occurs in the whole mass of AGCC and not only on the external layer of AGCC bead. On the other hand, if equilibrium adsorption is proportional to the bead size, there is a restrictive layer at the bead surface and sorption is limited to the surface. Guibal et al. have demonstrated that particle size does not influence equilibrium for chitosan beads, but increasing sorbent radius significantly decreases uptake capacities for chitosan flakes.[13] In this work, the sorption capacity of the alginate bead was drastically enhanced by immobilizing very small particle size of chitosan powders in alginate bead (Fig. 2). However, the capacity was confirmed to be independent of gel bead size (Fig. 3).

A greater K_s value indicates a steep initial slope of an isotherm, which in turn implies a high affinity of the adsorbent for the sorbate under dilute conditions.[16] The K_s values of the isotherms for Hg^{2+} sorption on the 2.7 mm adsorbents are in the order of AGCC(5 : 10) > AGCC(5 : 2) > alginate bead (Table I). This might be due to the high adsorption capacity of chitosan for Hg^{2+}. Otherwise, the K_s values of the isotherms for Hg^{2+} sorption on AGCC(5 : 10) are in the order of 1.8 mm adsorbent > 2.7 mm adsorbent (Table I). This is most likely because the smaller particles have more outside surface area per weight.

AGCC(5 : 10) saturated with Hg^{2+} solutions were cross section analyzed by SEM. The location of sorbed mercury is determined with an X-ray EDS analyzer. Figure 6 shows the distribution pattern of the Hg^{2+} ions taken along the lines crossing the AGCC(5 : 10) beads. A uniform distribution of the Hg^{2+} ions throughout the beads was observed. This distribution demonstrates the formation of open pores and channels during the formation process of the AGCC(5 : 10) beads, which allow the penetration of solution into the inner part of the beads during experiments. Furthermore, the homogeneous

TABLE I
Langmuir Isotherm Constants and Correlation Coefficients

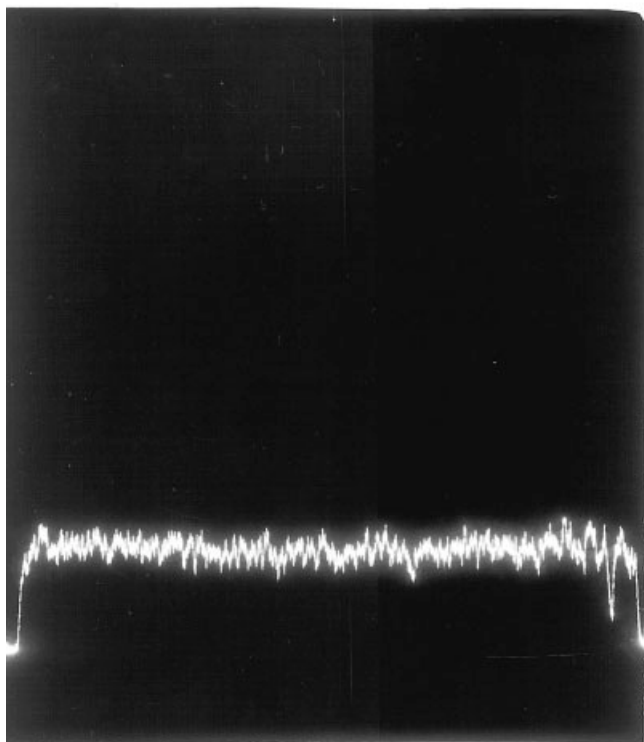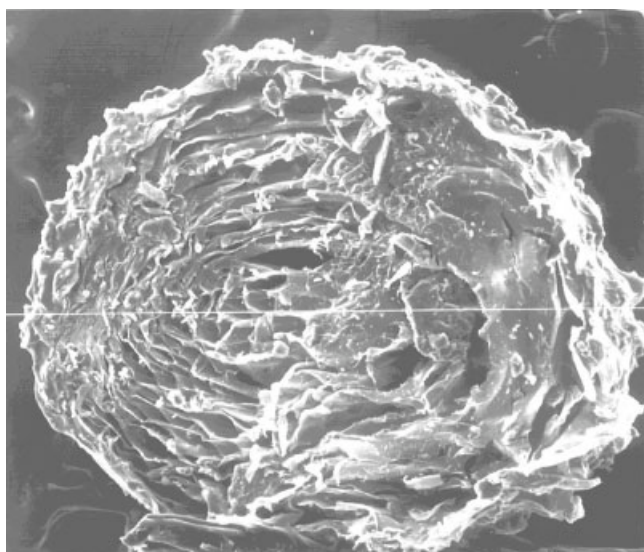| Adsorbent		Langmuir		
Type	Size (mm)	Q_{max} (mg/g)	K_s (L/mg)	R^2
Alginate bead	2.7	32	0.066	0.999
AGCC(5 : 2)	2.7	300	0.100	0.997
AGCC(5 : 10)	2.7	667	0.126	0.998
AGCC(5 : 10)	1.8	662	0.170	0.999

Figure 6 EDS analysis of Hg^{2+} ion distribution in AGCC.

distribution of chitosan on the entire structure of the AGCC(5 : 10) is demonstrated as well. The results demonstrate that Hg^{2+} ions are able to reach chitosan immobilized in the entire structure of AGCC(5 : 10). Similar results have been reported for protonated alginate beads.[27] Using SEM and X-ray EDS analyzer, it was demonstrated that after formation of the AGCC(5 : 10) beads, the porous alginate bead has homogenously immobilized chitosan, where Hg^{2+} metals can be sorbed (Fig. 2, Fig. 6). In addition, these observations agree with the high adsorption capacity of AGCC(5 : 10).

Adsorption kinetics

By plotting $C(t)/C(0)$ against time (min), where $C(t)$ is the solution metal concentration and $C(0)$ is the initial metal concentration, the experimental results are shown in Figures 7 and 8. Each plot shows the experiment results at an agitation rate of 200 rpm for initial concentrations of 10 and 50 ppm, respectively. Metal uptake by gel particles follows two-step kinetics. The extraparticle association (surface binding) occurs first and rapidly. Further metal uptake is controlled by diffusion through the particle pores. The rate-limiting step is diffusion inside the alginate gel beads.[47]
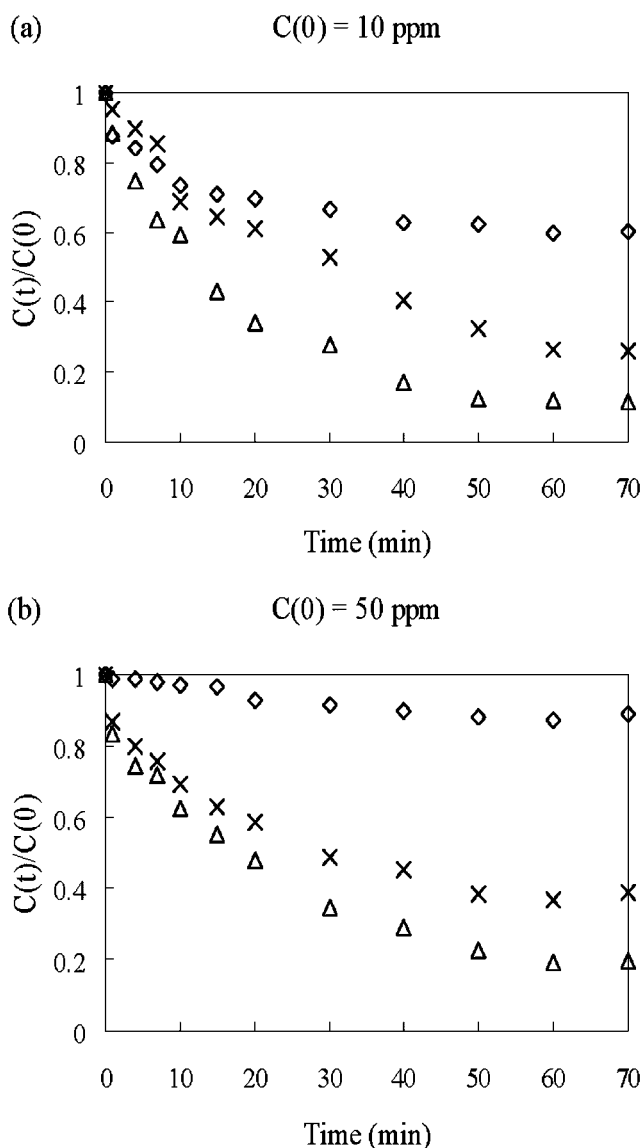

Figure 7 Influence of chitosan content of alginate bead on Hg^{2+} sorption kinetics using (a) 10 ppm and (b) 50 ppm mercury nitrate solution. The experiments were conducted for medium sized (diameter, 2.7 mm) alginate bead ($\diamond$), AGCC(5 : 2) ($\times$), and AGCC(5 : 10) ($\triangle$) at pH = 5, agitation rate = 200 rpm, and temperature = 25°C.
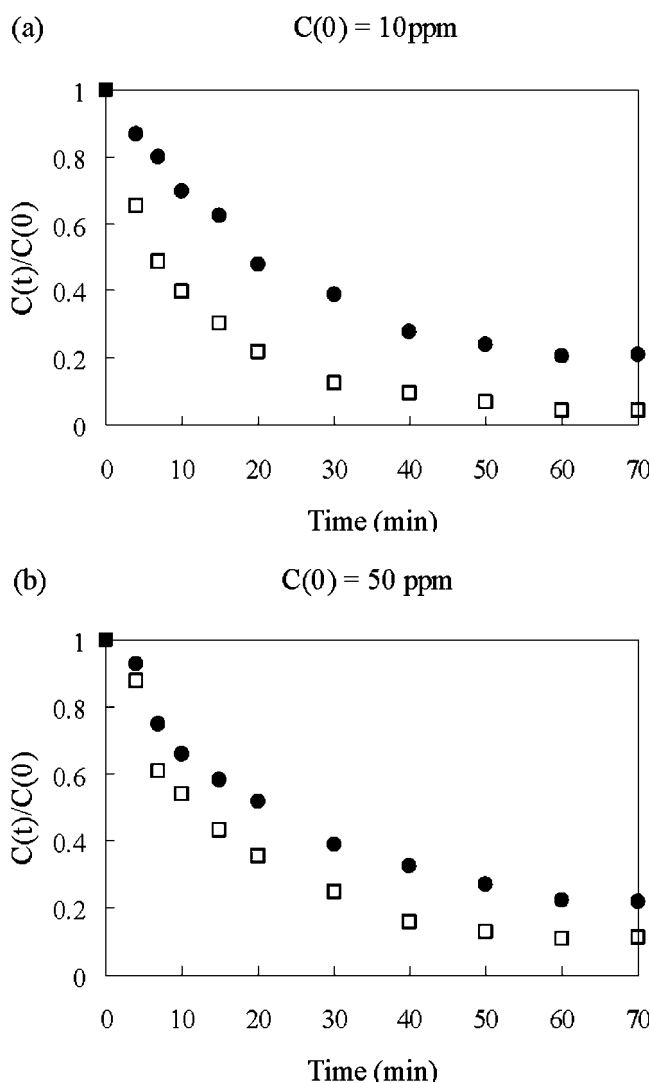
(a) C(0) = 10 ppm

(b) C(0) = 50 ppm

Figure 8 Influence of adsorbent size on Hg^{2+} sorption kinetics using (a) 10 ppm and (b) 50 ppm mercury nitrate solution. The experiments were conducted for AGCC(5 : 10) with diameter of 3.6 mm (●) and 1.8 mm (□) at pH = 5, agitation rate = 200 rpm, and temperature = 25°C.

The rates of Hg^{2+} adsorption by different adsorbents of the same size (diameter, 2.7 mm) are shown in Figure 7. Interestingly, the uptake rates for Hg^{2+} sorption are in the order of AGCC(5 : 10) > AGCC (5 : 2) > alginate bead. Addition of chitosan to alginate microsphere can result in significant enhancement of its uptake rate for Hg^{2+}. This might be attributable to the high adsorption capacity of chitosan for Hg^{2+} and high porosity of alginate beads.

As would be expected, decreasing the particle size of the AGCC(5 : 10) results in rapid increase in the initial sorption rate as shown in Figure 8. The dependence of the uptake rate on size is probably because the smaller particles have more outside surface area per weight, resulting in the observed faster initial uptake.[9] It was also reported that a decrease

in the size of immobilized biomass alginate bead leads to an increase in the rate of metal biosorption.[48]

Increasing the initial concentration leads to an increase in uptake rate because of the higher driving force (Figs. 7 and 8). Besides, the time to reach equilibrium of Hg^{2+} adsorption by AGCC(5 : 10) is only 60 min. The Hg^{2+} adsorption capacity and the time to reach equilibrium are presented in Table II, which also shows, for purposes of comparison, similar data from the literature. To increase the uptake capacity of mercury ions, several chemical modifications of chitosan beads which are crosslinked with glutaraldehyde were performed.[2,22,23] Among reported capacity result of adsorbents with feasible adsorptive kinetic property (adsorption equilibrium time = 100 min), the maximum uptake capacity (667 mg Hg^{2+}/ g-dry mass) of AGCC(5 : 10) was to be one of the highest capacities, up to now. In general, both high uptake capacity and fast time to equilibrium were demonstrated as the excellent characteristics of AGCC(5 : 10).

Desorption and regeneration

Desorption studies will help to elucidate the nature of adsorption process and to recover the Hg^{2+} ions from AGCC.[40] Moreover, it also will help to regenerate the AGCC, so that it can be used again to adsorb Hg^{2+} ions. Desorption experiments were performed by using $1N$ H$_2$SO$_4$ solution as the desorption agent. Desorption ratio for Hg^{2+} ions from the AGCC(5 : 10) loaded with 500 mg/L of Hg^{2+} ions was calculated by using eq. (2) and given in Figure 9. More than 95% of the adsorbed Hg^{2+} ions were desorbed with $1N$ H$_2$SO$_4$ solution. Adsorption/desorption cycles were repeated three times. When H$_2$SO$_4$ solution is used as the desorption agent, the Hg^{2+} ions were released from the solid surface into the desorption medium. Therefore, AGCC(5 : 10) can be used repeatedly without significantly loosing their adsorption capacities for the Hg^{2+} ions.

TABLE II
The Hg^{2+} Adsorption Capacity and the Time to Reach Equilibrium of Chitosan Containing Adsorbents Derived from Literature and Experimental Data

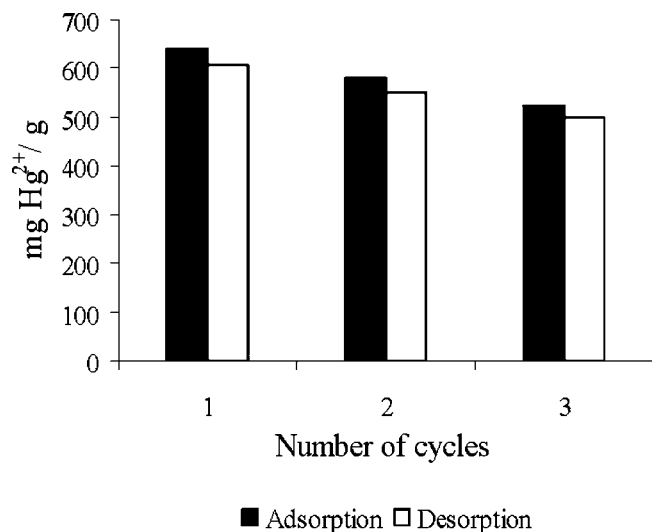| Adsorbent	Q_{max} (mg/g)	Time to reach equilibrium (min)	Paper source
Chitosan bead	294		[22]
Thiol-grafted chitosan bead	1,600	1,200	[2]
Aminated chitosan bead	476	100	[23]
AGCC(5 : 10)	667	60	This study
Alginate bead	32	60	This study

Figure 9 Adsorption/desorption cycles of AGCC(5 : 10).

CONCLUSIONS

Alginate and chitosan are all environmental friendly bioadsorbents for heavy metals. The chitosan flake was ground and sieved to collect the chitosan powder with particle size ranging from 0.075 to 0.106 mm. The collected chitosan powder was then crosslinked with glutaraldehyde to overcome solubility. It was confirmed that the crosslinked chitosan is insoluble in acidic and neutral media. A viscous sodium alginate solution containing certain amount of the crosslinked chitosan powders was directly dispensed drop wise into the calcium chloride solution to form spherical alginate gels. Three particle sizes with average diameters of 1.8, 2.7, and 3.6 mm were prepared. The SEM results reveal the uniform distribution of chitosan powders in the alginate gel bead.

Alginate gels containing chitosan, AGCC, have been successfully used as adsorbing agents for removal of Hg^{2+} from aqueous medium. The equilibrium was well described by Langmuir adsorption isotherms. And the adsorption of mercury ions was almost completed in 60 min at 200 rpm. Addition of chitosan to alginate microsphere results in significant enhancement of not only its adsorption capacity but also its uptake rate for Hg^{2+}. Decreasing the bead size of the AGCC results in rapid increase in the initial sorption rate for Hg^{2+}. However, the uptake capacity is independent of bead size. The SEM-EDX results demonstrate that Hg^{2+} ions are able to reach the chitosan immobilized in the entire structure of alginate beads.

The adsorbent, AGCC, can be regenerated and reused by acid treatment. The adsorbent was reused in three adsorption/desorption cycles with negligible decrease (up to 95% recovery) in sorption capacity. This adsorbent can be applied easily using existing treatment technologies.

These results suggest that AGCC is a strong candidate as an adsorbent for the removal of Hg^{2+} from wastewaters.

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