Removal of Hg^{2+} from Aqueous Solution Using a Novel Composite Carbon Adsorbent

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ABSTRACT: A novel composite carbon adsorbent (GCA) has been prepared by immobilizing activated carbon and genipin-crosslinked chitosan into calcium alginate gel beads via entrapment and applied to the removal of mercury (Hg^{2+}) ions from aqueous solution (e.g., drinking water). Two bead sizes and two mixing ratios of components were obtained and characterized. Batch experiments were performed to study the uptake equilibrium and kinetics of Hg^{2+} ions by the GCA. The Hg^{2+} adsorption capacity of GCA was found to be dependent of pH and independent of size of the adsorbent. The Hg^{2+} adsorption rate of GCA increases with decreasing its bead size. However, both adsorption capacity and rate of GCA for Hg^{2+} increase with increasing its chitosan content. Otherwise, it was shown that the GCA has higher Hg^{2+} adsorption capacity and rate than activated carbon, which might be caused by the incorporation of chitosan into the GCA. The maximum Hg^{2+} adsorption capacity of GCA was found to be 576 mg/g, which is over seven times higher than that of activated carbon. Our results reveal the uniform distribution of activated carbon and chitosan within the alginate gel bead and that Hg^{2+} ions can diffuse inside the bead. It also demonstrated the feasibility of using this GCA for Hg^{2+} removal at low pH values. The Hg^{2+} absorbed beads of the GCA can be effectively regenerated and reused using H$_2$SO$_4$. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2445–2454, 2009

Key words: alginate; chitosan; activated carbon; adsorption; heavy metals; mercury; adsorbent

INTRODUCTION

Modern industrial progresses increase the risk of water pollution with heavy metals. Mercury (Hg^{2+}) is one of the most toxic heavy metals, and it has been responsible for most serious outbreaks of metal poisoning, e.g., Minamata disease.[1] Exposure to Hg^{2+} can have toxic effects on reproduction, the central nervous system, liver, and kidney and causes sensory and psychological impairments.[2] Consequently, removal of Hg^{2+} ion from water (e.g., drinking water) is extremely critical.

Activated carbons are known as effective adsorbents for water treatment because of their high porosity with large surface area ($\sim$ 3000 m^2/g).[3] Although activated carbon has been used for Hg^{2+} removal from water stream,[4] different chemical modifications of activated carbons have been developed to improve their Hg^{2+} adsorption capacities.[5–8] Krishnan and Anirudhan prepared the sulfurized steam-activated carbons and used as adsorbents for Hg^{2+}

removal from aqueous solution.[5,8] Zhang et al. developed various types of activated carbons using H$_2$SO$_4$, H$_3$PO$_4$, and ZnCl$_2$ as chemical activation reagents, and found that the ZnCl$_2$-activated carbon has the highest capability for Hg^{2+} adsorption.[6] Similarly, Kadirvelu et al. used H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$ to perform the chemical activation of the activated carbon.[7] On the other hand, oxidized nanoporous-activated carbon was developed by Xiao and Thomas and demonstrated to have the highest capacity for Hg^{2+} ions adsorption at 275 mg/g.[9] Nevertheless, the maximum adsorption capacity of various natural polymers for Hg^{2+} has been reported to be significantly higher than that of the modified activated carbons. 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+}.[10,11] Recently, the adsorption capacity of chitosan for Hg^{2+}, 1127 mg/g, has been reported.[12] Therefore, this study intended to combine activated carbon and chitosan to prepare an effective composite carbon adsorbent, alginate gel beads containing chitosan (AGCC) and activated carbon, (abbreviated as GCA), for Hg^{2+} removal.

Chitosan is a nontoxic, biodegradable, and functional biopolymer formed by the N-deacetylation of

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chitin,[13] which is present in fungi, insects, and crustaceans. Chitosan has been known for its metal adsorption properties since 1970s,[13] and it has been shown to effectively remove metals such as Hg^{2+} and various metal species from aqueous solutions.[10–18] Chitosan also appears to be more economically attractive for removal of colors and organic compounds from wastewater than activated carbon.[19] However, the porosity and surface area of chitosan are significantly lower than those of activated carbon.[20] Chitosan is soluble in dilute mineral acids, except for sulfuric acid; therefore, it is necessary to be stabilized chemically for the recovery of metal ions in acidic solutions.[21] The most common crosslinker used with chitosan is glutaraldehyde; however, the glutaraldehyde contains cytotoxic chemical species.[22] It is, therefore, desirable to develop a nontoxic crosslinking reagent suitable for use in the purification of various water stream (e.g., drinking water). Genipin is about 5000–10,000 times less cytotoxic than glutaraldehyde, and it has been used as food dyes.[23] It was found that genipin can also react with the free amino groups in chitosan.[23] These results prompted us to use genipin to crosslink chitosan. It was reported that the maximum adsorption capacity of chitosan for Hg^{2+} was 815 mg/g[15]; however, later study reported only 430 mg/g.[16] This difference occurs because of 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.[11] Such reduction in particle size of chitosan, of course, increases its surface area to be adsorbed by the metal ions and it results in higher removal efficiency of heavy metal.[11] An even higher adsorption capacity, 1127 mg of Hg^{2+}/g, of chitosan with a smaller particle size (0.177 mm) was reported.[12] Otherwise, because of resistance to intraparticle mass transfer in raw chitosan, it is usually necessary to use very small particles to improve sorption kinetics.[14] Nevertheless, small particles have proved to be inappropriate for use in column systems as 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.[14,22] The metal adsorption capacity of chitosan powder was reported to be higher than that of chitosan gel bead.[24] Thus, 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 metal ions adsorption.[18]

Alginate, a nontoxic component of algal cell wall, has been previously used as a support material for the immobilization of several enzymes and microbial cells.[25,26] Alginate is a linear polysaccharide composed of (1 → 4)-linked residues of α-L-guluronic acid (G) and β-D-mannuronic acid (M). This polyelectrolyte is soluble in water but precipitated 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+}.[27] In our previous study, AGCC has been successfully prepared by immobilizing chitosan powder in alginate gel bead and used as adsorbing agent for removal of Hg^{2+} from aqueous medium.[18] Hence, a GCA was developed by the authors in an attempt to utilize AGCC to improve the Hg^{2+} adsorption capacity of activated carbon. Recently, Park et al. have developed an activated carbon-containing alginate bead (AC-AB) adsorbent to remove heavy metal ions from drinking water. However, there was no difference between the Hg^{2+} removal performance of water filter with extra AC-AB and that of conventional water filter.[26]

Although the surface area of chitosan (3.7 m²/g) is much lower than that of activated carbon (~ 3000 m²/g),[20] chitosan was reported to have higher adsorption capacity for Hg^{2+}.[10,11] The GCA was hence prepared for Hg^{2+} ions removal from water stream (e.g., drinking water) in this study. Chitosan powder was crosslinked with genipin and its solubility was measured before and after crosslinking. The crosslinked chitosan and activated carbon were then immobilized in alginate gel beads by liquid curing method. The resulting adsorbent is spherical shaped with diameter of 2.7 and 3.8 mm. The morphology of adsorbent was characterized by SEM. The release of entrapped particles from GCA and the swelling properties of GCA were also characterized. At pH 7, the equilibrium and kinetic characteristics of Hg^{2+} adsorption on the adsorbent were studied in batch experiments in terms of bead size and mixing ratios of components. The effect of pH on Hg^{2+} adsorption capacity was also investigated. The adsorption of Hg^{2+} ions by the GCA was confirmed to be significantly superior to that by activated carbon. We have demonstrated that the maximum uptake capacity of this GCA is 576 mg Hg^{2+}/g-dry mass, which is one of the highest capacities of carbon-containing adsorbents up to present. In addition, fast time (<70 min) to reach equilibrium of Hg^{2+} adsorption is another superior characteristic of GCA. Our previous study has demonstrated a higher adsorption capacity of AGCC for Hg^{2+}, i.e., 667 mg/g.[18] Nevertheless, chitosan has some disadvantageous properties, such as low surface area, low porosity, low affinity for basic dyes, and highly specific applications, when compared with activated carbon.[22] Besides, activated carbon has great capacity to adsorb a wide range of pollutants.[22] Because the GCA contains not only chitosan but also activated carbon, GCA might be more suitable for a wide variety of water treatment (e.g., drinking water treatment) in comparison with AGCC.

MATERIALS AND METHODS

Materials

Chitosan powder of 150 mesh (<0.106 mm) produced from crab shell wastes was obtained from Kiotek Corp., Taiwan. The degree of deacetylation of chitosan, 92 mol %, has been measured by an IR method.[28] The M_w of chitosan is 280,000, and the polydispersity index, M_w/M_n, is 2.8. The activated carbon of 325 mesh (<0.045 mm) was obtained from Prime Carbons Lanka, Sri Lanka. Genipin was purchased from Wako Pure Chemical Industries. Mercury nitrate was supplied by Merck as analytical-reagent grade. Sodium alginate, calcium chloride (CaCl$_2$), sulfuric acid, and acetic acid were purchased from Sigma-Aldrich.

Chitosan crosslinking

Chitosan was crosslinked in 0.5 mM genipin solution at room temperature for 8 h ($\sim$ 0.28 g chitosan in 40 mL genipin solution).[23,29] After crosslinking, the chitosan was rinsed with deionized water to remove any free genipin.

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 sample in the dilute acid and deionized water for 24 h with stirring.[18]

Preparation of composite carbon adsorbent

GCA ($X : Y : Z$) contains alginate, chitosan, and activated carbon with a weight ratio of $X : Y : Z$. The immobilization of crosslinked chitosan and activated carbon via entrapment was carried out as follows[18]: 10 g sodium alginate was dissolved in 500 mL of deionized water and mixed with 12 g crosslinked chitosan powder and 6 g activated carbon for preparation of GCA (10 : 12 : 6). The sodium alginate solution containing crosslinked chitosan and activated carbon was then added drop by drop by means of a peristaltic pump with a tube diameter of 0.5 mm into a stirred 0.5% CaCl$_2$ solution. The size of the droplets was controlled by applying a coaxial air stream. By doing so, the water-soluble sodium alginate is converted into water-insoluble calcium alginate beads. The beads were washed with deionized water to remove CaCl$_2$ and stored at 4°C before use. GCA (10 : 11 : 7), GCA (10 : 0 : 18), and plain alginate bead were also produced by the same method. GCA (10 : 0 : 18) and plain alginate bead were prepared for comparison purpose.

SEM studies

The GCA (10 : 12 : 6) with a diameter of 3.8 mm was freeze-dried. The dried GCA (10 : 12 : 6) was coated under vacuum with a thin layer of gold and examined by a JEOL (JSM5600) SEM.

Characterization of GCA

The mean weights of GCA beads were evaluated by removing only the excess of water on filter paper after their collection by filtration. The dry weights of GCA beads were determined by weighing the beads after drying in an oven at 70°C for 36 h. The water content of the wet adsorbent was measured using a gravimetric method. The loss of weight during drying was found to be 94.78, 94.55, and 94.24% for GCA (10 : 12 : 6), GCA (10 : 11 : 7), and GCA (10 : 0 : 18), respectively.

To evaluate the release of entrapped particles (activated carbon and chitosan) from GCA (10 : 12 : 6), a flask containing 300 mL deionized water and 2.5 g wet GCA (10 : 12 : 6) was agitated in a rotary shaker at 200 rpm, 25°C for 72 h. GCA (10 : 12 : 6) was separated from the water by a 0.991-mm mesh filter, which is permeable to the utilized activated carbon and chitosan (<0.106 mm). Subsequently, the filtrate was refiltered by Whatman filter membrane (pore size: 1.2 μm) and then the filter membrane was oven dried and weighed. Amount of the released particles from GCA (10 : 12 : 6) could be obtained by calculating the weight difference of filter membrane before and after filtration.

Swelling studies

Swelling studies were conducted in deionized water using wet adsorbents with a diameter of 3.8 mm. The term wet refers to the state of the adsorbent immediately after the preparation. Plain alginate bead, GCA (10 : 11 : 7), and GCA (10 : 12 : 6) were tested in this experiment. A total of 2.5 g wet adsorbent was immersed in 300 mL of deionized water, and at fixed time intervals the adsorbent was separated from the water. Immediately, the adsorbent was wiped gently with paper and weighed. The dynamic weight change of the adsorbent with respect to time was calculated according to the formula:[30]

$$\%\text{Weight change} = \frac{W_s - W_i}{W_i} \times 100\% \qquad (1)$$

where W_s is the weight of the adsorbent in the swollen state and W_i is the initial weight of the adsorbent.

Equilibrium uptake experiments

Adsorption of Hg^{2+} ions from aqueous solution was studied in batch system using mercury nitrate

solution. Batch experiments were carried out using GCA beads and activated carbon as adsorbents. A series of flasks containing 300 mL solution with various metal concentrations and adsorbent were agitated in a rotary shaker at 200 rpm, 25°C for 24 h, which is sufficient for the Hg^{2+} ion uptake process to reach final equilibrium. The weight losses during drying were found to be 94.78, 94.55, and 94.24% for GCA (10 : 12 : 6), GCA (10 : 11 : 7), and GCA (10 : 0 : 18), respectively. Therefore, 2.87 g wet GCA (10 : 12 : 6), 2.75 g wet GCA (10 : 11 : 7), 2.60 g wet GCA (10 : 0 : 18), or 0.15 g dry activated carbon were added in 300 mL solution, respectively, to make the dosage of adsorbent equal to 0.15 g-dry weight/300 mL. In this study, the adsorptive capacity of GCA and activated carbon for Hg^{2+} removal was determined through adsorption isotherm studies, whose parameters were calculated based on the dry weight of adsorbent. By adjusting with 0.1N HNO_3 or NaOH, the Hg^{2+} sorption experiments were conducted at pH = 7. After equilibrium, the adsorbent was filtered from the solution (Whatman filter membrane) and the filtrate was analyzed for Hg^{2+} content by a GBC Avanta Σ Atomic Absorption Spectrophotometer. Metal-free and adsorbent-free blanks were used as controls. Extent of the Hg^{2+} ion uptake by the adsorbent, based on dry weight, was determined by the following mass balance equation:

$$Q = \frac{V(C_0 - C_e)}{m} \qquad (2)$$

where Q and C_e are the adsorbent-phase metal concentration and the solution-phase metal concentration at equilibrium, respectively. 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 parameters were calculated based on the dry weight of the adsorbent.

The effect of pH on the adsorption capacity of Hg^{2+} on 3.8 mm GCA (10 : 12 : 6) was also investigated at pH value of 5, 6, 7, and 8, respectively. The initial concentration of Hg^{2+} ion was 480 mg/L and the adsorption capacity (Q) was calculated based on eq. (2).

SEM/EDS analysis of metal distribution

The isothermal adsorption of Hg^{2+} ion by 3.8 mm GCA (10 : 12 : 6) was conducted for the concentration (480 mg/L) of the Hg^{2+} ion solution at pH 7. After 24 h, the GCA (10 : 12 : 6) beads were separated from the Hg^{2+} ion solution, then washed several times with deionized water, and freeze-dried for further observations. The distribution of Hg^{2+} ions inside the Hg^{2+}-loaded beads was examined using a Hitachi S-2500 SEM with an attachment of X-ray

energy dispersion (EDS) analyzer after coating the beads with a thin layer of gold.[18]

Transient uptake experiments

Batch experiments for determination of the kinetics of Hg^{2+} adsorption on GCA beads were carried out using a continuously stirred 500-mL glass beaker.[18] A motor was used to drive a four-blade impeller with a diameter of 6 cm. The following experimental conditions were kept constant: volume of mercury nitrate solution = 300 mL, temperature = 25°C, stirring speed = 200 rpm, and initial metal concentration = 200 ppm. A total of 2.87 g wet GCA (10 : 12 : 6) and 2.75 g wet GCA (10 : 11 : 7) were added in 300 mL solution, respectively, to make the dosage of adsorbent equal to 0.15 g-dry weight/300 mL. By adjusting with 0.1N HNO_3 or NaOH, the Hg^{2+} sorption experiments were conducted at pH 7. During the kinetic experiments, samples were withdrawn at fixed time intervals and analyzed for metal content as described earlier. 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.

Breakthrough tests

A column (height 200 mm, diameter 30 mm) was filled with the adsorbent for the study of sorption in continuous fixed bed systems. A total of 105.36 g wet GCA (10 : 12 : 6) with a diameter of 3.8 mm was packed in the column to make the dosage of adsorbent equal to 5.5 g-dry weight per column. Packed bed experiments were carried out at 25°C. The mercury nitrate solution at pH 7 was introduced to a newly packed column by an upflow of flow rate at 15 mL/min using an inlet metal concentration of 300 or 700 mg/L. The samples in the outlet were taken at the preset time intervals and their Hg^{2+} concentrations were analyzed as described earlier.

Desorption

Desorption of Hg^{2+} ions was achieved by using 1N H_2SO_4. The 3.8 mm GCA (10 : 12 : 6) loaded with Hg^{2+} ion in the following conditions—initial concentration of Hg^{2+} ion: 480 mg/L; amount of GCA (10 : 12 : 6): 1 g-wet weight (0.0522 g-dry weight); volume of adsorption medium: 100 mL; pH: 7; temperature: 25°C; and adsorption time: 24 h. Then, the GCA (10 : 12 : 6) was placed in the desorption medium and stirred at 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 was calculated from the following expression[18]:
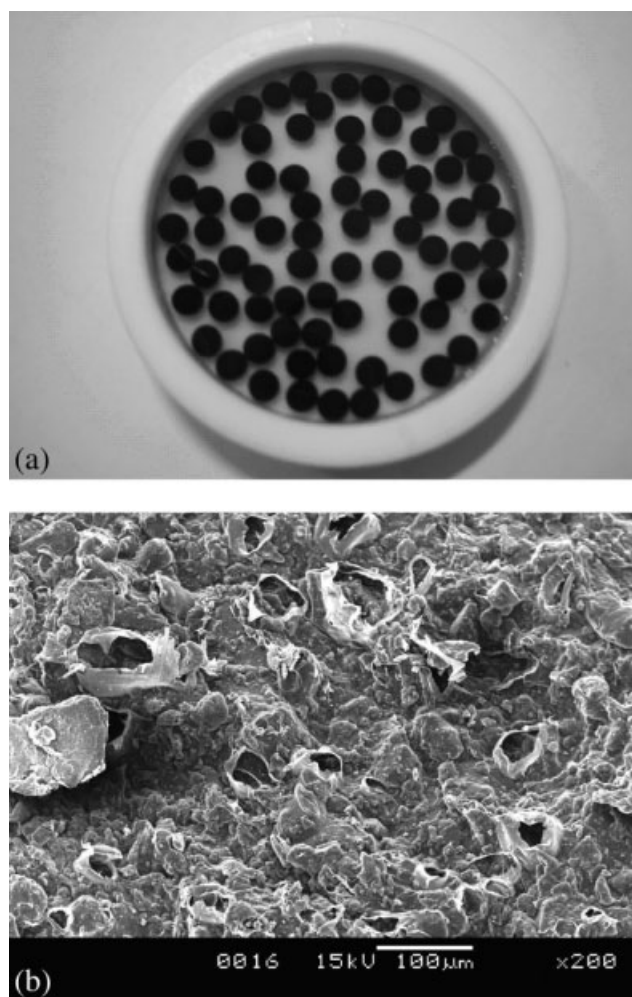
Figure 1 Morphologies of GCA (10 : 12 : 6) with a diameter of 3.8 mm: (a) photograph of GCA (10 : 12 : 6), (b) SEM surface image of GCA (10 : 12 : 6).

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

$$(3)$$

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, genipin, a natural and nontoxic crosslinking reagent, was used to crosslink chitosan. It was shown that after crosslinking, the crosslinked chitosan was found to be insoluble in 5% (v/v) acetic acid and deionized water. It is well known that the high hydrophilicity of chitosan because of its 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 genepin.[23,29] The reaction mechanism of chitosan with genipin has been previously studied.[31] It

was found that genipin undertakes a ring-opening reaction to form an intermediate aldehyde group because of the nucleophilic attack by the amino groups in chitosan. The genipin molecules reacting with a nucleophilic reagent such as chitosan undergo further polymerization to form a cyclic crosslinking structure.[29]

Properties of composite carbon adsorbent

We have demonstrated that immobilization of chitosan in the alginate bead provides advantages over the chitosan powder.[18] In this study, both chitosan and activated carbon were immobilized in the alginate gel bead. The GCAs 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 2.7 and 3.8 mm, respectively. As shown in Figure 1(a), the wet GCA (10 : 12 : 6) with a diameter of 3.8 mm is a black-colored bead. Figure 1(b) presents the morphology of GCA (10 : 12 : 6) obtained by using SEM. The beads are porous, indicating that their inside parts are accessible to Hg^{2+} ions in aqueous solution. Besides, the SEM micrograph also reveals a uniform distribution of chitosan and activated carbon in alginate gel bead.

With GCA (10 : 12 : 6), there was no release of activated carbon or chitosan observed by a batch contact with deionized water for 72 h at 25°C at a stirring rate of 200 rpm.

Figure 2 illustrates the swelling behaviors of the adsorbents in water. The degree of swelling of plain
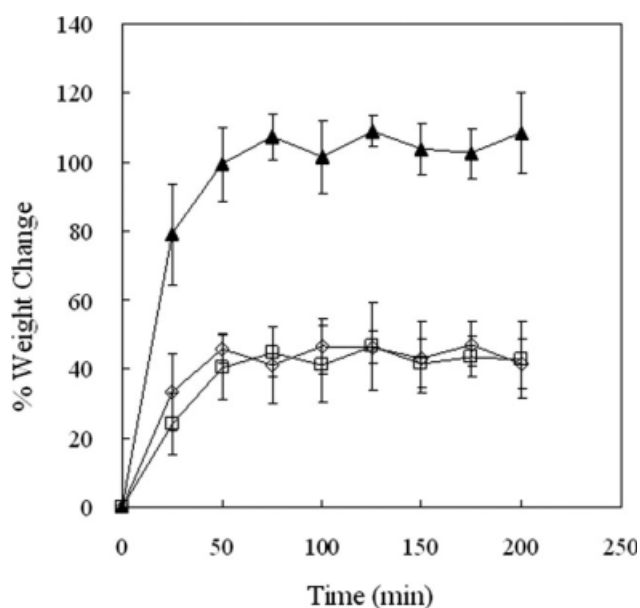

Figure 2 Swelling profiles of 3.8 mm wet beads in deionized water: plain alginate bead (▲), GCA (10 : 12 : 6) (◇), and GCA (10 : 11 : 7) (□). Values are mean ± standard deviation (S.D.) of three experiments.

alginate bead was higher than that of GCA (10 : 12 : 6) or GCA (10 : 11 : 7) (Fig. 2). The incorporation of crosslinked chitosan and activated carbon into alginate gel bead results in the reduction of swelling degree of the bead.

Adsorption isotherms

As the pH value of most of the drinking water is close to 7, the adsorption experiments were performed at pH 7. The adsorption time was 24 h. In this article, the adsorptive capacity of GCA and activated carbon for Hg^{2+} removal was determined through adsorption isotherm studies, whose parameters were calculated based on the dry weight of adsorbent. The experimental adsorption isotherms (Figs. 3 and 4) show the relationship between the quantity of Hg^{2+} adsorbed per unit dry mass adsorbent (Q) and the equilibrium concentration (C_e). All of the isotherms showed similar behavior, which can be described by using the Langmuir adsorption equation as:

$$\frac{C_e}{Q} = \frac{C_e}{Q_{max}} + \frac{1}{(Q_{max}) \cdot K_s} \quad (4)$$

where Q_{max} is 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 C_e for adsorption of Hg^{2+} on adsorbents are shown in Figure 5. These isotherms are linear over the entire concentration

Figure 4 Experimental adsorption isotherms of Hg^{2+} ions on GCA (10 : 12 : 6) with a diameter of 3.8 mm ($\diamond$) and 2.7 mm (+). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

range studied and the correlation coefficients are extremely high ($R^2 > 0.99$), implying that the sorption of Hg^{2+} closely follows the Langmuir model of sorption.[20] Linearized plots of (C_e/Q) versus (C_e) give Q_{max} and K_s values (Table I). The Hg^{2+} adsorption capacity is presented in Table II. For the purposes of comparison, similar data from the literature are also included in Table II.
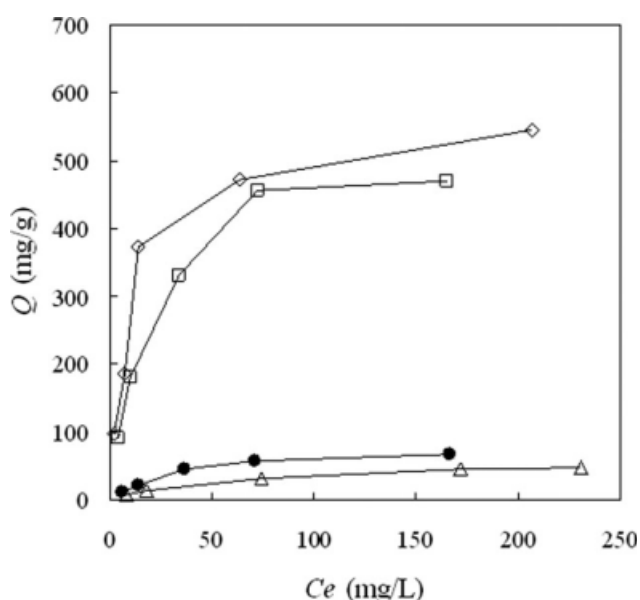

Figure 3 Experimental adsorption isotherms of Hg^{2+} ions on activated carbon (●) and composite carbon adsorbents with a diameter of 3.8 mm: GCA (10 : 12 : 6) (◇), GCA (10 : 11 : 7) (□), and GCA (10 : 0 : 18) (△).
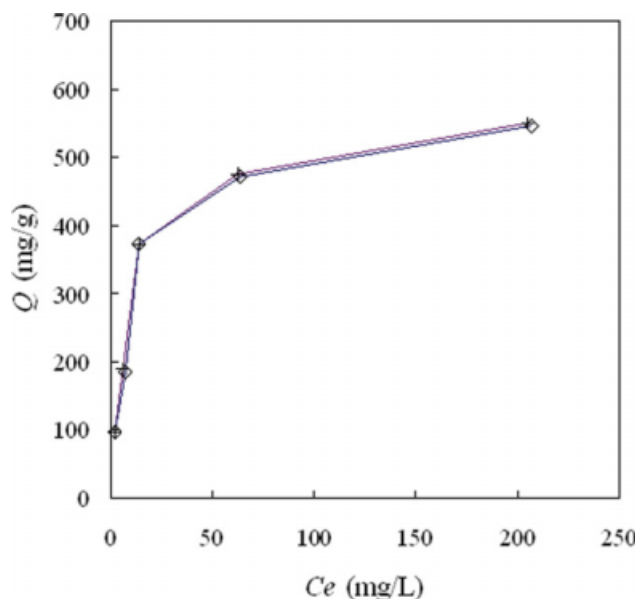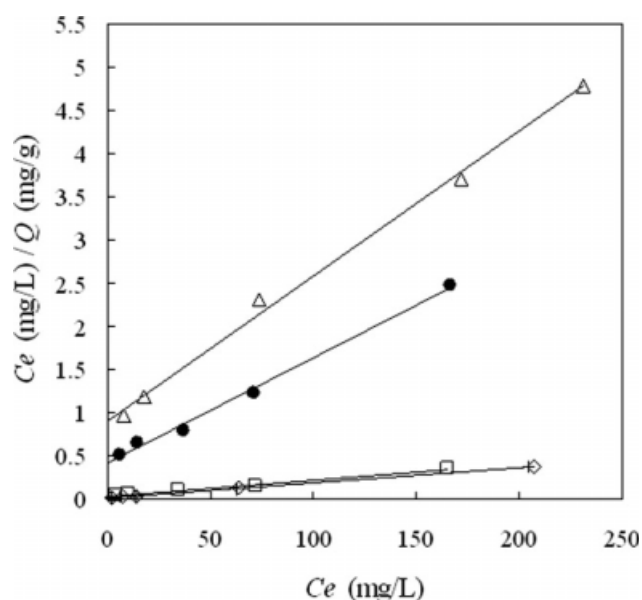

Figure 5 Langmuir isotherms of Hg^{2+} ions on activated carbon (●), 2.7 mm GCA (10 : 12 : 6) (+), and composite carbon adsorbents with a diameter of 3.8 mm: GCA (10 : 12 : 6) (◇), GCA (10 : 11 : 7) (□), and GCA (10 : 0 : 18) (△).

TABLE I
Langmuir Isotherm Constants and Correlation
Coefficients for Hg^{2+} Adsorption

Adsorbent		Langmuir		
Type	Size (mm)	Q_{max} (mg/g)	K_s (L/mg)	R^2
Activated carbon	(<0.045)	82	0.029	0.994
GCA (10 : 0 : 18)	3.8	60	0.018	0.996
GCA (10 : 11 : 7)	3.8	529	0.055	0.997
GCA (10 : 12 : 6)	3.8	574	0.088	0.999
GCA (10 : 12 : 6)	2.7	576	0.098	0.999

The adsorption capacity of GCA for Hg^{2+} increased significantly with increasing its weight ratio of chitosan to activated carbon (Table I). This may be due to the difference between the Hg^{2+} adsorption capacities of chitosan and activated carbon. The reported maximum adsorption capacity of chitosan powder for Hg^{2+} is 1127 mg/g,[12] whereas the capacity of activated carbon is only 82 mg/g (Table I). However, the Hg^{2+} adsorption capacity of alginate bead is 32 mg/g.[18] Hence, chitosan may play a critical role in enhancing the adsorption capacity of Hg^{2+} ions in GCA. Although crosslinking does somewhat reduce the adsorption capacity of chitosan, but this loss of capacity is necessary to ensure stability of the polymer.[10] Moreover, it was reported that the heterogeneous crosslinking of small particle size chitosan flakes gave comparable sorption capacities relative to raw and crosslinked materials.[14] The computed maximum capacity Q_{max} of Hg^{2+} on 2.7 mm GCA (10 : 12 : 6) has large value at 576 mg/g, which is the highest capacity among the literature reported carbon-containing adsorbents and is over seven times higher than that of activated carbon (Table II). The Hg^{2+} sorption capacity was found to be independent of the size of GCA beads

TABLE II
The Hg^{2+} Adsorption Capacity of Adsorbents Derived
from Literature and Experimental Data

Adsorbent	Q_{max} (mg/g)	Paper source
Activated carbon	174	7
Activated carbon[a]	172	9
Activated carbon[b]	208	9
Activated carbon	74	10
Activated carbon	82	This study
Sulphurized-activated carbon[b]	227	9
ZnCl$_2$-activated carbon	151	10
Chemical-activated carbon	56	11
Sulfurized steam-activated carbon	189	12
Oxidized nanoporous-activated carbon	275	13
GCA (10 : 12 : 6)	576	This study

[a] The adsorption was performed at 30°C.
[b] The adsorption was performed at 60°C.

(Table I), implying that sorption occurs in the whole mass of GCA bead rather than on the external layer of the bead. Although the Hg^{2+} adsorption capacity of chitosan powder (1127 mg/g or 815 mg/g)[12,15] is higher than that of GCA (10 : 12 : 6), the chitosan powder with small particle size is inappropriate for use in column systems because of column clogging and hydrodynamic limitations. In addition, activated carbon has great capacity to adsorb a wide range of pollutants in comparison with chitosan.[22]

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.[32] The K_s values of the isotherms for Hg^{2+} sorption on GCAs with a diameter of 3.8 mm are in the order of GCA (10 : 12 : 6) > GCA (10 : 11 : 7) > GCA (10 : 0 : 18) (Table I), mainly because of the higher Hg^{2+} adsorption capacity of the chitosan. On the other hand, the K_s value of the isotherms for Hg^{2+} sorption on GCA (10 : 12 : 6) of the 2.7 mm adsorbent is higher than that of the 3.8 mm adsorbent (Table I) because smaller particles possess greater outside surface area per weight than larger particles.

Influence of pH on sorption

The pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process, and thus, the role of the hydrogen ion concentration was examined in batch experiments. Figure 6 shows the effect of pH on the uptake capacity of Hg^{2+} on 3.8 mm GCA (10 : 12 : 6). The pH effect for Hg^{2+} adsorption was investigated in the pH range of 5–8. The sorption capacity increases with increasing the pH of the solution (Fig. 6). In acidic
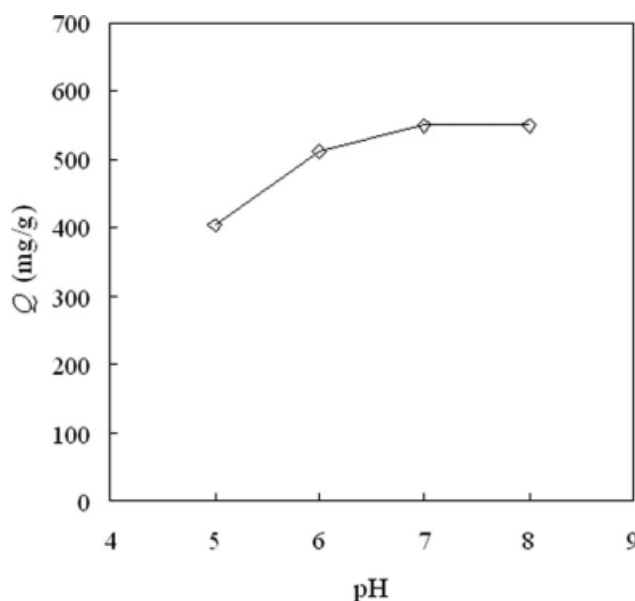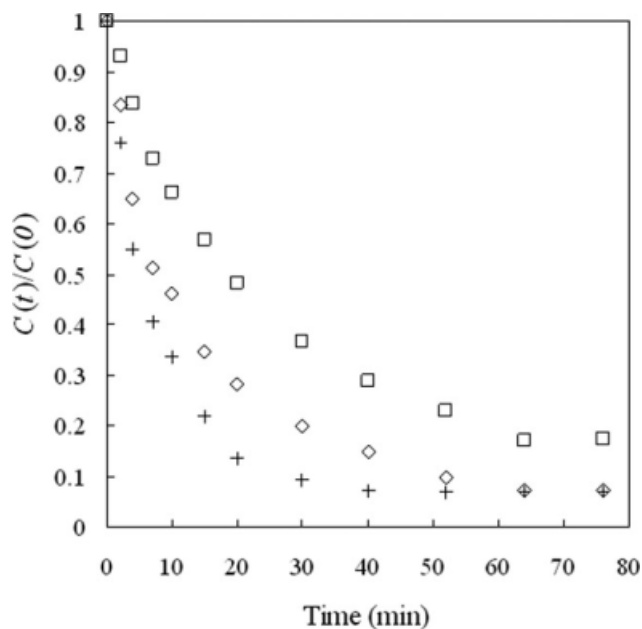

Figure 6 Effect of pH on Hg^{2+} ion uptake capacity.

Figure 7 Hg^{2+} sorption kinetics of composite carbon adsorbents: 3.8 mm GCA (10 : 11 : 7) (□), 3.8 mm GCA (10 : 12 : 6) (◇), and 2.7 mm GCA (10 : 12 : 6) (+). (pH = 7, agitation rate = 200 rpm, and temperature = 25°C).

solutions, a competition existed between Hg^{2+} ions and protons for sorption sites of the chitosan and its sorption capacity is thus decreased. Moreover, the protonation of amine groups of chitosan induces an electrostatic repulsion of Hg^{2+} cations. When the pH of the solution is increased, the competition effect decreases as well as the electrostatic repulsion. Dzul Erosa et al. reported a similar trend for cadmium sorption on chitosan sorbents.[33] In this study, the best results of the GCA were obtained in the pH range between 7 and 8. The experimental results also imply the possibility of desorption and regeneration of GCA by acidic solutions.

SEM/EDS study of sorptions

Cross section of the 3.8 mm GCA (10 : 12 : 6) saturated with Hg^{2+} solutions was analyzed by SEM. The location of sorbed Hg^{2+} is determined with an X-ray EDS analyzer. The distribution pattern of the Hg^{2+} ions taken along the line crossing the GCA (10 : 12 : 6) bead was evaluated. A fairly uniformed distribution of the Hg^{2+} content throughout the bead was observed (data not shown), implying that the open pores and channels of the GCA (10 : 12 : 6) bead allows for free penetration of Hg^{2+} ions into the inner part of the beads. Because chitosan may play a major role in the adsorption of Hg^{2+} ions, the homogeneous distribution of chitosan on the entire structure of the GCA (10 :1 2 : 6) is demonstrated as well. The results demonstrate that Hg^{2+} ions are able to reach chitosan immobilized in the entire

structure of GCA (10 : 12 : 6). Similar results have been reported for AGCC[18] and protonated alginate beads.[34] This SEM/EDS analysis indicates that the chitosan is homogenously immobilized within the porous alginate bead.

Adsorption kinetics

Plotting $C(t)/C(0)$ versus time (min) at pH 7 is shown in Figure 7, where $C(t)$ is the Hg^{2+} concentration and $C(0)$ is the initial Hg^{2+} concentration. The Hg^{2+} uptake by gel particles follows two-step kinetics. The extraparticle association (surface binding) occurs first and rapidly. Further Hg^{2+} uptake is controlled by diffusion through the particle pores and the rate-limiting step is diffusion inside the alginate gel beads.[35] However, the time to reach equilibrium of Hg^{2+} adsorption by GCA is less than 70 min in this experiment.

The Hg^{2+} adsorption rate of 3.8 mm GCA (10 : 12 : 6) is greater than that of 3.8 mm GCA (10 : 11 : 7) because of higher chitosan content of the former as would be expected (Fig. 7). Otherwise, decreasing the particle size of the GCA (10 : 12 : 6) results in higher initial Hg^{2+} uptake rate (Fig. 7) because smaller particles possess more outside surface area per weight.[36] A similar trend was also reported for the immobilized biomass alginate bead[37] and the AGCC.[18]

Breakthrough curves in fixed-bed columns

The breakthrough experiment using a fixed-bed column was performed for Hg^{2+} adsorption to verify the influence of initial influent concentration on the adsorption efficiency of GCA (10 : 12 : 6). The initial influent concentration was varied from 300 to 700 mg/L, and the adsorption time was 880 min. The results are shown in Figure 8, where C_i is the initial
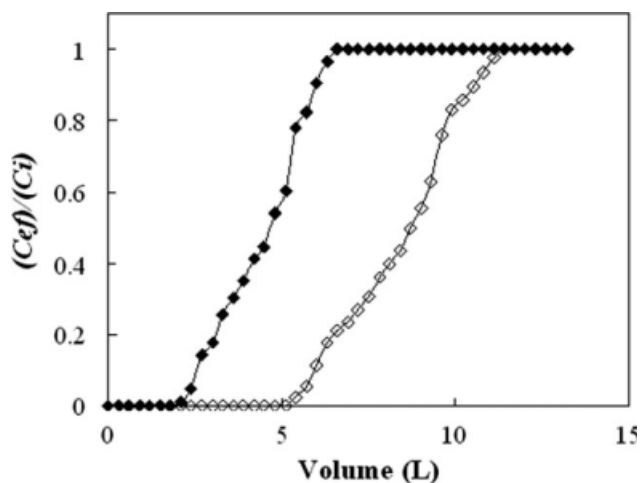

Figure 8 Experimental breakthrough curves for adsorption of Hg^{2+} ions from aqueous solution on GCA (10 : 12 : 6) with a diameter of 3.8 mm. (inlet metal concentration = 700 mg/L(◆) or 300 mg/L(◇), flow rate = 15 mL/min).

TABLE III
Bed Capacity of 3.8 mm GCA (10 : 12 : 6) for Hg^{2+} Adsorption

Inlet metal concentration (mg/L)	Bed capacity (mg Hg^{2+}/g adsorbent)
300	458
700	563

influent concentration and C_{ef} is the column effluent concentration. The dynamic uptake capacity for the adsorbent was obtained by calculating the area above the breakthrough curve until the line for which the Hg^{2+} concentration equals the initial concentration (Table III). This result shows that the GCA (10 : 12 : 6) bed has a good adsorption capacity and that its efficiency increases as the Hg^{2+} solution concentration is increased.

Desorption and regeneration

One of the important features of commercial adsorbents is their regeneration. To evaluate the regenerability of GCA adsorbent, repeated adsorption–desorption of Hg^{2+} was performed in a batch system. Our previous study has demonstrated that $1N$ H$_2$SO$_4$ is a suitable regenerant for AGCC.[18] As the activated carbon is commonly regenerated at high temperatures to oxidize the organics, acid elution is unable to remove organics from GCA. However, the scope of this study is limited to the regeneration of heavy metal uptake capacity. Desorption experiments were performed by using $1N$ H$_2$SO$_4$ solution as the desorption agent. Desorption ratio for Hg^{2+} ions from the GCA (10 : 12 : 6) loaded with 480 mg/L of Hg^{2+} ions was calculated by using Eq. (3). More than 97% of the adsorbed Hg^{2+} ions was desorbed with $1N$ H$_2$SO$_4$ solution, and the adsorption/desorption cycles were repeated three times (data not shown). 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, GCA (10 : 12 : 6) can be used repeatedly without significantly loosing their adsorption capacities for the Hg^{2+} ions. Using the advantageous features of the GCA in repeated cycles of loading and elution, this developed adsorbent may also provide a means to recover precious metal ions, such as gold, silver, platinum, and uranium.

CONCLUSIONS

This study clearly establishes that the GCA is an effective adsorbent for Hg^{2+} removal from aqueous solution. Immobilization of chitosan in alginate bead containing activated carbon results in significant enhancement of the adsorption capacity for Hg^{2+}. Both high uptake capacity and fast time (<70 min) to reach equilibrium have been demonstrated as an excellent adsorbent for Hg^{2+} removal from aqueous solution. This developed GCA remains effective after three adsorption/desorption cycles with negligible decrease (up to 97% recovery) in sorption capacity, which can be adopted easily using existing treatment technologies. The GCA has many advantageous features, such as high Hg^{2+} removal, low cost, and reusability, over current conventional filter materials.[26] Therefore, the GCA can be expected to have extensive applicability for water treatment processes, including drinking water purifiers.

References

1. Kurtland, L. T.; Faro, S. N.; Sieldler, H. World Neurol 1960, 1, 370.
2. Merrifield, J. D.; Davids, W. G.; MacRae, J. D.; Amirbahman, A. Water Res 2004, 38, 3132.
3. Dias, J. M.; Alvim-Ferraz, M. C. M.; Almeidaa, M. F.; Rivera-Utrilla, J.; Sánchez-Polo, M. J Environ Manage 2007, 85, 833.
4. Yardim, M. F.; Budinova, T.; Ekinci, E.; Petrov, N.; Razvigorova, M.; Minkova, V. Chemosphere 2003, 52, 835.
5. Krishnan, K. A.; Anirudhan, T. S. J Hazard Mater B 2002, 92, 161.
6. Zhang, F. S.; Nriagu, J. O.; Itoh, H. Water Res 2005, 39, 389.
7. Kadirvelu, K.; Kavipriya, M.; Karthika, C.; Vennilamani, N.; Pattabhi, S. Carbon 2004, 42, 745.
8. Krishnan, A. K.; Anirudhan, T. S. Ind Eng Chem Res 2002, 41, 5085.
9. Xiao, B.; Thomas, K. M. Langmuir 2004, 20, 4566.
10. Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D. Water Res 1999, 33, 2469.
11. Babel, S.; Kurniawan, T. A. J Hazard Mater B 2003, 97, 219.
12. Shafaei, A.; Ashtiani, F. Z.; Kaghazchi, T. Chem Eng J 2007, 133, 311.
13. Muzzarelli, A. A. Natural Chelating Polymers; Pergamon Press: Oxford, UK, 1973.
14. Guibal, E. Sep Purif Technol 2004, 38, 43.
15. McKay, G.; Blair, H. S.; Findon, A. Ind J Chem A 1989, 28, 356.
16. Peniche-Covas, C.; Alvarez, L. W.; Arguella-Monal, W. J Appl Polym Sci 1992, 46, 1147.
17. Gamage, A.; Shahidi, F. Food Chem 2007, 104, 989.
18. Chang, Y. H.; Huang, C. F.; Hsu, W. J.; Chang, F. C. J Appl Polym Sci 2007, 104, 2896.
19. El-Geundi, M. S. Adsorpt Sci Technol 1997, 15, 777.
20. Ng, J. C. Y.; Cheung, W. H.; McKay, G. J Colloid Interf Sci 2002, 255, 64.
21. Ruiz, M.; Sastre, A. M.; Guibal, E. React Funct Polym 2000, 45, 155.
22. Crini, G. Prog Polym Sci 2005, 30, 38.
23. Mi, F. L.; Tan, Y. C.; Liang, H. F.; Sung, H. W. Biomaterials 2002, 23, 181.
24. Jeon, C.; Höll, W. H. Water Res 2003, 37, 4770.
25. Jianlog, W.; Horan, N.; Stentiford, E.; Yi, Q. Process Biochem 2000, 35, 465.
26. Park, H. G.; Kim, T. W.; Chae, M. Y.; Yoo, I. K. Process Biochem 2007, 42, 1371.

27. Arica, M. Y.; Arpa, Ç.; Ergene, A.; Bayramoğlu, G.; Genç, Ö. Carbohydr Polym 2003, 52, 167.
28. Baxter, A.; Dillon, M.; Tayor, K. Int J Biol Macromol 1992, 14, 166.
29. Yuan, Y.; Chesnutt, B. M.; Utturkar, G.; Haggard, W. O.; Yang, Y.; Ong, J. L.; Bumgardne, J. D. Carbohydr Polym 2007, 68, 561.
30. George, P.; Nikolaos, B. Int J Pharm 2006, 323, 34.
31. Mi, F. L.; Shyu, S. S.; Peng, C. K. J Polym Sci Part A: Polym Chem 2005, 43, 1985.
32. Chu, K. H. J Hazard Mater B 2002, 90, 77.
33. Dzul Erosa, M. S.; Saucedo Medina, T. I.; Navarro Mendoza, R.; Avila Rodriguez, M.; Guibal, E. Hydrometallurgy 2001, 61, 157.
34. Ibanez.J. P.; Umetsu, Y. Hydrometallurgy 2002, 64, 89.
35. Chen, D.; Lewandowski, Z.; Roe, F.; Surapaneni, P. Biotechnol Bioeng 1993, 41, 755.
36. Evans, J. R.; Davids, W. G.; MacRae, J. D.; Amirbahman, A. Water Res 2002, 36, 3219.
37. Blanco, A.; Sanz, B.; Llama, M. J.; Serra, J. L. J Biotechnol 1999, 69, 227.