

Development of chitosan-based granular adsorbents for enhanced and selective adsorption performance in heavy metal removal

N. Li* and R. Bai**

*Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore, 119260

**Division of Environmental Science and Engineering, Faculty of Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore, 119260 (E-mail: esebairb@nus.edu.sg)

Abstract Novel chitosan-based granular adsorbents were developed for enhanced and selective separation of heavy metal ions. The research included the synthesis of chitosan hydrogel beads, the cross-linking of the hydrogel beads with ethylene glycol diglycidyl ether (EGDE) in a conventional and a novel amine-shielded method, the functionalization of the chitosan beads through surface grafting of polyacrylamide via a surface-initiated atom transfer radical polymerization (ATRP) method, and the examination of the adsorption performance of the various types of chitosan beads in the removal of heavy metal ions. It was found that chitosan beads were effective in heavy metal adsorption, the conventional cross-linking method improved the acidic stability of the beads but reduced their adsorption capacity, the novel amine-shielded cross-linking method retained the good adsorption capacity while it improved the acidic stability of the beads, and the grafting of polyacrylamide on chitosan beads not only enhanced the adsorption capacity but also provided the beads with excellent selectivity for mercury over lead ions. XPS analyses indicated that the adsorption of metal ions on chitosan beads was mainly attributed to the amine groups of chitosan, the novel amine-shielded cross-linking method preserved most of the amine groups from being consumed by the cross-linking process and hence improved the adsorption capacity of the cross-linked chitosan beads, and the many amide groups from the polyacrylamide grafted on the chitosan beads increased the adsorption capacity and also made possible selective adsorption of mercury ions because the amide groups can form covalent bonds with mercury ions.

Keywords Adsorption; chitosan beads; cross-linking; heavy metal ions; surface grafting

Introduction

Heavy metal contamination of various water resources is of great concern because of the toxic effects of heavy metals on human beings and other animals and plants in the environment, even at very low concentrations. Lead and mercury, for example, are highly toxic to flora, fauna, and human beings and are listed as priority pollutants by the US Environmental Protection Agency (Kiefer and Höll, 2001). Various methods, including chemical precipitation, ion exchange, reverse osmosis, electrolysis, and adsorption, have been used therefore to remove heavy metal ions from water, wastewater, and industrial effluents (Molinari *et al.*, 2004). In recent years, biosorption using materials of biological origin as the adsorbents for heavy metal removal has attracted more and more interest, largely due to the unique properties of these biomaterials being environmentally benign, low cost, effective at low metal concentrations, and easily re-useable (Muzzarelli, 1973; Roberts, 1992). Among these biomaterials, chitosan, a derivative from N-deacetylation of chitin – a naturally abundant polysaccharide from crustacean and fungal biomass – has particularly attracted attention because of its capability to chemically or physically adsorb various heavy metal ions (Castro Dantas *et al.*, 2001; Vincent and Guibal, 2001; Rhazi *et al.*, 2002).

doi: 10.2166/wst.2006.736

Although chitosan has many attractive properties, it also has several shortcomings. Firstly, the raw form of chitosan (in flakes or powder) is a crystallized polymer and metal ion adsorption could take place only at the amorphous region of the crystals, which thus limited the adsorption capacities of chitosan for various heavy metal ions (Lee *et al.*, 2001). Hence, attempts have been made to form chitosan hydrogel beads to reduce the crystallinity of chitosan (Li and Bai, 2005; Yan and Bai, 2005). Next, chitosan or chitosan hydrogel beads usually displayed poor acidic resistance and would gradually dissolve in a solution of pH 4 or less (Lee *et al.*, 2001; Ngah *et al.*, 2002; Li and Bai, 2005). Therefore, efforts have been made to improve the chemical stability of the hydrogel beads in acidic conditions through chemical cross-linking of the surfaces with cross-linking agents. However, most of the chemical cross-linking agents, e.g. EGDE, GA, and even ECH (Hsien and Rorrer, 1997; Schmuhl *et al.*, 2001; Vincent and Guibal, 2001; Ngah *et al.*, 2002), are prone to react with the amine groups of chitosan, and, as a result, the adsorption capacity of the cross-linked hydrogel beads are usually reduced largely because the amine groups of chitosan are also known to be the main chelating sites of adsorption for various heavy metal ions. To preserve the adsorption capacity of the chitosan hydrogel beads, it has been desirable to develop new cross-linking methods that can prevent the amine groups of chitosan from being consumed by the cross-linking reaction. In addition, the amine groups of chitosan, although effective for metal ion adsorption, do not have good selectivity for different types of metal ions. Since selective adsorption of various heavy metal ions can become an important means in separating heavy metal ions for recovery and reuse in the future, it is of great research and practical interest to develop chitosan adsorbents that show good selective adsorption performance. However, many attempts so far to modify chitosan beads have focused on improving the adsorption capacity or chemical/mechanical properties, and few researches have been directed to develop selective adsorption performance (Lasko and Hurst, 1999; Wu *et al.*, 1999).

In this study, chitosan hydrogel beads were prepared through a relatively simple method, and were initially cross-linked with EDGE through a conventional method. The chitosan hydrogel beads with or without cross-linking were examined for the adsorption of lead ions as a model heavy metal contaminant. The adsorption kinetics and adsorption mechanism were also investigated. Then, the chitosan hydrogel beads were cross-linked through a novel amine-shielded method and the adsorption of lead ions was conducted again to confirm the effectiveness of the new cross-linking method in improving the adsorption capacity of the cross-linked chitosan beads. Finally, the chitosan hydrogel beads were grafted with polyacrylamide on the surfaces through an ATRP method. The performance and selectivity of the polyacrylamide-grafted chitosan hydrogel beads were examined through mercury adsorption and mercury/lead competitive adsorption experiments.

Methods

Materials

Chitosan flakes (85% deacetylated) were purchased from Sigma Co. Ethylene glycol diglycidyl ether (EGDE), formaldehyde solution (20%), acrylamide (99.9%), HgCl_2 powder, $\text{Pb}(\text{NO}_3)_2$ standard solution (1000 mg/L), perchloric acid (70%) and acetic acid were provided by Merck. Tetrahydrofuran (THF, HPLC grade), triethylamine (Et_3N), N , N -dimethylformamide (DMF, 99.9 + % HPLC grade), copper(I) bromide (CuBr , 98%), copper(II) bromide (CuBr_2 , 98%), and titriplex III (disodium salt-ethylenediamine-tetraacetic acid, EDTA, 0.1 M), and 2-bromoisobutyryl bromide (98%) were supplied by Aldrich. Tris(2-aminoethyl)amine (TREN, 96%), obtained from Acros, was used

to prepare tris[2-dimethylamino]ethyl]amine (Me6TREN) ligand needed in the ATRP reaction (Ciampolini and Nardi, 1966). All other chemicals were of reagent grade purity, and deionized (DI) water was used to prepare all solutions.

Preparation and characterization of chitosan hydrogel beads

A 2 g amount of chitosan flakes was added into 100 mL 2%(w/w) acetic acid and the mixture was stirred at 70 °C and 200 rpm for 6 h. The chitosan solution was then injected in droplets into a 1 M NaOH solution to form hydrogel beads (denoted as CTS). To cross-link the hydrogel beads, 25 mL of the chitosan beads was suspended into a mixture of 25 mL DI water and 0.4 g EGDE in a beaker with continuous agitation, with the pH being adjusted to 12 by the addition of 0.1 M NaOH solution and the reaction being allowed at 70 °C for 6 h. The cross-linked beads (denoted as DCTS) were washed and then stored in DI water for further use.

Novel amine-shielded cross-linking of chitosan beads

100 mL of the chitosan beads and 100 mL of 20% formaldehyde solution were added to a flask and the contents were shaken at 250 rpm at room temperature for 2 h. The formaldehyde-treated chitosan hydrogel beads were separated from the solution, washed with DI water and then cross-linked with EGDE at 70 °C for 6 h in a similar condition described above. After the cross-linking, the beads were separated and added to 150 mL of a 0.5 M HCl solution and stirred at 200 rpm at room temperature for 12 h. The HCl-treated beads (denoted as NRCHBs) were washed and stored in DI water for further study.

Polymerization of acrylamide on chitosan beads through ATRP method

Before polymerization of acrylamide from the surfaces of chitosan beads, 2-bromoiso-butyryl bromide was reacted to the surfaces as the polymerization initiator. A test tube was charged with 21.51 mg (150 μ mol) of CuBr, 3.35 mg (15 μ mol) of CuBr₂, 1.08 g (15 mmol) of acrylamide and 0.5 g of the chitosan beads immobilized with the initiator. Then, 2 mL of DMF was added to the test tube and the content in the tube was bubbled with argon for 45 min to remove the oxygen. After the monomer was completely dissolved in the solution, 0.0345 mL (165 μ mol) of Me₆TREN was injected into the test tube. The reaction for acrylamide graft polymerization in the tube was allowed to proceed for 48 h. Finally, the resulting chitosan-g-polyacrylamide beads (denoted as CTS-PAAm) were separated and washed with DMF, 0.1 M EDTA and ethanol in sequence and stored in a desiccator for other analyses or adsorption experiments.

Heavy metal ions adsorption experiments

The kinetic studies of CTS, DCTS, and NRCTS beads were conducted with solutions of an initial pH 6 and an initial lead ion concentration of 15 mg/L. A 2.5 g amount of the hydrogel beads was added into 500 mL of the lead solution in a flask. Similarly, the kinetic adsorption of mercury on CTS and CTS-PAAm beads were conducted at an initial pH of 4 and an initial mercury concentration of 20 mg/L. A 0.25 g amount of the beads was added into 1000 mL of the mercury solution in a flask. The mixture in the flasks was shaken on an orbit shaker operated at 200 rpm at room temperature for a period of up to 24 h, or until adsorption equilibrium was established. The histories of lead or mercury ion concentrations in the solutions were determined by periodically taking and analysing solution samples. The adsorbed amounts of metal ions per unit weight of the beads at time t_i , $q(t_i)$ (mg/g), was calculated from the

mass balance equation as:

$$q(t_i) = \frac{\sum_{i=1}^n (C_{t_{i-1}} - C_{t_i})V_{t_{i-1}}}{m} \quad (1)$$

where C_{t_0} ($=C_0$) and C_{t_i} (mg/L) are the initial lead (or mercury) concentration and the lead (or mercury) concentrations at time t_i , respectively; V_{t_i} is the volume of the solution at time t_i , and m is the dry weight of the beads added into the flask.

The selective adsorption experiments were conducted with solutions containing both mercury and lead ions. 25 mg of the dry CTS-PAAM beads was added into individual flasks containing 100 mL of the solutions at pH 4 with initial mercury and lead concentrations varied from 10–200 mg/L in the solutions. For comparison, similar experiments were also conducted with CTS beads. The initial and final metal concentrations in all the adsorption experiments were determined using an ICP-OES.

FESEM observation

The surface morphologies of the CTS, DCTS, and NRCTS beads were examined with a field emission scanning electron microscope (FESEM, JEOL JEM 6700) at 5 kV. Samples were vacuum-dried in a desiccator and were platinum-coated by a vacuum electric sputter coater (JEOLJFC-1300) to a thickness of at least 500 angstroms before glue-mounted onto the sample stud for the FESEM analysis.

XPS study

XPS analyses of the CTS, DCTS, and NRCTS beads were carried out on a VGESCALAB MKII spectrometer with an Al K α X-ray source (1,486.6 eV of photons) to further verify the surface treatment, cross-linking, and adsorption mechanisms. The XPS spectra peaks were decomposed into subcomponents by fixing the 0% Lorentzian-Gaussian curve-fitting program with a linear background to the spectra through an XPSpeak 4.1 software package. The full width half maximum was maintained at 1.4.

Results and discussion

Chitosan hydrogel beads

Morphology of chitosan and cross-linked chitosan hydrogel beads. The morphologies of CTS and DCTS beads are shown in Figure 1. Both the CTS and DCTS hydrogel beads had a milk-white colour with a mean diameter of about 1 mm (Figure 1a). Compared

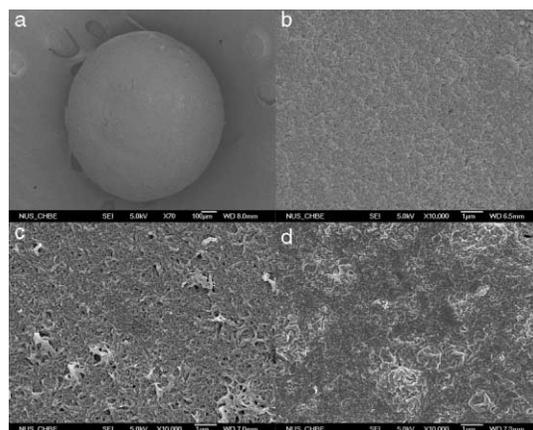


Figure 1 FESEM images of (a) CTS/DCTS macro-morphology, and the surface micro-morphologies of (b) CTS, (c) DCTS, and (d) NRCTS beads

to the surface of CTS in Figure 1b, the cross-linking reaction with EGDE obviously made the surface of DCTS very porous (see Figure 1c). It has been known for the cross-linking agent of EGDE to be prone to react with the amine groups instead of the hydroxyl groups in chitosan. Therefore, the porous structure of DCTS may be formed due to the bridging connection of EGDE molecules between the different amine groups in CTS through the intra-molecular and/or inter-molecular cross-linking interactions.

Dissolution property. The results of dissolution tests of CTS and DCTS are presented in Table 1. It can be observed that the cross-linking reaction significantly increased the chemical stability of the hydrogel beads in the acidic media (DCTS beads were insoluble in 0.1 M HCl solution, 0.1 M HAc solution, and 0.1 M H₂SO₄ solution). CTS hydrogel beads have been known to be unstable or to start to dissolve in solutions of pH < 4. In this study, the cross-linking reaction of CTS with EDGE has been found to extend the chemical stability of the hydrogel beads to solutions of pH < 1 and did not affect the chemical stability of the hydrogel beads in neutral and basic pH solutions. The high hydrophilicity of chitosan or chitosan hydrogel beads can be attributed to the primary amine groups in chitosan. Hence, the fact that the cross-linking reaction improved the acid dissolution resistance of the hydrogel beads suggests that some amine groups in chitosan were consumed or sheltered by the cross-linking reactions.

Adsorption behavior. The typical experimental results of lead adsorption on CTS and DCTS beads versus adsorption time are shown in Figure 2.

The CTS beads are found to have good adsorption capacity of lead ions (69.3 mg/g) and the cross-linking reaction reduced the adsorption capacity of the DCTS beads (45.1 mg/g). The dynamic behaviour of lead ion adsorption on both types of beads followed a similar change pattern consisting of an initial rapid step and then a second slow step. The DCTS beads are found to reach adsorption equilibrium in a shorter time than the CTS beads, possibly due to the higher adsorption capacity of CTS and the more porous structure of the DCTS beads (as shown in Figure 1b, c), which had smaller diffusion resistance for metal adsorption. Since the amine groups of chitosan are known to be the main binding sites for metal ions, the lower adsorption capacity of DCTS beads shown in Figure 2 again provide evidence that the cross-linking reaction of CTS with EDGE took place at the amine groups and thus reduced the available amine groups for metal adsorption.

Adsorption mechanism. To prove the metal adsorption mechanism, Figure 3 shows the typical N 1s XPS spectra of the DCTS beads before and after lead adsorption. Before lead ion adsorption, there is only one peak at 399.3 eV for the DCTS beads (Beamson and Briggs, 1992; Nalwa, 1997; Dambies *et al.*, 2001). This is attributed to the N atom in the —NH₂ and/or the —NH— groups on the surfaces of DCTS beads. After lead ion adsorption, however, a new peak at BE of 401.4 eV for the DCTS beads is observed. This indicates that some N atoms existed in a more oxidized state on the beads' surfaces due to lead ion adsorption. This phenomenon can be attributed to the formation of

Table 1 Solubility behaviour of various chitosan-based hydrogel beads

Types of beads	Dissolution condition				
	0.1 M HAc	0.1 M HCl	0.1 M H ₂ SO ₄	DI water	0.1 M NaOH
CTS	soluble	soluble	soluble	insoluble	insoluble
DCTS	insoluble	insoluble	Insoluble	insoluble	insoluble

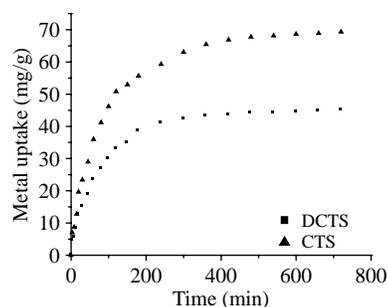


Figure 2 Adsorption kinetic results of lead ions on CTS and DCTS beads

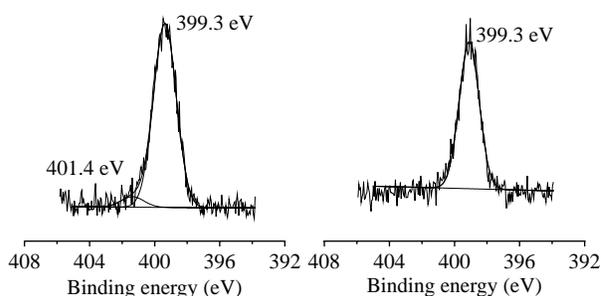


Figure 3 Typical N 1s XPS spectra of DCTS beads after (left) and before (right) lead ion adsorption

$R-NH_2Pb^{2+}$ complexes, in which a lone pair of electrons in the nitrogen atom was donated to the shared bond between the N and Pb^{2+} , and, as a consequence, the electron cloud density of the nitrogen atom was reduced, resulting in a higher BE peak observed. Therefore, the XPS spectra provide evidence of lead ions binding to the nitrogen atoms in the amine group of chitosan.

Chitosan beads with novel amine-shielded cross-linking

Although EGDE cross-linking improved the acidic resistance of the CTS beads, the adsorption capacity of the beads also was reduced greatly (see Figure 2) by the cross-linking reaction. Therefore, a novel amine-protected cross-linking method was developed in the study to both improve the acidic resistance and preserve the adsorption capacity of chitosan.

Cross-linking reaction. The novel cross-linking methods involved two steps. In Step 1, the amine groups on CTS beads were reacted with formaldehyde to form C–N bonds, as shown in Figure 4.

Then, the amine-shielded beads were reacted with the cross-linking agent EGDE. Since the amine groups have been converted into a C–N bond structure and were not

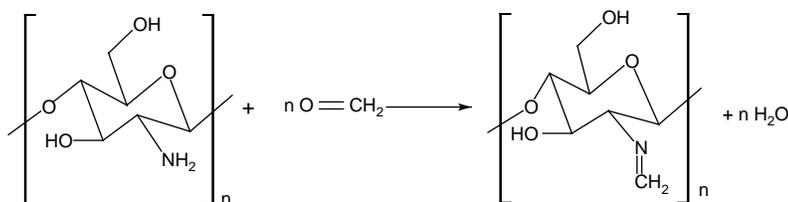


Figure 4 Novel cross-linking Step 1: amine-shielded reaction

available for the cross-linking reaction with EDGE, this forced the cross-linking agent of EGDE to react with the hydroxyl groups of chitosan to form the bridge structure, as shown in Figure 5.

After the cross-linking reaction, the shielded-amine groups in the C–N form were released and converted to the amine form again by soaking the beads in HCl solution. The surface morphology of the NRCTS beads is also shown in Figure 1 (see Figure 1d). Unlike the three-dimensional porous structure of DCTS, the NRCTS beads appear to show a denser surface. This is an indirect indication of the difference in the cross-linking reaction in the new method with that in the conventional cross-linking reaction described earlier. Again, the acidic dissolution study (results not shown) indicated that the NRCTS beads had good chemical stability in the acid medium, even at pH values down to 1, indicating that the novel cross-linking method was also effective.

Adsorption behaviour. Figure 6 shows the typical results of lead ion adsorption on the two types of the cross-linked chitosan beads, i.e. DCTS and NRCTS.

The adsorption capacities of DCTS beads and NRCTS beads are observed, in this case, to be at about 44.4 mg/g and 64.5 mg/g, respectively. In other words, the NRCTS beads are found to have a significantly greater adsorption capacity than the DCTS beads, clearly proving the advantage of the novel amine-shielded cross-linking method over the conventional cross-linking method. Nevertheless, the adsorption capacity of the NRCTS beads is found to be still slightly lower than that of the CTS beads (69.3 mg/g, see

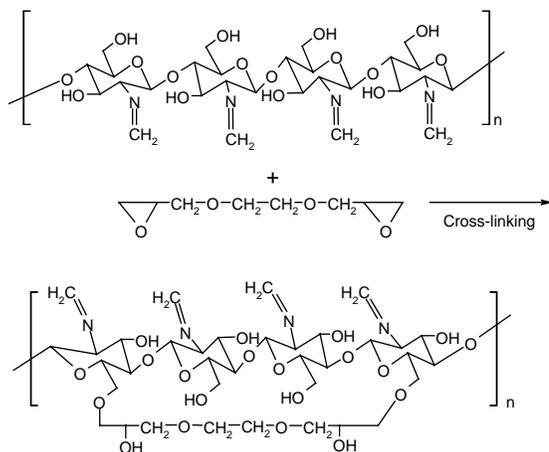


Figure 5 Novel cross-linking Step 2: reaction of EDGE with hydroxyl groups of chitosan to form bridges (i.e. cross-linking)

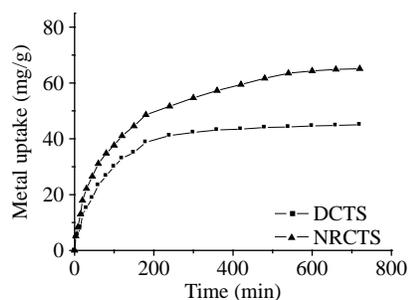


Figure 6 Adsorption kinetic results of lead ions on DCTS and NRCTS beads

Figure 2). This is probably due to the fact that a small amount of the amine groups may not be protected completely in the reaction with formaldehyde, or some of the protected amine groups in this case may not be released completely. This may be explained from the N 1s core-level XPS spectra of CTS and NRCTS beads in Figure 7.

As can be found in the figure, the N 1s XPS spectrum of the CTS beads is fitted to only one peak with binding energy (BE) of 399.42 eV for the nitrogen in the $-\text{NH}_2$ groups (Beamson and Briggs, 1992; Nalwa, 1997). The N 1s XPS spectrum of the NRCTS beads, however, has to be fitted to two peaks. The strong peak at the BE of 399.85 eV can be attributed to the nitrogen in the $-\text{NH}_2$ groups, indicating that the nitrogen atoms in the $-\text{N}=\text{CH}_2$ groups have been converted back into those in $-\text{NH}_2$. The weak peak at the BE of 398.41 eV is attributed to the nitrogen atoms in the $-\text{N}-\text{CH}_2$ groups, suggesting that in this case, a small number of the $-\text{N}-\text{CH}_2$ groups may remain after the acid treatment.

Polyacrylamide-grafted chitosan beads

Even though chitosan beads have good metal adsorption performance and the novel amine-shielded cross-linking method can retain the good adsorption capacity of the chitosan beads, the adsorbent usually did not show good selectivity toward a particular type of heavy metal ion. To achieve the selectivity of the adsorbent toward mercury ions, surface initiated ATRP of acrylamide was used to modify the chitosan beads, and the modified beads (CTS-PAAm) were examined for competitive and selective adsorption of mercury ions over lead ions.

Grafting of polyacrylamide. The ATRP initiator of bromides was found to be immobilized on the surfaces of CTS beads through the interaction/reaction with the $-\text{NH}_2$ or $-\text{OH}$ groups. Polymerization of acrylamide then started from the initiators on the surface-initiated CTS beads, and the chains of polyacrylamide grew with time by polymerizing additional acrylamide molecules into the polymer chain on the surface. This process provided the beads with many amide groups on the surface.

Adsorption kinetics, selectivity and mechanism. Rapid interaction of the metal ions to be separated with the adsorbent is desirable and beneficial for practical adsorption applications. The kinetic results of mercury adsorption on CTS and CTS-PAAm beads are shown in Figure 8.

It can be observed that mercury uptake on CTS-PAAm beads was a very fast process. The amount of adsorption increased rapidly in the first 20 min, contributing to about 90% of the ultimate adsorption amount, and then augmented slowly and approached the adsorption equilibrium in about 60 min, with an equilibrium uptake of around 78 mg/g

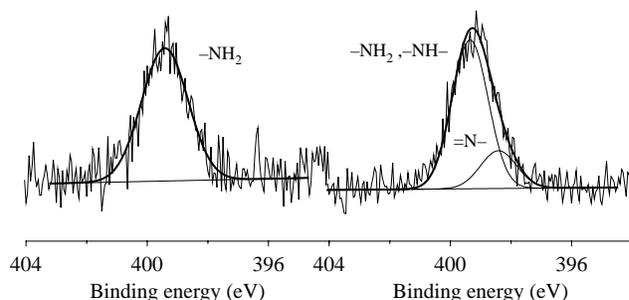


Figure 7 Typical N 1s XPS spectra of CTS beads (left) and NRCTS beads (right)

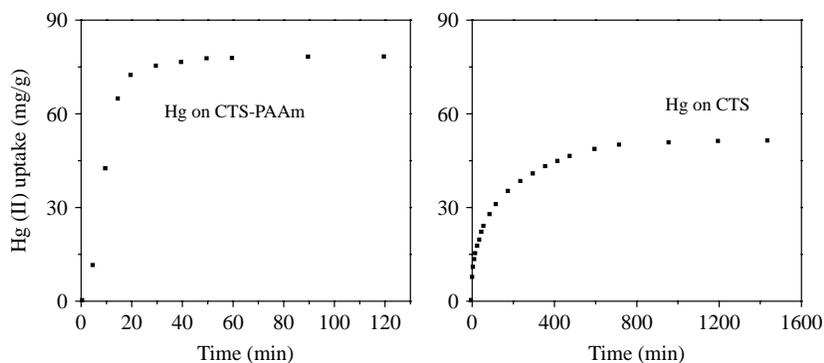


Figure 8 Adsorption kinetic results of mercury ions on CTS-PAAm (left) and CTS beads (right)

in this case. This type of adsorption behaviour is typical of the specific adsorption process in which adsorption rate is usually dependent upon the number of available adsorption sites on the surface of the adsorbent, and eventually controlled by the attachment of the metal ions on the surfaces. The high initial uptake rate and the short adsorption equilibrium time can be an indication that the surfaces of the CTS-PAAm beads had high density of active sites for mercury adsorption and the uptake mainly took place on the surfaces. In contrast, mercury uptake on the CTS beads was a much slower process and it took up to 1000 min to reach adsorption equilibrium, with a much lower equilibrium adsorption amount of about 50 mg/g. Hence, a practical advantage of using CTS-PAAm beads as an adsorbent would be its ability to remove more mercury in a much shorter process time.

Figure 9 shows the selective or competitive adsorption results of CTS and CTS-PAAm beads at initial solution pH 4 for mercury and lead ions. As can be observed in Figure 9, significant amounts of mercury were adsorbed by CTS-PAAm, and the amounts of lead adsorbed by CTS-PAAm were almost negligible. At adsorption equilibrium, the adsorption capacity at an initial concentration of 200 mg/L, for example, reached 294.1 mg/g for Hg^{2+} ions but only 18.0 mg/g for Pb^{2+} with CTS-PAAm. The amounts of mercury and lead adsorption on the CTS beads appeared to be much closer, and the corresponding adsorption capacities were 125 mg/g for Hg^{2+} and 51.3 mg/g for Pb^{2+} . In other words, at various initial metal concentrations, the results in Figure 9 show that the CTS-PAAm always had excellent selectivity to the adsorption of mercury against lead, but the CTS beads did not show such good selectivity toward any of the two metal species.

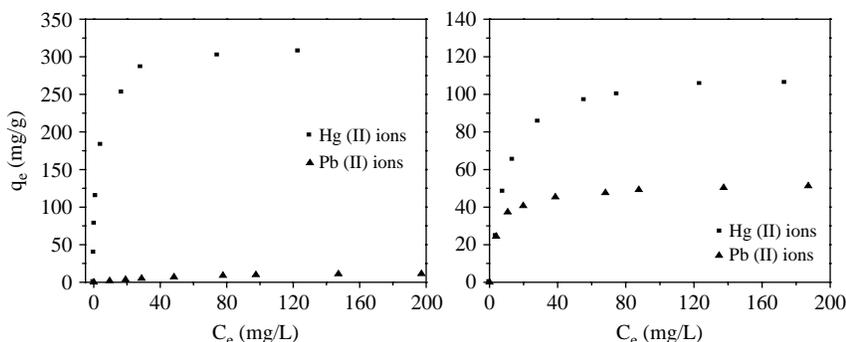


Figure 9 Competitive adsorption results of Hg ions and Pb ions on CTS-PAAm (left) and CTS beads (right)

As the fundamental difference between the functional groups on CTS and CTS-PAAm may be the amine group for the former and amide group for the latter, the high selectivity of CTS-PAAm toward mercury ions can be attributed therefore to the amide groups in polyacrylamide grafted on the chitosan beads. It has been reported that the C—O groups in amide have a tendency to attract the electron cloud of the N atom in the amide groups (Bulbul Sonmez *et al.*, 2002). Therefore, the electron cloud density of the N atom can be reduced. This makes it difficult for the N atom in amide to attract heavy metal ions through forming chelating bonds, as does the N atom in the amine group of chitosan. However, due to the special structure of mercury and the out layer electron cloud arrangement, mercury has extraordinary affinity for amide groups and is able to form strong covalent bonds with them. This provides the selective adsorption of mercury over other heavy metals by the polyacrylamide-grafted chitosan beads. Since the selectivity of CTS-PAAm beads is due to the special property of amide groups and the typical structure of mercury, it may be possible to extend the application of the current study to other cases. For example, copper, zinc, cadmium, and nickel, etc., have similar properties as lead, and uranium has similar structure and electron orbit arrangement as mercury. Attempts could be made therefore to selectively separate mercury or uranium from copper, zinc, cadmium, and nickel.

Conclusion

Chitosan hydrogel beads can be prepared successfully and used as an effective adsorbent for heavy metal removal. XPS study reveals that the adsorption of heavy metal ions on CTS takes place at the amine groups on the surfaces. Conventional cross-linking methods with EDGE can improve the acidic resistance of CTS, but the method consumes the amine groups and therefore reduces the adsorption capacity of CTS. The novel amine-shielded cross-linking method can retain the high adsorption capacity of CTS and, at the same time, improve the acidic resistance of CTS. Polyacrylamide-grafted chitosan beads exhibit enhanced adsorption capacity, fast adsorption kinetics for mercury ions, and show excellent selectivity towards mercury ions over lead ions.

References

- Beamson, G. and Briggs, D. (1992). *High Resolution XPS of Organic Polymers the Scienta ESCA300 Database*, John Wiley & Sons, Chichester.
- Bulbul Sonmez, H., Senkal, B.F. and Bicak, N. (2002). Poly(acrylamide) grafts on spherical bead polymers for extremely selective removal of mercuric ions from aqueous solutions. *Journal of Polymer Science Part A-Polymer Chemistry*, **40**(17), 3068–3078.
- Castro Dantas, T.N., Dantas Neto, A.A., de A Moura, M.C.P., Barros Neto, E.L. and Paiva Telemaco, E. (2001). Chromium adsorption by chitosan impregnated with microemulsion. *Langmuir*, **17**(14), 4256–4260.
- Ciampolini, M. and Nardi, N. (1966). Five-coordinated high-spin complexes of bivalent cobalt, nickel, and copper with tris(2-dimethylaminoethyl)amine. *Inorganic Chemistry*, **5**(1), 41–44.
- Dambies, L., Guimon, C., Yiacoumi, S. and Guibal, E. (2001). Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, **177**(2–3), 203–214.
- Hsien, T.Y. and Rorrer, G.L. (1997). Heterogeneous cross-linking of chitosan gel beads: kinetics, modeling, and influence on cadmium ion adsorption capacity. *Industrial & Engineering Chemistry Research*, **36**(9), 3631–3638.
- Kiefer, R. and Höll, W.H. (2001). Sorption of heavy metals onto selective ion-exchange resins with aminophosphonate functional groups. *Industrial & Engineering Chemistry Research*, **40**(21), 4570–4576.
- Lasko, C.L. and Hurst, M.P. (1999). An investigation into the use of chitosan for the removal of soluble silver from industrial wastewater. *Environ. Sci. Technol.*, **33**(20), 3622–3626.

- Lee, S.T., Mi, F.L., Shen, Y.J. and Shyu, S.S. (2001). Equilibrium and kinetic studies of copper (II) ion uptake by chitosan-tripolyphosphate chelating resin. *Polymer*, **42**(5), 1879–1892.
- Li, N. and Bai, R.B. (2005). Copper adsorption on chitosan-cellulose hydrogel beads: behaviors and mechanisms. *Separation and Purification Technology*, **42**(3), 237–247.
- Molinari, R., Poerio, T., Cassano, R., Picci, N. and Argurio, P. (2004). Copper(II) removal from wastewaters by a new synthesized selective extractant and SLM viability. *Industrial & Engineering Chemistry Research*, **43**(2), 623–628.
- Muzzarelli, R.A.A. (1973). *Natural Chelating Polymers: Alginic Acid, Chitin, and Chitosan*, Pergamon, New York.
- Nalwa, H.S. (1997). *Handbook of Organic Conductive Molecules and Polymers: Vol. 3. Conductive Polymers: Spectroscopy and Physical Properties*, John Wiley & Sons, Chichester.
- Ngah, W.S.W., Endud, C.S. and Mayanar, R. (2002). Removal of copper (II) ions from aqueous solution onto chitosan and crosslinked chitosan beads. *Reactive & Functional Polymers*, **50**(2), 181–190.
- Rhazi, M., Desbrières, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A. and Meray, M.E. (2002). Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste. *European Polymer Journal*, **38**(8), 1523–1530.
- Roberts, G.A.F. (1992). *Chitin Chemistry*, Macmillan, London.
- Schmuhl, R., Krieg, H.M. and Keizer, K. (2001). Adsorption of Cu (II) and Cr (II) ions by chitosan: kinetics and equilibrium studies. *Water SA*, **27**(1), 1–7.
- Vincent, T. and Guibal, E. (2001). Cr (VI) extraction using aliquat 336 in a hollow fiber module made of chitosan. *Industrial & Engineering Chemistry Research*, **40**(5), 1406–1411.
- Wu, F.C., Tseng, R.L. and Juang, R.S. (1999). Role of pH in metal adsorption from aqueous solutions containing chelating agents on chitosan. *Industrial & Engineering Chemistry Research*, **38**(1), 270–275.
- Yan, W.L. and Bai, R.B. (2005). Adsorption of lead and humic acid on chitosan hydrogel beads. *Wat. Res.*, **39**(4), 688–698.