Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Copper(II) from Aqueous Solutions by Chitosan Adsorption

Svetlana Verbych[a]; Mykhaylo Bryk[a]; Ganna Chornokur[a]; Bryan Fuhr[b]
[a] Ecological Research Center, National University of 'Kiev-Mohyla Academy', Kiev, Ukraine [b] Alberta Research Council, Edmonton, Canada

To cite this Article Verbych, Svetlana , Bryk, Mykhaylo , Chornokur, Ganna and Fuhr, Bryan(2005) 'Removal of Copper(II) from Aqueous Solutions by Chitosan Adsorption', Separation Science and Technology, 40: 8, 1749 — 1759
To link to this Article: DOI: 10.1081/SS-200059623
URL: http://dx.doi.org/10.1081/SS-200059623

Separation Science and Technology, 40: 1749–1759, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200059623

Removal of Copper(II) from Aqueous Solutions by Chitosan Adsorption

Svetlana Verbych, Mykhaylo Bryk, and Ganna Chornokur
Ecological Research Center, National University of 'Kiev-Mohyla Academy', Kiev, Ukraine

Bryan Fuhr
Alberta Research Council, Edmonton, Canada

Abstract: An investigation on the use of chitosan for the removal of copper from aqueous solutions has been carried out. Both kinetic data and equilibrium isotherms were obtained. The effects of contact time, initial copper concentration, background electrolyte, and pH on the uptake capacity of copper were studied. Initial copper concentration and pH were found to have the greatest effects on uptake. The copper uptake of chitosan was quantitatively evaluated using sorption isotherms. Results indicated a capacity of 1.8–2.2 mmol/g of dry mass. The capacity increases when solutions contain high concentrations of chloride ions. The variation of pH leads to competition between coordination of copper with chitosan with the optimal range being 5.4 to 6.0.

Keywords: Chitosan, adsorption, copper(II), heavy metal removal, wastewater

1. INTRODUCTION

Some industrial processes result in the release of heavy metals into the aquatic ecosystem. This has led to increasing concern about the effects of toxic heavy metals as environmental pollutants. Precipitation, coagulation, ion exchange, electrochemical, and membrane processes have been developed for the treatment of metal-bearing wastes before their discharge into the environment

Received 23 October 2004, Accepted 17 February 2005

Address correspondence to Svetlana Verbych, Ecological Research Center, National University Kiyv-Mohyla Academy of Ukraine, 2 Skovoroda St., 04070, Kiev, Ukraine E-mail: verbych@ukma.kiev.ua

(1). The need for economical, effective, and safe methods for removal of heavy metals from wastewater has directed attention to low-cost natural sorbents such as agricultural wastes, clay materials, biomass, and marine organisms (2, 3). Polysaccharide biopolymers isolated from shellfish are a new class of potentially inexpensive and environmentally friendly substances that exhibit a high specificity toward metal ions. One example is chitosan, a partially acetylated glucosamine biopolymer resulting from deacetylation of chitin (4). Polysaccharides with about 50% deacetylation seem to be most effective for adsorption since functional amine groups are available for interaction. Chitosan can be produced cheaply because chitin is the second most abundant biopolymer in nature next to cellulose. Chitosan has many useful characteristics such as hydrophilicity, biocompatibility, biodegradability, and antibacterial properties. Because of its excellent adsorptive behavior, chitosan has been employed as an effective coagulating agent in activated sludge plants and for recovering proteins from food processing factories (5–8). In addition, it is also a well-known adsorbent for transition metals because the amine ($-NH_2$) and/or hydroxyl ($-OH$) groups on chitosan chains can serve as coordination sites for these metals (9). The reactive amine group selectively binds to virtually all group III transition metal ions but does not bind to group I and II alkali and alkaline-earth metal ions (10). Extensive studies on the metal-binding properties and use of this polymer have been carried out by a number of researchers (11–19). Chitosan undergoes chelation with metal ions, releasing hydrogen ions according to the reaction shown in Fig. 1. This suggests that the adsorption of metal ions on chitosan is strongly dependent on pH in aqueous solutions due to the competition of proton and metal ions. However, there is insufficient information on the pH dependency of the adsorption of metal ions on chitosan. Most studies either obtained the sorption isotherms or merely compared the selectivity series based on the results of single-metal systems (20–23).

In the present work, a systematic study on the removal of copper by chitosan is reported. The pH dependence of uptake kinetics of metal on

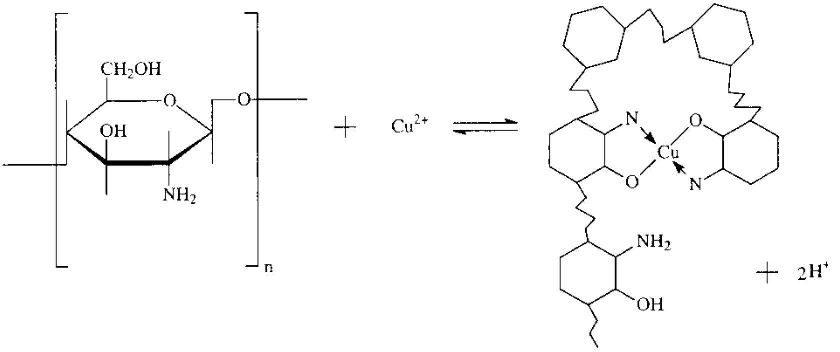

Figure 1. Chelation of copper(II) ion with chitosan.

chitosan flakes was studied. The sorption of copper in the presence of sodium chloride electrolyte was examined and compared to that in single metal systems.

2. MATERIALS AND METHODS

2.1. Chitosan and Reagents

Chitosan flakes produced from lobster shell were provided by the Moscow Textile Academy (Moscow, M. Kaluzhskaya, 1, Russia) and used in this form. The molecular weight of chitosan was found to be 1.7×10^5 by the Mark-Houwink equation from viscosity measurements (24). All other reagents ("Miranda-C", Kiev, Ukraine) were analytical grade. Distilled water (conductivity was $1.0\,\text{microS} \cdot \text{cm}^{-1}$) was used to prepare all the solutions. All glassware was supplied by Simax.

Stock solutions of copper sulphate and sodium chloride were made up to concentrations of 5×10^{-2} M and 1×10^{-1} M, respectively. These solutions were diluted with distilled water to concentrations of 1×10^{-5} to 5×10^{-4} M for $CuSO_4$ and 9×10^{-4} to 9×10^{-2} M for NaCl. The pH effect for copper adsorption was investigated in the pH range of 3–6.

2.2. Determination of pH_{zpc}

An approach outlined by Bryk and Tsapiuk (25) was applied to determine the pH of the zero point of charge (pH_{zpc}) of chitosan. To each of nine identical portions of 100 mL solutions with known pH values, 100 mg chitosan was added. Samples were agitated for 30 hours at low speed. After solutions achieved equilibrium (for 50 hours) their turbidities were examined by the use of a photoelectrocolorimeter KFK-2-UHL4.2 type (Zagorsk, Russia).

2.3. Metal Adsorption Experiments

Copper adsorption isotherms were constructed using data obtained from experiments during a well-mixed batch process allowed to proceed to equilibrium. Specifically, 100 mg chitosan flakes were contacted with 100 mL of $CuSO_4$ solution in a 125-mL Simax flask (Czech Republic), and agitated at 180 rpm on an orbital shaker OS 20 (St. Petersburg, Russia) for 2 hours. The temperature was controlled at 25°C by air conditioning. The pH was adjusted with 0.1 M HCl and NaOH.

Preliminary experiments had shown that the adsorption was complete after 50 hours. After adsorption, the copper solution was filtered from the flakes through paper filters (Filtrak, Germany). The residual copper solution was stored in a sealed vial for later analysis. After filtration the aqueous pH was measured with a Model pH-150MA instrument (Gomel, Belarussia).

Each run was carried out in duplicate. The Cu^{2+} concentration was measured at the beginning and end of the batch adsorption experiment by colorimetric analysis with diethyldithiocarbamate of lead (26). The final loading of Cu^{2+} adsorbed on the flakes was calculated based on the difference in Cu^{2+} concentration in aqueous before and after adsorption according to the following equation:

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

where Q is the metal uptake capacity (mmol/g of dry mass), C_0 is the initial concentration of Cu^{2+} (mmol/dm^3), C_f is the final concentration of Cu^{2+} at equilibrium (mmol/dm^3), V the volume of solution (dm^3), and m is the initial dry chitosan loading (g).

3. RESULTS AND DISCUSSION

3.1. Determination of pH_{zpc}

In Fig. 2, the isoelectric point of the chitosan is shown to be about pH_{zpc} 7. Maximum turbidity of the chitosan solution at this point was observed.

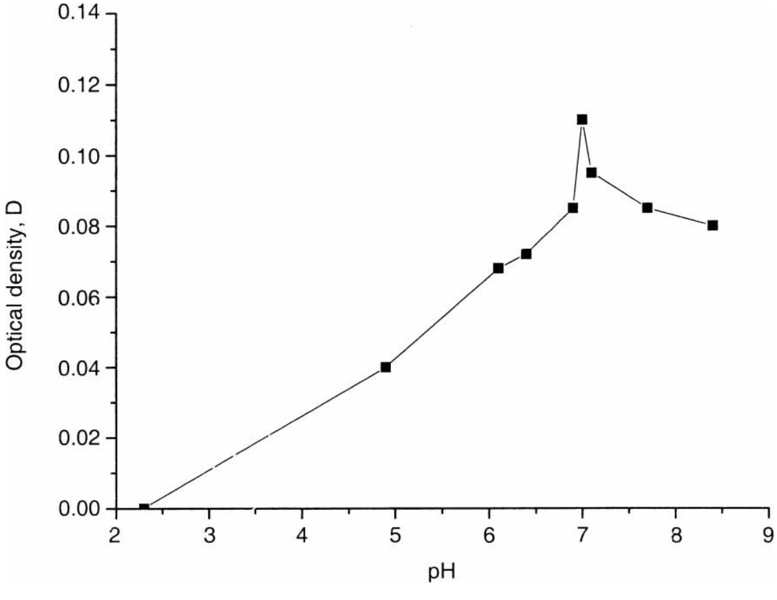

Figure 2. Optical density of chitosan solution vs. pH.

A key property of the biopolymer is the presence of amine ($-NH_2$) and hydroxyl ($-OH$) groups on its molecular chains. In acid solution, the groups become $-NH_3^+$ and $-OH$, respectively, which make chitosan soluble. The degree of dissociation depends on solution pH and results in changing of chitosan charge and consequently rearrangement of the polymer chains. In an acid environment, the nitrogen of the amine group is protonated, so that chitosan is positively charged and electrostatic repulsion between active groups occurs. This is the reason the polymer chains become unwrapped. The negative charge of the biopolymer, which occurs at high pH, has the same influence upon the spatial arrangement of polymer chains. This has been confirmed by data of chitosan electrokinetic potential (ζ) at different pH values (27). A positive ζ (10–20 mV) was determined at a pH between 4.7 and 3.0. In alkaline solution ζ becomes negative (-20 mV). At pH_{zpc} the number of positive and negative groups are equal and thus the total surface charge becomes zero and chains are curled into balls. Consequently, the uptake of metal ions on the biopolymer is very low at the zero point of charge. Therefore, in further experiments on Cu^{2+} uptake the adsorption was investigated within the pH range up to the isoelectric point. In another study it was established that the pH_{zpc} for chitosan was 8.6 (28) and at the same time Jeon and Holl (20) noted the pH_{zpc} values of natural and aminated chitosan beads were about 4.24 and 5.53, respectively. It is obvious that the nature of the biopolymer as well as the degree of deacetylation have a significant effect on pH_{zpc}.

3.2. Adsorption Kinetics

Two important physicochemical aspects for evaluation of the sorption process as a unit operation are the kinetics and the equilibrium of sorption (9, 13, 21). The uptake of Cu^{2+} with time at pH 5.4 at initial concentration of $6.7 \times 10^{-2}\,\mathrm{mmol/dm^3}$ is shown in Fig. 3. The concentration of Cu^{2+} remaining in solution after adsorption is marked on the axis vs. time. The rate of adsorption was quite rapid during the first few minutes and decreased after 5 hours. Amino groups of chitosan acted initially as copper coordination sites. The slower removal rate of metal after an initial rapid uptake can be due to the binding of Cu^{2+} by complexed metal ions. As an approximation, the removal of Cu^{2+} can be said to take place in two distinct steps, a relatively fast one followed by a slower one. The necessary time to reach this equilibrium is about 50 hours. Increasing the removal time to 70 hours did not show a noticeable effect. These observations are in agreement with the works of Salehizadeh and Shojaosadati (14), Jha, Lyengard, and Prabhakara Rao (28), and Benguella and Benaissa (22) with other metal ion-biomaterial systems.

During the course of Cu^{2+} removal by chitosan, it was noted that the pH of the solution changed from 5.4 to 5.8 at equilibrium. This was interpreted as

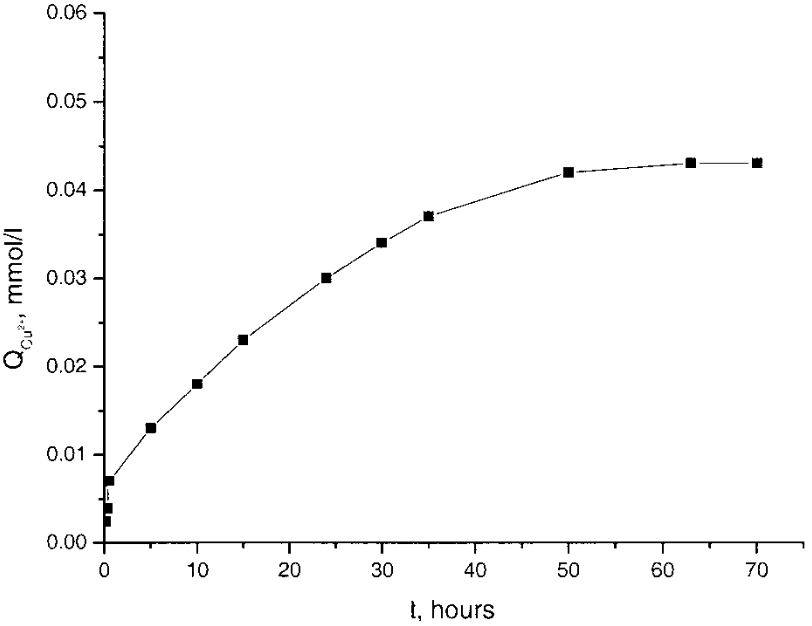

Figure 3. Kinetic of copper sorption by chitosan.

competition between Cu^{2+} and H_3O^+ for binding sites (16). As a result of this competition, only some of the glucosamine nitrogen atoms become available to Cu^{2+} for sorption.

Based on the results shown in Fig. 3, an equilibrium contact time of 50 hours was used for all further experiments.

3.3. Sorption Equilibrium

To study the equilibrium of Cu^{2+} removal by chitosan, the approach most frequently used consists of measuring the isotherm of sorption. The quantity of metal removed (Q) is plotted against the equilibrium concentration of metal ions in solution, and corresponds to the equilibrium distribution of metal ions between the aqueous and solid phases when the concentration increases.

During sorption equilibrium experiments, it was observed that the initial pH of the solution increased slightly and equilibrium pH varied with the initial concentration as shown in Table 1. Similar results were obtained with the uptake of cadmium on chitin (22), and adsorption of chromium (15) and cadmium on chitosan (29).

The equilibrium adsorption of Cu^{2+} on chitosan is shown in Fig. 4. A maximum adsorption capacity of approximately 2.2 mmol/g of dry mass is

Table 1. Initial and final solution pH values

Initial Cu^{2+} concentration ($mmol/dm^3$)	0.0078	0.047	0.094	0.156	0.31	0.47	0.78
Initial pH	5.6	5.6	5.6	5.6	5.6	5.6	4.1
Final pH	6.8	6.7	6.5	6.3	6.0	5.8	4.5

obtained. It is known that the uptake of transition metals is mainly effected via coordination with the amine groups ($-NH_2$) on chitosan. Two $-OH$ groups and one $-NH_2$ group are chelated by Cu^{2+} and the fourth site is probably occupied by a water molecule or the $-OH$ group on the third carbon atom according to the following equation:

$$Cu^{2+} + RNH_2 \longleftrightarrow Cu\ (RNH_2)^{2+} \tag{2}$$

It is also known that the amine groups of chitosan may react with H^+ according to:

$$RNH_2 + H^+ \longleftrightarrow RNH_3^+ \tag{3}$$

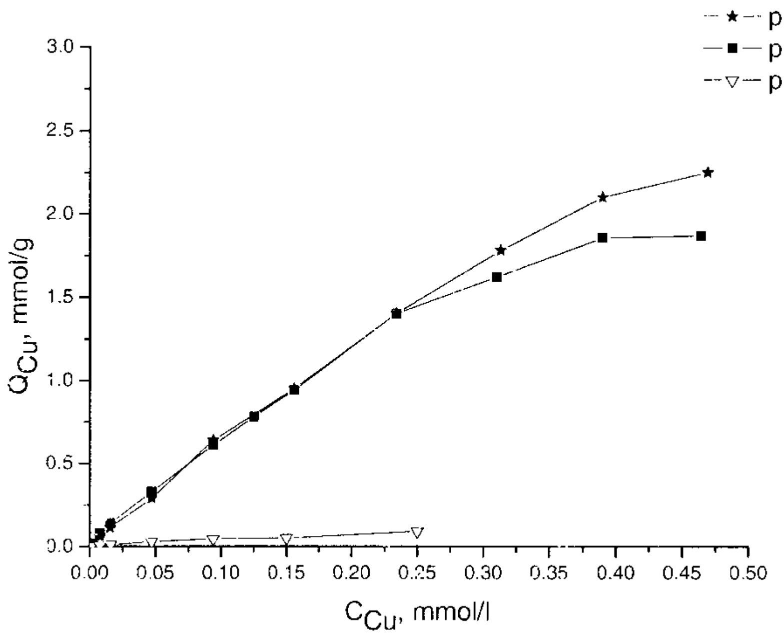

Figure 4. Equilibrium adsorption of Cu(II) by chitosan at different initial concentration ratios of Cu(II) to chitosan and different pH.

Because the protonation constant is log $K_p = 6.3$ (30), about 20% of the amino group of chitosan is protonated even at pH 6.9. The two reactions of Eqs. (2) and (3) compete during adsorption, which is supported by experimental observations where the solution pH increases after adsorption (see Table 1). For example, at $C_0 = 4.7 \times 10^{-1}\,\mathrm{mmol/dm^3}$ the solution pH changes from 5.6 to 5.8 after adsorption. It is found that the higher the value of C_0, the smaller the pH increment. Previous work has indicated that proper adjustment of solution pH leads to an increase in metal adsorption capacity on chitosan (28, 31). For instance, a steep rise in adsorption distribution ratio of copper to chitosan was found at pH 4–5 (11). Muzzareli et al. (32) examined the chelation of Cu^{2+} with chitosan membranes by ultraviolet, infrared, and electron spin resonance. They found that the average number of amino groups bound to one heavy metal ion changes with solution pH. About one to two amino groups bind with Cu^{2+} at pH < 5 because of the larger extent of protonated amino groups. The number of amino groups bound may increase up to two to three at pH 5–6. At pH 6–8, three amino groups and one hydroxyl group would bind with one Cu^{2+}.

Analysis of the isotherm results can be made in terms of the number of Cu^{2+} ions sorbed per number of N atoms in the bulk polymer. There are 3.2×10^{21} N atoms/g chitosan based on a nitrogen content of chitosan of 7.4% (10). A value of 1.01×10^{21} Cu^{2+} ions/g chitosan is calculated from the uptake capacity in Fig. 4 at pH 6. Thus, the ratio of N atoms in the polymer to the number of sorbed Cu^{2+} ions is 3. It is obvious that there is saturation of almost total N atom sites in chitosan by Cu^{2+}.

The effect of background sodium ion concentration on the adsorption of Cu^{2+} is presented in Fig. 5. The Cu^{2+} uptake of chitosan flakes was not affected by the presence of Na^+ at pH 8.6 and 17 mM over the Cu^{2+} concentration ranging from 1×10^{-2} to 5×10^{-1} mM. The uptake capacity value is almost the same as in the absence of background electrolyte. The effect of alkali metal ions on transition metal adsorption has not been investigated thoroughly, especially for Cu^{2+} binding on chitosan. Adsorption is sensitive to change in concentration of the supporting electrolyte if electrostatic attraction is the significant mechanism for metal removal. The results show that electrostatic attraction plays a negligible role in the concentration of background electrolyte up to 0.01 mM. However, further increase of NaCl solution up to 86 mM leads to a rise in Cu^{2+} uptake. As was noted previously, the ζ of the biopolymer varies from positive to negative as the pH increases. The dependence of background electrolyte concentration and counter ions present in solution on zeta potential is well known. It can be assumed that a high concentration of Cl^- in the electrolyte causes adsorption of these anions by polymer and decreases the positive value of the ζ. Consequently, chitosan possesses a negatively charged characteristic and shows additional ability to increase its uptake capacity to Cu^{2+}.

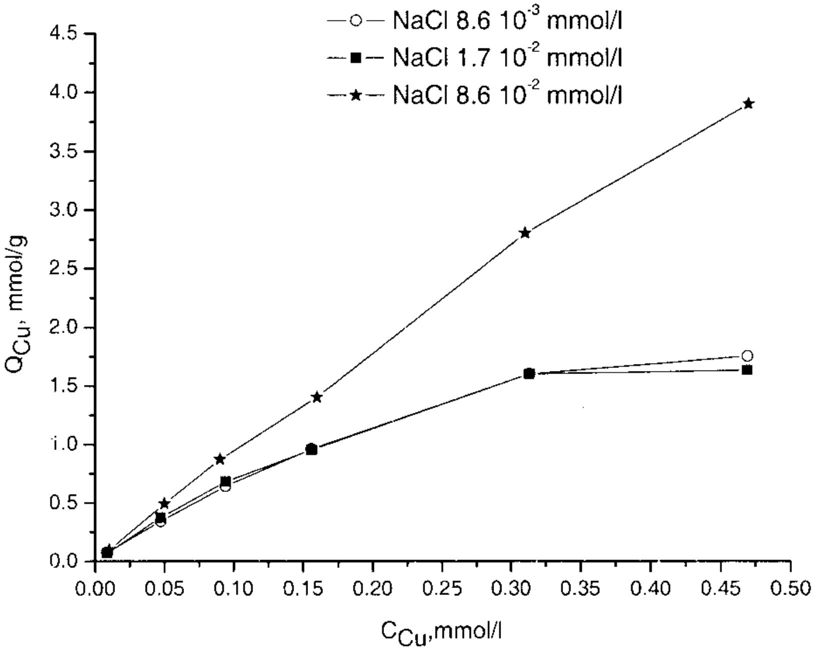

Figure 5. Equilibrium adsorption of Cu(II) by chitosan at different initial concentration ratios of Cu(II) to chitosan and different concentrations of NaCl.

The presence of a multiplicity of metals leads to an interactive effect. These effects as published by other researchers (33) can be extremely complex and the following three types of responses may be expected: (i) the effect of the mixture is greater than that of the individual effects of ions in the mixture (synergism); (ii) the effect of the mixture is less than that of the individual effects of ions in the mixture (antagonism); and (iii) no effect of the mixture (no interaction). The actual mechanisms of heavy metal adsorption, especially multicomponents, are not well understood and require further detailed studies.

4. CONCLUSIONS

The use of chitosan flakes for the removal of Cu^{2+} from water solutions has been examined. Chitosan shows excellent ability for Cu^{2+} adsorption with a capacity of 1.8–2.2 mmol/g dry mass. However, the capacity sharply rises when the solutions contain a high concentration of chloride ions. The variation of solution pH leads to competition between the coordination of Cu^{2+} with chitosan. The optimal pH range for copper adsorption is 5.4–6.0.

5. ACKNOWLEDGMENTS

This study was provided by Science and Technology Center in Ukraine, Grant number 2476.

REFERENCES

1. Veglio, R. and Beolchini, F. (1997) Removal of metals by biosorption: a review. *Hydrometallurgy*, 44 (3): 301–316.
2. Pollard, S.J.T., Fowler, G.F., Sollars, C.J., and Perry, R. (1992) Low cost adsorbents for waste and wastewater treatment: a review. *Science of the Total Environment*, 46: 31–52.
3. Chu, K.H. (2002) Removal of copper from aqueous solutions by chitosan in prawn shell: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, 90 (1): 77–95.
4. Coughlin, R.W., Deshaies, M.R., and Davis, E.M. (1990) Chitosan in crab shell wastes purities electroplating wastewaters. *Environ. Prog.*, 9 (1): 35–39.
5. Majeti, N.V. and Kumar, R. (2000) A review of chitin and chitosan applications. *Reactive and Functional Polymers*, 46: 1–27.
6. Khor, E. and Lim, L.Y. (2003) Implantable applications of chitin and chitosan. *Biomaterials*, 24: 2339–2349.
7. Genc, O., Soysal, L., Bayramoglu, G., Arica, M.Y., and Bektas, S. (2003) Procion Green H-4G immobilized poly(hydroxyethylmethacrylate/chitosan) composite membranes for heavy metal removal. *Hazard Mat.*, B97: 111–125.
8. Juang, R.-S., Xu, Y.-Y., and Chen, C.-L. (2003) Separation and removal of metal ions from dilute solutions using micellar-enhanced ultrafiltration. *J. Membrane Sci.*, 218: 257–267.
9. Kawamura, Y., Mitsuhashi, M., and Tanibe, H. (1993) Adsorption of metal ions on polyaminated highly porous chitosan chelatin resin. *Ind. Eng. Chem. Res.*, 32 (2): 386–391.
10. Muzzarelli, R.A.A. (1973) *Natural Chelating Polymers*; Pergamon Press: Oxford, 163–180.
11. Ang, R.-S., Wu, F.-C., and Tseng, R.-L. (1999) Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents. *Wat. Res.*, 33 (10): 2403–2409.
12. Oyrton, A.C., Monteiro, J., and Airoldi, C. (1999) Some thermodynamic data on copper-chitin and copper-chitosan biopolymer interactions. *Journal of Coll. and Int. Sci.*, 212 (2): 212–219.
13. Inoue, K., Baba, Y., Yoshizuka, K., Noguchi, H., and Yoshizaki, M. (1988) Selectivity series in the adsorption of metal ions on a resin prepared by crosslinking copper(II)-complexed chitosan. *Chemistry Letters*, 8 (3): 1281–1284.
14. Salehizadeh, H. and Shojaosadati, S.A. (2003) Removal of metal ions from aqueous solutions by polysaccharide produced from *Bacillus Firmus*. *Wat. Res.*, 37 (17): 4231–4235.
15. Eiden, C.A., Jewell, C.A., and Wightman, J.P. (1980) Interaction of lead and chromium with chitin and chitosan. *J. Appl. Pol. Sci.*, 25 (8): 1587–1599.
16. Guibal, E., Saucedo, I., Jansson-Charrier, M., Delanghe, B., and Le Chloirec, P. (1994) Uranium and vanadium sorption by chitosan and derivates. *Wat. Sci. Tech.*, 30 (9): 183–190.

17. Juang, R.-S. and Chiou, C.-H. (2001) Feasibility of the use of polymer-assisted membrane filtration for brackish water softening. *J. Membr. Sci.*, 187: 119–127.
18. Muslehiddinoglu, J., Uludag, Y., Ozbelge, H.O., and Yilmaz, L. (1998) Effect of operating parameters on selective separation of heavy metals from binary mixtures via polymer enhanced ultrafiltration. *J. Membr. Sci.*, 140: 251–266.
19. Volchek, K., Krentsel, E., Zhilin, Yu., Shtereva, G., and Dytnersky, Yu. (1993) Polymer binding/ultrafiltration as a method for concentration and separation of metals. *J. Membr. Sci.*, 79: 253–272.
20. Jeon, C. and Holl, W.H. (2003) Chemical modification of chitosan and equilibrium study for mercury ion removal. *Wat. Res.*, 37 (18): 4770–4780.
21. Juang, R-S., Wu, F.-C., and Tseng, R.-L. (1999) Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents. *Wat. Res.*, 33 (10): 2403–2409.
22. Benguella, B. and Benaissa, H. (2002) Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Wat. Res.*, 36 (10): 2463–2474.
23. Llorens, J., Pujola, M., and Sabate, J. (2004) Separation of cadmium from aqueous streams by polymer enhanced ultrafiltration: a two-phase model for complexation binding. *J. Membr. Sci.*, 239: 173–181.
24. Kurenkov, V.F. (1990) *Practical Work in Chemistry and Polymer Physics*; Khimija: Moskow, 304.
25. Bryk, M.T. and Tsapiuk, E.A. (1989) *Ultrafiltration*; Nauk. Dumka: Kiev, 288.
26. Lurye, Yu.Yu. (1971) *Standardizated Methods of Water Analysis*; Khimija: Moskva, 376.
27. Zhao, Z.P., Wang, Z., and Wang, S.-C. (2003) Formation, charged characteristic and BSA adsorption behavior of carboxymethyl chitosan/pes composite MF membrane. *J. Membr. Sci.*, 217 (1–2): 151–158.
28. Jha, I.N., Lyengard, L., and Prabhakara Rao, A.V.S. (1988) Removal of cadmium using chitosan. *J. Env. Eng.*, 114 (4): 962–975.
29. Billie, J.S. and Wightman, J.P. (1983) Interaction of heavy metals with chitin and chitosan. II. cadmium and zinc. In *Adsorption from Solution*; Ottewill, R.H., Rochester, C.H. and Smith, A.L., eds.; Academic Press: London, 235–244.
30. Muzzarelli, R.A.A. (1977) *Chitin*; Pergamon Press: New York, 94–101.
31. Juang, R.-S. and Shao, H.-J. (2002) A simplified equilibrium model for sorption of heavy metal ions from aqueous solutions on chitosan. *Wat. Res.*, 36 (12): 2999–3008.
32. Muzzarelli, R.A.A., Tanfani, F., Emanuelli, M., and Simonetta, G. (1980) The chelation of cupric ions by chitosan membranes. *J. Appl. Biochem.*, 2 (2): 380–389.
33. Sag, Y. and Kutsal, T. (1996) The selective biosorption of chromium(VI) and copper(II) ions from binary metal mixtures by *R. Arrhizus*. *Proc. Biochem.*, 31 (6): 561–572.