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Carbohydrate Polymers 55 (2004) 249–254

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Copper adsorption through chitosan immobilized on sand to demonstrate the feasibility for in situ soil decontamination

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Received 9 June 2003; revised 13 September 2003; accepted 16 September 2003

Abstract

The contamination of soils and waters by metals all over the world continues to present a serious danger to the environment and human health. The development of innovative metal clean-up technologies remains a challenge as current procedures have many limitations, such as being expensive, disruptive, and only efficient for certain concentrations. With high molecular weight and repetitive functional groups, biopolymers provide excellent chelating material for metals. Chitosan is a well-known and efficient metal chelator, but its practical use is limited due to the relatively high costs of constructing clean-up devices (filters) from chitosan alone. In the current study we attempt to find a more cost-effective solution by investigating a new adsorbent material based on chitosan immobilized on sand, namely, chitosan-coated sand (5% chitosan content). This new material was studied for its copper adsorption capacity at contact times of 2, 4, and 6 h and the equilibrium result was compared with copper adsorption capacities of chitosan and sand alone. Hopefully this concept will lead to an application as a large-scale permeable reactive barrier. Copper recovery from an adsorbent with the possible reuse of the adsorbent material was also evaluated in leaching tests. The equilibrium isotherms for Cu adsorption on chitosan-coated sand were described by the Langmuir model. These preliminary results indicate the possibility of using chitosan-coated sand to build inexpensive large-scale barrier filters for metal removal from moving contaminated groundwater plumes.

Keywords: Copper adsorption; In situ soil decontamination; Chitosan; Chelation; Biopolymers

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1. Introduction

As a result of today's widely industrialized society large areas of soil and water have been contaminated with toxic metals, raising serious environmental and health issues. Industrial and mining wastes are the most significant sources of environmental pollution by heavy metals (Quek, Wase, & Forsteret, 1998). Over the years, a wide range of clean-up technologies has been developed to remove toxic metals from water (Water treatment handbook, 1979) and soils (Jakpa, Lodolo, & Miertus, 1998). Currently, the most widely used remediation technologies are based on physical–chemical processes, including filtration, chemical precipitation, ion exchange, adsorption, electro-deposition, and membrane systems for water treatment, and excavation followed by burial at a hazardous waste site for soil treatment. These technologies have a series of problems, stemming from their high cost, disruptive nature, and inadequacy at removing trace levels of metals in most cases. Recently, biological technologies such as bioremediation and phytoremediation are regarded as future solutions to many contamination problems, because of the many advantages they possess such as, being cost-efficient, non-disruptive, and easy to maintain. However, there are still problems with these methods, as microorganisms do not have the ability to degrade metals but rather to transform them, and phytoremediation is only effective for low to moderate contamination and may take long periods of time.

The development of innovative metal clean-up technologies remains a challenge. In this context, the use of chelating materials holds great potential for metal adsorption and removal from both water and soils. The use of such chelating materials for metal ion removal has been widely studied in the laboratory, but has not been applied in the field. This technique takes advantage of the multiple structures of the chelating units to bind and remove metal

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0144-8617/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2003.09.009

ions of a specific size in the presence of other ions (Deans & Dixon, 1992). Such an approach is inherently attractive since only the toxic metal ions are removed while other harmless ions can be released into the environment. Moreover, the removed metals can be recovered and the chelating agents can be reused. Some of the best chelating materials are biopolymers, which are high molecular weight compounds and also can be produced by different living organisms. One of the most abundant biopolymers in the biosphere is chitin, with a linear structure composed of *N*-acetyl-glucosamine residues, and its de-acetylated derivative chitosan. In nature, the main sources of chitin/chitosan are from the animal and plant kingdoms, including the shells of crustaceans and mollusks, the algae commonly known as marine diatoms, and the cell walls of fungal species. With such abundant and inexpensive natural sources and a structure containing many reactive sites including the repetitive amino groups, chitosan provides an excellent chelating material for metals. A good indication of the high metal chelation power of chitosan as compared to other metal chelators, is proved by the study of Kang, Choi, and Kweon (1999), who obtained high stability constants of amidoximated chitosan-*g*-poly (acrylonitrile) copolymer for adsorption of Cu^{2+}. The interactions of metals with chitosan are complex, probably simultaneously dominated by adsorption and chelation. To study this, it is of utmost importance to use well-characterized chitosan, which is generally problematic, because available characterizing methodology is limited (OnsØyen & Skaugrud, 1990). However, there are several interesting studies regarding the interaction between chitosan and different metallic ions (Deans & Dixon, 1992; Eiden, Jewell, & Wightman, 1980; Lerivrey et al., 1986).

The use of chitosan to chelate metallic ions for wastewater treatment was one of the first applications for chitosan (Khor, 2001). The ability of chitosan to adsorb metallic ions from aqueous solutions has been extensively studied by different authors (Deans & Dixon, 1992; Findon, McKay, & Blair, 1993; Jha, Iyengar, & Prabhakara Rao, 1988; Schmuhl, Krieg, & Keizer, 2001; Wan Ngah & Liang, 1999) for several metals, such as Cu, Pb, Au, Cr, and Cd. In such studies, chitosan was used alone, as cross-linked chitosan, or in the form of several derivatives (e.g. carboxymethyl and hydroxamic acid derivatives). Deans and Dixon (1992) also compared a large number of adsorbent materials based on biopolymers (chitosan, chitin, cellulose, alginic acid, carrageenan) and their carboxymethyl and hydroxamic acid derivatives, obtaining good metal removal percentages depending on metal type, concentration, and the adsorbent used. Such investigations, although appealing in theory, have limited potential for practical applications. This is because in order to remediate contaminated waste streams, filters must be built along the stream, which would require large quantities of chitosan, if used alone, and the entire process would be expensive. However, if a proper and inexpensive material is used as immobilization support for chitosan, much lower quantities of chitosan are needed to build the filters, while the overall metal adsorption capacity may not be affected. In spite of the inherent practical advantages, there is no literature reference of adsorption studies using chitosan immobilized on a geologically readily available support.

The aim of this work is to investigate metal adsorption capacity of chitosan immobilized on sand as compared to chitosan or sand used alone. The metal used was Cu(II) in $CuSO_4$ solution. Adsorption isothermal data could be interpreted by the Langmuir equation. Batch studies were carried out to identify the time controlling steps for copper isotherm by determining the maximum capacity of the three aforementioned adsorbents used. Finally, desorption and leaching studies were performed to determine the possibility of stable copper removal or recovery from chitosan-coated sand system.

2. Material and methods

Reagents. In this study the following reagents were used: chitosan with a high purity reflected by a nitrogen content of 7.57% (MegaCare Inc., S. El Monte, CA); copper sulfate ($CuSO_4{\cdot}5H_2O$); hydrochloric acid (HCl); sodium hydroxide (NaOH); acetic acid (HAc); sand (EM Science, Gibbstown, NJ). All of the reagents used were of a highly pure grade. The deionized water was used for all reagent solutions.

Preparation of chitosan-coated sand. Five grams of chitosan was mixed with 100 g sand, and 300 ml 5% HCl (pH 1.5) was added. The acid was added for chitosan solubilization, allowing its uniform distribution on sand particles. The mixture was then stirred for 5 h at room temperature. The resulting solution was neutralized with NaOH (1N, pH 13), which was added drop by drop until chitosan-coated sand was formed by precipitating the chitosan from solution on sand surface. Then, it was filtered from the solution, washed and dried in a vacuum oven. After grinding and sieving, the particles were passed through ASTM sieve size #35 and particles greater than 0.5 mm were collected and used as the adsorbent for the isotherm test. Coated sand increases the surface area of chitosan. All pH values were measured with pH meter (ORION, Model 1230).

Adsorption studies. Cu(II) solutions of different concentrations (100, 500, 1000 and 2000 mg/l) were prepared in deionized water using $CuSO_4$. The batch adsorption equilibrium studies of Cu were carried out at room temperature and with $CuSO_4$ of pH 4.2, beakers filled with 2.5 g adsorbent (chitosan-coated sand with 5% by weight chitosan content, chitosan, and sand) and 30 ml metal solution (of each concentration used). The contact times were 2, 4 and 6 h. A shake machine, reaching a static speed of 50 rpm, provided continuous mixing. After sample filtration, Cu concentration in the supernatant was analyzed

Table 1
Copper adsorption parameters from studies with chitosan-coated sand, pure chitosan, and sand

Concentration of Cu^{2+} solution (mg/l)	Cu^{2+} adsorbability (%) (Cu^{2+} adsorption capacity, mg Cu^{2+}/g chitosan)			
	Chitosan-coated sand		Chitosan, 4 h contact	Sand, 4 h contact
	2 h contact	4 h contact		
100	98 (25)	99 (25)	99 (25)	16 (0.20)[a]
500	90 (114)	99 (124)	92 (116)	13 (0.78)
1000	78 (196)	93 (235)	66 (166)	12 (1.39)
2000	52 (265)	52 (260)	36 (184)	8.50 (2.04)

[a] In this case mg Cu^{2+}/g of sand only.

with an atomic adsorption (AA) spectrophotometer (Perkin Elmer AAnalyst-300).

The *percentage adsorption* of Cu was calculated according to:

$$\text{Percentage adsorption} = \frac{(C_0 - C)100}{C_0}$$

where C_0 is the initial Cu^{2+} concentration (mg/l) and C is the final Cu^{2+} concentration (mg/l).

The *adsorption capacity* was calculated for each adsorbent (reported per gram chitosan or sand), based on the difference of Cu concentration in aqueous solutions before and after adsorption, the volume of aqueous solution, and the amount of adsorbent used by weight, according to:

$$\text{Adsorption capacity} = \frac{(C_0 - C)V}{W}$$

where C_0 is the initial Cu^{2+} concentration (mg/l), C the final Cu^{2+} concentration (mg/l), V the volume (l) of Cu^{2+} solution, and W is the weight (g) of the adsorbent used.

Leaching and desorption studies (only for chitosan-coated sand experiments). Dilute acetic acid solutions of pH 4 and 2.9 were used. A 30 ml quantity of 5% HCl was added to each beaker (from the adsorption studies) and the solutions were shaken for 2 h. Then, Cu concentration in each supernatant was determined with the AA Spectrometer. Our experimental data were obtained as the average of at least two runs.

3. Results and discussion

3.1. Adsorption studies

Cu adsorbability and its adsorption capacity are the main parameters derived from the adsorption studies. These parameters are presented in Table 1 for the studies with chitosan-coated sand (2 and 4 h contact time), pure chitosan, and sand alone, respectively. Table 2 presents the ratio of N and Cu content of each adsorbent from the studies with chitosan-coated sand and chitosan alone.

The best Cu adsorption capacity was obtained for the highest Cu concentration used in all current studies of 2000 mg/l, regardless of the adsorbent type. However, different values of Cu adsorption capacity were obtained for each adsorbent used in this study. The best adsorption capacity was obtained in the case of chitosan-coated sand with a value of 260 mg Cu adsorbed per gram chitosan (contained in chitosan-coated sand), followed by chitosan with 184 mg Cu adsorbed per gram chitosan (used alone), and sand with only 2.04 mg Cu adsorbed per gram sand. This was both surprising and encouraging at the same time. Thus, by coating the sand with chitosan, we created an adsorbent that is not only less expensive than chitosan, but also displays much better adsorption capacity than any of its components used alone (sand or chitosan). The explanation may lie in the three-dimensional structure, which is different for each of the adsorbents used, and thus may fit differently with Cu's ionic size. As known, the chelating groups of chitosan (amino groups especially) allow for different chelating combinations, making the interaction with metal complex. By combining chitosan with sand, chitosan may have changed its three-dimensional structure to one that fits better for the interaction with Cu. The possibility that the metal adsorption process will be affected by the stereochemistry of particular adsorbents is in accordance with the hypothesis advanced by Deans and Dixon (1992), based on testing different biopolymers and their carboxymethyl and hydroxamic acid derivatives.

Comparing the adsorbability values, there are very small differences between chitosan and chitosan-coated sand, both materials exhibiting very high Cu adsorbability (up to 99 and 98%, respectively) for concentrations up to 500 mg Cu/l. Then, the adsorbability dropped slightly to 1000 mg

Table 2
The ratio of N/Cu from different Cu adsorption studies

Adsorbents	N/Cu(II)
Chitosan-coated sand	
2 h contact	1.81
4 h contact	1.50
6 h contact	1.57
Pure chitosan	2.28

Cu/l, followed by a sharp increase from 1000 to 2000 mg Cu/l. Still, although the adsorption percentage of Cu dropped with the concentration increase after 500 mg Cu/l, the adsorption capacity increased, reaching its maximum for 2000 mg Cu/l as discussed before. The decrease in adsorption percentage was clearly lower compared to the increase in Cu concentration. Sand had a very low adsorbability when used alone, despite its good metal precipitating characteristics. There are many possible explanations for this, including the type of sand used, and the possible re-dissolution of precipitated Cu after the equilibrium was reached. This suggests that if contaminated water was flowing through possible sand filters (without staying in contact with sand for longer periods) much better adsorption of Cu could be achieved by sand alone, as the precipitated Cu could not be re-dissolved. This may be in accordance with the study of Petrisor et al. (2002), who reported sand as a very good heavy metal adsorbent from column flow studies.

Doubling the contact time between Cu solution and the adsorbent (chitosan-coated sand) had a very slight effect on Cu adsorbability and adsorption capacity, with almost no increase in Cu uptake by the adsorbent. Thus, 2 h or perhaps even less time is adequate for achieving good Cu adsorption.

Chitosan's ability to adsorb copper ions from aqueous solutions has been studied by other authors as well (Deans & Dixon, 1992; Findon et al., 1993; Schmuhl et al., 2001). However, the aforementioned studies were using chitosan alone or derivatives of chitosan (e.g. carboxymethyl and hydroxamic acid derivatives). Thus, no other study reported in the literature has described chitosan bound to a support as our chitosan-coated sand, which showed a much better Cu adsorption capacity than chitosan used alone.

The maximum Cu adsorption capacity of chitosan (used alone) obtained in this study, with a value of 184 mg Cu adsorbed/g chitosan, is much higher than Cu adsorption capacity reported for chitosan in other studies. Findon et al. (1993) reported a maximum adsorption capacity of chitosan for Cu ions of 40 mg Cu adsorbed per gram chitosan, while Schmuhl et al. (2001) reported higher values of Cu adsorption capacity of 78 mg Cu per gram chitosan, which is still less than half the values from the current study. The explanation of these differences in results may be due to several factors. First of all, the chitosan source used in each study was different and to make a reasonable comparison of adsorption capacity, the purity of chitosan used was required to be known. The chitosan used in our study was of a high degree of purity, having a high nitrogen content of 7.57%, which is close to the theoretical value of the nitrogen of 7.91% calculated based on chitosan structure. For the benefit of future studies, we indicate the nitrogen content for our chitosan, but there is no similar information in the referred papers (Findon et al., 1993; Schmuhl et al., 2001), which makes any direct comparison difficult at this time. Chitosan obtained from sources other than that used in the current study will be further tested alone and as chitosan-coated sand in our future investigations.

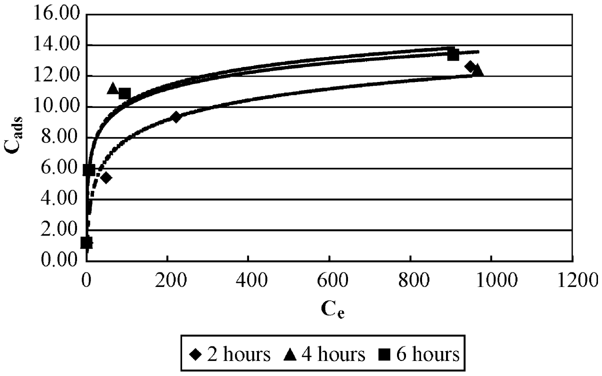

Fig. 1. Isotherm plot for the adsorption of Cu(II) ions by chitosan-coated sand after 2, 4 and 6 h of contact.

The smaller the ratio of nitrogen concentration to that of Cu for each adsorbent used after the completion of adsorption studies (Table 2), the better is the adsorbent capacity since most of the amino groups would bind Cu. Thus, from this perspective, chitosan-coated sand was a better adsorbent compared to chitosan being used alone. Additionally, 4 h of contact between adsorbent and Cu solution was found to be the most effective length of time to achieve a good N/Cu ratio.

3.2. Mechanism

Since chitosan-coated sand proved to be efficient in Cu removal during our study, a more detailed analysis of results was carried out. Fig. 1 shows the equilibrium isotherms for the adsorption of copper ions by chitosan-coated sand at different contact times (2, 4 and 6 h), at room temperature. Obviously, the 4-h one can be used for equilibrium studies. The solute concentration in the solid phase C_{ads} (mg/g) was plotted as a function of the solute concentration in the liquid phase C_{eq} (mg/l) at equilibrium.

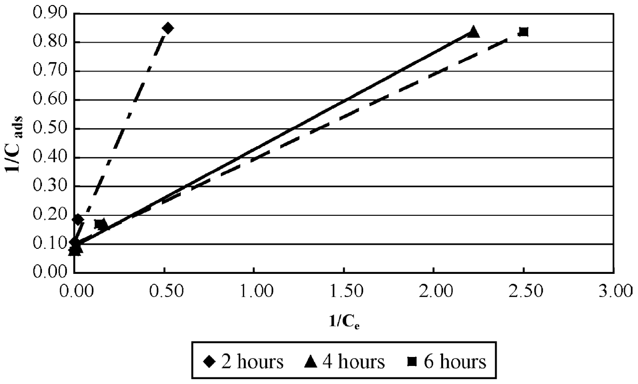

Fig. 2. The Langmuir model for the adsorption of Cu(II) ions by chitosan-coated sand after 2, 4 and 6 h of contact. The lines represent adsorption.

Table 3
The Langmuir constant constants derived from literature and experiment data (data reported on chitosan)

Paper source	Langmuir constant		
	K_L (l/g)	b (l/mg)	C_{max} (mg/g)
Findon et al. (1993)	1.17	0.02	59
McKay, Blair, and Findon (1989)	6.83	0.03	288
Udaybhaskar, Iyengar, and Prabhakara Rao (1990)	34.90	0.62	56
This study			
Pure chitosan only	251.09	1.67	150
2 h Cu isotherm	14.78	0.08	189
4 h Cu isotherm	62.50	0.27	228
6 h Cu isotherm	70.73	0.32	219

When the solute remaining in solution is in dynamic equilibrium with that on the solid surface, there is a defined distribution of solute between the liquid and solid phases, which is generally expressed by one or more series of isotherms (Findon et al., 1993). In our case, the experimental values of the isotherms were used in the linear forms of the Langmuir equation. This equation is valid for monolayer adsorption. The model contains a limited number of sites and predicts a homogeneous distribution of adsorption energies.

The Langmuir equation is represented by the following:

$$C_{ads} = \frac{K_L C_{eq}}{1 + bC_{eq}} = \frac{C_{max} b C_{eq}}{1 + bC_{eq}}$$

where $C_{max}b = K_L$In this study, the following reciprocal from the Langmuir equation was used,

$$\frac{1}{C_{ads}} = \frac{b}{K_L} + \frac{1}{K_L C_{eq}}$$

where C_{ads} is the amount of Cu(II) adsorbed (mg/g), C_{eq} equilibrium concentration of Cu(II) in solution (mg/l), K_L the Langmuir equilibrium constant (l/g), and b the Langmuir constant (l/mg). The constant b in the Langmuir equation is related to the energy or the net enthalpy of the adsorption process, while the constant K_L can be used to determine the enthalpy of adsorption.

The relation between $1/C_{ads}$ and $1/C_{eq}$ yields a straight line, as shown in Fig. 2. As can be seen from the plot, the experimental adsorption isotherm values fit into linearized forms of the Langmuir equation.

From these data, the two constants, K_L and b, can be calculated by slope and interception. Confirming the applicability of the Langmuir adsorption isotherm, the values of C_{max} can be obtained by the value of K_L/b. These constants are presented in Table 3, which also shows, for purposes of comparison, similar data from the literature. Our constants are within the values indicated by other authors (Table 3), which proves the validity of the Langmuir model to describe Cu adsorption isotherm by chitosan. Compared to other studies, we obtained quite a good maximum adsorption capacity ($C_{max} = 228$ mg Cu adsorbed per gram of chitosan) when used as chitosan-coated sand. This indicates the potential of chitosan-coated sand in large-scale practical applications.

There is no reference in the literature concerning the use of chitosan-coated sand in the adsorption of metals. However, there are many studies indicating that adsorption of metals by chitosan is described by different experimental models, depending on the metal. Most studies in the case of Cu, reported the Langmuir model as best describing the equilibrium isotherms. Findon et al. (1993) found that the adsorption of Cu onto chitosan could be described by the Langmuir equation. A study of the copper removal capability of prawn shell was demonstrated by Chu (2002) where the extended Langmuir model or the competitive Langmuir model was adopted due to the competition between proton and copper for binding sites on the prawn shell. For any passive treatment technology involving the remediation of metal ions in groundwater, the chitosan-coated sand can be easily constructed as a permeable reactive barrier.

3.3. Leaching and desorption studies

Chitosan-coated sand demonstrated efficient Cu adsorption capacity as shown in our adsorption studies. Furthermore, we have investigated Cu desorption from chitosan-coated sand using leaching with water and strong HCl. Such desorption studies were aimed at evaluating the possibility of Cu recovery from the adsorbent, as well

Table 4
Copper leaching with HCl from chitosan-coated sand

2-h Cu adsorption isotherm studies			4-h Cu adsorption isotherm studies		
Cu adsorbed (mg/l)	Cu recovered (mg/l)	Cu recovery (%)	Cu adsorbed (mg/l)	Cu recovered (mg/l)	Cu recovery (%)
98.27	98.00	99.7	97.67	80.20	82.1
443.7	422.1	95.1	467.6	402.7	86.1
797.8	752.2	94.3	822	726	88.3
1157	1079	93.3	1157	1033	89.3

Table 5
Copper leaching with water (pH 7), acetic acid (pH 4.0), and acid (pH 2.9) from chitosan-coated sand

	Original Cu concentration (mg/l)	Cu adsorbed (mg/l)	Cu leached (mg/l)	Cu leaching (%)
Water (pH 7)	100	98.6	1.46	1.48
	500	475	0.66	0.14
	1000	866	5.75	0.66
	2000^{a}	989	29.2	2.95
Acid (pH 4.0)	100	99.6	4.40	4.44
	500	488	22.1	4.53
	1000	897	42.2	4.70
	2000^{a}	1177	110	9.35
Acid (pH 2.9)	2000^{a}	996	517	51.9
	2000^{a}	1198	623	52.0

[a] Differences are due to in-homogeneity of the samples taken.

as elucidating the nature of the adsorption process. We also investigated the case of any active aggressive geological liquids such as those of pH 4 and 2.9. Most naturally occurring acid streams are above pH 3. The results of leaching tests for chitosan-coated sand are presented in Table 4 (leaching with HCl from both adsorption experiments of 2 and 4 h of contact) and Table 5 (leaching with water, as well as both pH 4 and 2.9 acids).

Very low concentrations of Cu were leached by water, up to only 2.95% Cu. This is an indication of the stability of bound Cu, which is not easily removed in practice. The stability of Cu retained in sand can be found in Table 4. Most of the Cu adsorbed on chitosan-coated sand could, however, be leached out by strong HCl acid with more than 95% Cu leached in a 2-h contact test, indicating the good potential for recovering the adsorbed Cu with subsequent reuse of adsorbent (Table 5). An increase in contact time between adsorbent and Cu solution resulted in a slight decrease (to 80%) of Cu leached with HCl. This suggests that a longer contact time of adsorbent with Cu solution may affect the type of Cu bindings determining more stable bindings, however it did not affect the Cu adsorbability overall. Changes in Cu concentrations have no effect on Cu desorption from chitosan-coated sand, as compared to Cu adsorbability, which is strongly influenced by the concentration of Cu in solution.

The results of our desorption studies indicate the potential for recovering Cu from chitosan-coated sand, with important practical implications when building filters along a contaminated stream of groundwater. Chitosan-coated sand could be useful in creating permeable reactive barrier for the recovery of metals.

Acknowledgements

This work was supported by the US Department of Energy (DOE), under the contract US DOE DE-AC 2601 NT 41307. We would also like to express our thanks and gratitude for their valuable technical assistance in preparing this manuscript to Laura Wennstrom, Mary Quach, and Divya Devaguptapu.

References

Chu, K. H. (2002). Removal of copper from aqueous solution by chitosan in prawn shell: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *B90*, 77–95.

Deans, J. R., & Dixon, B. G. (1992). Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. *Water Research*, *26*(4), 469–472.

Eiden, C. A., Jewell, C. A., & Wightman, J. P. (1980). Interaction of lead and chromium with chitin and chitosan. *Journal of Applied Polymer Science*, *25*, 1587–1599.

Findon, A., McKay, G., & Blair, H. S. (1993). Transport studies for the sorption of copper ions by chitosan. *Journal of Environmental Science and Health*, *A28*(1), 173–185.

Jakpa, T., Lodolo, A., & Miertus, S. (1998). An overview of soil remediation technologies. *Genetic Engineering and Biotechnology*, *3*(4), 1–11.

Jha, I. N., Iyengar, L., & Prabhakara Rao, A. V. S. (1988). Removal of cadmium using chitosan. *Journal of Environmental Engineering*, *114*(4), 962–975.

Kang, D. W., Choi, H. R., & Kweon, D. K. (1999). Stability constants of amidoximated chitosan-*g*-poly(acrylonitrile) copolymer for heavy metal ions. *Journal of Applied Polymer Science*, *73*, 469–476.

Khor, E. (2001). *Chitin: Fulfilling a biomaterials promise*. Amsterdam: Elsevier.

Lerivrey, J., Dubois, B., Decock, P., Micera, G., Urbanska, J., & Kozlowski, H. (1986). Formation of D-glucosamine complexes with Cu(II), Ni(II) and Co(II) ions. *Inorganica Chimica Acta*, *125*, 187–190.

McKay, G., Blair, H. S., & Findon, A. (1989). Equilibrium studies for the sorption of metal ions onto chitosan. *Indian Journal of Chemistry*, *28A*, 356–360.

OnsØyen, E., & Skaugrud, Ø. (1990). Metal recovery using chitosan. *Journal of Chemical Technology and Biotechnology*, *49*, 395–404.

Petrisor, I. G., Komnitsas, K., Lazar, I., Voicu, A., Dobrota, S., & Stefanescu, M. (2002). Biosorption of heavy metals from leachates generated at mine waste disposal sites. *The European Journal of Mineral Processing and Environmental Protection—Biotreatment and Biosorption I—Special Issue*, *2*(3), 158–167.

Quek, S., Wase, D., & Forster, C. F. (1998). The use of sago waste for the sorption of lead and copper. *Water SA*, *24*(3), 251–256.

Schmuhl, R., Krieg, H. M., & Keizer, K. (2001). Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies. *Water SA*, *27*(1), 1–7.

Udaybhaskar, P., Iyengar, L., & Prabhakara Rao, A. V. S. (1990). Hexavalent chromium interaction with chitosan. *Journal of Applied Polymer Science*, *39*, 739–747.

Wan Ngah, W. S., & Liang, K. H. (1999). Adsorption of gold(III) ions onto chitosan and *N*-carboxymethyl chitosan: Equilibrium studies. *Industrial and Engineering Chemistry Research*, *38*, 1411–1414.

Degremont, G., *Water treatment handbook* (1979). Halstead Press, New York.