

# Removal of metals from aqueous solutions using natural chitinous materials

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**Abstract** Four naturally derived chitinous materials, commercial cryogenically milled carapace (CCMC), mechanically milled carapace (MMC), chitin and chitosan, were assessed for their ability to remove a range of alkali, alkaline earth, transition and heavy metals from aqueous media in flow-through column trials. The materials showed a poor affinity for the alkali metals and alkaline earth metals but significantly greater affinity for transition and heavy metals. In general, chitin was the least efficient material for removal of transition and heavy metals (~35%) while chitosan was most effective (>99%). CCMC and MMC both removed >90% of transition and heavy metals tested from solution. Batch studies conducted using copper as a reference metal demonstrated that removal was dependent on a number of variables including pH, contact time, particle size, metal concentration, metal type and the physio-chemical characteristics of the materials. Detailed analysis of the results from these studies indicate that removal is a complex process and that metals can be sequestered from solution by a number of mechanisms including adsorption, absorption and precipitation.

**Keywords** Biosorbents; chitin; chitosan; crabshell; heavy metals transition metals

## Introduction

With growing pressures on water resources and the increase in toxic pollutants entering reservoirs, rivers and groundwater, the supply of high quality potable water and the treatment of wastewater to regulatory standards will present unique challenges for water authorities during the coming years. A specific concern is the presence of toxic transition and heavy metals such as copper, zinc, cadmium, lead and mercury. These metals can be introduced into aquatic systems through effluent discharges from various industrial operations including; mining (Kumar *et al.*, 1998), chemicals manufacture (Gupta, 1998), electroplating (Kratochvil *et al.*, 2000) and distilling and brewing operations (Mader *et al.*, 1997). Many of these metals can be bio-accumulated by aquatic organisms causing serious health and environmental concerns even at low concentrations (Chang *et al.*, 1998). Although source reduction and efficient waste management programmes are the preferred long-term solutions, upgrading existing treatment systems and the implementation of new and novel technologies will continue to play an important role.

Processes such as coagulation and chemical precipitation (Charentanyarak, 1999), slow sand filters (Wheatley *et al.*, 1998), membrane technologies (Croll, 1992) and ion exchange resins (Chiarle *et al.*, 2000) are routinely employed to remove toxic metals from aqueous wastes. A range of expensive synthetic and mineral materials are currently available for use in these processes. However, a variety of low-cost, natural products have shown potential for the detoxification of metal bearing effluents over recent years (Bailey *et al.*, 1999) including shrimp shells (Chui and Wong, 1984) chitin and chitosan, (Muzzarelli, 1973; Eiden *et al.*, 1980; Peniche *et al.*, 1992), wood barks (Gloaguen and Morvan, 1997), peat (McKay *et al.*, 1999), seaweed (Volesky and Kratochvil, 1998), sugar beet (Gerente *et al.*, 2000), crab shells (Lee *et al.*, 1999; An *et al.*, 2001) and spent grain (Low and Liew, 2000).

The objective of this study was to compare the efficiency of four naturally derived chitinous materials CCMC, MMC, chitin and chitosan for the removal of metals from

aqueous media. All materials can be produced from waste generated during shellfish processing operations.

## Materials and methods

### Mechanically milled carapace

(MMC): Carapace of the crab *Cancer pagurus* (containing 20–50% chitin; Welinder, 1975) was collected from fishing vessels at Scrabster Harbour, Thurso, Caithness, UK. The carapace was thoroughly washed with distilled water to remove surface debris and air-dried at room temperature (18–22°C) overnight. The dry carapace was roughly broken by hand, milled with a domestic food processor to increase surface area and mechanically sieved to give particles in the size ranges <250, 250–800, 800–2,000 and >2,000 µm.

### Commercial cryogenically milled carapace

(CCMC): This was obtained from Carafiltration Ltd. York, UK. The material had been ultrasonically cleaned to food grade quality, milled cryogenically –120°C to maintain structural integrity and mechanically sieved to a constant particle size (250–800 µm). When processed under these conditions, each milled particle has an inherent macro and microporosity, which enhances the surface area to volume ratio.

### Chitin

Chitin flakes (derived from crab carapace) was obtained from Sigma Chemical Company UK. Chitin was milled using a domestic food processor and mechanically sieved to give particles in the size ranges <250, 250–800, 800–2,000 and >2,000 µm.

### Chitosan

This was prepared by deacylation of chitin by mixing chitin flakes (100 g) with NaOH (2.4 L, 50% w/v) for 5 days at ambient temperature (18–20°C). The deacylated product was mechanically sieved to give particles in the size ranges <250, 250–800, 800–2,000 and >2,000 µm.

### Metal solutions

All chemicals and reagents used were of analytical grade. Stock solutions of metal ions were prepared by dissolving metal salts in Ultra Pure water obtained from a Millipore Direct Q3 System. Ultra Pure water was also used in all dilutions and in the preparation of standards used in calibration.

### Batch studies

Batch studies were conducted by measuring the metal concentration of a standard metal solution (100 ml) before and after biosorbent addition (5 g). All studies were conducted under conditions of regulated contact time, particle size, concentration and pH. All studies were conducted at room temperature (19–21°C) and samples were mechanically agitated on a rotary shaker (350 rpm) during the contact period. Batch studies were conducted in triplicate to assess reproducibility.

### Column studies

Flow through column studies were performed by delivering metal solutions of known concentrations (500 mg/L) at a constant flow rate (6.4 ml/min) to 20 grams of material of the 250–800 µm size fraction. Effluent samples were collected at 15-minute intervals and residual metal concentration determined using atomic absorption or flame photometry.

### Control of pH

Solution pH can dramatically influence the sorption capacity of a material for metals with different materials (B Volesky pers. comm.). For example, copper speciation from free  $\text{Cu}^{2+}$  ions to the solid hydroxide  $\text{Cu}(\text{OH})_2$  form begins to occur in solution at pH values  $> 5$  (Stumm and Morgan, 1996). In this study, experiments with copper were conducted with and without pH control to assess copper removal by sorption processes. The pH adjustments were made by addition of 5M  $\text{H}_2\text{SO}_4$  or 1M LiOH.

### Chemical and physical analysis of biosorbents

Surface topography and Energy Dispersive X-Ray Analysis (EDAX) of materials were studied using a Phillips XL 20 Scanning Electron Microscope. The specific surface area of each material was determined by the Brauner Emmett and Teller (BET) single point method using a "Micromeritics" (Flowsorb III 2305/2310) surface area analyser with nitrogen as the adsorbate gas at 77 K. Elemental analysis carbon (C), hydrogen (H), and nitrogen (N) of materials was performed using a Carlo Ebra NA2500 elemental analyser calibrated with acetanilide standards.

### Determination of dissolved metal concentrations

Transition and heavy metal were determined using a Perkin Elmer Atomic Absorption Spectrophotometer (AAS; Model No 357). Alkali and alkaline earth metals were determined using a Sherwood Flame Photometer (Model No 410). Instrument calibrations were performed within the linear working range for each metal (e.g. for copper 0–10 mg/L). Absorbance values were recorded in triplicate to assess reproducibility and mean values used for concentration calculations.

## Results and discussion

### CHN, EDXA and SEM analysis

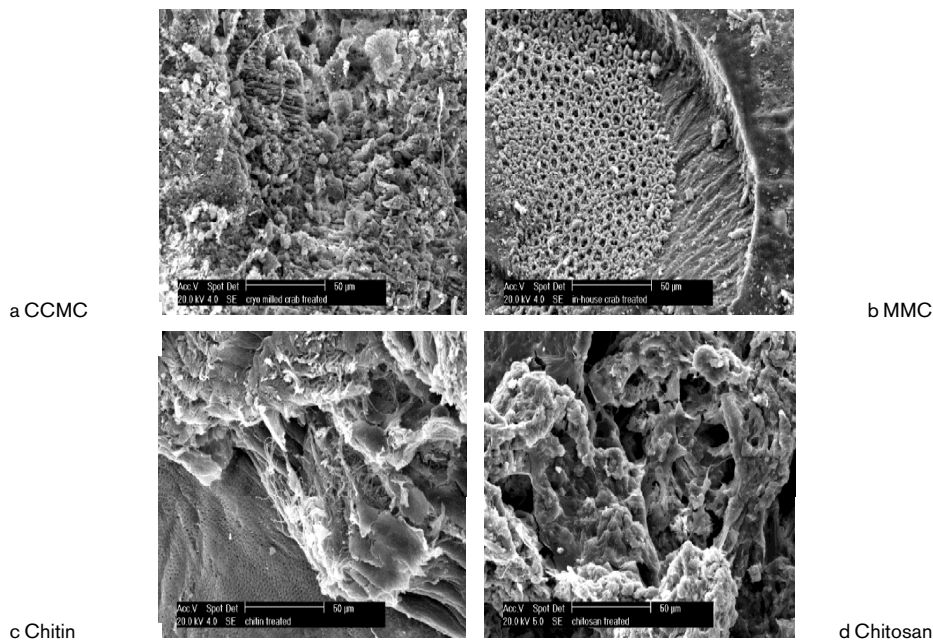
Chitin and chitosan contain approximately three times as much C, H and N as MMC and CCMC and possess approximately a quarter of the surface area (Table 1). The higher surface area of CCMC with respect to MMC may denote the preservation of the open porous structure when milled under cryogenic conditions.

The CCMC and MMC particles exhibit extensive macro and micro porosity (Figure 1a and b), Hegdahl *et al.* (1977) reported the abundance of pore canals ( $150,000\text{--}220,000 \text{ mm}^2$ ) permeating the cuticle of the *Cancer pagurus* this may account for the higher surface area of these materials (Table 1). Chitin and chitosan have closed fibrous structures and exhibit a reduced internal porosity which may account for the smaller surface area recorded for these materials (Table 1).

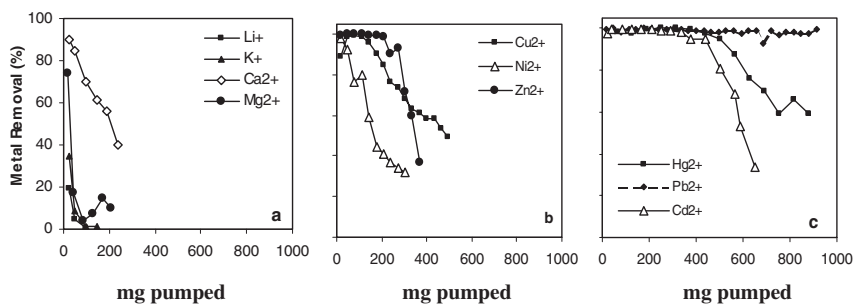
Materials showed a poor uptake for alkali and alkaline earth metals (Figure 2a). However, significantly higher removal was observed for the transition metals, particularly divalent copper (Figure 2b). Removal of the heavy metals was highly efficient e.g. Pb, Hg and Cd  $>99\%$  (Figure 2c). These results support the findings of Muzzarelli (1973, 1997) who reported the effectiveness of chitin, chitosan and their derivatives for the removal of

**Table 1** Physio-chemical characteristics of chitinous materials of 250–800  $\mu\text{m}$  particle size

Material	C (%)	H (%)	N (%)	Surface area ( $\text{m}^2/\text{g}$ )
Mechanically Milled Carapace (MMC)	15.08	1.70	1.12	19.3
Commercial Cryogenically Milled Carapace (CCMC)	11.40	1.52	1.26	22.5
Raw crab chitin	46.65	6.74	5.97	5.99
Chitosan	32.43	5.14	4.48	3.94



**Figure 1** SEM micrographs showing the structural topography of chitinous materials. a = CCMC, b = MMC, c = chitin and d = chitosan (All scale bars = 50  $\mu\text{m}$ )

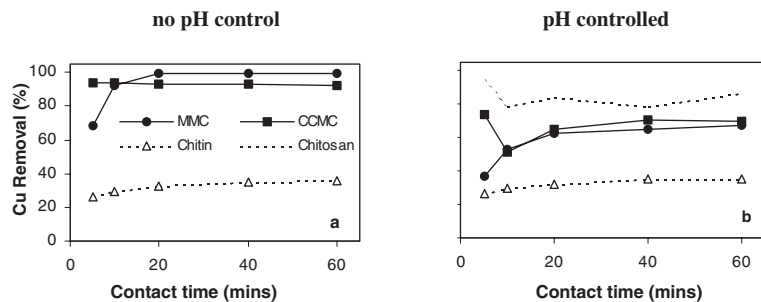


**Figure 2** Removal of metals tested in column studies. a = alkali and alkaline earth metals, b = transition metals and c = heavy metals. All metals were assessed at a concentration of 500 mg/L, initial solution pH = 4.5 and no pH control with 20 grams material of 250–800  $\mu\text{m}$  particle size

metal ions from wastewater because they selectively bind to virtually all group III transition metals but do not bind to alkali and alkaline earth metals.

#### Effects of pH

Without pH control, effluent final pHs were 7.3, 8.6, 4.5 and 5.0 for MMC, CCMC, chitosan and chitin respectively with copper removal efficiencies of 99%, 93%, 86% and 35% respectively (Figure 3a). With pH control, effluent final pH values were 4.5, 4.3, 4.3 and 5.0 and reduced removal efficiencies of 62, 65, 84 and 32% respectively were recorded after 20 minutes of contact time (Figure 3b). In effect, copper removal increased by 5–30% for all materials as solution pH increased above 5. This increase in metal removal can be attributed to precipitation of insoluble  $\text{Cu}(\text{OH})_n$  when the bulk solubility limit is reached (Schneider *et al.*, 2001). It was concluded from this study that without pH control, sorption and precipitation mechanisms accounted for approximately 70% and 30% of the total copper removal respectively (Figures 3a, b and 4a, b)



**Figure 3** The influence of contact time on the removal of  $\text{Cu}^{2+}$  from solution. a = no pH control – initial pH 4.5; b = pH controlled – initial pH 1.8, final pH controlled to 4.3–4.5. All studies conducted using 250–800  $\mu\text{m}$  particle size material, Cu concentration 500 mg/L

These results are consistent with earlier studies investigating the sorption mechanisms of transition metals onto chitin (Muzzarelli, 1973) and chitosan (Yang and Zall, 1984) and reflect the high metal scavenging efficiency of these polymers. Their effectiveness has been attributed to reactive surface functional groups (acetylamino and amino) on the polymer structural chain (Eiden *et al.*, 1980). The high number of free amino groups per monomer unit on the chitosan polymer chain are considered to be more effective for binding copper than the acetyl groups in chitin (Sturm and Hesse, 2000). This could account for the low removal capacity of chitin observed in this study. More recent research has reported on the effectiveness of chitosan, chitin and crabshell for the chelation of heavy metal ions (Peniche *et al.*, 1992; Sag and Aktay, 2000; An *et al.*, 2001).

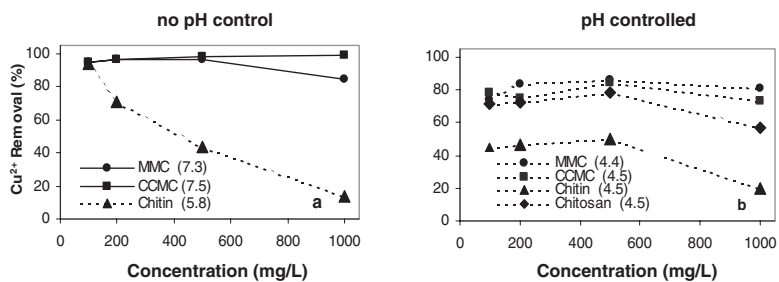
#### Effect of contact time

Contact times in excess of 20–40 minutes resulted in no significant improvement in removal efficiency either with or without pH control (Figures 3a and 3b). Based on these results it was concluded that 40 minutes contact time would be sufficient and was used in all other batch experiments.

Efficient uptake of a range of metals over comparable times by natural materials has been observed recently by a number of workers including McKay *et al.* (1999) and Sag and Aktay, (2000). It is considered that sorptive uptake of metals from solution by porous materials involves three consecutive stages: (1) mass transport of metals to the external surfaces of the material, (2) intra-particle diffusion into pores and (3) adsorption on interior surfaces. In general, stage (1) is relatively fast compared to stages (2) and (3). Yang and Zall (1984) studied the adsorption kinetics of copper onto chitosan as a function of time and concluded that intra-particle diffusion was the rate-determining step. Efficient metal removal by MMC and the CCMC (Figures 3a and b) may be due to their extensive porosity and surface area (Figure 1 and Table 1).

#### Effect of metal ion concentration

Optimum removal efficiencies of 96, 98, 70 and 43.5% were recorded for MMC, CCMC, chitosan and chitin at concentrations of 500, 1,000, 500 and 100 mg/l respectively at final effluent pH values of 7.3, 7.5, 4.5 and 5.8 respectively (Figure 4a). A slight decrease in removal is observed for MMC, chitosan and chitin at concentrations above 500 mg/L and a significant decrease in removal capacity is observed for chitin at concentrations >100 mg/L. For pH controlled studies (Figure 4b), optimum removal capacities of 86, 84, 79 and 50% were recorded at a concentration of 500 mg/L with final solution pHs of 4.4, 4.5, 4.3 and 4.5 for MMC, CCMC, chitosan and chitin respectively.

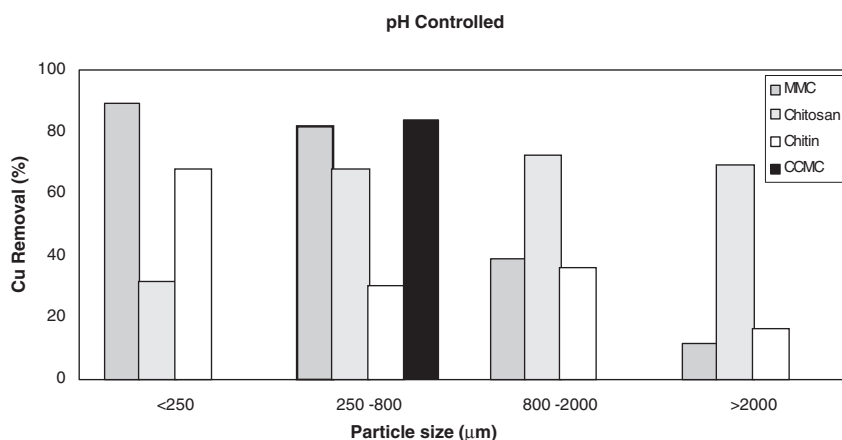


**Figure 4** The influence of initial concentration on the removal of  $\text{Cu}^{2+}$  from solution. a = no pH control – initial pH 4.5; b = pH controlled – initial pH = 1.8, final pH controlled to 4.3–4.5. All studies 40 minutes contact time, 250–800  $\mu\text{m}$  particle size material. Values in parentheses represent the final solution pH

### Effects of particle size

In general, as particle size is decreased there was a corresponding increase in copper removal (Figure 5). Under the conditions investigated, MMC removed >90% with <250  $\mu\text{m}$ , steadily decreasing to 11.5% with the >2,000  $\mu\text{m}$  size fraction. CCMC was only available at 250–800  $\mu\text{m}$  particle size and removed >84%. This removal trend was also observed for chitin with 68% decreasing to 16% for <250  $\mu\text{m}$  and >2,000  $\mu\text{m}$  respectively. However, this trend was not so pronounced for chitosan and removal capacities of 32, 67, 72 and 69% were observed for <250, 250–800, 800–2,000 and >2,000  $\mu\text{m}$  respectively. McKay *et al.* (1986) reported similar removal patterns with small variations in copper removal with chitosan particles as size was decreased from 1.0 to 0.21 mm. As chitin and chitosan have small internal surface area (Table 1) and porosity (Figure 2) the removal of metals is most likely to be by chemisorption onto active surface sites on the polymer chain.

This relationship between particle size and removal capacity of metals has also been observed for other natural materials e.g. wood (Gloaguen and Morven, 1997) and peat (McKay *et al.*, 1999). The increase in removal capacity with decreasing particle size suggests that the metals preferentially adsorb onto external surfaces and do not fully penetrate into the particles. The extensive surface area of CCMC and MMC at the 250–800  $\mu\text{m}$  size fraction (Table 1) and the open pore structure of the CCMC (Figure 1a) could account for the high copper removal observed. The highly porous nature and the extensive surface area of the crustacean cuticle have been well documented by Welinder (1975) and Hegdahl (1977a, b and c) in studies with *Cancer pagurus*.



**Figure 5** The effect of particle size on Cu removal from solution. Experimental conditions: Contact time 40 minutes, concentration 500 mg/L, initial pH 1.8 and maintained between 4.3–5 during contact

SEM-EDAX analysis of the spent materials used in this study indicated the formation of adsorbed metal clusters at the exterior surfaces of materials. This accumulation of metals has also been observed by Eiden *et al.* (1980) and Maruca *et al.* (1982) from studies involving chitosan powder and by Suder and Wightman (1983) investigating the uptake mechanisms of  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  onto chitin and chitosan using SEM-EDAX analysis. These workers concluded that a combination of nodular formation, ion adsorption and absorption accounts for the total metal uptake.

## Conclusions

Chitinous materials derived from crustacean products are effective for the removal of metals from aqueous solutions. Raw crabshell chitin was the least efficient material for the removal of metals tested (35%) while chitosan was most effective (>95%) for the removal of transition and heavy metals from solution over a wide concentration range. Although commercial cryogenically milled carapace was marginally more efficient than mechanically milled carapace, both were capable of removing >90% of transition and heavy metals from solution. However, mechanically milled carapace is significantly cheaper and less labour intensive to obtain and prepare. It thus constitutes an attractive, low cost and environmentally benign material for possible applications in the primary and tertiary treatment of metal bearing effluents. Furthermore, the basic nature and structural stability of crab carapace in low pH solutions, may offer significant potential for the detoxification of highly acidic metal bearing effluents. The main metal removal mechanisms are considered to be adsorption, absorption and precipitation depending on solution pH, contact time, initial metal concentration and the physio-chemical characteristics of the materials.

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## References

- An, H.K., Park, B.Y. and Kim, D.S. (2001). Crab shell for the removal of heavy metals from aqueous solutions. *Water Research*, **35**, 3551–3556.
- Bailey, S.E., Olin, T.J., Bricka, M. and Adrian, D. (1999). A review of potentially low cost sorbents for heavy metals. *Water Resources*, **33**, 2469–2479.
- Chang, L.W., Furst, A. and Fan, A.M. (1998). Metals Toxicology. In: *Encyclopaedia of Environmental Analysis and Remediation*, Vol. 4, pp 2750–2759 edited by Robert A. Myres.
- Charentanyarak, L. (1999). Heavy metal removal by chemical coagulation and precipitation. *Water Science and Technology*, **39**(10–11), 135–138.
- Chiarle, S., Ratto, M. and Rovatti, M. (2000). Mercury removal from water by ion exchange resins adsorption. *Water Research*, **34**(11), 2971–2978.
- Croll, B.T. (1992). Membrane Technology – The Way Forward. *Journal of the Institution of Water and Environmental Management*, **6**(2), 121–129.
- Eiden, C.A., Jewell, C.A., Wightman, J.P. (1980). The interaction of lead and chromium with chitin and chitosan. *J. Applied Polymer Science*, **25**, 1587–1599.

- Gloaguen, V. and Morvan, H. (1997). Removal of metal ions from aqueous solution by modified barks. *Journal of Environmental Science Health*, **A32**, 901–912.
- Gupta, V.K. (1998). Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag. *Industrial and Engineering Chemistry Research*, **37**(1), 192–202.
- Hegdahl, T.F., Gustavsen, F. and Silness, J. (1977a). The structure and mineralisation of the carapace of the crab (*Cancer pagurus* L.). 1 The endocuticle. *Zool. Scripta*, (6), pp. 89–99.
- Hegdahl, T.F., Gustavsen, F., and Silness, J. (1977b). The structure and mineralisation of the carapace of the crab (*Cancer pagurus* L.). 2 The exocuticle. *Zool. Scripta*, (6), pp.101–105.
- Hegdahl, T.F., Gustavsen, F. and Silness, J. (1977c). The structure and mineralisation of the carapace of the crab (*Cancer pagurus* L.). 1 The epicuticle. *Zool. Scripta*, (6), pp. 215–220.
- Kratochvil, D., Pimentel, P.F. and Volesky, B. (2000). *Removal of Trivalent Chromium By A Seaweed Biosorbent*, Department Of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada.
- Kumar, M.N.V. *et al.* (1998). Methods of metal capture from wastewater. In: *Advances in Waste Water Treatment Technologies*, pp. 23–46. Global Science Publishing.
- Lee, M.Y., Park, J.M. and Yang, J.W. (1999). Micro precipitation of lead on the surface of crab shell particles. *Process Biochemistry*, **32**, pp. 671–677.
- Low, K.S. and Liew, S.C. (2000). Sorption of cadmium and lead from aqueous solutions by spent grain, *Process Biochemistry*, **36**, 59–64.
- Mader, C., Sommer, G. and Thurl, S. (1997). Changes in the contents of trace elements lead, cadmium, copper and zinc during beer production. *Monatsschrift Fur Brauwissenschaft*, **50**(7–8), 138–141.
- McKay, G., Ho, Y.S. and Ng, J.C.Y. (1999). Biosorption of copper from wastewaters: a review. *Separation and Purification Methods*, **28**(1), 87–125.
- Muzzarelli, R.A.A. (1973). *Natural Chelating Polymers*, Pergamon Press. pp. 23–80.
- Peniche-Covas, C., Alvarez, L.W. and Arguelles-Monal, W. (1992). The adsorption of mercuric ions by chitosan. *J. Applied Polymer Science*, **46**, 1147–1150.
- Schneider, I.A.H., Rubio, R. and Smith, W. (2001). Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation? *Int. J. Miner. Process.* **62**, 111–120.
- Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters* 3rd Edition. John Wiley & Sons, New York.
- Sturm, K.D. and Hesse, K.J. (2000). Chitin and chitosan: natural polymers from the sea. *Ocean Challenge*, **10**(1), 20–24.
- Volesky, B. and Kratochvil, D. (1998). Biosorption of Cu from ferruginous wastewater by algal biomass. *Water Research*, **32**, 2760–2768.
- Welinder, B.S. (1975). The Crustacean cuticle: III. Composition of the Individual layers in the *Cancer pagurus* cuticle. *Comp. Biochemical. Physiology*, **52A**. 659–663.
- Wheatley, A.D., Smith, M.D., Parr, J. and Muhammad, N. (1998). Microbial uptake of heavy metals in slow sand filters. *Environmental Technology*, **19**, 633–638.
- Yang, T.C. and Zall, R.R. (1984). Absorption of metals by natural polymers generated from seafood processing wastes. *Ind. Eng. Chem. Prod. Res. Dev.*, (23), 168–172.
- Yesmin, S. and Aktay, Y. (2000). Mass transfer and equilibrium studies for the sorption of chromium ions onto chitin. *Process Biochemistry*, **36**, 157–173.