Chitosan for Removal of Mercury from Water*

K. G. RAMACHANDRAN NAIR and P. MADHAVAN
Central Institute of Fisheries Technology, Cochin - 682 029

Chitosan from prawn waste was used for the removal of mercury from solutions. Mercuric chloride solutions containing 250, 500, 1000, 10000 and 1,00,000 ng of Hg^{+2}/ml were treated with chitosan samples of different particle size for different periods. The effect of initial concentration of mercury in the solution, particle size of chitosan and time of treatment on the adsorption of Hg^{+2} were studied. The residual mercury content after treatment for ten min. with chitosan of 40 mesh size from a solution of initial concentration 10,000 ng/ml was 10 ng/ml whereas it was 50 ng/ml for chitosan of larger particle size (10–20 mesh). From solutions of lower concentrations complete removal of mercury was possible by chitosan treatment. Though the particle size and time of treatment have significant effect, the concentration of mercury in solution is more influential on the removal of mercury from solution.

Chitosan is a polymer of 2-deoxy-2-amino D-glucose which can be prepared by deacetylation of chitin present in the exoskeleton of prawns, crabs and lobsters. Methods have already been developed for the extraction of chitin and its conversion to chitosan (Madhavan & Nair, 1974, 1975; Radhakrishnan & Prabhu, 1971). Chitosan has the property of chelation of metal ions and the quantity of metal ions adsorbed varies considerably with different metals (Muzzarelli & Rocchetti, 1974; Muzzarelli & Tubertini, 1969; Madhavan & Nair, 1977; Yoshinari & Subramanian, 1976). Of the different metals studied mercury has shown maximum adsorption by chitosan. The metal binding property of chitosan from prawn, crab and squid were reported earlier (Nair & Madhavan, 1982).

The chlor-alkali plants discharge large quantities of Hg^{+2} from the mercury cells used in the process (Bligh, 1970). The pulp and paper mills also discharge mercury. The aquatic animals from such polluted water have shown to accumulate significant quantity of mercury making them unsuitable for human consumption (Kurland, 1960; Wobeser *et al.*, 1970; Scherer *et al.*, 1975). The permitted level of mercury in drinking water is below 0.001 mg/l (1 ng/ml) (WHO, 1978). Removal of mercury from effluents poses serious problems to industries. The metal binding property of chitosan, if properly made use of, may go a long way in solving this problem.

Materials and Methods

Chitosan prepared from prawn shell waste by the process reported earlier (Madhavan & Nair, 1974) was used. In order to find the effect of particle size of chitosan on the adsorption of Hg^{+2}, chitosan of two different particle size namely, 10–20 mesh and 40 mesh were employed. A solution of Hg^{+2} (1 mg/ml) was prepared by dissolving analar mercuric chloride and the experimental solutions of concentrations 250, 500, 1000, 10,000 and 1,00,000 ng/ml were prepared by dilution. To find the influence of period of treatment and concentration of Hg^{+2} in the solutions 100 ml of the solution was treated with 1 g chitosan of each particle size and the contents were uniformly shaken for 10, 20, 30, 40, 60, 90 and 120 min and filtered through Whatman filter paper No. 1. The residual mercury in the solution was estimated using a Mercury Analyser (MA. 5800 A, Electronics Corporation of India). To investigate the influence of the quantity of chitosan on the residual mercury content different known quantities such as 50, 100,

*Abstract of this paper was presented in the Poster Session of 3rd Indian Convention of Food Scientists and Technologists at Central Food Technological Research Institute, Mysore, 2–4, June 1983

Table 1. *Influence of initial concentration of Hg^{+2} particle size of chitosan and time of treatment on the quantity of mercury adsorbed*

Period min	*Initial concentration of Hg, ng/ml	Residual mercury, ng/ml	
		**Chitosan, 40 mesh	**Chitosan, 10–20 mesh
10	250	Nil	Nil
10	500	Nil	Nil
10	1000	Nil	Nil
10	10000	10	50
20	10000	10	50
30	10000	8	40
40	10000	Nil	30
60	10000	Nil	10
90	10000	Nil	Nil
10	100000	600	2500
20	100000	400	1250
30	100000	350	1200
40	100000	275	1000
60	100000	250	550
90	100000	200	300
120	100000	175	300

*Volume of solution 100 ml
**Quantity of chitosan 1 g

200, 500, 700 mg and 1 g were added to 100 ml solutions containing 10,000 ng/ml and the residual mercury was estimated after 30 min. Also 1, 2, 3 and 4 g were added to 100 ml solutions containing, 1,00,000 ng/ml and residual mercury was estimated after 60 min.

Results and Discussion

There was no residual Hg^{+2} in solution with an initial concentration of 250, 500 and 1000 ng of mercury/ml after 10 min contact with 1 g chitosan. In the case of solution having 10,000 ng, residual mercury ranged from 10 to 50 ng/ml depending on the particle size of chitosan after 10 min whereas this ranged from 175 to 300 even after 2 h in solution having 1,00,000 ng/ml (Table 1).

The particle size of chitosan was also found to influence the rate of adsorption of mercury. In the case of 250 ng, 500 ng, and 1000 ng of mercury/ml there was no residual mercury after treatment for 10 min whereas this was 10 ng/ml in solution of 10,000 ng/ml when treated with chitosan of 40 mesh size for 10 min and 50 ng/ml with chitosan of mesh size 10–20. This difference was very much significant with solution of 1,00,000 ng of mercury/ml (Table 1). So particle size was found to influence the adsorption of Hg^{+2} on chitosan in accordance with earlier observations (Muzzarelli, 1971).

The residual mercury content was related to the chitosan added to the solution. It varied from 300 ng to 40 ng within 1 h, the minimum with 1 g and maximum with 50 mg of chitosan of 10–20 mesh size, the initial concentration being 10,000 ng/ml (Table 2a).

Table 2a. *Influence of quantity of chitosan on the adsorption of mercury from lower concentration*

Initial concentration of Hg^{+2}	10,000 ng/ml
Volume of solution	100 ml
Time of treatment	30 min
Particle size of chitosan	40 mesh

Weight of chitosan mg	Residual Hg^{+2} ng/ml
50	300
100	250
200	150
300	100
500	80
700	70
1000	40

When solution containing 1,00,000 ng/ml of mercury (100 ml) with 1 g of chitosan of 40 mesh size, the residual content was 250 ng/ml after 1 h and it was reduced to 60 ng/ml when treated with 4 g chitosan for the same time (Table 2b). This shows that simple addition of excess amount of chitosan cannot accomplish complete removal of mercury from solution of higher concentration. It can be seen from Table 2b that 100 ml solution of Hg with concentration 1,00,000 ng/ml when treated with 1 g of chitosan for 60 min the residual Hg content has reduced to 250 ng/ml and to 100 ng/ml with 2 g chitosan. But Table 1 shows that 100 ml solutions upto 10,000 ng/ml concentration of Hg treated with 1 g chitosan, the residual Hg is reduced to 10 ng/ml. This shows that the concentration of mercury in solution is more significant than the ratio of chitosan to the total quantity of mercury present in the solution, in the removal of mercury by chitosan.

Table 2b. *Influence of quantity of chitosan on the adsorption of mercury from higher concentration*

Initial concentration of $Hg+^{2}$	1,00,000 ng/ml
Volume of solution	100 ml
Time of treatment	60 min
Particle size of chitosan	40 mesh
Quantity of chitosan g	Residual $Hg+^{2}$ ng/ml
1	250
2	100
3	80
4	60

Again from the same results it can be interpreted that 100 ml solution of concentration 1,00,000 ng/ml when treated with 1g chitosan for 60 min, the residual mercury comes down to 250 ng/ml (Table 2b) and to 175 ng/ml after 120 min (Table 1). But the residual mercury falls to a non-detectable level from 100 ml solution of 250 ng/ml concentration with 1 g of chitosan in 10 min. When these two observations are combined and treatment repeated after one hour, complete removal of mercury is possible with a treatment of 2g chitosan for 70 min which is not achieved by 120 min treatment with 1g of chitosan (Table 1) or 60 min treatment with even 4 g of chitosan. Hence it can be inferred that the concentration of Hg in solution at every stage of treatment is more important in the removal of Hg than the ratio of the total quantity of chitosan used and the total quantity of the $Hg+^{2}$ present in the solution, the time of treatment or particle size, though these factors also have significant effect in the removal of mercury.

The experimental results show that chitosan can be used for complete removal of mercuric salts from water or from industrial effluents. Depending upon the initial concentration of mercury the quantity of chitosan, number and duration of treatment are to be adjusted to enable complete removal of mercury from solutions or industrial effluents.

References

Bligh, E. G., (1970) *Fish. Res. Bd Can.* as referred in "*The Effect of Effluent Components from Chloralkali Plants on Aquatic Organisms.*" A literature review by Linda Gregory-1974–Technical Report No. 228

WHO (1978) *International Standards for Drinking Water.* 3rd Edn., p. 32

Kurland, L. T., Faro, S. N. & Seidler, H. (1960) *Wld. Neurol.* **1,** 370

Madhavan, P. & Nair, K.G.R. (1974) *Fish. Technol.* **11,** 50

Madhavan, P. & Nair, K.G.R. (1975) *Fish. Technol.* **12,** 81

Madhavan, P. & Nair, K.G.R. (1977) *Proc. 1st International Conference on Chitin/Chitosan, Boston, U.S.A.* May, 1977, 444

Muzzarelli, R.A.A. & Rocchetti, R. (1974) *Talenta,* **21,** 1137

Muzzarelli, R.A.A. & Tubertini, o. (1969) *Talenta,* **16,** 1571

Muzzarelli, R.A.A. (1971) *Proc. Krem. Tek. Z. Cong. Copenhagen.* 3, v/3

Nair, K.G.R. & Madhavan, P. (1982) *Proc. 2nd Int. Conf. Chitin and Chitosan, Sapparo,* Japan, July, 1982, p. 187

Radhakrishnan, A.G. & Prabhu, P. V. (1971) *Res. & Ind.* **16,** 265

Scherer, E., Armstrong, F.A.J. & Nowak, S. H. (1975) *Effect of Mercury Contaminated Diet Upon Walleyes,* Stizostedion vitreum vitreum (Mitchill) Technical Rep. 597, *Fish. Mar. Ser. Canada.* p. 4

Wobeser, G., Nielsen, N. O., Dunlop, R. N. Atton, F. M. (1970) *J. Fish. Res. Bd Can.* **27,** 830

Yoshinari, T. & Subramanian, V. (1976) In *'Environmental Biogeochemistry', Vol. 2, Metal Transfer and Ecological Mass Balance,* (Nariagu, J. O., Ed.) Ann Arbor Science Publ. Ann. Arbor