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Removal of Heavy Metals from Water by the Direct Addition of Chitosan Prepared from Prawn and Squilla Shells

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Abstract

Chitosan was prepared from prawn shell (*Fenneropenaeus indicus*) and squilla (*Oratosquilla nepa*) and quality characteristics such as moisture, ash, viscosity and degree of deacetylation were determined. The efficacy of the prepared chitosan to remove heavy metals when directly added to water samples at 1% level was assessed. Water samples with the addition of known quantities of lead, zinc, cadmium, copper and iron and water samples collected from different locations in Vembanad Lake were used in this study. Significant reduction in the concentration of heavy metals was observed after treatment with chitosan. Chitosan from prawn shell was found to be more effective in the removal of heavy metals from water. Treatment with prawn chitosan removed 68% cadmium from spiked samples, whereas squilla chitosan removed 37%. In the case of water samples collected from Vembanad Lake, treatment with chitosan from prawn shell removed approximately 50% of cadmium and the same treatment resulted in removal of lead to non-detectable levels in all the samples.

Introduction

The phenomenal increase in the export of frozen prawn products from India presents the problem of a huge quantity of waste material comprising head and shell, which comes around 100000 tonnes annually on a rough estimate. A negligible portion of this waste is used directly as manure and the rest is being discarded. Direct disposal of such huge quantity of shell waste to water bodies or land often causes environmental problems; a scientific assessment of the impacts of such a large-scale discard is not yet carried out. Apart from prawn, squilla also constitutes considerable portion of trawler catch in certain seasons. *Oratosquilla nepa*, the species of squilla available in Indian water, is not generally used for human consumption because it does not contain much meat and hence almost entire catch is thrown back into the sea.

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An industrial product *viz.*, chitosan can be prepared by processing the waste of prawns, crabs and squilla. Chitosan finds extensive applications in food industries, wound healing, water purification, wine clarification, and photography and textile industries. Radhakrishnan & Prabhu (1971) had studied the preparation of chitosan from prawn waste by different methods for deacetylation of chitin using 50% aqueous KOH and equal volumes of 50% aqueous NaOH and ethyl alcohol. Later, Madhavan & Nair (1975) perfected a method for the preparation of chitosan from prawn waste. Madhavan et al. (1986) reported a modified method for deacetylation of chitin to produce chitosan by treatment with concentrated alkali. The metal binding property of chitosan prepared under different temperature conditions were studied by Madhavan & Nair (1978). Chitosan is a natural chelating polymer with diverse applications for the harmful chemicals and toxic heavy metals (Muzzarelli & Tubertini 1969; Yang 1984).

The content of lead, cadmium, and so on in the effluents from battery and metal plating industry can be reduced by treating the effluents with chitosan (Masri & Randfall 1978). In wastewater treatment, chitosan can also be used as chelating polymer for binding toxic heavy metals (Muzzarelli 1981). The role of chitin to remove Cd was demonstrated by Poirier & Cossa (1981). Chitosan can also be used as an agent to remove harmful chemicals from polluted streams and effluents (Chia 1994). Krishnamurthy & Frederick (2006) suggested that the biopolymers such as chitin, chitosan and modified starch could be used to remove or reduce the concentration of heavy metals from water. Chitosan is an excellent chelation polymer, which can be used for the purification of water intended for handling and processing food products (Das et al. 2003).

Vembanad Lake supports the rich aquatic fauna and the fields around the backwater are suitable for aquaculture. These areas support traditional, seasonal and perennial prawn fishery. The nutrients and pollutants introduced into the estuary control the distribution and abundance of less tolerant species in ecologically sensitive areas in the backwaters to a great extent. Cochin backwaters, considered one of the polluted estuaries in India, receive contaminated freshwater inputs and discharges of effluents and partially treated sewage from many points throughout its tidally mixed zone. The concentration of heavy metals is found to be higher in Cochin region of the lake owing to the discharge of effluents from Eloor industrial belt. The study by Priju & Narayana (2007) suggests that industrial effluents are the major source of metal enrichment (Cu, Ni, Zn and Cd) in the Vembanad lagoon system. Remani et al. (2004) reported that heavy metals such as Cu, Cd, Zn, Ni and Pb are heavily distributed in Chitrapuzha river which drains to the lake.

This study deals with the utilization of chitosan for the removal of heavy metal residues from spiked samples and natural water samples collected from selected locations in Vembanad Lake.

Materials and Methods

Water samples were collected from five different locations of Vembanad Lake *viz.*, Chambakkara, Kumbalangi, Cherai, Chellanam and Marine drive (locations I, II, III, IV and V, respectively). Standard solutions of Cd, Zn, Pb, Fe and Cu of 10 ppm concentration were prepared by diluting the stock solution (Merck, Germany).

Chitosan was derived from the shell of *Fenneropenaeus indicus* and squilla (*O. nepa*) by the method used in the study by Madhavan & Nair (1974). Chitosan powder at 1% level was directly added to the water samples kept at ambient temperature for 30 minutes. The samples were filtered and analysed with atomic absorption spectrophotometer (Varian AA 420, USA) in air-acetylene flame using the respective hollow cathode lamps (AOAC 1990). All the samples were analysed in triplicates, and the average value was noted.

Moisture and ash content were determined (AOAC 1975). Degree of deacetylation was determined by measuring the absorbance of chitosan solution in 1% acetic acid (Muzzarelli & Rochetti 1985) using spectrophotometer (Spectronic Genesys 5, Spectronic Instruments, Inc., Rochester, NY, USA). Viscosity of 1% chitosan solution (1 g of chitosan in 98 g of distilled water and 1 g of glacial acetic acid) was measured with Brookfield viscometer (LV DVE -230, Brookfield, Germany). AR grade acids and reagents were used for analyses.

Results and Discussion

Quality characteristics of chitosan used for this study are given in Table 1. Viscosity of prawn chitosan and squilla chitosan was 314.4 Cp and 213.14 Cp, respectively. Viscosity of prawn chitosan was found to be high compared to that of squilla chitosan. In the study by Thankappan & Madhavan (1995) the viscosity of chitosan obtained from *F. indicus* was 460, whereas in this study it was 314.4 Cp, which could be due to the reduced molecular weight because of the higher degree of deacetylation. The degree of deacetylation of the prawn chitosan (98.4%) was found to be higher than that of the squilla chitosan (75.5%). Ash content of prawn chitosan (0.72%) was also higher than that of the squilla chitosan (0.63%).

The result of treatment of standard water samples with prawn and squilla chitosan is given in Table 2. Prawn chitosan was found to have better capacity to remove heavy metals from the standard water samples compared with squilla chitosan. On treatment with prawn chitosan, maximum reduction (90%) was found in Cu concentration and similar reduction was also found in Zn concentration. When squilla chitosan was used only 50% reduction in Cu was observed. Under the same conditions, only 68% and 36% Cd was removed by prawn chitosan and squilla chitosan, respectively. In general, the retention of heavy metals was double in the case of water samples treated with squilla chitosan. The effectiveness of prawn chitosan in removing heavy metals could be due to the higher degree of deacetylation (Table 1), which increases the binding sites for heavy metals. The free amino groups are abundant in chitosan, where the lone pair electrons of nitrogen bond with transition metal ions. The increase in the number of amino groups increases the capacity of chelation. Chitosan from different sources has different binding ability for heavy metals (Nair & Madhavan 1984; Chui et al. 1996).

Table 1. Quality characteristics of chitosan used for the study

Parameters	Prawn chitosan	Squilla chitosan
Moisture (%)	3.6 ± 0.12	3.2 ± 0.11
Degree of deacetylation (%)	98.4 ± 1.3	75.5 ± 0.8
Viscosity (Cp)	314.4 ± 11.4	213.1 ± 8.5
Ash (%)	0.72 ± 0.01	0.63 ± 0.01

Table 2. Concentration of heavy metals in spiked water samples after treatment with prawn and squilla chitosan

Heavy metal	Initial conc. (ppm)	Concentration after treatment (ppm)	
		Prawn chitosan	Squilla chitosan
Zn	10	1.126	5.261
Fe	10	2.889	5.571
Cu	10	1.027	2.931
Pb	10	2.120	5.90
Cd	10	3.213	6.320

The results of treatment of water samples collected from Vembanad Lake with prawn chitosan are given in Tables 3 and 4. The incidence of heavy metals indicated in two locations *viz*., water sample from locations I and V. The water samples contained all the five metals assessed. It is noteworthy that the sample collected from location V had the highest concentration of the metals under study. Zn was present in all the water samples collected and found to be within the range of 0.0059-0.026 ppm. Fe was found in the range of 0.321-1.242 ppm, which is the maximum among all the heavy metals studied, in all the samples collected from five locations. Cu was detected only in two locations. Substantial quantity of Pb was present in all the samples analysed (0.230-0.790 ppm) and Cd was in the range of 0.123-0.216 ppm.

Table 3. Removal of Zn, Pb and Cd in water samples from selected locations

Locations	Zn conc.(ppm)		Pb conc.(ppm)		Cd conc.(ppm)	
	Initial	After treatment	Initial	After treatment	Initial	After treatment
I	0.008	ND	0.450	ND	0.164	0.089
II	0.019	ND	0.690	ND	0.205	0.100
III	0.026	ND	0.230	ND	0.123	0.070
IV	0.0059	ND	0.703	ND	0.187	0.091
V	0.018	ND	0.790	ND	0.216	0.110

After allowing 30 minutes contact time of chitosan with water samples, Zn and Pb were reduced to non-detectable levels in all the five samples. Similarly, Cu was removed from both the samples to non-detectable level after the treatment. Fe was found in all the water samples and maximum Fe content (1.242 ppm) was found in the water sample collected from location V. The removal rate of iron was found to be varying from location to location. In the case of location I, the retention was 25%, whereas in location II it was approximately 10%. The different adsorption rates in each location could be due to the compositional variations and interactions of chemicals present in the sample. The concentration of Pb was significantly higher in water sample from location V. When treated with chitosan, Pb was reduced to non-detectable levels in all the samples. The concentration of Cd was highest in the water sample from location V. In all the samples studied nearly 50% of Cd was removed after treatment with chitosan.

Table 4. Removal of Fe and Cu in water samples from selected locations

Locations	Fe conc.(ppm)		Cu conc.(ppm)	
	Initial	After treatment	Initial	After treatment
I	0.474	0.103	0.016	ND
II	0.872	0.074	ND	ND
III	0.321	0.019	ND	ND
IV	0.358	0.017	ND	ND
V	1.242	0.233	0.017	ND

Chitosan derived from the shell waste of *F. indicus* was found to be effective compared to other chelating agents in removing heavy metals. Retention of the heavy metals after treatment with chitosan in the water samples was well below the maximum allowable concentration of water to be used in food industry (Table 5). However, 50% retention was observed in case of cadmium in all the samples.

Table 5. Maximum allowable concentration of selected heavy metals in drinking water (Lakshmanan 2007) [*WHO - World Health Organization; #USPHS - United States Public Health Service]

No.	Metal	*WHO (mg/L)	#USPHS (mg/L)
1	Zinc	15	Not exceeding 5
2	Lead	0.05	0.05
3	Cadmium	0.01	0.01
4	Copper	1.5	1
5	Iron	1	0.3

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