

Bioadsorption of Arsenic by Prepared and Commercial Crab Shell Chitosan

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Abstract: The present research investigated the arsenic removal performance of prepared and commercial crab shell chitosan by adsorption filtration method. The ability of chitosan to remove arsenic from prepared arsenic contaminated solution was examined by Atomic Absorption Spectrometry (AAS). It is found that the saturation volume of prepared chitosan for 10 mg L⁻¹ As³⁺/As⁵⁺ solution was 8.55 L and its arsenic removal capacity was 6244.2 mg kg⁻¹. For commercial chitosan, the saturation volume for low and high molecular weight chitosan was 1.3 and 0.45 L and their arsenic removal capacity were 461.8 and 149.5 mg kg⁻¹, respectively. The FT-IR study also confirmed that prepared chitosan's arsenic removal capacity was higher than that of low and high molecular weight commercial chitosan due to the free amino group.

Key words: Chitin, arsenic contamination, groundwater, adsorption filtration, removal capacity

INTRODUCTION

Arsenic contamination in ground waters is now a worldwide problem and often referred to as a 21st century calamity (Mohan and Pittman, 2007). Recently, arsenic pollution has been confirmed in the Argentina, Bangladesh, China, Chile, Canada, India, Japan, Hungary, Mexico, New Zealand, Poland, Taiwan and USA. Among the 23 countries, Bangladesh and West Bengal (India) are in the greatest risk for arsenic contamination in groundwater (Rahman *et al.*, 2005; Van Geen *et al.*, 2003; Chakraborti *et al.*, 2003; Jain and Ali, 2002). Several researches revealed that many millions of people have been exposed to water containing >0.01 mg L⁻¹ As (the WHO guideline value) drawn from alluvial aquifers in the Bengal Basin (Sengupta *et al.*, 2008). It is now suspected that more than 100 million people worldwide ingest excessive amounts of arsenic through drinking water contaminated from natural geogenic sources (Lenny *et al.*, 2008).

People of Bangladesh and West Bengal are totally dependent on groundwater for their drinking to household chores. Skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite and nausea are common diseases where people consume arsenic contaminated water in long term (Kazi *et al.*, 2008; Lin *et al.*, 2008; Lubin *et al.*, 2007; Cantor *et al.*, 2006; Mandal and Suzuki,

2002). On the other hand, acute poisoning causes vomiting, oesophageal and abdominal pain and bloody rice water diarrhoea (Duker *et al.*, 2005; Ng *et al.*, 2003). For this reason, arsenic free water is the crying need for marginalized people who can not afford cost of health in Bangladesh and west Bengal.

In recent years, different types of adsorbing materials such as granular ferric hydroxide (GFH), granular ferric oxide (GFO), activated alumina (AA), modified activated alumina (MAA) and granular titanium dioxide (TiO₂) have been developed and implemented (Westerhoff *et al.*, 2006; Bang *et al.*, 2005; Jing *et al.*, 2005). But very few studies have been done with biopolymer chitosan. Chitosan, a poly-*N*-acetylglucosamine, obtained by the deacetylation of chitin (Crini and Badot, 2008; Orrego and Valencia, 2008; Dambies *et al.*, 2000). After cellulose, chitin is the most common polysaccharide found in the nature extracted from crustacean shells, such as prawns, crabs, insects and shrimps is a white, hard, inelastic, nitrogenous polysaccharide (Xu *et al.*, 2008; Xu-fen *et al.*, 2007; Rinaudo, 2006). Some recent research divulged that natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion concentrations. Chitin and chitosan are considered as natural polymers which have excellent properties such as biocompatibility, biodegradability to harmless products, nontoxicity, physiological inertness, antibacterial properties, heavy metal ions chelation, gel forming properties and

hydrophilicity and remarkable affinity to proteins (Krajewska, 2004; Ravi Kumar, 2000). In addition, Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.9%). Amine and hydroxyl groups on their chemical structures act as chelation sites for metal ions making them useful chelating agent.

Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable (Crini, 2006). Adsorption is evolving as a front line of defense because of its simplicity, ease of operation and handling, regeneration capacity and sludge free operation (Thirunavukkarasu *et al.*, 2003; Nurul *et al.*, 2006). Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement in removing trace element from contaminated water (Dambies *et al.*, 2002). In particular, chitosan can be used as a promising adsorbent for arsenic removal from contaminated ground water as inorganic forms of arsenic most often exist in water supplies. Two forms are common in natural waters: arsenite and arsenate referred to as arsenic (III) and arsenic (V). The present research project is a part of our searching for better and nature based adsorbent that can successfully remove arsenic and reduces the cost of getting clean water for poor people in Bangladesh. Particularly, this project investigated the performance of prepared and commercial high and low molecular weight chitosan in removing arsenic from contaminated water in laboratory condition.

MATERIALS AND METHODS

Sample collection: The present study was carried out from February, 2006 to November, 2007 and crab shell was collected from Bio-Chemical and Seafood Export Co., Dhaka, Bangladesh. Low and High molecular weight commercial chitosan were obtained from Marina Chemicals, Dhaka, Bangladesh and used as received throughout this study without any preliminary purification and further modification.

Isolation of chitin from crab shells: Dehooded crab shells was collected, dried, crushed and decalcified by treatment with 10% HCl, the acid being changed everyday. The dorsal cover of the shell was peeled off on the third day. Its inner layer was removed by rubbing it away with the fingers. Thereafter, the rest of bone was broken into smaller bits. Decalcification was complete in about four days which can be represented in the following reaction.



The resulting chitin protein complex of the dorsal cover was deproteinized by the treatment of 10% (w/v) NaOH at 103 to 105°C in an autoclave. The septa region was deproteinized in six hour treatments under similar conditions.

Preparation of chitosan from chitin: Chitin shells, collected from crab shell were dried and again crushed and boiled successively with very dilute HCl for several hours and then it was filtered in a Buchner funnel. The solid was added to sodium hydroxide (20% aqueous solution) and refluxed for four hours and was filtered. The reaction mass was finally added to the deionized water and was again boiled for several hours. After cooling and washing, it was finally dried at 105°C. The powder thus obtained was boiled with 3 N acetic acid and the solution was cooled and filtered. The resulting slurry was neutralized with 15% KOH solution in a large beaker and the precipitate was then filtrated and thoroughly washed with hot water and deionized water. This resulting chitosan precipitates was dried at 105°C and crushed to optimum particle size (100-200) mesh. The IR spectrum of prepared chitosan was taken in KBr disc.

Column preparation: Three columns were made with 5 g uniformly grained prepared chitosan, low and high molecular weight commercial chitosan that collected from Marina Chemicals, Dhaka, Bangladesh and the prepared 10 mg L⁻¹ As³⁺/As⁵⁺ solution with deionized water was passed through the columns until the break through volume as well as saturation volume of the three materials was reached. Water samples that passed through the columns were collected in the sample bottles after several time intervals. The flow rates of the columns were measured and it was range 3-3.5 mL per minute, respectively. All columns were made by Pyrex glass of length 47 cm and diameter 2 cm and length of all the column materials was 5 cm.

Arsenic detection method: Arsenic analysis was carried out using SHIMADZU model AA-6800 Atomic Adsorption Spectrophotometer (AAS) in Bangladesh Atomic Energy Commission, Dhaka. The AAS was calibrated for the arsenic by running different concentrations of standard solutions. Average values of three replicates were taken for each determination. Analytical conditions for the measurement of arsenic in water using AAS are follows: wavelength (nm) 193.7, Slit (nm) 0.5, lamp current (mA) 12, calibration range (µg L⁻¹) 0.001-0.006 and detection limit (µg L⁻¹) 0.003.

RESULTS AND DISCUSSION

To prepare chitosan it is required to isolate chitin in its pure form. Here, we obtained chitin from crab shells that contain calcium and protein at a large scale. Therefore, extracted chitin remains covered with calcium and even after decalcification and deproteinization treatment several times with HCl and NaOH in reflux condition. It was estimated from the study that about 0.2705 g calcium remained per gram of crab shells.

The IR spectra of chitosan were taken and compared with the IR spectra of chitin. The Infrared spectra clearly showed a marked change due to the removal of acetyl groups from the amino nitrogen. In the IR of chitin and chitosan all the stretching frequencies for the different functional groups were almost same. But the stretching frequency of C = O was missing in the spectrum of chitosan.

Secondary amide in the solid state usually showed the C = O absorption near 1640 cm^{-1} . In the spectrum of chitin there were two strongly perpendicular bands near the frequency at 1652 cm^{-1} . According to the spectrum of chitosan which was obtained from deacetylation of the chitin, the C = O stretching frequency at 1640 cm^{-1} was missing but two bands occurred at 1625 cm^{-1} that is also supported by the study by Shin *et al.* (2001). This band is due to the antisymmetric deformational vibration due to the formation $-\text{NH}_3^+$ because chitin is dissolved in HCl during the reaction. The band appearing at 1521 cm^{-1} may be assigned to the symmetric $-\text{NH}_3^+$ deformational mode. In addition, the IR spectrum of the prepared Chitosan was confirmed from pure Chitosan. The physical and chemical property of the prepared chitosan was compared with the original (97% pure) chitosan and it was observed that this pure chitosan was inactive in both acid and base but the prepared chitosan was slightly soluble in acid and it was basic impurity. Here, CaCO_3 was present in a large scale.

To investigate the arsenic removal efficiency of prepared crab shell chitosan, 10 mg L^{-1} of arsenic solution ($\text{As}^{3+}/\text{As}^{5+}$, 1:1) was passed through the chitosan packed column (5 g) and it was found that the average arsenic adsorbing capacity of prepared chitosan was 52%. The amount of arsenic passed through the prepared chitosan composite is $12008.077\text{ mg kg}^{-1}$ and the amount of arsenic absorbed 6244.2 mg kg^{-1} in Table 1. The earlier studies by Dambies *et al.* (2002) and Chen *et al.* (2008) revealed that modified chitosan gel beads prepared by the molybdate adsorption and coagulation methods showed relatively better performance to remove both states of arsenic though it was more efficient to remove As (V) than As (III). Though the mechanism of the adsorption was not clear enough but it was suggested that the sorption

Table 1: Arsenic ($\text{As}^{3+}/\text{As}^{5+}$ at 1:1 ratio) removing performance by prepared chitosan

Amount of adsorbent (g)	Initial As conc. (mg L^{-1})	Volume passed (L)	Dilution factor	Arsenic conc. (mg L^{-1})	Amount adsorbed (mg)
5	10	0.05	0	0.3820	0.4809
		0.10	0	2.7315	0.3634
		0.50	0	2.1235	3.1506
		1.00	2	5.7181	2.1409
		1.50	2	4.7891	2.6054
		2.00	4	7.0899	1.4550
		3.00	4	6.6375	3.3625
		3.40	4	7.5663	0.9694
		3.60	4	5.4018	0.9196
		3.80	4	5.5137	0.8972
		4.05	4	6.1316	0.9671
		4.30	4	6.6375	0.8406
		4.60	4	6.8475	0.9459
		4.90	4	7.2116	0.9759
		5.25	4	6.4800	1.0560
		5.60	4	6.2300	1.3195
		5.90	4	5.0100	1.7466
6.40	4	8.0620	0.9690		
7.00	4	5.3290	2.5690		
7.55	4	7.8730	1.1698		
8.00	4	7.0560	1.3248		
8.50	4	9.8100	0.0950		

Table 2: Arsenic ($\text{As}^{3+}/\text{As}^{5+}$ at 1:1 ratio) removing performance by low-molecular weight commercial chitosan

Amount of adsorbent (g)	Initial As conc. (mg L^{-1})	Volume passed (L)	Dilution factor	Arsenic conc. (mg L^{-1})	Amount adsorbed (mg)
5	10	0.05	4	6.531	0.1734
		0.10	4	7.182	0.1409
		0.20	4	7.606	0.2394
		0.45	4	8.972	0.2570
		0.70	4	6.608	0.8480
		1.05	4	8.107	0.6625

mechanism is a complexation between arsenate ions and molybdate ions.

However, the arsenic removing performance of the commercial low and high molecular weight chitosan was relatively much lower than that of prepared chitosan. The amount of arsenic passed through the low molecular weight chitosan (LMWC) was $1721.48\text{ mg kg}^{-1}$ and the adsorption was 464.8 mg kg^{-1} in Table 2. Similarly, the amount of arsenic passed through the high molecular weight commercial chitosan was 711.90 mg kg^{-1} and the amount of arsenic absorbed 149.5 mg kg^{-1} in Table 3. The FT-IR spectra of the low and high molecular weight commercial chitosan offered obscure information about the groups, it may be due to the presence of impurity.

To estimate the each adsorption amount of the three chitosan materials, influent (C_0) and effluent (C_e) concentration were calculated and it was observed that initially the adsorption amount of the prepared chitosan was expectedly high and it was gradually decreased over time. However, the adsorption amount was not uniformly decreased with time and a probable reason was that the

Table 3: Arsenic (As^{3+}/As^{5+} at 1:1 ratio) removing performance by high-molecular weight commercial chitosan

Amount of adsorbent (g)	Initial As conc. ($mg L^{-1}$)	Volume passed (L)	Dilution factor	Arsenic conc. ($mg L^{-1}$)	Amount adsorbed (mg)
5	10	0.05	2	4.400	0.280
		0.10	4	7.820	0.109
		0.15	4	7.980	0.101
		0.20	4	8.240	0.088
		0.25	4	8.630	0.680
		0.30	4	8.960	0.052
		0.35	4	9.300	0.035
		0.40	4	9.740	0.013
		0.45	4	9.980	0.001

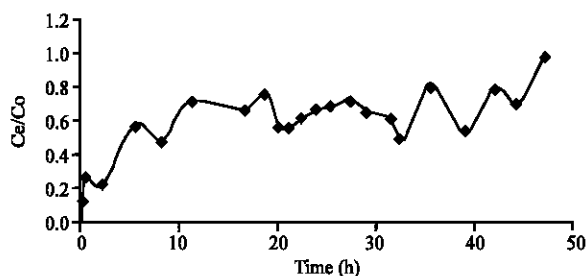


Fig. 1: Effect of prepared chitosan column on arsenic adsorption

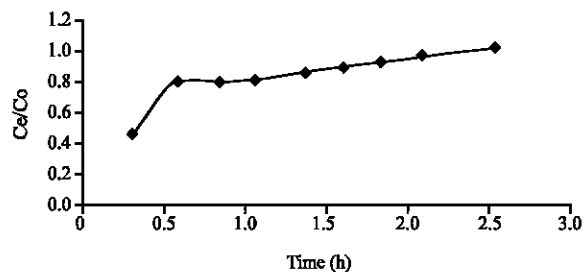


Fig. 2: Effect of commercial high molecular weight chitosan column on arsenic adsorption

passing rate of the prepared arsenic solution through the column was not same. Surface area and contact time also played a vital role for the adsorption of arsenic in prepared and commercial chitosan.

The effect of flow rate was more significant for prepared chitosan than that of high and low molecular weight commercial chitosan. About 48 h was required to reach 100% breakthrough of prepared chitosan (Fig. 1) whereas 2.5 h was required for both high and low molecular weight commercial chitosan (Fig. 2-3). This study revealed that the prepared chitosan required much more time to reach 100% breakthrough point than that of the chitosan bead study by Chen and Chung (2006).

The use of polymer as adsorbents and in particular chitosan is an enormous complicating factor. The shape of the uptake isotherms (Fig. 1-3) showed that the uptake process is a complex one. Simple ion adsorption on the

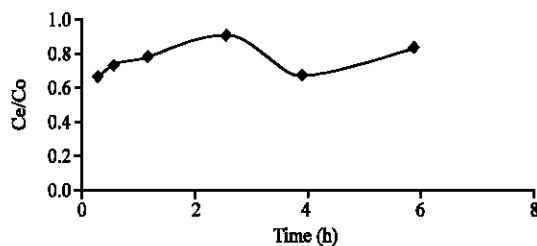


Fig. 3: Effect of commercial low molecular weight chitosan column on arsenic adsorption

chitosan surface does not appear to be the dominant mechanism as is inferred from literature. It is concluded from the previous study where under moderate magnification, metal containing aggregates were observed on the polymer. So, a possible uptake mechanism is the formation of metal-containing nodules on the polymer surface.

Absorption presumably by diffusion of metal ions into the polymer is also playing a part in the total process. Further chitosan embedded or laced with calcium carbonate in the composite materials may create some cryptand sites of right size so that some metals are simply caged at those sites. Thus a combination of nodular formation, cryptand site formation, ion adsorption and ion absorption account for the total uptake. The greater uptake is attributed due to the free amino group of chitosan having its lone pair electrons can act as a specific chemical bonding sites for arsenic ions capable of forming complex ions. Research by Guibal (2004) also confirmed that metal cations can be adsorbed by chelation on amine groups of chitosan in near neutral solutions.

CONCLUSION

Overall, prepared chitosan from crab shell exhibited efficient arsenic removal in adsorption filtration methods whereas low and high molecular weight commercial chitosan showed least performance due to impurity and incomplete deacetylation process. From these findings, it is suggested that prepared crab shell chitosan can be used as a promising bioadsorbent for removing arsenic.

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