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Highly Deacetylated Chitosan as Low-cost Adsorbent Material for Removal of Heavy Metals from Water

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Authors' contributions

This work was carried out in collaboration between all authors. Author ABO designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors ABO and OW managed the analyses of the study. Author ABO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Background and Aim: Chitin, a naturally occurring polysaccharide was isolated from the shells of crabs. The chitin was chemically modified to give alkali chitin, carboxymethyl chitin, highly deacetylated CM chitosan and highly deacetylated chitosan. The highly deacetylated chitosan was used as an adsorbent for removal of heavy metals from surface and groundwater samples collected from Lagos metropolis.
Experimental: The process was performed by using chitosan to reduce the concentration of heavy metals from the water samples by packing a column with the chitosan in a burette. 100 ml of the water samples were passed through the packed column and 2.5 ml of concentrated nitric acid was added to the filtrate in a 250 ml beaker. The mixture was evaporated on a hot plate to about 20 ml. The filtrate was transferred to a 100 ml volumetric flask and it was diluted to the mark and mixed thoroughly. A portion of the digested samples was taken for required metal determination using Atomic Absorption Spectroscopy.

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Results: The heavy metal adsorption capacity of the deacetylated chitosan was assessed by running surface and groundwater samples through a column packed with deacetylated chitosan. The percentage removal of Pb, Cd and Cu from the water samples was as follows; lead in the borehole (57%), lagoon (39%), well water (8%). cadmium in borehole (80%), lagoon (43%), well water (54%) and copper in borehole (61%), lagoon (44%) and well water (0%).
The chemical integrity of the chitin derivatives was confirmed through IR studies.

Keywords: Chitin; chitosan; heavy metals; adsorbent; FTIR; AAS.

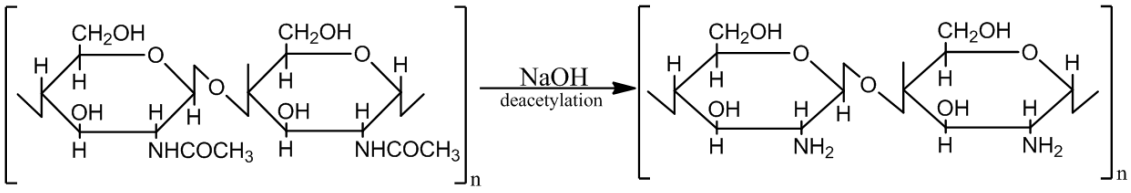
1. INTRODUCTION

Chitosan and its derivatives are examples of value-added materials. They are produced from chitin, which is a natural carbohydrate polymer found in the skeleton of crustaceans, such as crab, shrimp. Chitosan is a polymer obtained from deacetylation of chitin [1]. Chitosan is a natural, non-toxic, copolymer composed of N-acetyl-D-glucosamine and D-glucosamine unit. It is obtained in three different ways, these are; thermochemical deacetylation of chitin in the presence of alkali, by enzymatic hydrolysis in the presence of a chitin deacetylase, or naturally found in certain fungi as part of their structure [2].

Chitosan has an amine functional group which strongly reacts with metal ions, considerable research has been done on the uptake of metal cations by chitosan. The amine group on the chitosan binds metal cations at pH close to neutral. At low pH, chitosan is more protonated and therefore able to bind anions by electrostatic attraction [3].

The main parameters influencing the characteristic of chitosan are its degree of deacetylation and molecular weight. Deacetylation describes a reaction that removes an acetyl functional group from the molecular chain of chitin. When the degree of deacetylation of chitin reaches 50% depending on the origin of the chitin, it becomes soluble in aqueous acidic media and is called chitosan. The solubilization occurs by protonation of $–NH_2$ functional group on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic medium. The degree of deacetylation can be employed to differentiate between chitin and chitosan because of free amino groups in the polysaccharides.

Chitosan is biopolymer of high molecular weight. Like its composition, the molecular weight of chitosan varies with the raw material sources and the method of preparation. In general, high temperature-dissolved oxygen and shear stress can cause degradation of chitosan. For example, at a temperature over 280°C thermal degradation occurs and polymer chains rapidly breakdown thereby lowering molecular weight. Also, maximal depolymerization is caused by utilization on of high temperature or concentrated acids such as hydrochloric acid followed by acetic acid and sulphuric acid results in molecular weight changes with minimal degradation with the use of EDTA [4]. Chitosan can chelate five to six times greater concentrations of metals than chitin [5]. Metals mainly occur in the earth's crust, however, urbanization and industrialization lead to their release into the biosphere where they have become part of the air, soil, water, and biota. As a consequence of metabolic similarity of toxic metals with non-toxic elements they can cause negative effects on human and plants. Some metals such as copper and zinc are essential micro-nutrients although they are also toxic in higher concentration



Scheme 1. Chitin deacetylation

[6]. On the other hand, other metals such as cadmium, lead, arsenic and mercury can damage numerous biochemical pathways even at low concentration [7]. One half of the world's population lives now in urbanized areas, hence are subjected to the effect of toxicity caused by these elements, which presents a serious issue for public health. In the light of this, heavy metals are metals having a density greater than 5 g/cm^3 [8]. This classification includes transition metals and higher atomic weight metals of group III to V of the periodic table. The term 'heavy metals' originate with reference to the harmful effects of cadmium, mercury and lead, all of which are denser than iron. Various treatment technologies employed for the removal of heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption [9]. Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. The adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent and is reversible and the adsorbent can be regenerated [9].

The purpose of this study is to evaluate the efficiency of highly deacetylated chitosan as adsorbent for the removal of heavy metals from water.

2. MATERIALS AND METHODS

The materials used for the research work were crab shells obtained from Makoko fish market located at Adekunle in Yaba, Lagos State, the chemicals used were of analytical grade, water samples from three different locations and the instruments used for characterization; FTIR and Atomic Absorption Spectrophotometer . The crab shells were cleaned and scraped under running water. The washed crab shells were dried for ten days at room temperature. The water samples were collected by immersing the cans below the water surface for the surface and well water samples and directly from the tap for the borehole. The water samples were tightly capped and refrigerated until the analysis commenced.

2.1 Sample Sites/ Location Description

Sample	Source	Location
1	Borehole water	Solous, Isheri, Lagos State.
2	Lagos Lagoon	Bordering University of Lagos, Lagos State.
3	Well water	Bariga, Lagos State.

2.2 Isolation of Chitin

The shells obtained from the crabs were dried for ten days. The dried crab shells were crushed and 100g of the pulverized shells were weighed into a 1000ml beaker and treated in boiling Sodium hydroxide (4% $^{v}/_{v)}$ for one hour in order to dissolve the proteins and sugars. After boiling, the beaker was removed from the hot plate and allowed to cool for 30 minutes at room temperature. After cooling, 1% HCL was prepared and used to soak the boiled crab shells in a 250ml beaker for 24 hours. The HCL was decanted after 24 hours.

2g of NaOH was weighed in 100ml of water to obtain 2% NaOH, after which 50ml was measured from the prepared 2% NaOH and added to the demineralized shells which were boiled for one hour to decompose protein to water-soluble amino acids. The chitin obtained was washed with distilled water and allowed to air dry.

2.3 Preparation of Highly Deacetylated Chitosan

100 ml of 40% sodium hydroxide was prepared by weighing 60g of sodium hydroxide flakes in 90ml of water. 50g of chitin was weighed and put in a round bottom flask and the dissolved sodium hydroxide was added to the sample.

150ml of isopropan-2-ol was added to the above mixture and reflux first for 8 hours after which the degree of deacetylation was checked by taking the IR spectrum.

The spent sodium hydroxide and isopropan -2-ol solution in the flask were decanted and fresh 100 ml of 40%$^{w}/_{w}$ NaOH and 100 ml of isopropan-2-ol were added to the chitosan in the flask. The content was allowed to reflux for further 10 hours after which the reaction was stopped.

The chitosan was washed with water containing 0.5 g of EDTA to chelate all metal ions present. It was further washed with bidistilled water and then with methanol and air dried.

2.4 Adsorption

The process was performed by using chitosan to reduce the concentration of heavy metals from the water samples by packing a column with the chitosan in a burette. 5 ml of concentrated nitric acid was added to 200 ml of the water samples in a 250 ml beaker. The mixture was evaporated on a hot plate to about 20 ml. The filtrate was transferred to a 100 ml volumetric flask and it was diluted to the mark and mixed thoroughly. 100 ml of the water samples were passed through the packed column and portions of the digested samples were taken for required metal determination using Atomic Absorption Spectroscopy.

3. RESULTS

Chitin from the crabs used for the research was obtained in good yield of 67% and 79%. Calibration curves were obtained using a series of varying concentrations of the standards for the three metals. In this study, the concentration of Pb, Cu, and Cd were successfully determined in the water samples by AAS technique.

Table 2 shows the level of the metals in the studied water samples. The results stated here in the table are those obtained for the concentration of Lead, Copper, and Cadmium in the digested water samples using AAS method.

Table 1. Correlation coefficient for metal ions

Metal ions	Pb^{2+}	Cu^{2+}	Cd^{2+}
Method of analysis	AAS	AAS	AAS
Correlation coefficient	0.9746	0.9934	0.999

The effect of pH in this research was due to the rupture of the internal hydrogen bonds caused by a swelling of chitosan, followed by the protonation of the amino group with water as a proton donor [5].

$$\text{Chitosan} -NH_2 + H_2O \rightleftharpoons \text{Chitosan-}NH_3^+ + OH^-$$

In addition, chitosan acts as a weak base. At low pH, amino group of the chitosan takes the proton available in the water sample according to;

$$\text{Chitosan} -NH_2 + H^+ \rightleftharpoons \text{Chitosan-}NH_3^+$$

This reduces the concentration of H^+ ions and raises the pH of the solution thereby improving the adsorption performance of chitosan.

Table 2. Concentration of metal ion in water samples obtained by AAS (untreated water)

Sample	pH	Pb^{2+} (mg/L)	Cu^{2+} (mg/L)	Cd^{2+} (mg/L)
Borehole water	3.9	6.19	0.28	0.20
Lagoon water	7.4	4.52	0.18	0.07
Well water	6.7	4.15	0.12	0.13

Table 3. Concentration of heavy metal ion in sample after treatment with Chitosan

Sample	pH	Pb^{2+} (mg/L)	Cu^{2+} (mg/L)	Cd^{2+} (mg/L)
Digested Chitosan Borehole Water	10.95	2.68	0.11	0.04
Digested Chitosan Lagoon Water	10.21	2.74	0.10	0.04
Digested Chitosan Well Water	10.68	3.82	0.12	0.06

N.B: the percentage removal of Lead from the water samples is in the order of Borehole > Lagoon> Well Water. The Percentage removal of Cadmium from the water sources is in the order of Borehole water>Well Water>Lagoon. The Percentage removal of Cadmium from the water samples is in the order of Borehole water>Lagoon>Well water

Table 4. Maximum permissible level of metal ion in drinking water

Metal	SON (mg/L)	WHO (mg/L)
Pb	0.01	0.01
Cd	0.003	0.003
Cu	2	1

(W.H.O 2007)

Comparing Tables 2 and 4, Pb (Borehole water (Solous) 6.19), (Lagoon 4.52),(Well water 4.15) and Cd (Borehole water (Solous) 0,20),(Lagoon 0.07), (Well water 0.13) are higher than the permissible level in drinking water by SON (Pb 0.01), (Cd 0.003) and WHO (Pb 0.01), (Cd 0.0030) and that of Cu (Borehole water (Solous) 0.207, Lagoon 0.175, Well water 0.123) are below the allowable standards of SON for Cu is 2 and WHO for Cu is 1 [10]. The water samples may not be declared as being totally safe for drinking due to the risk of bioaccumulation in the human body. The high concentration of these metals can be attributed to leaching from the dumpsite close to the Borehole (Solous). The high concentration of Pb, Cu and Cd comes from industries that empty effluents into the Lagoon and also the burning of refuse at the dumpsite. Therefore, the use of chitosan as an adsorbent to reduce the concentration of Pb, Cu and Cd are shown in the Tables.

3.1 FTIR Analysis

The chemical integrity of chitosan was determined using infra-red spectroscopy. The functional groups present in chitosan were determined using infra-red spectroscopy. Three main absorption bands were identified in the sample.

The band in the range of 3695-2500 cm^{-1} corresponds to the vibration of OH, NH, and CH groups, the complex band in the range of 1657.9 - 1400 cm^{-1} corresponds to absorption of carbonyl and amide groups (Amide I band at 1641.95 cm^{-1} and Amide II band 1550 cm^{-1}); the strongest absorption band at 861.16 cm^{-1} is characteristic of the glycosidic linkage of the chitosan which matches the reported result in Fig. 1.

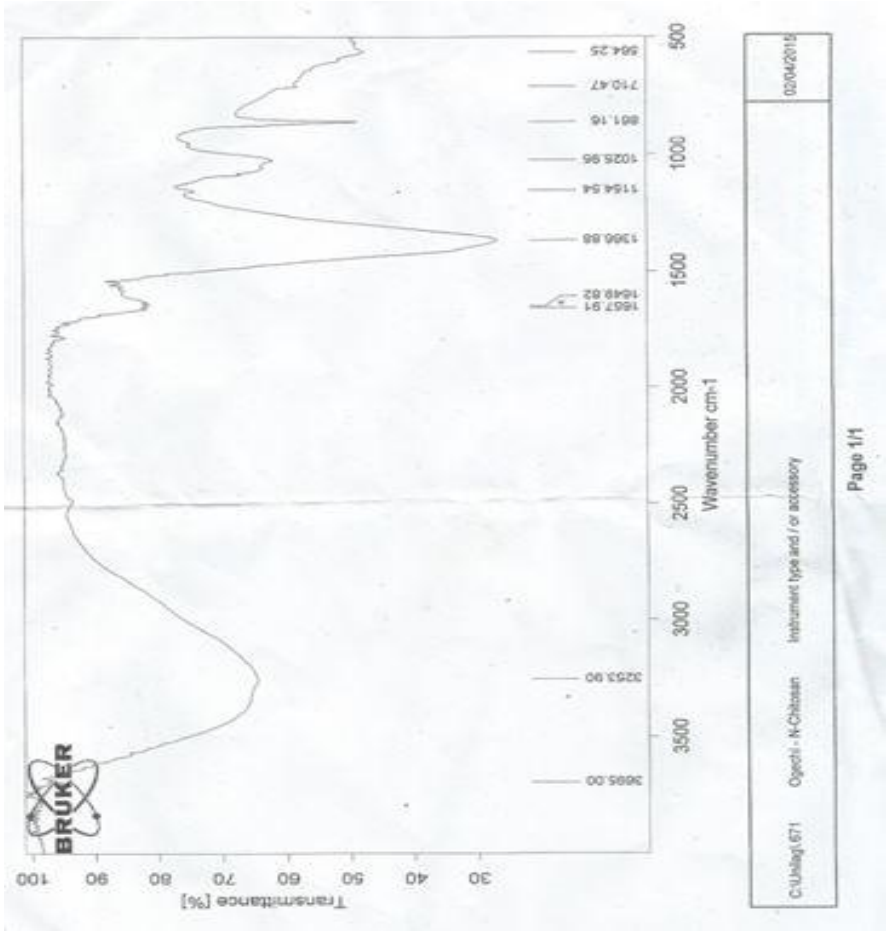


Fig. 1. The characterization of the chitosan using IR spectrum

4. DISCUSSION

The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. For this purpose, various techniques are evolved which include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flocculation, flotation and electrochemical methods. It is evident from several literature surveys that ion-exchange, adsorption and membrane filtration are the most common way in wastewater management system [11]. Amongst all these process adsorptions shows the better potential in the removal of waste heavy metals from the water. The utility of several biopolymers may ensure the removal of the waste products from the water. The study of Wang et al., *2010* give such impact of adsorption of amino-functionalized $Fe_3O_4@SiO_2$ magnetic nanoparticles, that ensures effective and recyclable adsorbant quality which remove heavy metal ions from water [12] but comparatively unfeasible than that of Chitosan which is technically much more feasible. Study of Babel *et. al*., 2003 emphasizes that chitosan (815, 273, 250 mg/g of Hg^{2+}, Cr^{6+}, and Cd^{2+}, respectively), zeolites (175 and 137 mg/g of $Pb^{2+}$and Cd^{2+}, respectively), waste slurry (1030, 560, 540 mg/g of Pb^{2+}, Hg^{2+}, and Cr^{6+}, respectively), and lignin (1865 mg/g of Pb^{2+}) are high adsorbent capacity containing substances, more precisely in the treatment of inorganic heavy metals [13].

5. CONCLUSION

A review of various processes and adsorbents for heavy metal removal shows that adsorption process has great potential for the elimination of heavy metal from water sample using the crab shell Chitosan as a low-cost biopolymer adsorbent. In addition, the study concluded that the use of Chitosan for heavy metal removal appears to be technically feasible, eco-friendly and with high efficacy. However, further studies are needed to unveil the complete removal mechanism of Chitosan for heavy metals.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Renge VC, Khedkar SV, Pandey Shraddha V. Removal of heavy metals from wastewater using low cost adsorbents: A review. Scientific Reviews and Chemical Communications. 2012;2(4):580–584.
2. Amuda OS, Adelowo FE, Ologunde MO. Kinetics and equilibrium studies of adsorption of chromium(VI) ion from industrial wastewater using *Chrysophyllum albidum* (Sapotaceae) seed shells. Colloids and Surfaces B: Biointerfaces. 2009;68:184-192.
3. Guibal E. Interaction of metal ions with Chitosan- based Sorbent. A review Separat. Purificat. 2004;38:43-74.
4. Muzzarelli RAA. Analytical Chim Acta. 1997;69:35.
5. Salam OEA, Reiad AN, ElShafei MM. A study of removal characteristics of heavy metals from wastewater by low-cost adsorbents. Journal of Advanced Research. 2011;2:297–303.
6. Deniz B, Merve H, Sermin E. Evaluation of lead removal onto black cumin by using multi linear regression. BALWOIS 2012 - Ohrid, Republic of Macedonia. 2012;1-6.
7. Aderinola OJ, Clarke EO, Olarinmmoye, OM, Kusemiju V, Anatekhai MA. Heavy metals in surface water, sediments, fish and periwinkles of Lagos lagoon. American –Eurasian J. Agric. & Environ. Sci. 2009;5(5):609-617.
8. Evans JR, Davids WC, MacRae JD, Amirbahman A. Kinetics of cadmium uptake by chitosan- based crab shells. Water Res. 2002;36:3219-3226.
9. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management. 2011; 92(3):407–418.
10. WHO. Pharmaceutical Use. In: Quality Assurance of Pharmaceuticals: A Compendium of Guidelines and Related Materials. 2nd Updated Edn. World Health Organisation, Geneva. 2007;2:170-187.
11. Fenglian Fu, Qi Wang. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management. 2011;92:407-418.

12. Jiahong Wang, Shourong Zheng, Yun Shao, Jing liang Liu, Zhaoyi Xu, Dong Qiang Zhu. Amino-functionalized Fe_3O_4@SiO_2 core–shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. 2010;349(1):293-299.

13. Sandhya Babel, Tonni Agustiono Kurniawan. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials. 2003;B97:219–243

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