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Development and Application of Chitosan Extracted from Crab Shell for Water Purification

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ABSTRACT

The properties of chitosan enable it to attach itself to a variety of organic contaminants (bacteria, algae, urea and sweat), minerals metals and oils. Chitosan, therefore, drastically increases the effectiveness of filtration systems, being sand or decent ridges which normally cannot capture fine particles and dissolved pollutants. Crab shell was collected from Rivers State in southern part of Nigeria and characterized using XRF and Chitosan was extracted from it using the conventional method of pretreatment, demineralization, HCl deproteinizationand NaOH deacetylation and also the chitosan was characterized using XRF, SEM, and FTIR. Results obtained from XRF shows that CaO is in high percentage of 88.74%, CeO_2 in low percent of 0.01% and Al_2O_3 0f 2.2% in crab shell after the Chitosan characterized Al_2O_3 increases to 7.7% while CaO decreases to 85.49%. The FTIR spectra of the chitosan gave characteristic band 0f 3433.41 cm^{-1} for –NH2 and 1647. 41cm^{-1} for carbonyl group and the SEM shows non smooth space in the morphology of the chitosan indicating high degree of deacetylation. The prepared chitosan was used at different dosage and contact time in Gubi Dam raw water treatment some physical, chemical and microbial properties of the water were analyzed before and after purification and was found to be a good coagulant/ flocculant aid and disinfectant.

Key words: Chitosan, Deacetylation, Demineralization, Deproteinization.

1.0 INTRODUCTION

Chitosan is a natural polymer that is abundant, easily obtained, renewable and is second to cellulose (Badawy and Rabea, 2011). It is commonly found in the cell walls of most fungi and some algae. It exists in several zygomycetes species in its deacetylated form; it is referred to as chitosan. The degree of deacetylation is one of the most important chemical characteristics which could influence the performance of Chitosan in many of its application; in addition the degree of deacetylation determines it content of free amino groups which play an important role in water purification (Dutta, 2004). Chitosan is produced by the thermo chemical deacetylation of chitin (The principal industrial source of chitin is shells of shrimps, lobsters and crabs). Chitosan has favourable biological properties such as biodegradability, biocompatibility and non toxicity. It was found to improve the fluidity of powdery mixtures and has satisfactory adhesive property and good industrial applications such as lubricant, disintegrant, thickening, stabilizing and suspending agent in pharmaceutical, textile and paper industries (Fernandez-Kim, 2004). It is also a chelating agent for the removal of harmful metals in industrial and nuclear wastes, and a support for ion exchange, chelation and affinity chromatography (Kannan, 2010).

Water is one of the essential items needed for survival of living things and growth. It also maintains an ecological balance between various groups of organisms and their environment. Heavy metals are widely used in industries like paint, textile, steel fabricating industries etc. These industries discharge large quantities of toxic wastes and the untreated effluents from these industries when discharge into bodies of water without proper purification cause water pollution. A wide range of physical and chemical processes for the removal of these pollutants from such water, such as coagulation, ultrafilteration, adsorption, ion exchange, reverse osmosis, oxidation, ozonation are used to ensure proper treatment. Among these, the coagulation method has proven to be an excellent method to remove pollutants from contaminated water due to its advantages over other processes (Fernandez-kim, 2004). Turbidity in water is caused by suspended matter, such as clay, silt, finely divided organic and inorganic

matter, soluble colored organic compounds, and plankton and other microscopic organism. Turbid water has muddy or cloudy appearance and it is aesthetically unattractive. The turbidity increases as sewage becomes stronger (Abdelaal *et al.*, 2005).

The history of the use of natural coagulant for water purification is long. Natural organic polymers have been used for more than 200 years in India, Africa and China as effective coagulants and coagulant aids at high turbid water (Bodrezor *et al*, 2003). They may be manufactured from plant seeds, leaves, roots and animals remain. Natural coagulants have bright future and are concerned by many researchers because of their abundant source, low price, and environmentally friendly, multifunction and biodegradable nature in water purification.

The aim of this research was to extract chitosan from crab shell and investigate its effectiveness for water treatment.

The objectives of this research were;

i. Characterization of crab shell using X-ray spectroscopy,
ii. Extraction of chitin from the crab shell and it conversion to chitosan,
iii. Characterization of the produced Chitosan,
iv. Treatment of Gubi Dam raw water using prepared chitosan.

2.0 METHODOLOGY

The extraction of chitosan from crab shell waste includes crab shell waste collection and purification, Deprotinization, Demineralization and Deacetylation. These processes are discussed as follows:

2.1 Crab shell waste collection and preparation

The Crab shell waste was collected from Rivers state of southern part in Nigeria. It was thoroughly washed with tap water to remove unwanted materials; this was then dried for 24 h at 65 ^{o}C in an oven until constant weight. The dried shell was crushed using a laboratory mortar and pestle to increase the surface area and stored in an air tight container ready for use.

2.2 Deprotinization

50 g of the crushed shell was deprotinized in a 250 ml beaker by the addition of 0.62 M boiled NaOH for 1 h to dissolve out protein and sugar present. (Fernandez-Kim, 2004).

2.3 Demineralization

25 g of the deprotinized sample was deminaralized by soaking for 24 h in 100 ml of 0.68 M HCl. This was achieved to remove $CaCO_3$ from it. The deminaralized sample was then treated with 50 ml of 0.60 M $NaOH_{aq}$ for 1 h. Thus, albumen decomposed into water soluble amino acid leaving behind, chitin as residue, which was washed with deionized water and dried.

2.4 Deacetylation

The deacetylation process was done to remove acetyl group from chitin by adding 75 ^{o}C 100 ml of 25 M concentration of NaOH to the deminaralized sample (Chitin) and boiled at for 2 h on a hot plate and then placed under a hood and cooled for 30 min at room temperature. After which the sample was washed continuously with water and filtered, solid matter which was chitosan retained. The chitosan was left uncovered and oven dried for 24 h.

3.0 WATER PURIFICATION

The water purification included raw water sample collection, Jar test, physical, chemical and microbial analysis of the raw and purified water which can be discussed as follows:

3.1 Raw Water Sample Collection

Gubi Dam raw water was sample from raw water unit of Gubi water treatment plant for analysis before and after purification.

3.2 Jar Test

Jar test was conducted on Gubi Dam raw using a flocculator to determine the optimum dose of Chitosan needed for the purification that will give desired properties of the treated water for human consumption.

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3.3 Physical properties analysis of raw and chitosan treated water

The physical properties (Turbidity, Colour and temperature) of water were determined by the use of photometer 7100 model, thermometer, and turbidity meter respectively.

3.4 Chemical properties of raw and treated water

Chemical properties (Nitrate and Arsenic) of the treated and untreated water were determine using photometer 7100 model.

3.5.5 Microbial property

This is an important property to consider in drinking water before consumption to ensure good health of lives; the microbial properties considered are faecal and coliform bacteria.

4.0 RESULT

The results for the characterization and for treated and treated water were presented below

Table 1: XRF for Oxide Analysis of Crab Shell

Metallic oxides	Percentage Composition
Al_2O_3	2.20
P_2O_5	5.31
SO_3	0.41
CaO	88.70
TiO_2	0.12
MnO	0.19
Fe_2O_3	0.24
Ag_2O	1.30
ln_2O_3	0.74
BaO	0.27
CeO_2	0.01
Tm_2O_3	0.43
Lu_2O_3	0.08
Total	100.00

Table 2: XRF for Prepared Chitosan Showing Oxide Composition

Metallic oxides	Percentage composition (%)
Al_2O_3	7.70
CaO	85.47
TiO_2	0.02
MnO_2	0.17
Fe_2O_3	0.12
Y_2O_3	4.80
Ag_2O	1.44
BaO	0.10
CeO_2	0.02
SmO_3	0.03
YbO_3	0.06
LuO_3	0.07
Total	100.00

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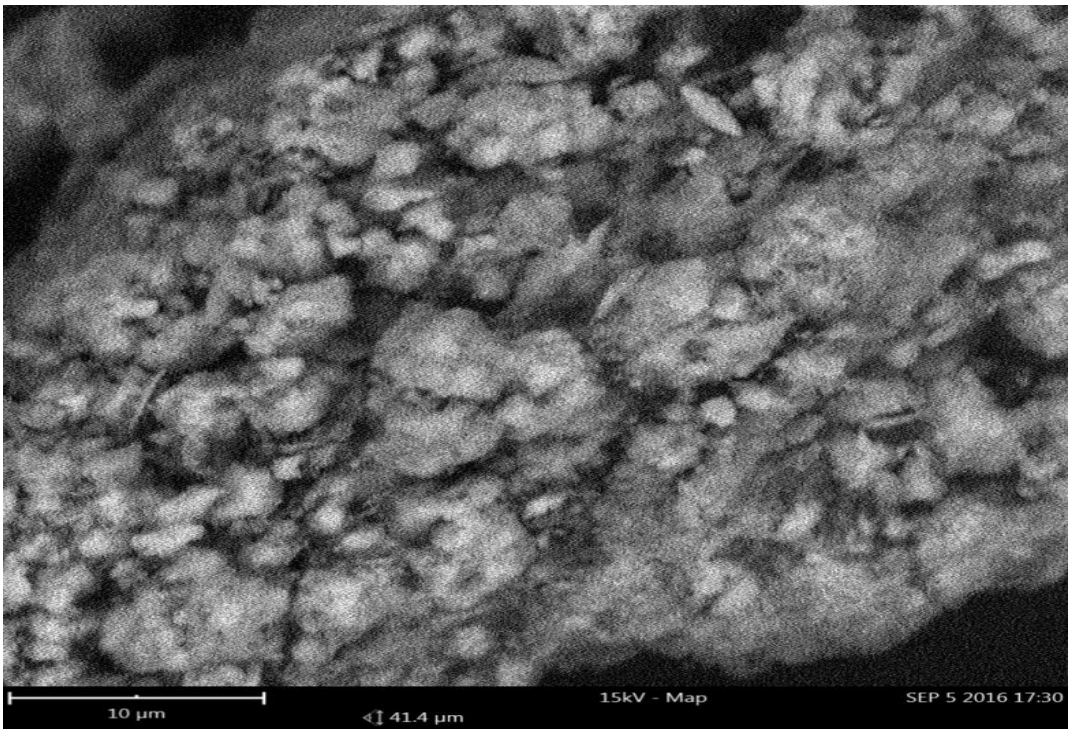

Figure 1: Scanning Electron Microscope of Chitosan

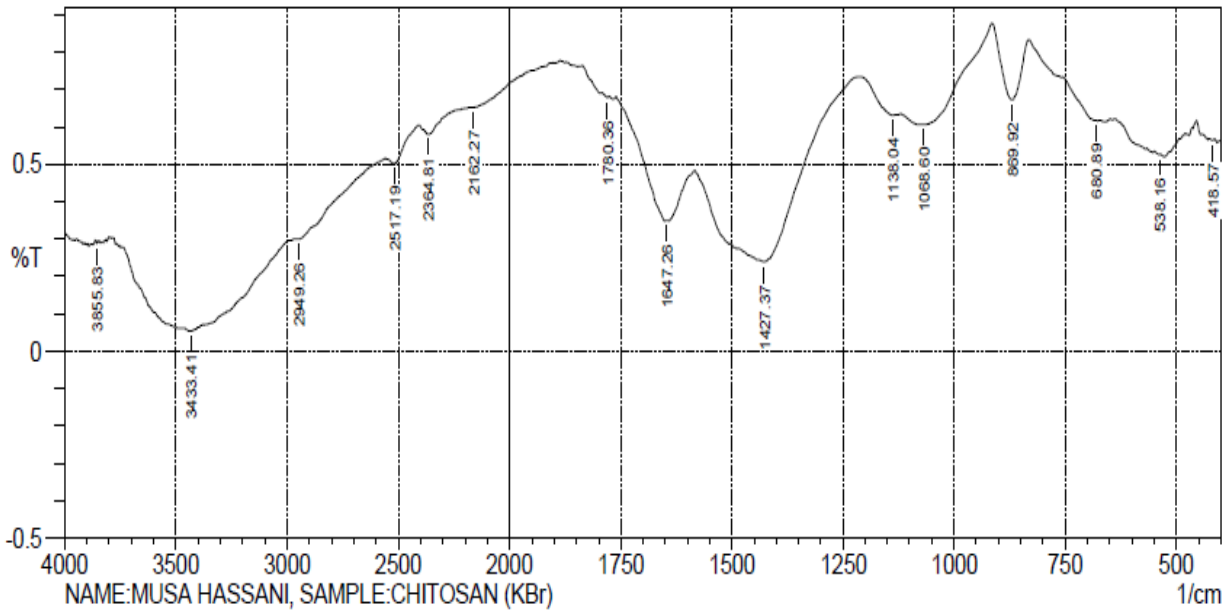

Figure 2: Fourier Transform Infrared of Chitosan

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Table 3: Comparison of Properties of Water for Different Dosages of Chitosan at 10 Minutes Contact Time.

Parameters	Units	Raw water	Maximum permitted value	Chemically treated water	0.5g chitosan dose	1.0g chitosan dose	1.5g chitosan dose	2.0g chitosan dose	2.5g chitosan dose
Colour	TCU	45	15	0.00	25	5	5	0	0
Turbidity	NTU	2.53	5	0.44	1.91	1.74	0.20	0.08	0.06
Tempt.	^{o}C	27.5	Ambient	30	28.0	28.2	28.1	28.2	28.2
Copper	mg/l	0.08	1	0.04	0.00	0.00	0.00	0.00	0.00
Arsenic	mg/l	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
NO_2	mg/l	0.67	50	0.20	0.48	0.19	0.17	0.17	0.15
Flouride	mg/l	0.85	1.5	0.15	0.37	0.24	0.24	0.24	0.20
Ph		7.15	6.5-8.5	7.25	7.25	7.32	7.33	7.35	7.35
Total Coliform Bacteria	cfu/ml	89	10	5	20	13	0	0	0
Total faecal bacteria	cfu/ml	15	0	0	7	0	0	0	0

Table 4: Comparison of Properties of Water for Different Dosages of Chitosan at 15 Minutes Contact Time.

Parameters	Units	Raw water	Maximum permitted value	Chemically treated water	0.5g chitosan dose	1.0g chitosan dose	1.5g chitosan dose	2.0g chitosan dose	2.5g chitosan dose
Colour	TCU	45	15	0.00	23	4	5	0	0
Turbidity	NTU	2.53	5	0.44	1.90	1.72	0.20	0.07	0.06
Temperature	^{o}C	27.5	Ambient	30	28.1	28.3	28.1	28.2	28.2
Copper	mg/l	0.08	1	0.04	0.00	0.00	0.00	0.00	0.00
Arsenic	mg/l	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
NO_2	mg/l	0.67	50	0.20	0.48	0.180	0.17	0.17	0.14
Flouride	mg/l	0.85	1.5	0.15	0.36	0.22	0.21	0.21	0.15
pH		7.15	6.5-8.5	7.25	7.31	7.32	7.34	7.35	7.35
Total Coliform Bacteria	cfu/ml	89	10	5	16	10	0	0	0
Total faecal bacteria	cfu/ml	15	0	0	5	0	0	0	0

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Table 5: Comparison of Properties of Water for Different Dosages of Chitosan at 20minutes Contact Time

Parameters	Units	Raw water	Maximum permitted value (NIS)	Chemically treated water	0.5g chitosan dose	1.0g chitosan dose	1.5g chitosan dose	2.0g chitosan dose	2.5g chitosan dose
Colour	TCU	45	15	0.00	23	3	5	0	0
Turbidity	NTU	2.53	5	0.44	1.80	1.71	0.20	0.04	0.04
Temperature	^oC	27.5	Ambient	30	28.2	28.3	28.1	28.2	28.3
Copper	mg/l	0.08	1	0.04	0.00	0.00	0.00	0.00	0.00
Arsenic	mg/l	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
NO_2	mg/l	0.67	50	0.20	0.47	0.18	0.17	0.17	0.13
Flouride	mg/l	0.85	1.5	0.15	0.35	0.20	0.20	0.19	0.14
pH		7.15	6.5-8.5	7.25	7.30	7.33	7.34	7.35	7.35
Total Coliform Bacteria	cfu/ml	89	10	5	16	9	0	0	0
Total faecal bacteria	cfu/ml	15	0	0	4	0	0	0	0

Table 6: Effect of Contact Time on Water Properties Removal at Optimum Dose of Chitosan.

Time (minute)	Colour (TCU)	Coliform bacteria (cfu/ml)	Faecal bacteria (cfu/ml)
0	45	89	15
2	35	20	7
4	30	10	5
6	5	7	0
8	0	0	0
10	0	0	0

5.0 DISCUSSION OF RESULT

This section discusses the results obtained which were shown in section 4.0. The results are that of preliminary analysis (XRF, SEM, and FTIR) and water analysis.

5.1 X-ray fluorescence (XRF) analysis

The XRF analysis was used to determine the composition of each element and it corresponding oxide present .Table 1 and 2 shows the oxide composition of the crab shell and chitosan respectively. The oxide composition of the crab shell and the chitosan produced from the result it was found that the percentage composition of Al_2O_3 which is one of the active oxides in water coagulation increased from 2.2% in Crab shell to 7.7% in Chitosan as a result of demineralization of the crab shell during the process of producing the chitosan (Cuero, 2000).

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5.2 Scanning electron microscope (SEM) analysis

Scanning electron microscope (SEM) is a type electron microscope that produced images of a sample by scanning it with a focused beam of electrons. Figures 1, present SEM micrograph illustrating the morphology of chitosan prepared after HCl acid demineralization and NaOH deacetylation. Under electron microscope examination, Chitosan showed non homogeneous and non-smooth surface as a result of deacetylation which removed some bonding and exposing more sheaths in the Chitosan and shrinkage which corresponds to the SEM morphology of extracted Chitosan as reported by Monaral *et al.* (2011).

5.3 Fourier transforms infrared (FTIR) analysis

Fourier transform infrared (FTIR) is a technique which is used to obtain an infrared spectrum absorption or emission of a solid, liquid or gas. An infrared spectrometer simultaneously collects high spectral resolution data over a wide spectral range. FTIR characteristics of the chitosan was performed with FTIR-8400S instrument with a frequency range of 4000 to 500 cm^{-1} it is clearly seen from Figure 2 that the absorption patterns of the spectrum is similar to that of the literature and suggesting good quality of chitosan biopolymers has been obtained. Detailed examination of the spectrum reveals that the spectra have characteristics bands for chitosan and all assignment to peak will be made according to Coates (2000).

The spectra was observed to have a band located at 650.80 cm^{-1} indicating the stretching vibration of alkynes (C-H), which are more evident in the chitosan spectrum (Kumar *et al.*, 2015). Absorption band at 860.92 cm^{-1} was assigned to C-C stretching, at 1068.60 cm^{-1}, the absorption was assign to skeletal C-C vibration, while 1138.04 cm^{-1} was assigned to C-N secondary amine and 1427.37 cm^{-1} was assign to C=C aromatic ring carbonate ion. 1647.26 cm^{-1} represent stretching vibration of the carbonyl C=O, 1780.36 cm^{-1} was assigned to open chain acid and hydride and 2162.81 cm^{-1} assigned to C=C group. Other characteristic absorption for chitosan is at 2717.19 cm^{-1} assigned to C-H and 2949.26 cm^{-1} assigned to C-H stretching of aliphatic compound and 3433.41 cm^{-1} indicating the bending vibration of $-NH_2$.

5.4 Water Analysis

Tables 3, 4 and 5 in shows the result of the properties of the raw water, chemically treated water and chitosan treated water at 10, 15 and 20 min contact time respectively and. From these results, it was found that the chitosan performed well in removing the properties of water for all the dosages chosen when compared with the Nigerian Industrial Standard (NIS) values.

At 10 min contact time, the chemical used in treating the raw water performed better than the chitosan dosage of 0.5 and 1.0 g for the removal of colour, turbidity, NO_2, fluoride, and total coliform bacteria while at optimum dosage of 2.0g the Chitosan performed better than the chemical in removing, turbidity, copper, NO_2, and total coliform bacteria (Shanmugapriya *et al.*, 2011).

At 15 min contact time, the chitosan used at 1.5, 2.0 and 2.5 g dosage in treating the raw water performed better in removing colour, turbidity, copper, NO_2, fluoride coliform bacteria and faecal bacteria than chemical treatment while chemically treated water was better than 0.5 and 1.0 g dosed chitosan treated water.

The lower dose of chitosan was because of its high degree of deacetylation of 80.80% and the Al_2O_3 of 7.7% as illustrated in Table 2. The increase in pH was due to the sodium hydroxide used during deacetylation, as the mass of chitosan increased there was little increase in pH of the water. The nitrogen in the amino group acts as an electron donor and is presumably responsible for selective chelation with metal and neutralize the surface charge of the colloidal materials present in water to form flocs which result in adjusting the properties of water to desired value that make water portable for human consumption. Less sludge was produced compared with alum at equivalent dose but however the sludge formed by Chitosan was crystalline in nature due to the crystalline form of the Chitosan.

Table 4 shows the effect of contact time against percentage removal on some properties such as colour, faecal bacteria and coliform bacteria of the chitosan treated water, as the contact time increases the rate of removal increase with is to that of work reported by (Bodrezor *et al*, 2003). Colour decrease from 45 to 35 CTU at 2 min while at 8 min there was total reduction to 0 min, for coliform bacteria the reduction at first 2 min was from 89 to 20 cfu/ml indicating effectiveness in water purification and optimum reduction was achieved at 8 min similar to that colour while faecal Bacteria there was reduction from 15 to 7 cfu/ml at the first 2 min and the total reduction was achieved at 6 min.

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6.0 CONCLUSION

Base on the experimental results obtained in this research work, the following conclusions were drawn.

1. Crab shell was characterized using XRF both elemental and oxide were analyzed and found to contain 88.74 % of calcium oxide and 2.2 % Al_2O_3.

2. Chitin was extracted from crab shell and converted to chitosan using HCl demineralization and NaOH deacetylation.

3. Chitosan was characterized using XRF, SEM, and FTIR. It was found to contain 7.7 % Al_2O_3 and non smooth surface, indicating high degree of deacetylation.

4. The prepared chitosan was tested for water purification and found to be a good coagulant/flocculants aid at optimum dosage of 2.0 g and worked perfectly as disinfectant.

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