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Isolation and characterization of selected biopolymers from Maize Cobs and Crab Shells obtained in Niger State, Nigeria

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Abstract

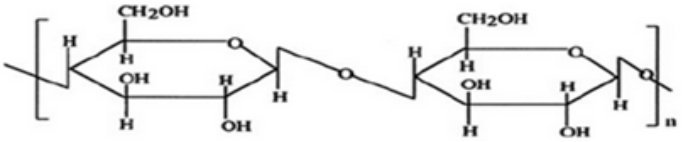
Cellulose, chitin and chitosan are widely spread biopolymers in nature. These biopolymers have economic significance due to their wide applications in industries and biomedicine. They can be locally sourced in abundance from agricultural wastes. In this study, cellulose and chitin as biopolymers were isolated from maize cobs and crab shells respectively via simple techniques. The isolated chitin was processed into the more valuable material (chitosan) by deacetylation process. The three isolated biopolymers were characterized by using X-ray diffraction and Fourier transform infrared spectroscopy (FTIR). XRD analysis indicated the crystalline nature of the chitin and chitosan and also showed that the isolated cellulose is amorphous in nature. The FTIR spectra displayed the peaks corresponding to the characteristic functional groups (O-H, C-H and C=O) common to the prepared biopolymers. It can be concluded that maize cobs and crab shells can be chief sources of cellulose and chitins and this can assist in reducing the environmental pollutions caused by the indiscriminate discarding of these local waste materials.

Keywords: Biopolymer, characterization, maize cobs, crab shells.

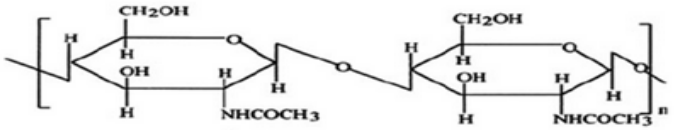
Introduction

Biopolymers are heavy biomolecules consisting of covalently connected repeating monomeric units produced by living organisms[1]. The fact that biopolymers are biodegradable, non-toxic and have renewable sources makes them possesses economical advantages over synthetic non-renewable polymers and are usually engaged as starting materials in the production of numerous value-added materials[2]. These biopolymers have various *uses* in industries like veterinary, foods, wood and paper, fibres and clothes, cosmetic and pharmaceutical[3]. Previous studies have shown that these polymers can be obtained from numerous sources using different techniques[4,5]. Among the naturally available biopolymers, cellulose, chitin and chitosan are the most abundant on earth[6]. Cellulose is found in plant cell wall in a form of nanofibrils[7], while chitin and chitosan are present in shells and tissues of some marine animals, insects and fungi[8]. Cellulose; chitin and chitosan serve as skeleton systems in plants and marine animals respectively[9]. Cellulose when nitrogenated becomes chitosan, although both polymers are reported to be linear semi-crystalline in nature[10]. Cellulose macromolecules consist of repeat anhydroglucose units while those of chitin and chitosan are built from amino partially substituted anhydroglucose (Figure-1).

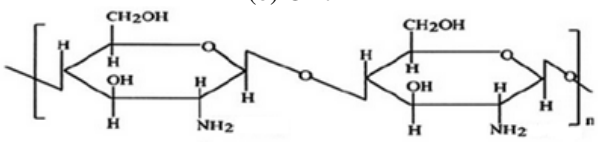
Annually, serious environmental challenges are posed by huge quantities of these biopolymers in the form of agricultural wastes generated and indiscriminately discarded without adequate exploitation of their worth for wealth creation[11]. These agricultural wastes which includes maize (stem and cobs) and crab shells are among the available sources of cellulose; chitin and chitosan obtained in large quantities as major wastes locally and from food industries. Exploiting local sources which are abundant and less expensive for the production of biopolymers can be a smart approach to alleviate the cost related issues on large scale production of these biopolymers. In view of this, this study utilized maize cobs and crab shells as agricultural wastes to produce cellulose, chitin and chitosan via simple and cheap means.



(a) Cellulose



(b) Chitin



(c) Chitosan

Figure-1: Chemical structures of (a) cellulose, (b) chitin and (c) chitosan.

Materials and methods

Materials: Maize cobs were collected from local farmlands somewhere in Korokpa, Paiko, Nigeria during the last dry season of the year 2018. Crab shells were obtained from local fish markets at New Bussau, Nigeria. Sodium hydroxide, hydrochloric acid, sodium hypochlorite, sulphuric acid and distilled water of analytical grades were used in this study.

Samples preparation: The maize cobs were weighed, cut with a kitchen knife and sun dried for five (5) hours. The sun dried cobs was pulverized using mortar and pestle to produce powdered cobs. The crab shells were carefully washed with distilled water to remove impurities. The washed shells were sun-dried for two weeks, ground using mortar and pestle and sieved using a 2.0 mm sieve for easy extraction. The ground samples were stored in opaque glass bottles for further use.

Preparation of cellulose: To prepare cellulose, 100g of the powdered maize cobs was treated with 50cm^3 of a 1M of sodium hydroxide for 30 minutes to remove lignin. The mixture was filtered using cotton cloth to obtain slurry, which was in turn further treated with 250cm^3 of 1 M sulphuric acid to digest the slurry at 80°C for an hour and subsequently filtered to give a residue that was carefully washed with distilled water and bleached using 3.2% w/v of sodium hypochlorite for 20 minutes at 80°C, washed with distilled water until neutral pH to produce the cellulose. This cellulose produced was air dried for 48 hours.

Preparation of Chitin: The preparation of chitin from the ground crab shells was carried out via two main stages of extraction: deproteinization, and demineralization. For the deproteinization, 5g of crab shell was treated in 250cm^3 beaker using 100 cm^3 1.25M NaOH for 3 hrs at room temperature, after which the mixture was allowed to settle; remnant sodium hydroxide was removed using deionized water until neutral pH. Filtration was done using Whatmann filter paper No 4 and the residue was oven dried at temperature of 80 ^{0}C for 45 minutes to obtain deproteinized crab shells.

The dimerialization was carried out by heating 3 grams of the deproteinized crab shells using 100cm^3 1.25M HCl for 5hrs at temperature of 80^{0}C in 250cm^3 conical flask. After heating, the mixture was left to cool and settle; excess HCl was separated by decantation. The residue washed using deionized water to neutral pH and subsequently filtered using Whatmann filter paper No 4. The residue obtained was oven dried at 80^{0}C for 45 minutes to obtain chitin.

Preparation of Chitosan: To prepare chitosan, 1g of the chitin in 100cm^3 beaker was deactylated using 0.5M of NaOH for 2 hrs at temperature of 100^{0}C. Thereafter, the mixture was allowed to cool and settled; excess NaOH removed by decantation. The residue was washed with deionized water to neutral pH, filtered using Whatmann filter paper No 4 and oven dried at 80^{0}C for 45 minutes to produced chitosan.

Characterization of the prepared Biopolymer samples: The Fourier transform infrared (FT-IR) spectrum of the prepared chitin, cellulose and chitosan samples were determined using a Frontier FT-IR Perkin Elmer, UK over the range of 4000-400 cm^{-1} in order to determine the key functional groups available. The phase structures of the prepared chitin, cellulose and chitosan samples were examined using X-ray diffractometer (XRD)-6000 Shimadzu Scientific Instruments.

Results and discussion

FTIR spectra of cellulose, chitin and chitosan are shown in Figure-2. The absorption peaks were observed in two wave number region of 3500-2500cm^{-1} and 1750-500cm^{-1}. The existence of absorption bands on the respective spectrum of the biopolymer samples correspond to the characteristic bands of polymer matrix of chitin, cellulose and chitosan[12]. From the Figure-2, the peak at 3338cm^{-1} is typical for stretching vibration of the -OH group alongside molecular hydrogen bond vibrations in cellulose[12]. The peak at 2905cm^{-1} is ascribed to C-H stretching vibration of all hydrocarbon components in polysaccharides[13]. Usual peaks attributed to cellulose were noticed in the region of 1600–1000cm^{-1}. The peak observed at 1591cm^{-1} matches the vibration of moisture molecules absorbed in cellulose[14]. The absorption peaks at 1415, 1321, 1050, 1023 cm^{-1} and 900cm^{-1} correspond to the stretching and bending vibrations of -CH_2 and -CH, -OH and C-O bonds respectively in cellulose. The peak at about 1415cm^{-1} determines the crystalline arrangement of the cellulose, while the peak at 900cm^{-1} is attributed to the amorphous state in cellulose[15].

The IR spectrum of the prepared chitosan shown in Figure-2 illustrates important absorption peaks to recognize the typical functional groups in the chitosan. From the figure, the stretching vibrations of -OH bond of the prepared chitosan was found at 3257cm^{-1} [16] and that for C–H was observed at 2892cm^{-1} [17]. The absorption peaks at 1632cm^{-1} and 1409.97cm^{-1} could be associated with the presence of the N-H in-plane bend and O-H deformation in-plane respectively[18]. The peaks at 1009cm^{-1} could be assigned for symmetric stretching of C–O–C bridge of O-H groups[19], while the 684cm^{-1} bands could be due amines wagging[20].

The crab chitin showed a weak band at about 1632cm^{-1} which corresponds to the N-H out-planes of amides[21]. The bands at 1429cm^{-1} and 1050cm^{-1} are ascribed to the respectively C-C and C-O stretching[22]. The band at 2932cm^{-1} could be attributed to the stretching of C–H[23]. The broad band at 3337cm^{-1} corresponds to the superimposed N-H and O-H stretching[24].

X-Ray Diffraction (XRD) pattern of the Extracted Chitosan: The phase structures of the isolated biopolymers (cellulose, chitin and chitosan) were studied using x-ray diffractometer and the XRD patterns are displayed in the Figure-3. X-ray diffractogram of cellulose shows one significant diffraction peak at 2θ angle of 20.17^0 with a corresponding crystal plane as

(002), this is in agreement with the result reported for cellulose by Park[25]. From the Figure-2, the XRD pattern of chitosan showed significant diffraction peaks centered at 2θ of 12.56^0 and 19.30^0 with a corresponding crystal planes as (002) and (101) respectively[26].

Figure-3 shows the XRD pattern of the isolated chitin with two characteristic peaks at 2θ of 12.67^0 and 19.20^0 which were assigned (020) and (110) miller indices. This diffraction peaks matched well with chitin powder[27]. The other peaks on the diffractogram of chitin and chitosan may be attributed to impurities originated from micro-molecules that formed the components of these polymers[28].

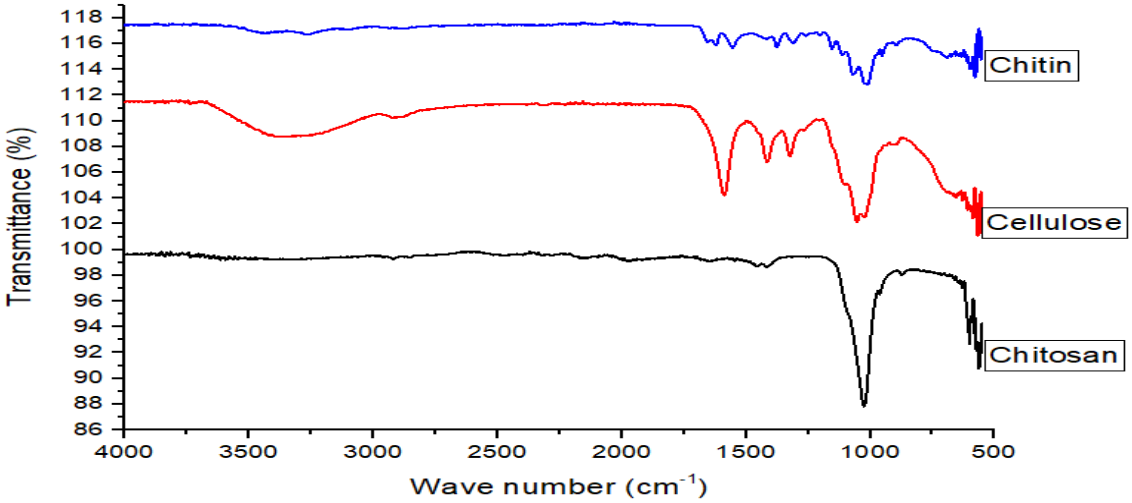


Figure-2: FTIR spectra of isolated cellulose, chitin and chitosan.

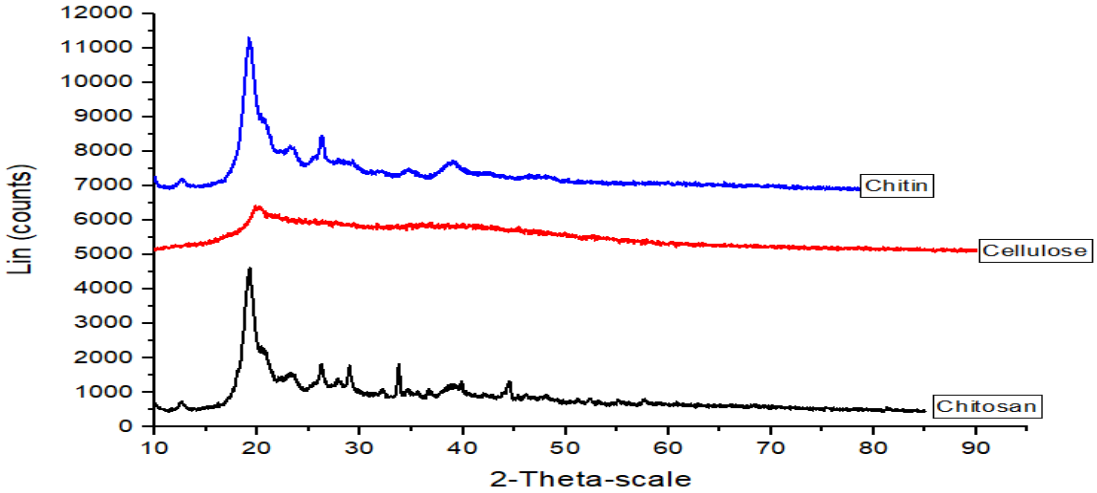


Figure-3: X-ray diffractogram of chitin, cellulose and chitosan.

Table-1: Crystallinity Index of the prepared Biopolymers.

Biopolymers	Peak position (2θ)	Counts	Intensity	d-spacing (A^0)
Cellulose	20.17	1711/5.2	329	4.399
Chitin	12.67	797/6.2	129	6.982
	19.20	4851/8.9	545	4.619
Chitosan	12.56	732/5.8	126	7.006
	19.30	4414/5.3	833	4.639

However, the diffractogram pattern of the cellulose sample (Figure-3) shows that the cellulose isolated in this study is more amorphous and less crystalline compared to chitin and chitosan[27]. This may be attributed to the existence of more hydrogen bonds[28]. Replacement of secondary hydroxyl group by amino group in chitosan and acetylamino group in chitin leads to shifts of the diffraction peaks to smaller angles (Table-1) and thus, result in the increase of intensity of peaks and d-spacing typical of crystalline lattice of biopolymers[29].

Conclusion

This work establishes the feasibility of isolating cellulose, chitin and chitosan from maize cobs and crab shells respectively. The results of XRD characterization of the isolated materials indicate that the cellulose prepared is amorphous in nature while chitin and chitosan are semi-crystalline in nature with the crystallinity of the chitin higher than that of the chitosan. The FTIR spectra of the prepared biopolymers confirmed the presence of the characteristic absorption bands of O-H, N-H, CH, C-O and C-C which conform to their chemical structures. The biopolymers obtained from the aforementioned local sources could be employed in a variety of applications.

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References

1. Dassanayake R., Acharya S. and Abidi N. (2018). Biopolymer-Based Materials from Polysaccharides: Properties. Processing, Characterization and Sorption Applications. 10.5772/intechopen.80898.

2. Maghchiche A. (2019). A Review: Application of Biopolymers in the Pharmaceutical Formulation. 10.5281/zenodo.2577643.

3. Shokri J. and Adibki K. (2013). Application of Cellulose and Cellulose Derivatives in Pharmaceutical Industries. *Cellulose-Medical, Pharmaceutical and Electronic Applications*. Doi: 10.5772/55178.

4. Vroman I. and Tighzert L. (2009). Biodegradable Polymers. *Materials*, 2, 2, 307-344. Doi: 10.3390/ma2020307.

5. Bano I., Arshad M., Yasin T., Ghauri M.A. and Younus M. (2017). Chitosan: A potential biopolymer for wound management. *International journal of biological macromolecules*, 102, 380-383. 10.1016/j.ijbiomac.2017.04.047.

6. Peter N.C., Ryan W., Vivek S.B., Jason K., Ashutosh M., Gregg T.B., Stephen R.D., Michael E.H. and Michael F.C. (2019). Nanomechanics of cellulose deformation reveal molecular defects that facilitate natural deconstruction. *Proceedings of the National Academy of Sciences of the United States of America*, 116, 20, 9825-9830. Doi.org/10.1073/pnas.1900161116.

7. Elieh-Ali-Komi D. and Hamblin M.R. (2016). Chitin and Chitosan: Production and Application of Versatile Biomedical Nanomaterials. *International journal of advanced research*, 4(3), 411-427.

8. Younes I. and Rinaudo M. (2015). Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Marine drugs*, 13(3), 1133-1174. Doi: 10.3390/md13031133.

9. Benabid F.Z. and Zouai F. (2016). Natural Polymers: Cellulose, Chitin, Chitosan, Gelatin, Starch, Carrageenan, Xylan and Dextran. *Journal of Natural Products*, 4, 348-357.

10. Kumar S., Smith S.R., Fowler G., Velis C., Kumar S.J., Arya S. and Cheeseman C. (2017). Challenges and opportunities associated with waste management in India. *Royal Society Open Science*, 4(3), 160764. doi:10.1098/rsos.160764.

11. Ezeonu C.S., Tagbo R., Anike E.N., Oje O.A. and Onwurah I.N. (2012). Biotechnological tools for environmental sustainability: prospects and challenges for environments in Nigeria-a standard review. *Biotechnology Research International*, 450802. doi:10.1155/2012/450802.

12. Turki A., Oudiani A., Msahli S. and Faouzi S. (2018). Infrared Spectra for Alfa Fibers Treated with Thymol. *Journal of Glycobiology*. 07. 10.4172/2168-958X.1000130.

13. Popescu M., Froidevaux J., Navi P. and Popescu C. (2013). Structural modifications of Tilia cordata wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy. *Journal of Molecular Structure*, 1033, 176-186. 10.1016/j.molstruc.2012.08.035.

14. Majid N.A.A., Bakar S.M.K., Fadzly R.N.F., Ismail M.R. R., Norhamidi M. and Muhammad A. (2016). Influence of alkaline treatment and fiber loading on the physical and mechanical properties of kenaf/polypropylene composites for variety of applications. *Progress in Natural Science*, *Materials International*, 26, 6, 657-664.

15. Park S., Baker J.O., Himmel M.E., Parilla P.A. and Johnson D.K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology for Biofuels*, 3, 10. Doi: 10.1186/1754-6834-3-10.

16. Ji N., Qin Y., Xi T., Xiong L. and Sun Q. (2017). Effect of chitosan on the antibacterial and physical properties of corn starch nanocomposite films. *Starch-Stärke*, 69(1-2), 1600114. doi.org/10.1002/star.201600114.

17. Lefatshe K., Muiva C.M. and Kebaabetswe L.P. (2017). Extraction of nanocellulose and in-situ casting of

ZnO/cellulose nanocomposite with enhanced photocatalytic and antibacterial activity. *Carbohydrate polymers*, 164, 301-308. 10.1016/j.carbpol.2017.02.020.

18. Sambo R.E., Nuhu A.A. and Uba S. (2019). Preparation and Characterisation of Shrimp Waste-Derived Chitin, Chitosan and Modified Chitosan Films. *Nigerian Research Journal of Chemical Sciences*, 6, 213-230.

19. Talari A.C.S., Martinez M.A.G., Movasaghi Z., Rehman S. and Rehman I.U. (2017). Advances in Fourier transform infrared (FTIR) spectroscopy of biological tissues. *Applied Spectroscopy Reviews*, 52(5), 456-506.

20. Amado A.M., Fiuza S.M., Batista de Carvalho L.A. and Ribeiro-Claro P.J. (2013). On the relevance of considering the intermolecular interactions on the prediction of the vibrational spectra of isopropylamine. *Journal of Chemistry*, 2013. doi.org/10.1155/2013/682514.

21. Kumirska J., Czerwicka M., Kaczyński Z., Bychowska A., Brzozowski K., Thöming J. and Stepnowski P. (2010). Application of spectroscopic methods for structural analysis of chitin and chitosan. *Marine drugs*, 8(5), 1567-1636. 10.3390/md8051567.

22. Singh G., Faruk A. and Bedi P.M.S. (2018). Spectral Analysis of Drug Loaded Nanoparticles for Drug-Polymer Interactions. *Journal of Drug Delivery and Therapeutics*, 8(6), 111-118. Doi.org/10.22270/jddt.v8i6.2030.

23. Motschulsky S., Liu J.S., Lina Y., Chushu Z., Jie B., Feng Z., Mingjing Q., Chen J. and Qingli Y. (2012). Extraction and Characterization of Chitin from the Beetle. *Holotrichia parallela, Molecules*, 17, 4604-4611. Doi: 10.3390/molecules17044604.

24. Bagchi S., Falvo C., Mukamel S. and Hochstrasser R.M. (2009). 2D-IR experiments and simulations of the coupling between amide-I and ionizable side chains in proteins: application to the Villin headpiece. *The Journal of Physical Chemistry. B*, 113(32), 11260-11273. Doi: 10.1021/jp900245s.

25. Park S., Baker J.O., Himmel M.E., Parilla P.A. and Johnson D.K. (2010). Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnology Biofuels*, 24(3), 10. Doi: 10.1186/1754-6834-3-10.

26. Li L.H., Deng J.C., Deng H.R., Liu Z.L. and Xin L. (2010). Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes. *Carbohydrate research*, 345(8), 994-998. Doi: 10.1016/j.carres.2010.03.019.

27. Ding F., Shi X., Jiang Z., Liu Li., Cai J., Li Z., Chen Si. and Du Y. (2013). Electrochemically stimulated drug release from dual stimuli responsive chitin hydrogel. *Journal of Material Chemistry B*., 1, 1729-1737. 10.1039/C3TB00517H.

28. Kumirska J., Czerwicka M., Kaczyński Z., Bychowska A., Brzozowski K., Thöming J. and Stepnowski P. (2010). Application of spectroscopic methods for structural analysis of chitin and chitosan. *Marine drugs*, 8(5), 1567-1636. 10.3390/md8051567.

29. Ioelovich M. (2014). Crystallinity and hydrophility of chitin and chitosan. *J. Chem*, 3(3), 7-14.