



SINCE 2013

NAAS SCORE : 4.32
(2017 to 2020)

SJIF 2020 = 6.618

IPI Value 2019: 1.90

IPI Value 2020: 1.90

IPI Value 2021: 2.53

Received on:

26th February 2022

Revised on:

10th March 2022

Accepted on:

15th March 2022

Published on:

1st April 2022

Volume No.

Online & Print

36

Page No.

01 to 11

IRJC is an international open access print & online journal, peer reviewed, worldwide abstract listed, published quarterly with ISSN, Free-membership, downloads and access.

APPLICATION OF CELLULOSE CONTAINING LABILE CATIONIC GROUP IN REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTION

ALIYU DANMUSA MOHAMMED^{1*} AND

ANSAR BILYAMINU ADAM²

¹DEPARTMENT OF CHEMISTRY, UMARU MUSA YAR'ADUA UNIVERSITY, PMB 2218, KATSINA, KATSINA STATE NIGERIA

²DEPARTMENT OF CHEMICAL SCIENCE, FEDERAL UNIVERSITY WUKARI, TARABA NIGERIA.

Corresponding author email: aly27moh27@gmail.com

ABSTRACT:

Chemical modification of cellulose was successfully carried out using different amounts of sodium tripolyphosphate. Cellulose was extracted using 2% sodium hydroxide and 10% H₂O₂ solution from the stem of *Calotropis procera*, the stem was dried after which the lignin content was removed. Incorporation of sodium tripolyphosphate (STTP) on the cellulose matrix, showed an increase in thickness and size of the cellulose microfibrils. The absorption band appeared at 1287 cm⁻¹ in the Fourier transform infrared spectroscopy (FTIR), and is attributed to P=O stretching of the modified cellulose. Scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD) analyses were used to characterize the modified cellulose. The results of adsorption for the following heavy metals were found to be 71.43 mg/g, 41.84 mg/g for Pb²⁺, Cu²⁺ respectively. The adsorption equilibriums data satisfactorily fitted Langmuir isotherm equation better than Freundlich isotherm. The study indicates that the modified cellulose could be used as adsorbent for the removal of Pb²⁺ and Cu²⁺ ions from aqueous solution.

KEYWORDS: Cellulose; Cross linking; Heavy metal, microfibrils; Sodium tripolyphosphate; X-ray diffraction.

INTRODUCTION:

Water is one of the essential items needed for living beings for the survival and growth. It also maintains an ecological balance between various groups of organisms and their environment. The quality of water is of initial concern for mankind since it is directly linked with human welfare [1].

Domestic wastewaters usually contain pathogens, suspended solids, nutrients and other organic materials [2]. The wastewater produced from different kinds of industries normally contains very fine suspended solids, dissolved solids, inorganic and organic particles, metals and other impurities [3].

Cellulose is the most abundant polymer on Earth, composed of glucose units, it is biodegradable and resistance to hydrolysis and hence can be regarded as a very important raw material for several purposes. Recently, cellulose has been in the public eye due to its possible use in the production of biofuels and other numerous applications [4]. Moreover, it can be chemically modified to yield cellulose derivatives. The derivatives are widely used in various industrial sectors in addition to being used as a source for commodity goods. Cellulose based materials are in the focus of numerous studies due to an increasing demand for environmental-friendly and biocompatible products in various applications. Efficient utilization of cellulose as a material source has been challenging, especially in chemical industry, it is hardly ever used as a chemical raw material because of its poor solubility resulting mainly from the highly extended hydrogen bonding of its anhydroglucose repeat units [5].

Various natural fibers such as cotton and higher plants have cellulose as their main constituent [6]. Cellulose is the main building material out of which plants are made, and plants are the primary or first link in what is known as the food chain (which describes the feeding relationships of all living things). Cellulose is the most abundant naturally occurring biopolymer [7]. Various natural fibers such as cotton and higher plants have cellulose as their main constituent [6]. It consists of long chains of anhydro-D-glucopyranose units (AGU) with each cellulose molecule having three hydroxyl groups per AGU, with the exception of the terminal ends.

Cellulose is insoluble in water and most common solvents; the poor solubility is attributed primarily to the strong intramolecular and intermolecular hydrogen bonding between the individual chains [8].

Ionic charges of cellulose could facilitate the isolation of nano fibrillated cellulose [16,6]. The cellulose fibrils are aligned in diverse angles within the cell wall, but after isolation they form entangled network structures due to strong hydrogen bonding between hydroxyl groups.

Liimatainen *et al.*, (2011) have reported to have produced cellulose-based polyelectrolytes from birch wood pulp by oxidation with sodium periodate, and then cationized the substrate with Girard's reagent. They were able to incorporate more than one cationic group per monomer, thus obtaining a very high degree of substitution (and consequently high charge density).

The potentials of *Calotropis procera* leaves in purification of water and its ability to drastically reduced total viable count of microorganism and its performance in coagulation and sludge conditioning capabilities have been reported to be similar to aluminum sulphate (alum) [9].

Cellulose can be chemically modified to yield derivatives which are used widely in different industrial sectors in addition to conventional applications. As an example, in 2003, 3.2 million tons of cellulose was used as a raw material in the production of regenerated fibers and films in addition to cellulose derivatives [10].

Native cellulose has a relatively low reactivity towards adsorption or flocculation in water treatment [11], thus, the introduction of new functional groups on the surface of cellulose can increase its surface polarity and hydrophilicity, which can, in turn, enhance the adsorption of polar adsorbents and the selectivity of the cellulose for the target pollutant. However, the chemical modification of this natural polymer is slightly difficult because of the low reactivity. This is influenced also by the large number of hydrogen bonds which decrease the potential solubility in most common solvents.

Chemical modification of cellulose is performed to improve process ability and to produce cellulose derivatives (cellulosics) which can be tailored for specific industrial applications. Cellulosics are in general strong, reproducible, recyclable and biocompatible, used in various biomedical applications such as blood purification membranes and the like [12].

Cellulose derivatives are designed and fine-tuned to obtain certain desired properties. This is done by altering the inherent hydrogen bond network and by introducing different substituents. These substituents either prevented the spontaneous formation of hydrogen bonding completely or created new interactions between the cellulose chains.

MATERIAL AND METHOD:

Acetic acid, nitric acid, hydrogen peroxide, sodium hydroxide and Sodium tripolyphosphate (STTP) (Sigma Aldrich) were used as received. Cellulose was extracted from the stem of *Calotropis procera*.

Samples Collection and Pre-treatment

The samples from *Calotropis Procera* were collected from Umaru Musa Yar Adua University, Katsina State, Nigeria, and identified by biology department. The sample were sun dried for 8-10 days. The leaves and small branches were separated from the stems. The stems were washed with water 4-5 times. Cleaned stems were put into an open water tank at ambient temperature for 8 days. Retting was done to loosen the bandage of fibers with stems which were expected to affect the quantity of fibers and its extraction rate. The retted stems were cleaned with water and dried thoroughly.

Extraction of cellulose

The extraction procedure reported by [13] was used with little modification, the extraction procedure was carried out with initial 5.0 g of dried stems of *Calotropis procera*, using 2% sodium hydroxide solution and 10% H₂O₂ solution and heated at 100 C for one hour to remove the lignin content. The extracted cellulose was washed with distilled water, centrifuged at 1000 rpm for 10 minutes and dried in an oven for 1 Hr.

Phosphorylation of cellulose

Conventional phosphorylation of starch was achieved according to the method proposed by [14] with little modifications. About 2.86 g of sodium tripolyphosphate (STTP) was weighed and 167 mL of distilled water added to cellulose with constant stirring. The mixture was centrifuged for 10 min at 6000 rpm in a centrifuge. The modified cellulose was dried in an oven at 40- 45 C for 20 minutes.

FTIR

The IR absorption spectra of the sample was scanned from 4000 cm⁻¹ to 600 cm⁻¹ to obtain the functional groups of the cellulose and the modified sample.

Scanning electron microscopy

Samples extracted Substrates were directly "flat-mounted" on aluminum SEM stubs, using a two-sided adhesive film to adhere the filter to the stub, and covered by a thin gold coating [9]. Changes in morphological surface of cellulose and the modified cellulose were observed.

X-ray diffraction

Morphological changes in the crystalline structure of cellulose were analyzed using a High-resolution X-ray diffractometer (XRD). The crystallinity of cellulose was determined from X-ray diffraction curves based on the [15].

RESULTS AND DISCUSSION:

SEM Analysis

Scanning electron microscope of unmodified and modified cellulose were shown in Figs1a, 1b and 1c respectively.

The Surface morphology of the samples are studied using SEM analysis. Fig. 1 (a) shows the microfibrillar structure of cellulose network consisting of several micrometers. However, with incorporation of STTP on the cellulose matrix, there is an observed increase in thickness and size of the cellulose microfibrils. This can be attributed to the agglomeration of STTP molecules onto the structural backbone of the cellulose molecules. Hence, Fig. 1 (c) shows thicker and larger microfibrils than Fig 1 (b), while Fig. 1 (b) shows a larger microfibrils than 1 (a). Therefore, the more STTP within the cellulose structure the more the surface thickness of the microfibrils. These changes are due to more agglomeration of the particles over the surface of the cellulose backbone. Moreover, it arises from the crosslinking reactions that have taken place and, as a result, the molecular orientation of the polymer was changed. Similar observations were reported by [16].

The changes observed in the morphological images confirms that structural changes have occurred due to the intermolecular bridging reactions of the cross-linking agent with sodium tripoly polyphosphate molecules.

X-ray diffraction analysis

Figure 2 (a-c) show the X-ray diffraction of unmodified and modified cellulose respectively. The XRD diffraction curves of unmodified and modified cellulose were measured by using X-ray diffractometer.

The crystalline peaks in Figs. 3 (b) and (c) at 15° and 16.7° have disappeared respectively, into a single broad peak, while the sharp crystalline peak at 23.1° in Fig. 2 (d) has now decreased in intensity. This is as a result of more modifying agent been incorporated onto the cellulose matrix, resulting in greater expansion of amorphous region over the crystalline region in the cellulose structure.

Summarily, this trend can be attributed to the fact that chemical reactions or modification of polysaccharide such as starch or cellulose takes place within the amorphous region. Hence, the more the degree of modification the more the expansion of the amorphous region [16].

FTIR analysis

The FTIR spectral show the vibrational frequencies of both unmodified and modified cellulose in the frequency range of $650 - 4000 \text{ cm}^{-1}$ as shown in Figure 3 (a) and (b) respectively.

The FTIR spectra of cellulose and modified cellulose obtained from phosphorylation are shown in Fig. 3 (a) and (b) at a wave number range of 650 to 4000 cm^{-1} . The absorption peak at 3212 cm^{-1} is due to -OH stretching vibration and 2807 cm^{-1} from asymmetric stretching vibration of C-H. In Fig. 3 (a), the C-O-C stretching and C-O-H bending vibrations are observed at 1030 and 1432 cm^{-1} respectively, additional absorption band in Fig. 3 (b) appeared at 1287 cm^{-1} is attributed to P=O stretching of the modified cellulose. The appearance of these bands successfully confirmed the chemical modification of *Calotropis procera* with sodium tripolyphosphate. Similar observations were reported by [17]

Adsorption Study

It was revealed that the adsorption gradually increased with time and attained equilibrium after 80 minutes. The rapid intake initially could be due to the availability of the more surface sites on the adsorbent for adsorption. The plot of C_e/q_e versus C_e gives straight lines with correlation coefficients of 0.99 and 0.99 for Pb^{2+} , Cu^{2+} respectively which indicate that the adsorption of the metal ions onto the adsorbent fitted the Langmuir isotherm well than Freundlich isotherm equation. The maximum adsorption capacity of each metal ion, constants and correlation coefficients were represented in Table 1.

CONCLUSION:

Cellulose was successfully synthesized and modified using different amounts of sodium tripolyphosphate as modifying agent. The FTIR absorption band in Fig h appeared at 1287 cm^{-1} and is attributed to P=O stretching of the modified cellulose. Addition of more modifying agent incorporated onto the cellulose matrix resulted in greater expansion of amorphous region over the crystalline region in the cellulose structure which was confirmed by XRD analysis. The crosslinking reaction which resulted from the incorporation of STTP on the cellulose matrix showed an increase in thickness and size of the cellulose microfibrils. This can be attributed to the agglomeration of STTP molecules onto the structural backbone of the cellulose molecules. This has been confirmed further from the SEM analysis. The adsorption equilibriums data satisfactorily fitted Langmuir isotherm equation better than Freundlich isotherm. Thus, it can be concluded that the modified cellulose could be used in the treatment of toxic metals effluents polluted with Pb^{2+} and Cu^{2+} ions.

ACKNOWLEDGEMENTS:

The authors are grateful to Umaru Musa Yar'adua University for financial support in carrying out the research work.

REFERENCES:

1. H V. Jadhav : Element of Environmental Chemistry, (Himalaya Publishing Home, India) (1992) pp. 38.
2. R. Devi, R. Dahiya: Removal from domestic wastewater generated in decentralised sectors. *Bio-resources Technology*. 99, (2008) 344–349.
3. C. S, Lee, J. Robinson, M. F. Chong : A review on application of flocculation in wastewater treatment, *Process safety and environmental Protection*. 92, (2014) 489.
4. Y. Habibi, "Key advances in the chemical modification of nanocelluloses," *Chemical Society Reviews*, vol. 43, no. 5, pp. 1519–1542, 2014. View at: Publisher Site | Google Scholar.
5. A. Elidrissi, S. El barkany , H. Amhamdi, A. Maaroufi, B. Hammouti. New approach to predict the solubility of polymers Application: Cellulose Acetate at various DS, prepared from Alfa "Stipa - tenassicima" of Eastern Morocco. *J. Mater. Environ. Sci.* 3 (2) (2012) 270-285. ISSN: 2028-2508.
6. V.V. Myasoedova. *Physical chemistry of non-aqueous solutions of cellulose and its derivatives* JohnWiley and Sons, Chirchester 2000.
7. B. Hinterstoisser. L. Salmen. Application of dynamic 2D FTIR to cellulose. *Vibrational Spectroscopy* 2000, 111–118.
8. A. M. Bocek: Effect of hydrogen bonding on cellulose solubility in aqueous and nonaqueous solvents. *Russian Journal of Applied Chemistry* 2003,76, 1711–1719.
9. B.O Shittu. T.O.S. Popoola. O. Taiwo: Potentials of Calotropis procera Leaves for Wastewater treatment. Proceedings of the Inter. Conf. on Sci. and National Development held at University of Agriculture, Abeokuta 2004, 97.
10. D. Klemm. B. Heublein. H.P. Fink. A. Bohn, "cellulose: fascinating biopolymer and sustainable raw material," *Angewandte chemical international edition* 2005,44,22, 33583393.
11. A.W. Rudie. A. Ball. N. Patel. Ion exchange of H⁺, Na⁺, Mg²⁺, Ca²⁺, Mn²⁺, and Ba²⁺, on wood pulp. *Journal of wood chemical technology*, 2006,26, 259.
12. I. Akira: Chemical modification of cellulose. In 'Wood and Cellulosic Chemistry' (eds.: Hon D. N-S., Shiraishi N.) Marcel Dekker, New York, 2001, 599–626.
13. O. Brendel, PPM Iannetta, D. A. Stewart: Rapid and Simple method to Isolate Pure Alpha Cellulose. *Phytochemical Analysis* 2000,11, 7-10.
14. E. F. Paschal: Phosphorylation with inorganic salt. *Methods carbohydr. Chem* 1964_4,296.
15. K. Schenzel, S. Fischer, E. Brendler. New Method for Determining the Degree of Cellulose I Crystallinity by Means of FT Raman Spectroscopy. *Cellulose* 2005, 12, 223–231 . <https://doi.org/10.1007/s10570-004-3885-6>.
16. A.D. Mohammed. D.A. Young. H.C.M. Vosloo: Synthesis of high-performance superabsorbent glycerol acrylate-cross-linked poly (acrylic acid). *Journal of Research Chemical Intermediates* 2016, 43, 2187-2191.

17. A.A. Nafie., Elfatih A.H., Al Sayed A.A, G.A. Mohamed, Induced Grafting of Polyacrylamide onto Gum Arabic. *Journal of Physical Science* 2012,23, 43–53.

Table 1.

Metal ion	<i>Langmuir model</i>			<i>Freundlich model</i>			
	q_{max} (mg/g)	Q_L	R^2	R_L (L/mg)	K_F (mg/g)	N	R^2
Pb²⁺	71.42857	1.1764	0.9984	0.0010	2901.3	3.2268	0.8854
Cu²⁺	41.841	0.4530	0.9973	0.0003	466.32	3.5385	0.7538

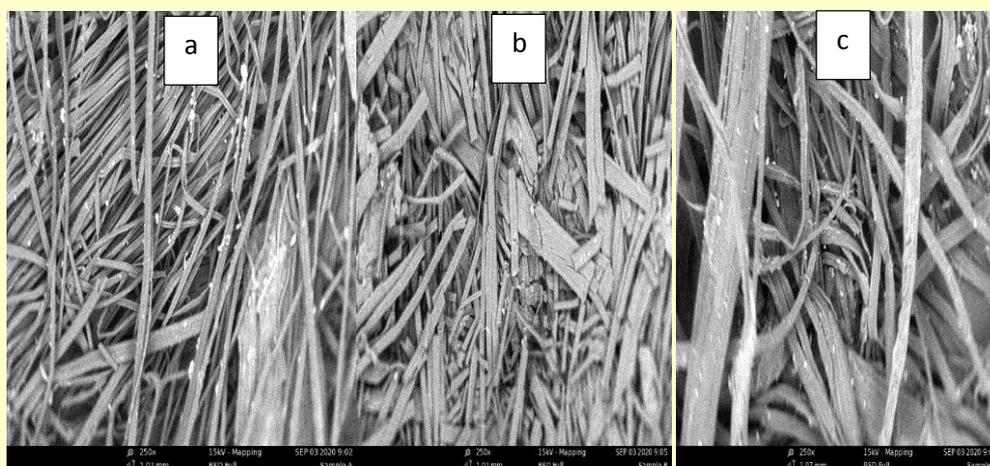


Figure 1: SEM Images of (a) unmodified cellulose, (b) modified cellulose with 0.56g STTP and (c) modified cellulose with 2.86g STTP

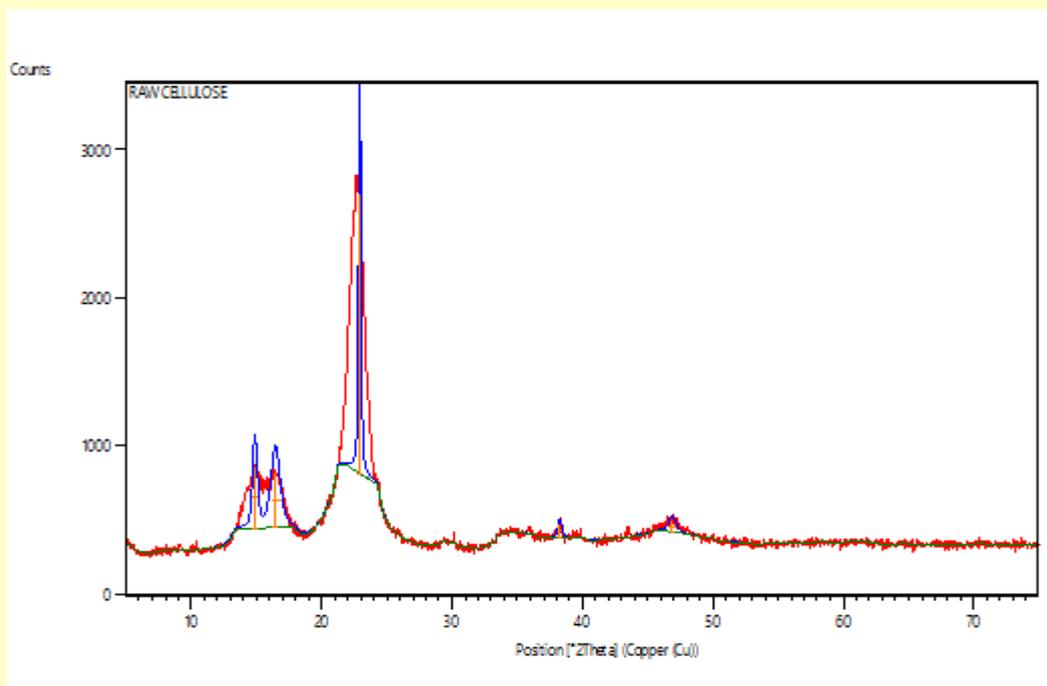


Figure 2 (a): X-ray diffraction of unmodified cellulose

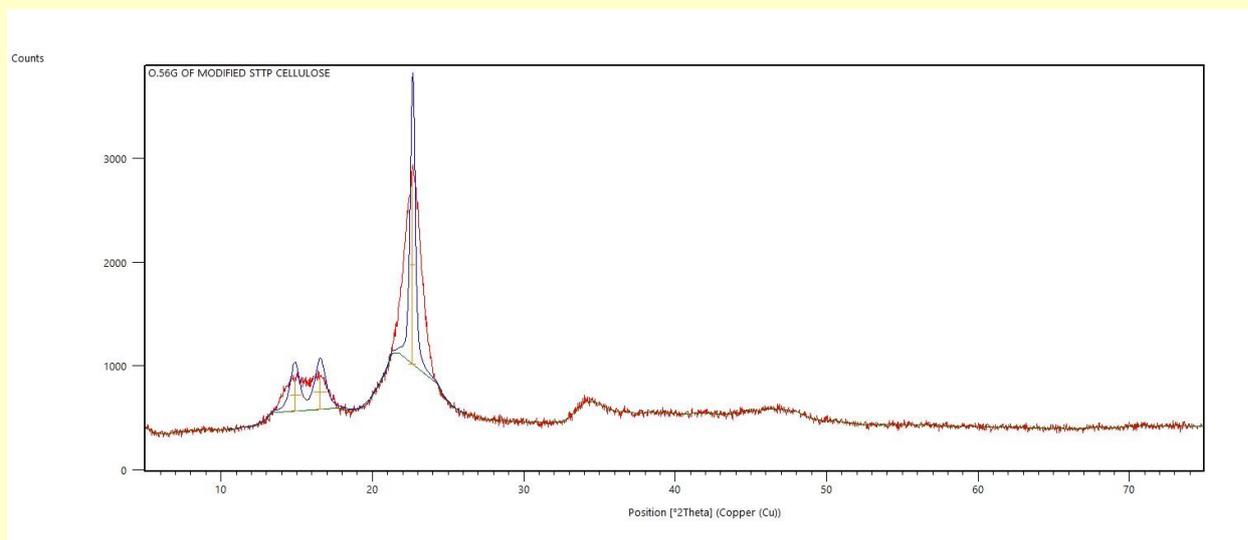


Figure 2 (b): X-ray diffraction of modified cellulose with 0.56g STTP

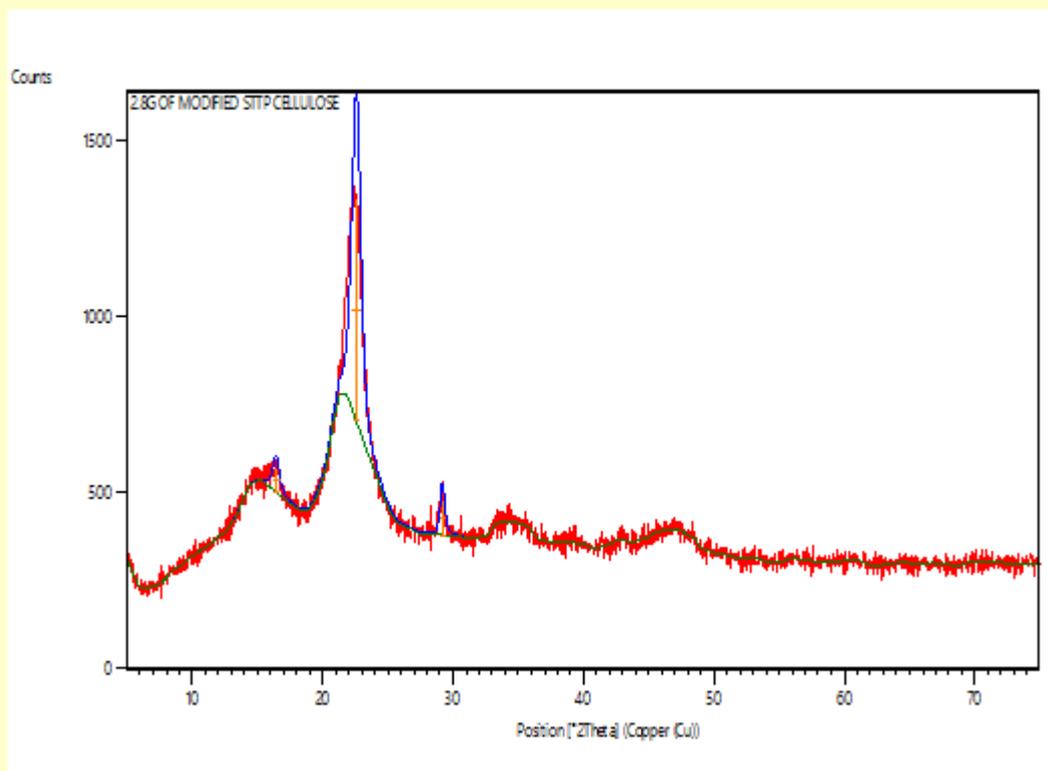


Figure 2 (c): X-ray diffraction of modified cellulose with 2.86 g STTP

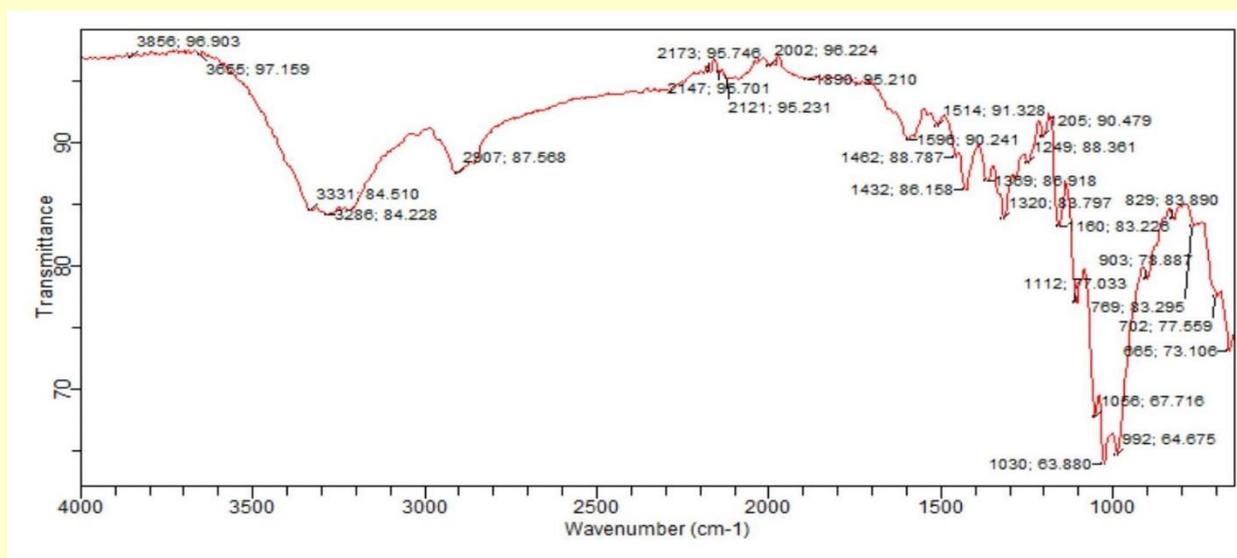


Figure 3 (a): FTIR spectrum of unmodified cellulose

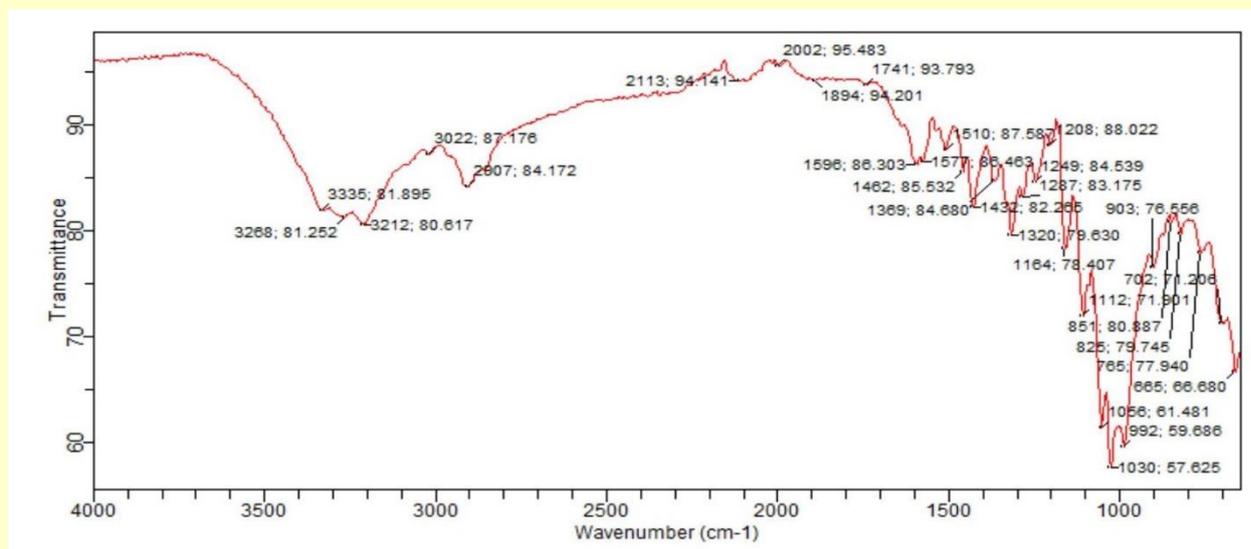


Figure 3 (b): FTIR spectrum of modified cellulose