



Preparation of oxidized cellulose from Shambat Cotton Lint Using phosphoric acid and nitric acid with sodium nitrite Solvent System

Inaam A. M. Salim¹ Emam A AWAJI² Sara F Aajmi³

1-Department of Chemistry, Faculty of Science, University of Kordofan, El Obeid, Sudan

2- Department of Chemistry, university collage nayria, University of hafr albatin, Saudi Arabia

3- Department of Chemistry, university collage nayria, University of hafr albatin, Saudi Arabia

ABSTRACT: Cotton cellulose has interesting properties which can be controlled to a large degree by chemical modification. This study was designed to prepare cellulose derivative with different functional group. from Sudanese Shambat cotton lint. Cellulose is the most abundant polymer on earth and hence can be regarded as a very important raw material for several purposes. The chemical structures of these derivatives were investigated using infrared spectroscopy and thermal analysis (TGA, DSC). Cotton cellulose was directly dissolved in phosphoric acid (85%). The reaction of cellulose with a mixture of H_3PO_4 / HNO_3 in the presence of $NaNO_2$ at room temperature for different time intervals has been investigated to produce oxidized cellulose. The results revealed an increase in carboxyl content with increasing reaction time. FTIR spectra of the oxidized different cellulose samples, confirmed the presence of a strong absorption band at around 1740 cm^{-1} that was attributed to the band of carbonyl group of carboxylic moiety. Solubility in some organic solvents was tested for the prepared derivative to explore possible new uses and applications. The study recommended that the use of modified cellulose derivatives as heavy metal adsorbents for its high abundance, low cost and the ease with which it can be modified chemically.

keywords: cotton lint, cellulose, oxidation, H_3PO_4 , shambat

1. Introduction:

Oxidation in organic chemistry refers to the elimination of hydrogen atoms from a substrate, or to the replacement of a hydrogen atom bonded to carbon by a more electronegative element, oxygen in particular. As amore general concept, the oxidation of an organic compound involves the transfer of electrons from the substrate to the oxidant, a process that is usually accompanied by the breaking of carbon–hydrogen or carbon–carbon bonds. Such a reaction, which can formally be regarded as occurring between a nucleophile (the substrate) and an electrophile (the oxidant), is greatly affected by factors that alter the nucleophilicity or electrophilicity of the respective reactants; steric effects are often also important [1].

The oxidation of carbohydrates is an important tool for obtaining compounds having interesting chemical and physical properties. Such oxidation products constitute useful intermediates for the synthesis of more complex molecules, and they also display, in many cases, varied biological activities. Selective oxidation of primary hydroxyl groups or the glycolic oxidation of polysaccharides yields polycarboxylates having thickening, gel-forming, and metal-sequestering properties.

Several water-soluble polysaccharides, e.g., starch and inulin, could be completely oxidized with high selectivity. However, for non-water-soluble polysaccharides like cellulose, much longer reaction times were necessary which caused degradation of the polymer due to β -elimination and oxidative degradation [2].

Oxidized cellulose (oxycellulose) is cellulose in which some of the terminal primary alcohol groups of the glucose residues have been converted to carboxyl groups Figure (1). The products that have lower carboxyl contents are the most desirable. The oxidized cellulose fabric, such as gauze or cotton resembles the parent substance; it is insoluble in water and acids but soluble in dilute alkalis. In weakly alkaline solutions, it swells and becomes translucent and gelatinous. When wet with blood, it becomes slightly sticky and swells, forming a dark brown gelatinous mass. So, it is used in various surgical procedures, by direct application to the oozing surface except when used for homeostasis, it is not recommended as a surface dressing for open wounds. The oxidized cellulose product can be used for producing novel film forming systems. The oxidized cellulose material, are bio -adhesive, can be applied on the human skin or hair and can be included in cosmetics. Oxidized cellulose were used also in anti-acne cream, anti-acne lotion, sunscreen spray anti-fungal cream [3]. Cellulose is highly susceptible to oxidizing agents which cause breakdown to products of lower molecular weight called "oxycelluloses". A wide variety of different forms of oxycelluloses may be produced depending on the oxidizing agent and the conditions of oxidation. Unruch and Kenyon [4] have recognized six products, all containing aldehydic, ketonic or carboxylic groups.

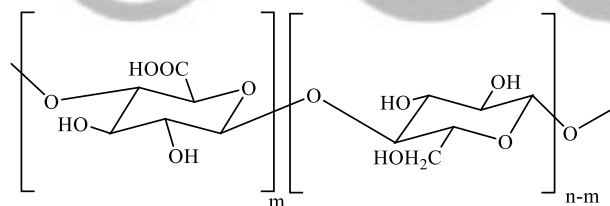


Figure (1): Structure of oxidized cellulose

The primary consideration in the preparation of biodegradable oxidized cellulose having 3% or higher carboxylic groups is the uniformity and extent of oxidation. Of the various oxidizing agents investigated, nitrogen dioxide has been the most extensively studied for cellulose. It selectively converts the C-6 primary hydroxyl group to the carboxyl group. Nitrogen dioxide can be used in the gaseous form or as a solution in an appropriate organic solvent [5]

2. MATERIALS AND METHODS

2.1. Cotton source:

The cotton lint sample of Shambat variety was obtained from the Cotton Breeding Section, Agricultural Research Corp. Wad Medani. It was treated first with the Shirley analyzer machine for removal of trash content, and further treatments of the sample was carried out according to practical requirements.

2.2. Cotton mercerization:

Cotton was mercerized in 15% NaOH solution at 0°C for 1.0 hr. [6]. (Buschle-Diller and Zeronian, 1992). The alkali swollen material was washed with distilled water until the pH of the filtrates remained unchanged. The mercerized product was air-dried and kept at 60°C under vacuum.

2.3. Oxidations of cotton cellulose in phosphoric acid and nitric acid with sodium nitrite:

Nitric acid and phosphoric acid were mixed in 1:2, (v/v) ratio. To a 70 ml solution of the acid mixture prepared in four beakers, 5.0 gm of cotton lint, cut into small pieces, was added. Once the cotton pieces were completely soaked, 1.0 gm of sodium nitrite was added all at once. An immediate formation of reddish brown fumes occurred. To prevent the release of these fumes to the air, the reaction containers were covered with a Petri dishes. The reaction mixtures were allowed to react at room temperature, with occasional stirring using a glass rod, for 12, 24, 36 or 48 hrs. The reaction mixtures, appeared green in color, the reactions were terminated by slowly adding an excess of water (about five times the volume of the reaction mixture). The diluted reaction mixtures were filtered, and the white fluffy solid obtained was filtered and washed with water until the filtrate showed a pH of about 4. They were finally washed with acetone and then air-dried at room temperature. The dried oxidized cellulose was milled and then used for characterization.

2.4. Carboxyl content analysis:

The same procedure as described in the United States Pharmacopeia (USP, 1995) [7] was used. 0.5 gm of the oxidized cotton cellulose sample was accurately weighted and dispersed in 50 ml of a 2% solution of calcium acetate for 30min. The mixture was titrated with standardized 0.1 N NaOH solution using phenolphthalein as an indicator. The volume of NaOH solution consumed was corrected for the blank. The carboxyl content in the sample was calculated from the following relationship:

$$\text{COOH content (w/w)\%} = \frac{N \times V \times MW_{\text{COOH}}}{\text{Weight of the Sample (mg)}} \times 100$$

where N is the normality of NaOH, V is the volume (in ml) of NaOH, consumed in titration after correcting for the blank and MW_{COOH} is the molecular weight of the carboxylic group.

2.5. Determination of carbonyl content:

The carbonyl content of the products was determined by the hydroxylamine method (Green, 1963) [8]

An accurately weighed amount of oxidized cellulose (0.5 gm) and 50 ml of hydroxylamine hydrochloride (prepared by dissolving 5gm of hydroxylamine/HCl in 12 ml sodium hydroxide 1N solution and then diluting with water to 100 ml) were placed separately in 250 ml round bottom flasks (one of the flasks has a side arm for evacuation) the flasks were evacuated with a vacuum pump. The side arm is then closed and the hydroxylamine hydrochloride solution is then transferred into the flask that contain the oxidized cellulose sample. The reaction mixture was then heated at 50°C for 2 hrs. After cooling to room temperature a 25 ml of the reaction mixture was removed and titrated against 0.1 N HCl solution. Blank titration was conducted in the same manner. The carbonyl content in the product was calculated using the following equation:

$$\text{Carbonyl group} = \frac{\text{MW}_{\text{CO}}(\text{B}-\text{S})}{10 \text{ Weight of sample}} \times 100$$

Where B and S volumes of 0.1NHCl used in titration of blank and sample solution respectively. MWCO is the molecular weight of the carbonyl group.

2.6. Determination of aldehyde content:

The amount of aldehyde groups present in the products was determined according to the procedure reported by Friedlander [8]. The oxidized cellulose sample was reacted with a solution of 0.2M sodium chlorite and acidified with 0.1M acetic acid for 72hrs at room temperature in the dark. The reaction mixture was filtered and the residue obtained was washed with distilled water and then dispersed in 0.1M HCl for 30 min in an ice bath. The latter was filtered and the solid obtained was freed from acid by washing with water. The wet material was then air dried and stored in the dark. The aldehyde content in the product was calculated by subtracting the carboxyl content value determined in the starting OC sample from that of the chlorite –treated OC sample.

2.7. Ketone content analysis:

The amount of ketone groups in the product was determined by subtracting the aldehyde content from the carbonyl content determined as described above

3. Results and discussion:

3.1. Cotton cellulose oxidation:

The use of high concentration of NaOH (15%) for cotton mercerization would weaken the aggregation of the bundles of cotton cellulose fibres and subsequently facilitates the dissolution. The effect of reaction time on the carboxyl content and yields of oxidized cellulose are presented in Table (1). Oxidized cellulose in high yield and with different levels of carboxyl content can be prepared by reacting cellulose with a mixture of H₃PO₄, HNO₃ and NaNO₂ at room temperature for different reaction time. In general, the carboxyl content increased linearly when reaction the time was increased as shown in Figure (2) while the yield of the final product decreased after oxidation.

These results indicate that oxidation of cellulose by concentrated phosphoric acid with addition of sodium nitrite is appropriate since cellulose is not hydrolyzed heavily, and oxidation proceeds smoothly. The reason being perhaps that phosphoric acid has weak acidity and a strong ability to swell cellulose.

Since the phosphoric group was not detected in oxidized cellulose, it can be considered that the phosphoric acid group did not combined chemically with the cellulose while enhancing its solubility.

Table (1) Effect of reaction time on the carboxyl content and yield of oxidized cellulose using H₃PO₄, HNO₃ and NaNO₂ at room temperature.

Time(hrs.)	COOH content %	Yield after oxidation
12	8.0	80%
24	12.5	77%
36	16.5	73%
48	21.4	73%

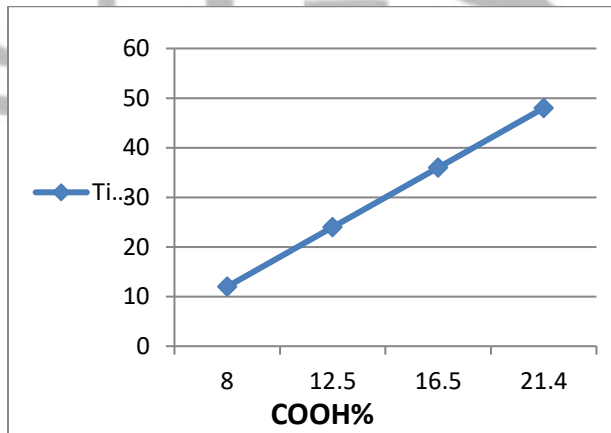


Figure (2) Effect of reaction time on the carboxyl content of oxidized cellulose using H₃PO₄, HNO₃ and NaNO₂

3.2. Carbonyl, aldehyde and ketone content in oxidized cellulose:

As shown in Table (2) the amounts of carbonyl groups determined in the four products were 2.4, 6.1, 6.6 and 6.8 %, whereas the carboxyl content in the samples, after treatment with sodium chlorite, corresponded to 8.8, 13.1, 17 and 21.5, respectively. These results shows that all the samples contain low

aldehyde content, and the carbonyl content determined in the product was only due to the ketones as shown in Figure (3).

Table (3) Carbonyl, aldehyde and ketone content in oxidized cellulose

Time(hrs)	COOH%	COOH%NaClO ₂ Treated	Aldehyde %	Carbonyl %	Ketone %
12	8.0	8.8	0.80	2.4	1.60
24	12.5	13.1	0.60	6.1	5.50
36	16.5	17.0	0.50	6.6	6.10
48	21.4	21.5	0.06	6.8	6.74

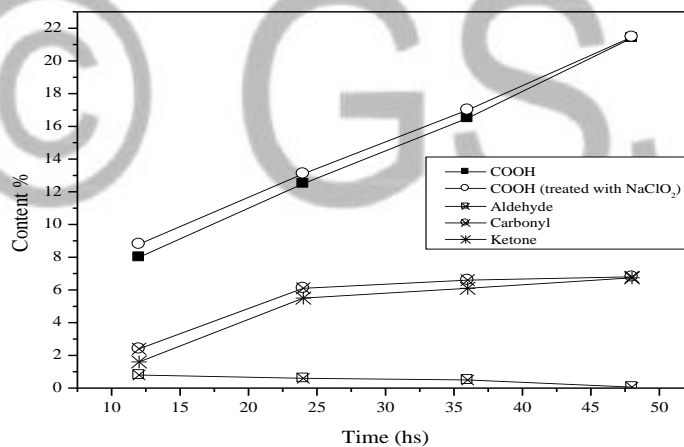


Figure (3) Carbonyl, aldehyde and ketone content in oxidized cellulose.

3.4. Fourier transform infrared (FTIR) spectroscopy: -

From Figure (4) and (5) it was observed that oxidized cellulose exhibits two characteristic FTIR bands at near 1735 and 925cm^{-1} that increase with increasing degree of oxidation. The absorbance at about 1735cm^{-1} is characteristic of carbonyl groups, which intensity decreased in order of time of oxidation, while the band around 925cm^{-1} is generally assigned to the formation of hemiacetal bonds between the aldehyde groups and neighboring hydroxyl groups. Also the spectra of oxidized cotton cellulose samples show a broad absorption band at 3438cm^{-1} , that confirms the stretching frequency of the $-\text{OH}$ group. In addition to the band at 2908cm^{-1} that confirm $\text{C}-\text{H}$ stretching vibration. The bands around 1431 and 1369cm^{-1} are assigned to $-\text{CH}_2$ vibration. From these result it can be concluded that, $\text{HNO}_3/\text{H}_3\text{PO}_4-\text{NaNO}_2$ mixture is a good oxidizing agent for the primary hydroxyl group of cellulose because there is no need to a reduction step after oxidation. From all these results, cotton cellulose is considered to be good for homogenous reaction.

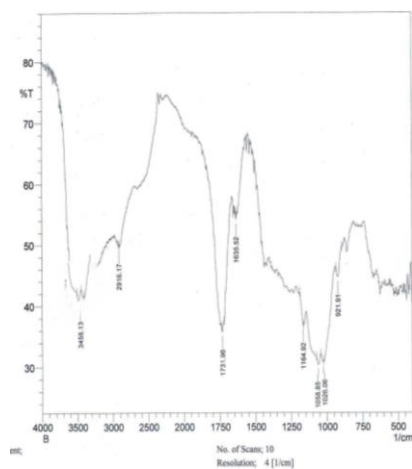
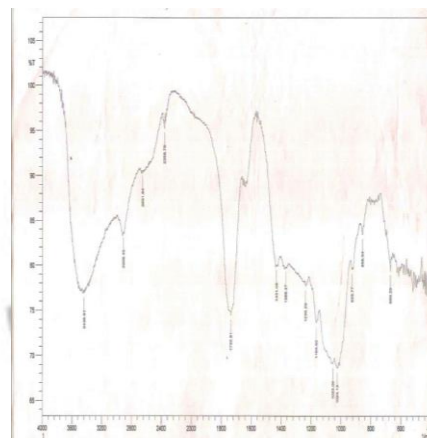


Figure (4) FTIR spectrum of oxidized cellulose (reaction time 24hrs)



Figure(5)FTIR spectrum of oxidized cellulose (reaction time 48hrs)

3.5. Thermogravimetric Analysis (TGA):

In the thermal degradation studies of oxidized cellulose (OC) two distinct weight loss zones were observed as shown in Figures (6) and (7). The initial weight loss is due to the presence of small amount of moisture in the sample are appears up to 113°C . Knowing that this moisture content is important as it has a major bearing on the end use properties and processing performance of OC. The second rapid loss is due to loss of CO_2 from OC and occurred at $213-291^{\circ}\text{C}$. It has been observed that in the initial stages of weight loss ($213-291^{\circ}\text{C}$) the oxidized sample started to decompose at lower temperatures than that of unmodified cotton cellulose (300°C). All oxidized cellulose samples showed a weight loss due to the moisture content between $108-113^{\circ}\text{C}$. The results presented show that the moisture content in the product increases with increasing carboxyl content. This is because the higher the carboxyl content the greater the affinity of the

material for interaction with water molecules. The decline in weights above about 290°C is attributed to the degradation of the materials [9].

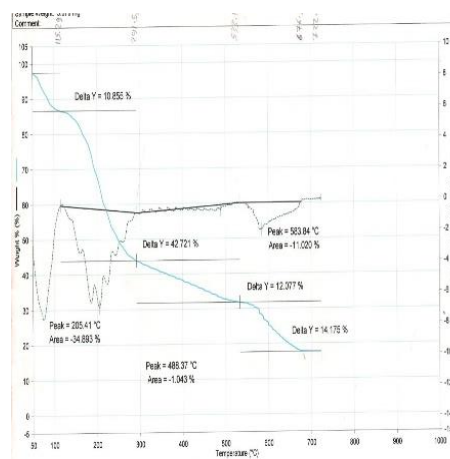
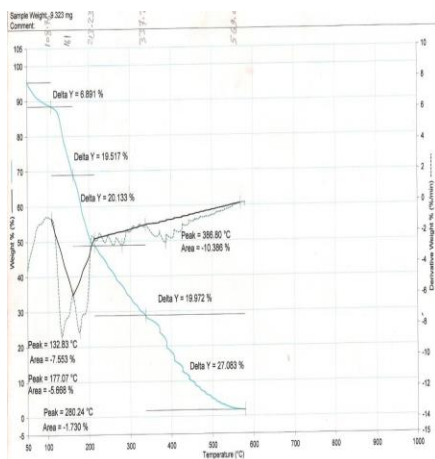


Figure (6)
TGA curve of oxidised cellulose
(reactin time 24hrs)

figure(7)
TGA curve of oxidized cellulose (reactin time 48 hrs)

3.6. solubility of the oxidized cotton cellulose derivative in some organic solvents

Dissolving a polymer is a process that occurs in two stages. First solvent molecules slowly diffuse into the polymer to produce a swollen gel. Production of a persistent swollen gel occurs when the polymer intermolecular forces are high because of cross-linking, crystallinity, or strong hydrogen bonding. In the second stage the solution takes place if the intermolecular forces are overcome by the introduction of strong polymer solvent interactions. The gel gradually disintegrates into a true solution. The solution process can be quite slow for materials of high molecular weight [8]. The results of solubility of the oxidized cotton cellulose derivative in different organic solvents are shown in Table (4).

Table (4) Solubility of the oxidized cotton cellulose derivative in some organic solvents

Solvent	Oxidized cellulose
DMA	+
DMF	+
DMSO	+
ACETON	-
THF	-
DIOXANE	-
CH3C1	-
Formic acid	-

(++) =Soluble, (+) =Partially soluble, (–) = Insoluble

4. Conclusions:

Oxidized celluloses were biodegrade Thus, it has been possible to develop new types of cellulose esters, halogendeoxy celluloses, ethers and oxidized cellulose as polymers of the future , for example, toward a wide range of high-quality applications on the industrial scale, which have been established in the markets. Cellulose the highly purified products of high carboxyl content have made oxidized cellulose to be a valuable additive in many products.

6. References:

[1] **Varela, O. (2000)**. Oxidative reactions and degradations of sugars and polysaccharides, Advances in carbohydrate chemistry and biochemistry, Vol. (58), pp: 308 – 359.

[2] **Arjan,E.J.; Paglairo, M.; Herman, V.B.; and Arai, C.C. (1997)** .Autocatalytic oxidation of primary hydroxyl functions in glucans with nitrogen oxides.Carbohydrate Research.Vol(304) pp:117-123.

[3] **Kumar,V. and Yang,T. (2002)**. HNO₃/H₃PO₄-NANO₂ mediated oxidation of cellulose - preparation and characterization of bio absorbable oxidized celluloses in high yields and with different levels oxidation. Carbohydrate Polymers. Vol (48), pp:403-412.

[4] **C. C. Unruch and W. O. Kenyon**, Text. Res. J. 15,1 {1946}

[5] **United States Pharmacopia (1995).Oxidized cellulose. pp: 318.**

[6] **Green, J.W. (1963)**. Determination of carbonyl groups in carbohydrates. Carbohydrate chemistry. New York. Vol (3), pp: 49 – 51.

[7] **Friedlander, B.I. (1996)**. An infrared Spectroscopic Study of oxidation of cellulose. Ph.D. Thesis University of Toronto, Canada.

[8] **Klemm, D.; Philipp, B.; and Heinze, T. (1998)**. Comprehensive cellulose chemistry (6thed) Wiley, VCH, Weinheim, Germany **Kumar, V., (2000)**. Powdered oxidized cellulose united states patent 662749.

[9] **Billmeyer, F. W. (1984)**. Textbook of Polymer Science.(3rdEdition). John Wiley & Sons Inc .Singapore. pp:151-153.

© GSJ