Journal of Textiles, Coloration and Polymer Science
https://jtcps.journals.ekb.eg/

Utilization of Egyptian cotton waste fibers for production of Carboxymethyl cellulose (CMC)

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Abstract

THE AIM of present work was to use waste cotton fiber from the textile industry as a raw material and extract cellulose to prepare carboxymethyl cellulose from it by adapting a modified etherification methodology. Cotton waste fibers are an abundant waste, but it has great potential for use as a cellulose source for the production of carboxymethyl cellulose (CMC). The chemical composition of Egyptian cotton fibers, such as cellulose, sugar, and waxy matter was determined. Scouring and bleaching pretreatments were used to prepare the cotton samples. Then cellulose extracted was carboxymethylated using sodium hydroxide and monochloroacetic acid in aqueous ethanolic medium using different concentration of sulfuric acid. Carboxymethyl cellulose was characterized using Fourier transform infrared spectroscopy (FTIR). Results confirming the transformation of cotton fiber waste to carboxymethyl cellulose.

Keywords: Egyptian cotton, Waste fibers, Carboxymethyl cellulose, Etherification.

INTRODUCTION

Cotton is one of the most important agricultural crops in many countries. One of the side products of cotton cleaning factories is approximately 3-5% of un-spinnable short fibers which is considered as waste material meanwhile it contain about 90% cellulose, which can be used for producing value added products such as carboxymethyl cellulose (CMC).(1)
Cellulose is the major component of cotton fiber that is mostly comprised of cellulose with several non-cellulosic components surrounding the cellulose core. These non-cellulosic components are mostly originated in the cuticle layer and the primary wall, which surrounds cotton fiber (2,3).
Cellulose is an insoluble polymer, in order to increase the cellulose absorbance properties we must convert the cellulose to carboxymethyl cellulose which is a water soluble derivative of cellulose with -D-glucose and-D-glucopyranose 2-O-(carboxymethyl)-mono-sodium salt which are connected via -1, 4-glycosidic bonds (4). CMC has many applications throughout the food industry, detergents, cosmetics, pharmaceuticals, textiles, paper, adhesives and ceramics It also acts as a viscosity modifier, thickener and emulsifier (4,5). And there are researches on how to utilize commercial CMC in preparation of polymeric blends for the packaging material, which can save considerable time involved in the recovery of CMC from sugarcane bagasse. CMC has several grades and types according to the degree of substitution, viscosity and particle size (6).
CMC is a water-soluble anionic polysaccharide polymer, produced by etherification of cellulose. It is considered as biodegradable in nature and biological waste water treatment systems by aerobic and anaerobic microorganisms. Purified CMC is a white- to cream-colored, tasteless, odorless, free-flowing

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(Received 11/01/2023, accepted 20/01/2023)
DOI: 10.21608/JTCPS.2023.186804.1158

powder. The sodium form of carboxymethyl cellulose is commonly known as CMC, but food-grade CMC is also known as cellulose gum (4-6).

The global agriculture sector produces billions of tons of agricultural biomass annually. However, this progress has also led to the generation and accumulation of agricultural wastes with little commercial value. Only a small amount of agricultural wastes are used as animal feeds (7) Many researchers have studied the production of CMC from agricultural waste cellulose sources such as the synthesis of CMC from different agro-cellulosic sources, such as paper sludge , hyacinth , wood residue , cotton linters, bagasse.(8-10) rice straw , wheat straw (11,12) and from corn peels and husk.(13,14)

The aims of this research is to use waste cotton fiber from the textile industry as a raw material and prepare carboxymethyl cellulose by converting the cellulose to its derivatives known as carboxymethyl cellulose (CMC), which has many applications throughout several industries.

MATERIALS AND METHODS

Cotton fiber

Short staple cotton fibers used in this study was obtained from the un-spinnable waste fibers from cotton spinning department at Cotton Research Institute, Agricultural Research Center, Egypt.

Chemicals

All chemicals used in this research were of analytical grade purchased from local supplier.

Sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2) , sulfuric acid (H_2SO_4), sodium carbonate, monochloroacetic acid ($ClCH_2CO_2H$), glacial acetic acid, ethanol (99.08%) , methanol absolute , sodium silicate; Na_2SiO_3, magnesium chloride; $MgCl_2$ $6H_2O$, and non-ionic wetting agent; Triton X – 100

Preparatory process

- **Opening and cleaning**

Cotton fibers were cleaned and opened through trash separator to remove trash in the fiber, using Microdust Trash Analyzer instrument (MDTA3).

- **Scouring**

Conventional scouring of cotton fabric involves a high-temperature with a solution containing alkali, wetting agent, and detergent. The raw cotton fibers was scoured using aqueous sodium hydroxide (3 g/ L) and nonionic wetting agent (Triton X 1 g/ L) at boiling for 1 hour at liquor ratio of 1:50. Then samples were washed with hot water followed by cold water

- **Bleaching**

The scoured cotton fibers were bleached using H_2O_2 depending on weight of the cotton fiber samples in bath containing 1.5 g/l sodium hydroxide, 0.4 g/l sodium silicate, 0.2 g/l sodium carbonate, 0.2 g/l magnesium chloride, and 25 ml/l 35% hydrogen peroxide. The liquor ratio was 1:50 at boiling for 1 hour. The samples were finally washed with hot water followed by cold water.(15)

- **Treatment with sulfuric acid (H_2SO_4)**

The scoured and bleached samples were treated with different concentration of sulfuric acid (5, 10 wt% H_2SO_4) for 1 hour at 70-80 ◦C. The treated cotton fiber was washed several times with distilled water.

- **Alkalization**

Cellulose alkalization followed by adding 20 wt% NaOH solution at 70 ◦C for 2 h.

- **Etherification**

Etherification was carried out using monochloroacetic acid (MCA) as the organic acid. The carboxymethylation reaction was started by adding (3 g) monochloroacetic acid (MCA) to the reaction mixture placed on magnetically stirrer hot plate at temperatures 60 ◦C-70 ◦C for 3 h. then the mixture was filtered and the residue was suspended in 100 mL of ethanol for 1h. Then neutralized was done using diluted glacial acetic acid to adjust pH to 7. The residue was filtered again and washed using methanol to remove undesired by-product. The residue from the filtration was oven dried at 60 ◦C, the matter

obtained was carboxymethyl cellulose (CMC). (7,16,17)

Testing and Analysis

All testing samples was carried out in laboratories where standard atmospheric conditions at 65 ± 2% relative humidity and 21 ± 2°C temperature were maintained.

- **Cotton fiber Chemical composition**

Cotton Chemical analysis used to determine almost all cotton fiber components, such as moisture, sugar, wax, ash and cellulose content of the cotton waste fibers used as raw material for CMC production were measured according to ASTM-D2495-07(2019), ISO 18068(2014), ASTM D2495-07(2019) and ASTM D629–99, respectively.

- **Mechanical properties: Tensile strength and elongation percentage**

Cotton bundle tensile strength (g/tex) and elongation, % were determined by STELOMETER instrument (Model 154 M, Germany) at 1/8 inch gauge length according to (ASTM: D1445-67) at the fiber testing Lab, Cotton Research Institute.

- **Carboxymethyl cellulose characterization**

The functional groups of extracted cellulose and CMC samples were identified using a Fourier transform–infrared (FTIR) spectroscopy. Pellets were made separately from CMC and FTIR spectra were recorded with FTIR 6300 instrument from Jasco Inc., Japan. All the spectra recorded in the range 4000 cm^{-1} - 500 cm^{-1} were averaged over 32 scans at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

- **Cotton Fiber Chemical composition**

The compositional data of the cotton fiber waste used as raw material for CMC production is presented in Table 1, which illustrated that the α-cellulose content of the sample is almost 90% of the cotton fiber and the non-cellulosic matters such as: soluble sugar content which is the important indicator affecting cotton fiber quality and spinning process because higher sugar content causes not only directly affects ginning rate and the quality of cotton, and affects quality and the efficiency of spinning. Other impurities are waxes which are esters of complex monohydric alcohol with fatty acid finally the ash content represent the mineral matter of cotton.

Table 1. Chemical composition of cotton fiber

Constituent	Percentage in cotton waste sample (%)
α-Cellulose	90
	90.1
	89.5
Mean	89.87
S.D.	0.32
Sugar	0.16
	0.18
	0.18
Mean	0.17
S.D.	0.01
Wax	0.85
	0.77
	0.79
Mean	0.80
S.D.	0.04
Ash	0.999
	0.998
	0.999
Mean	1.00
S.D.	0.00
Moisture	6.8
	6.5
	7.2
Mean	6.83
S.D.	0.35
Other Substances	1.191
	1.452
	1.331
Mean	1.32
S.D.	0.13

We can notice that cotton fibers have a variety of impurities that must be removed by pretreatment processes known as scouring and bleaching of cotton that provide a fiber that is both absorbent and free of impurities After scouring and bleaching, cotton is nearly 99% cellulose.

The main step of carboxymethylation is the formation of alkali cellulose which modifies the crystalline structure of cellulose. This form increases the accessibility of the sample to chemicals by swelling (18).
In alkalization pretreatment, α-cellulose was suspended in alcohol by adding the alkali 20% NaOH (w/v), then carboxymethylation by adding mono-chloroacetic acid MCA. CMC is produced by an aqueous alkali-swollen cellulose reaction with monochloroacetic acid and a surplus of alcohol. Hydroxyl groups in cellulose are usually replaced by carboxymethyl groups in the order of C2 > C6 > C3 (19)
These reactions are summarized as basification and etherification as shown below:

- Cotton cellulose

$$[C_6H_{10}O_5]_n \longrightarrow [C_6H_7O_2(OH)_3]n$$

- In alkalization pretreatment

$$[C_6H_7O_2(OH)_3]n + nNaOH \longrightarrow [C_6H_7O_2(OH)_2ONa]n + nH_2O$$

- In etherification

$$[C_6H_7O_2(OH)_2ONa]n + nClCH_2COONa \longrightarrow [C_6H_7O_2(OH)_2OCH_2COONa]n + nNaCl$$

Samples treated with different concentrations (5 and 10%) of H_2SO_4 it was revealed that concentration of 10% H_2SO_4 was ideal for this procedure.(16)

As the concentration of acid increased up to 10% H_2SO_4 for pretreated scoured and bleached samples, there was increase in CMC formation and for hemicellulose removal. But using high concentration of acid above (10%) that lead to degradation of cellulose as reported in researches (20,21)
As we see from figure 1. The cotton cellulose fibers were treated with alkaline solution 20% NaOH. Etherification was carried out when adding MCA as the organic acid that was replaced by substitution of NaOH on cellulose fibers. The ratio of NaOH/MCA is critical for etherification. It was reported that the degree of substitution (DS) of CMC increased with sodium hydroxide concentration. The increase in the degree of substitution of CMC improved the ability of CMC to immobilize water in a system. But above concentration 20% of NaOH, the degree of substitution was decreased, probably due to the degradation of cellulose structure and glycolate formation leading to inactivation of monochloroacetate and its utilization by this side reaction. This explanation and observation has reported in literature (16)

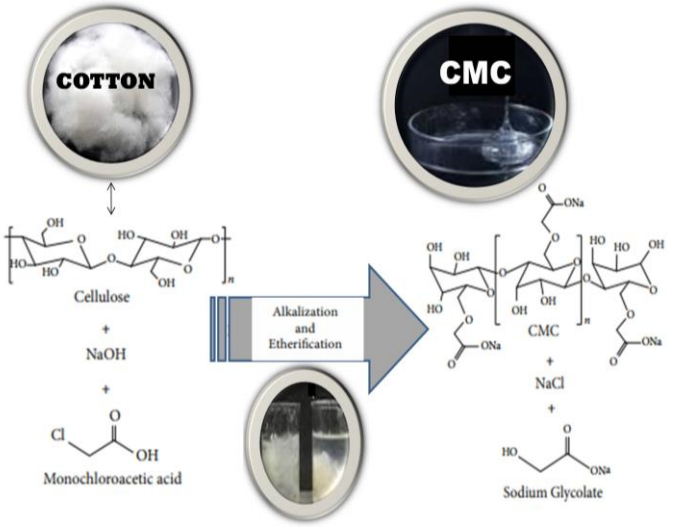


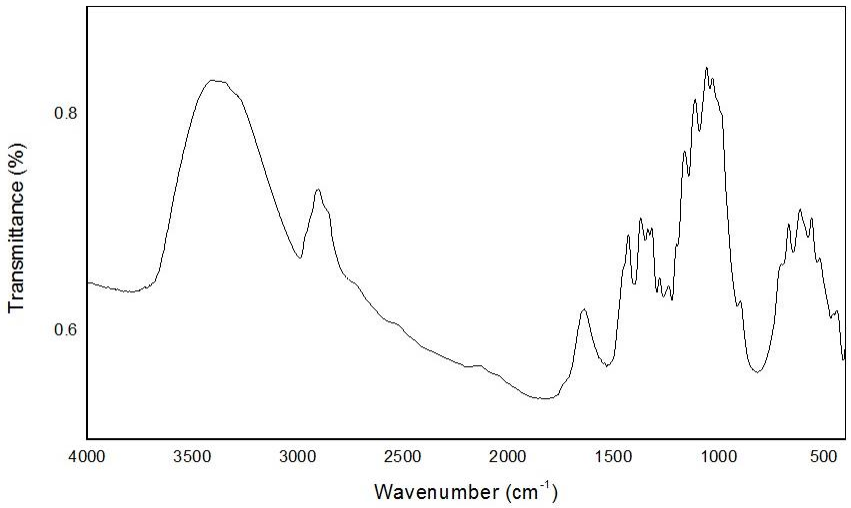
Figure1. Preparation methodology of CMC from Cotton fiber

- **Mechanical properties: Tensile strength and elongation percentage**

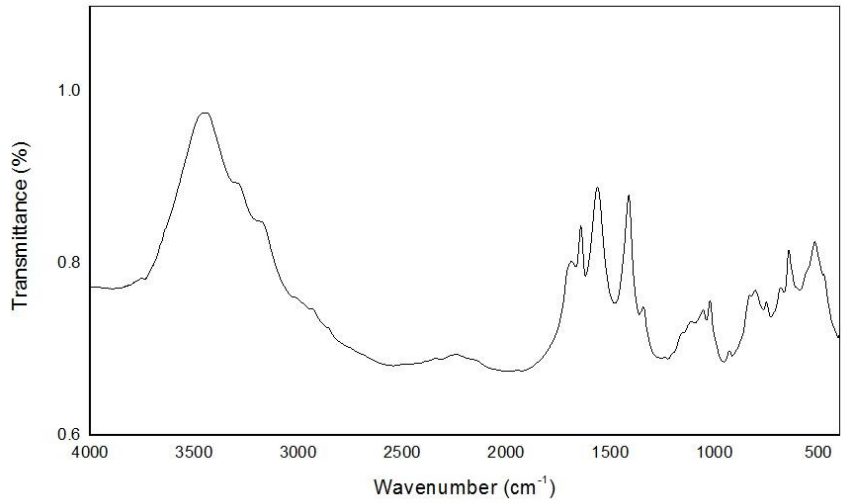
Cotton bundle tensile strength and elongation were determined and results are illustrated in table 2 below:

Table 2. Mechanical properties of cotton fiber

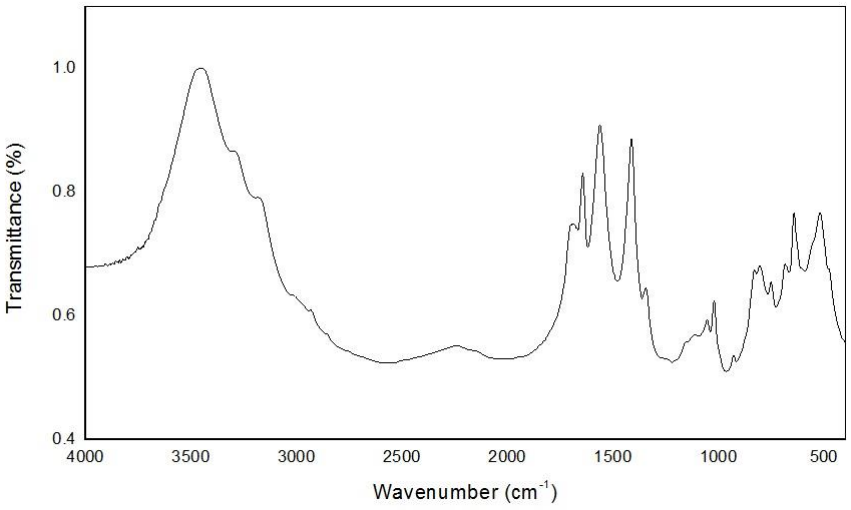
Mechanical properties		Cotton waste Sample
Fiber strength (g/tex)		28.8
		28.5
		29.3
	Mean	28.87
	S.D.	0.4
Fiber elongation (%)		6.2
		6
		6.3
	Mean	6.17
	S.D.	0.15



a)



b)



c)

Figure 2. FTIR spectrum of the raw cotton, and prepared CMC; a) Raw cotton, b) CMC prepared with 5% H2SO4 and c) CMC prepared with 10% of H2SO4

- **The FTIR characterization of CMC**

FTIR spectroscopy of raw cotton, and prepared CMC Samples treated with different concentrations (5 and 10%) of H_2SO_4, have been shown respectively in Figure2 (a, b and c)

The presence of strong absorption band at 1620 cm^{-1} in both treated samples confirmed the presence of carboxymethyl functional groups COO−.

spectrum shows peaks at 3350 and 3400 cm^{-1} is due to stretching frequency of hydroxyl group (O-H stretch), The bands around 2900 and 2920 cm^{-1} is due to carbon–hydrogen (C H) stretching vibration specially in raw cotton sample, 1640 cm^{-1} (absorbed H_2O bending), while the bands around 1423 and 1328 cm−1 are assigned to CH_2 scissoring and hydroxyl group (OH) bending vibration, respectively.

In raw sample we can confirm the Presence of impurities like lignin which can be noticed by adsorbed peaks at 1200 and 1220 cm^{-1} due to aromatic C=C and C-O phenolic bonds, Presence of mentioned peaks in impurity FTIR spectrum (Figure 2-a), and absence of these peaks in treated samples FT-IR, shows our method is able to extract pure cellulose and effectively prepared CMC.

Appearance of peaks at 1700 cm^{-1} (C=O stretch carboxylic acid) and 1620 cm^{-1} (C-O stretch carboxylic acid) in the prepared CMC spectrum (Figure 2-b and Figure 2-c) is the indication of successful completion of etherification reaction, and that was in agreement with Kardam et.al. 2014 (22)

Conclusions

Hydrolysis of the cellulose fibers with 5% and 10% (w/v) H_2SO_4 for 1 h at 60◦C-70◦C was observed to be optimum because the isolated cellulose from cotton waste was successfully converted to CMC by etherification using sodium monochloroacetic acid.

Results show that cotton waste has high potential for recycling cellulose content Furthermore, the developed method of producing a value-added product by utilizing cotton waste may help to alleviate environmental issues.

Conflicts of interest

There are no conflicts to declare.

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استخدام عوادم ألياف القطن المصري لإنتاج كربوكسي ميثيل السليلوز

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الهدف من الدراسه هو استخدام عوادم ألياف القطن الفائضه والغير مستخدمه في صناعة الغزل و النسيج كمادة خام لاستخراج السليلوزمنها ومن ثم لتحضير مركب كربوكسي ميثيل السليلوز عن طريق معاملات ومعالجات كيميائية. وحيث أن عوادم ألياف القطن هي مصدر مهم للسليلوز وقد تم تحليل شعيرات عوادم القطن لمعرفة التركيب الكيميائي لألياف القطن المصري مثل السليلوز والسكر والمادة الشمعية ....الخ. ثم تم تطبيق المعالجات الأوليه (الغلي والتبييض) لتحضير عينات القطن والتخلص من المواد الغير سليلوزية بها. ثم تمت معالجة السليلوز المستخلص باستخدام هيدروكسيد الصوديوم وحمض الخليك أحادي الكلور في وسط كحولي وباستخدام تركيزات مختلفه من حامض الكبريتيك المركز. تم التأكد من تحضير مركب كربوكسي ميثيل السليلوز باستخدام التحليل الطيفي بالأشعة تحت الحمراء (FTIR) وأكدت النتائج تحول عوادم القطن إلى مركب كربوكسي ميثيل السليلوز.

وقد أظهرت النتائج أنه أمكن اعادة تدوير عوادم ألياف القطن للاستفادة من محتوى هذه الالياف من السليلوز علاوة على ذلك فإن طريقة معالجة التحويرات الكيميائية أدت الى إنتاج منتج ذي قيمة مضافة وبالتالي عائد اقتصادي كما انها تساعد في الحد من المشكلات البيئية.

الكلمات المفتاحية: القطن المصري ، عوادم ، اعادة تدوير ، كربوكسي ميثيل سليلوز