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Preparation of Cotton Gauze Coated with Carboxymethyl Chitosan and its Utilization for Water Filtration

Hassan Ibrahim[1*] &, El-Amir M. Emam[2]& Tawfik M. Tawfik[3] & Ahmed T El-Aref[1]
[1]Textile Research Division, National Research Centre,
Dokki, Giza

[2]Faculty of Applied Arts, Textile Printing, Dyeing and Finishing Department,
Helwan University, Cairo

[3]Faculty of Applied Arts, Textile Printing, Dyeing and Finishing Department,
Benha University,
Egypt

*Corresponding author: H. M. Ibrahim: hmaibrahim@gmail.com

ABSTRACT

Contaminated water represented the main source of communicable diseases; therefore the decontamination process of waste water is essential to remove these pathogenic bacteria. The filtration process is a more favorable process than other chemical methods due to the harmful hazards of chlorinated materials used. In the present work cotton gauze coated with carboxymethylchitosan is used as water filter for gram-positive and gram-negative bacteria disinfection. We choose cotton gauze as cellulosic substrate as it is cheap, easily available and has an open structure suitable for continuous filtration systems. Carboxymethyl chitosan (CMCS) as water soluble chitosan derivative has been prepared in accordance with the methodology in our previous study by the reaction of chitosan with monochloroacetic acid in the presence of sodium hydroxide for 3 hours at 60oC (20). The prepared CMCS was characterized by using nitrogen content and FT-IR spectra. The FT-IR spectra demonstrated the conversion of chitosan to carboxymethyl chitosan. Carboxymethylchitosan treated Cotton gauze has been prepared via pad-dry-cure method, to be used for water filtration against gram-positive and gram-negative bacteria. The cotton gauze was characterized before and after treatment with CMCCS using various tools such as nitrogen content, FT-IR spectra, scan electron microscope (SEM) and thermal gravimetric analysis (TGA). FT-IR spectra confirm the presence of CMCS on cotton gauze. Antibacterial activity of this cotton gauze has been evaluated by using a bacterial count method. The results show that water filters cause a reduction of bacterial count. This reduction of bacteria depends on the amount of chitosan on the fiber. Based on our results, this composite had great promising to be used as bacterial filter.

Keywords: chitosan, carboxymethylchitosan, cotton, gauze, antibacterial activity, water filtration, modification

1. Introduction:

Contaminated water has been identified as causing some types of communicable diseases, such as diarrhea, cholera and typhoid. Insufficient management of waste water has exposed several millions of people to biological contamination dangers from bacteria such as Staphylococcus aureus and Escherichia coli. Therefore, removing or inactivating these bacteria has been a goal for several decades due to their impact on human health. Water decontamination to eliminate bacteria has been completed via both chemical and physical methods. Chemical processes use chlorinated compounds; however there were several restrictions due to its harmful effects towards human health. Physical treatments such as sedimentation and filtration can offer alternative solutions. [1-3].

Chitosan is a copolymer of glucose amine and N- Acetyl glucose amine. Chitosan has unique properties from its compatibility, biodegradability. In addition, it is a safe material with promise in uses such as wound dressing, wound healing, antibacterial, antioxidant, water and blood filtration [4-8]. It is insoluble in organic solvents, but it is soluble in weak acids. Therefore, carboxymethyl chitosan can be used as water soluble derivative instead of chitosan itself as antibacterial material in biological, biomedical and water filtration applications [9-12].

Chitosan and its derivatives accelerate bacterial cell aggregation and bacterial cell wall membrane disorganization causing loss of cellular fluids and bacterial death. Therefore, chitosan can be used as an antibacterial textile finishing agent, antitumor and biomedical applications [1, 12, 13]. In addition, chitosan and its derivatives were used for heavy metal ions removal due to the presence of hydroxyl and amino groups as coordination sites for heavy metal such as chromium and copper ions[12, 14]. Based on these promising properties, chitosan and its derivatives are attractive finishing agents of cotton gauze for water filtration especially for dye removal and bacterial disinfections [1, 15-19].

In the present work, carboxymethyl chitosan was prepared by the reaction of chitosan with monochloroacetic acid in the presence of sodium hydroxide(20). Carboxymethylchitosan (CMCS) was characterized by using nitrogen content, carboxyl content and FT-IR spectra. FT-IR spectra confirmed the conversion of chitosan into carboxymethyl chitosan. The pad-dry-cure method was used to coat cotton gauzes with the prepared CMCS. First the morphology of the treated cotton gauze was evaluated by using SEM. Next the antibacterial activity of the treated cotton gauze was evaluated using a bacterial count method.

2. Materials and Methods:

2.1. Materials

Low molecular weight Chitosan (CS) (Aldrich, viscosity 300 cps, degree of deacetylation (75-85%), Printofix® Binder MTB01 EG (APEO-free binder based on acrylate based copolymer, Egcodar), Sodium hydroxide (Modern Lab chemicals), monochloroacetic acid (Fluka), were used without further purification. Methyl alcohol, ethyl alcohol, acetic acid, sulfuric acid (Adwic), isopropyl alcohol (Sisco Research Laboratories), carbon disulfide (Fluka) and all other chemicals used were analytical grade. The two bacterial strains, were E. coli ATCC 11229 (gram-negative), S. aureus ATCC 6538 (gram-positive). Staphylococcus aureus (S. aureus) is a gram positive bacteria and Escherichia coli (E. coli) is a gram negative bacteria. These bacterial strains were selected for testing as they are the most frequent bacteria in found in wound infections and are representative of gram-positive and gram-negative bacteria. Fresh inoculants for antibacterial assessment were prepared on nutrient broth at 37°C for 24 hours.

2.2. Methods

2.2.1. Preparation of carboxymethylchitosan:

Carboxymethylchitosan (CMCS) was prepared in accordance with the methodology described in literature[20, 21]. As follows; chitosan (5gm), sodium hydroxide (50%), isopropanol (80ml), and distilled water (20ml) were added into a three necked flask (250ml) to swell and alkaline at room temperature for one hour The monochloroacetic acid (2.5M) was dissolved in isopropanol (20ml), and added drop wise into the reaction mixture over a 30 minute-period; the reaction took place for three hours at 60°C and was, then stopped by adding 80% ethyl alcohol. The solid was filtered and rinsed in 70-90% ethyl alcohol to desalt and dewater and then dried at room temperature.

The CMCS solutions with concentrations ranging from 2 to 4 wt.% were prepared by dissolving 0.2, 0.3 and 0.4 g of CMCS in 10 ml distilled water for 1 hour

2.2.2. Carboxymethylchitosan coated cotton gauze preparation:

The cotton gauze (49g/m2) was first alkalinized with a solution of 250 g/L of NaOH and 0.03 g/L of Tergitol NP 14, 1:20 (v/v) liquor ratio. As the reaction was exothermic, temperature rise was monitored and when it returned to 25◦C, denouncing the complete cotton alkalinization [1, 22, 23]. Carboxymethylchitosan was applied on cotton gauze using a pad-dry-cure method. The cotton fabric, cut to the size of 30×30 cm, was immersed in the solution containing CMCS (1, 3 and 5%) and acrylic binder (1%) for 30 min and then it was passed through a padding mangle. A 100% wet pick-up was maintained for all of the treatments. After padding, the fabric was dried at 100 0C for 5 minutes followed by curing for 3 minutes at 150°C. Then it was washed and dried to be ready in further characterization[24].

2.3. Characterization of carboxymethylchitosan & cotton Gauze:

Nitrogen content was determined using a micro- Kehjeldal Procedure [25]. FT-IR spectra of the samples were measured using a FT- IR spectrophotometer (Nexus 670, Nicolet, USA) in the region of 4000-400cm-1 with a spectra resolution of 4 cm-1. Thermal analysis measurements were measured using simultaneous thermal gravimetric analyzer (Perkin Elmer thermo-gravimetric analyzer, TGA7, USA). Surface roughness (SR) was measured using a Surfacoder 1700a. Thermal gravimetric analysis (TGA) was performed at a temperature range beginning at25 °C to 600 °C under inert nitrogen atmosphere with heating rate of 10 °C min-1 using the instrument: SDT Q600 V20.9 Build 20, USA. Micrographs using Scanning Electron Microscopy (SEM) of the untreated and treated gauze coated with carboxymethylchitosan fabrics surfaces using a scanning electron probe micro analyzer (type JXA 840A)–Japan were obtained. Surface morphologies were imaged at different magnifications, using 30kV accelerating voltage.

2.4. Evaluation of antibacterial activity via bacterial count method:

The antibacterial activity was evaluated before and after water filtration against S. aureus gram positive bacteria and E. coli gram negative bacteria by colony counting method [21]. A liquid culture was prepared by mixing 0.5 g peptone and 0.3 g beef extract in 100 ml water. 1 cm diameter blended film samples were cut and put into 10 ml of liquid culture, to which 10 µl of microbe culture was inoculated. All samples were incubated for 24 h at 37 °C. From each incubated sample, 100 µl of solution was removed, diluted and distributed onto an agar plate. All plates were incubated for 24 hours and the colonies formed were counted. The percentage reduction was determined as follows:

$$\text{Reduction in CFU (Colony Forming Units) \%} = \frac{(C - A)}{C} \times 100$$

where A is CFU/ml after contact (end test) and B is CFU/ml at zero contact time.

2.5. Antibacterial Filtration

The functionalized gauzes were tested in dynamic conditions with bacteria inoculum continuously flowed through the filter several times. A scheme of the system is shown in *Figure 1* as shown in a previous study [1]. It consists of a water pump, sterile plastic filter holder (25 mm internal diameter) and autoclavable tubing. The gauzes were cut in 25 mm disks. Three layers of the same fabric were placed in the filter holder. 50 ml of bacteria inoculum 1.5–3.0 $x10^5$ CFU/ml in a reservoir were magnetically stirred and pumped at 4.8 ml/min flow rate in the system. In this way, the volume of bacteria inoculum was pumped in about 10 min and the contact time between the inoculum solution and the fabric was 4 s in each passage. The contact time was calculated as a ratio between the flow rate and the void volume of the gauze placed in the filter holder. The inoculum was cycled for about 50 min in the system, therefore the entire volume of bacteria inoculum passed through the filter 5 times (precisely at 0, 10.2, 20.2, 30.0, 39.6 and 49.0 min). Every 10 min 1 ml of bacteria inoculum was taken from the reservoir and pleated in yeast extract agar.

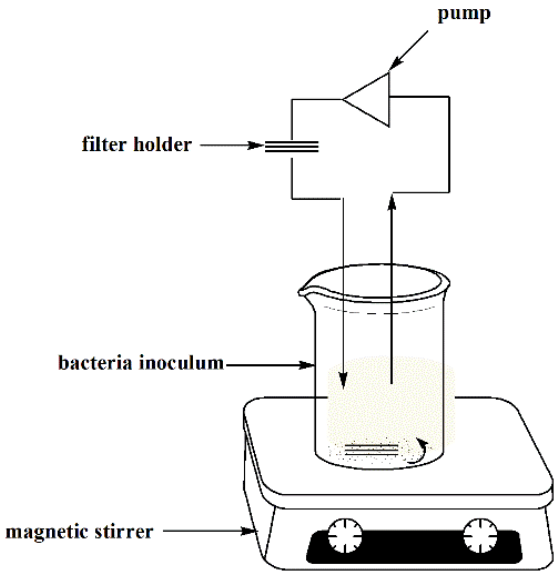


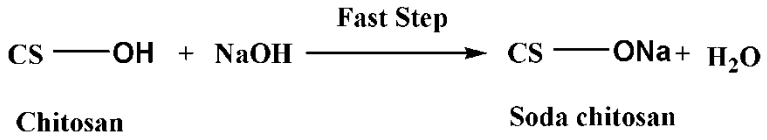
Figure 1. Scheme of Continuous filtration system

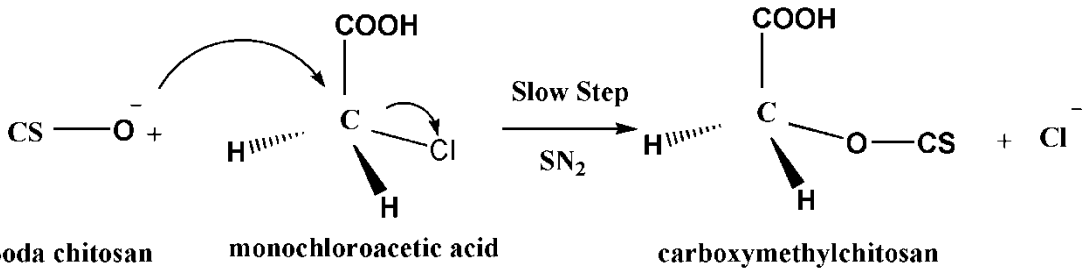
3. Results and Discussion:

3.1. Preparation of carboxymethylchitosan:

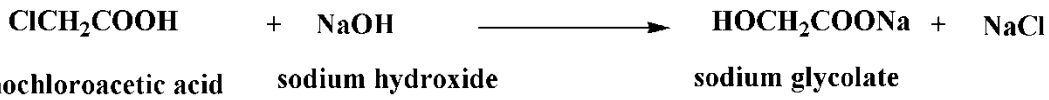
Carboxymethylchitosan was prepared based on our previous study and the optimum values at: 2.5 M monochloroacetic acid concentration, 50% sodium hydroxide concentration, 3 hrs. reaction time and 60°C reaction temperature in reaction medium formed from isotopic mixture of H_2O/isopropyl alcohol ration 20:80 [20, 26].

Carboxymethylchitosan prepared in two steps the first is conversion of chitosan to soda chitosan followed by nucleophilic substitution reaction (SN_2), to it depends on both monochloroacetic acid and chitosan, where soda chitosan act as nucleophile and monochloroacetic acid as target electrophile with chloride anion as good departure leaving group as follows:





Nevertheless, this reaction accompanied by side reaction occurs between sodium hydroxide and monochloroacetic acid and formation of sodium glycolate that as follows:



Nitrogen content and FT-IR used to confirm the structure of the prepared carboxymethyl chitosan where nitrogen content changed from 6.9 for chitosan to 3.9 for carboxymethyl chitosan, which corresponds to degree of substitution (DS) equal 0.63.

Figure 2. shows the FT-IR of the prepared carboxymethyl chitosan shows characteristic peak of typical carboxymethyl chitosan, at 3420 cm^{-1} corresponding to OH and NH stretching, 2927 cm^{-1} and 1639 cm^{-1} for CH and CO bonds, 1420 $cm^{-1}$for asymmetric stretching vibration of COO group, two peaks at 1528 $cm^{-1}$and 1513 $cm^{-1}$for NH_3^+, peaks at 1413 cm^{-1} and 1377 cm^{-1} for symmetric deformation of CH and NH bonds and peaks at 1175 cm^{-1} and 878 cm^{-1} for CO and COC bonds [20, 26].

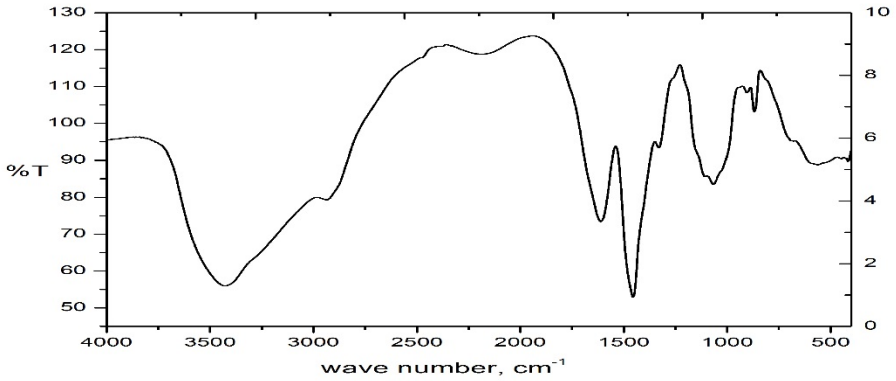


Figure 2. FT-IR spectra of the prepared carboxymethylchitosan

3.2. Morphological Analysis:

In Figure 3. SEM images of untreated (Figure 3a) and carboxymethylchitosan treated (Figures 3b, 3c, 3d) samples are reported. The formation of aggregations, due to the deposition of carboxymethyl chitosan, can be observed. In addition, these aggregations not present on cotton fibers. After immersion in water, some aggregations still found on the cotton gauze after half an hour of streaming of water Figure 4.

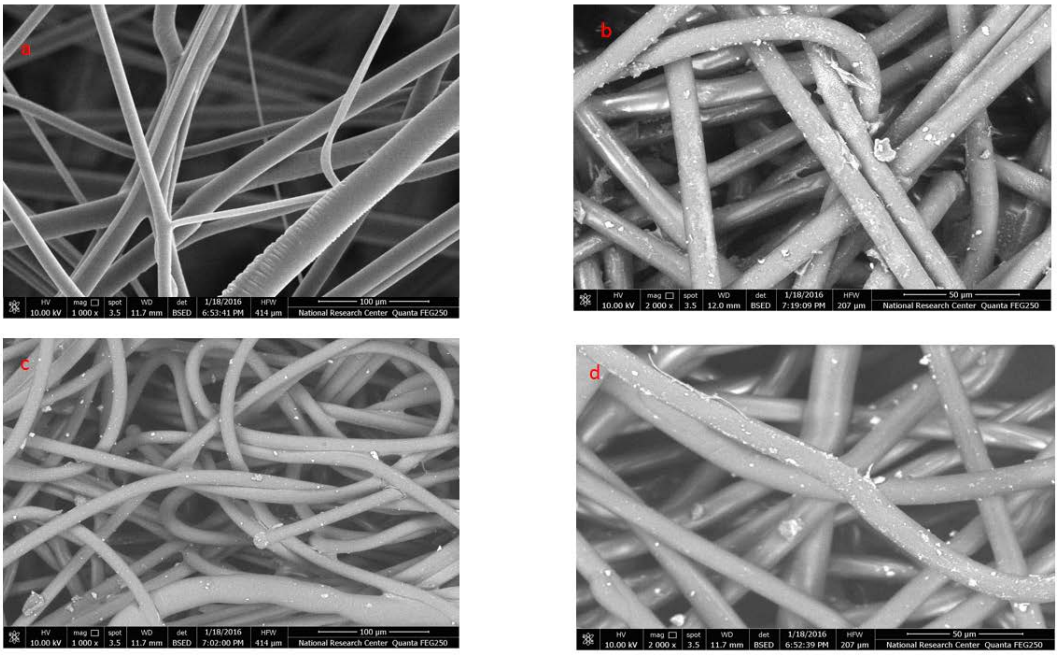


Figure 3. SEM images of untreated cotton gauze (a), 1% (b), 3% (c) and 5% (d) carboxymethylchitosan add-ons

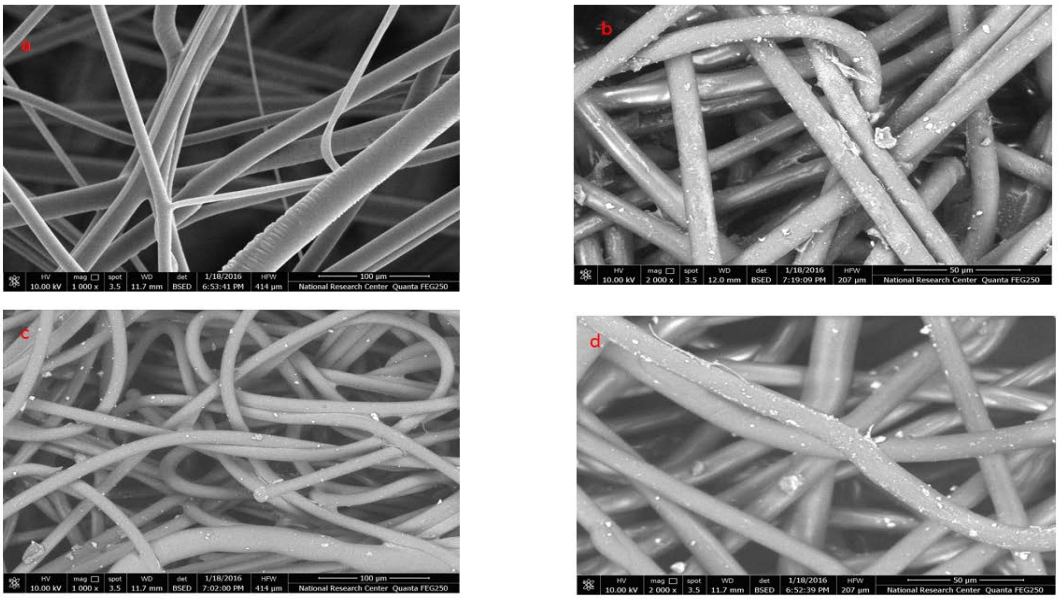


Figure 4. SEM images of untreated cotton gauze (a), 1% (b), 3% (c) and 5% (d) carboxymethylchitosan add-ons, after 30 minutes of water streaming

3.3. Roughness:

The results of average roughness of cotton gauze are listed in Table 1. The average roughness values decreased by increasing the amount carboxymethyl chitosan for untreated cotton gauze and 3% carboxymethyl chitosan treated cotton gauze from 25.4 µm to 6.1 µm. As a result, as the amount of carboxymethyl chitosan increased, a homogeneous coating was formed on the cotton fiber with uniform distribution.

In addition, results of water immersion for CMCS treated cotton gauze are also reported in Table 1. The average roughness of treated samples increased after streaming of water for 10 min., 30 min., and 24 hours due to removal of CMCS from cotton gauze surface under the effect of streaming of water[15].

Table 1. Average roughness of untreated and CMCS treated water streaming ton gauze

Sample	Average roughness [µm]			
	A	B	C	D
untreated	25.4	25.4	25.4	25.4
1% CMCS	18.3	19.5	21.0	22.4
3% CMCS	10.6	14.9	17.6	21.9
5% CMCS	6.1	8.0	13.2	14.5
A: without water streaming, B: After 10 min. water streaming, C: After 30 min. water streaming &D: After 24 h. water streaming				

3.4. Infrared Spectroscopy:

The FT-IR analysis was carried out on the prepared samples treated with different CMCS add-on and compared with the untreated cotton gauze sample to find CMCS characteristic peaks as shown in Figure 5. Comparison of FT-IR spectra of untreated and CMCS treated cotton gauze samples (evidence with peaks at 1420cm^{-1}, which comes from the asymmetric stretching vibration of the COO^- group) confirm the substitution of carboxymethyl groups onto the chitosan chain [27]. Two bands at 1528 and 1513cm^{-1} assigned to NH_3^+ indicate that the carboxymethylation occurred at OH positions [27, 28].The stretching vibration of C–O in the CH_2COOH group gives rise to the peak at 1207cm^{-1}. Peaks located in the range of 1175-878cm^{-1} are the result of vibrations of C–O and C–O–C and some other bonds that comprise the polysaccharide chain [29, 30]. The other peaks can be due to both cotton and chitosan component of the sample.

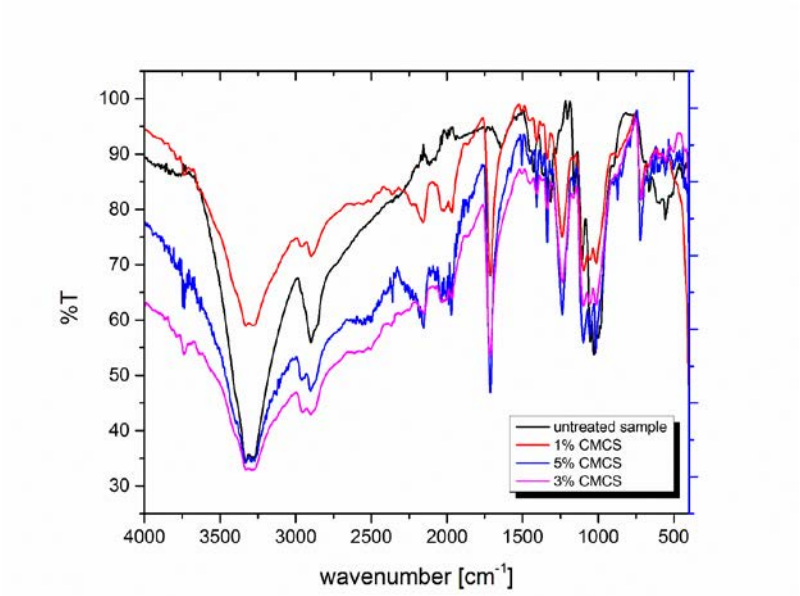


Figure 5. FT-IR analysis of the prepared samples with different CMCS add-on and untreated samples

3.5. Thermal Gravimetric Analysis:

The presence of carboxymethyl chitosan on treated cotton samples was evaluated by residual weight after thermal analysis at 800^0C. The residual percentage weights evaluated by TGA on 3% and 5% CMCS treated samples are in good agreement with the applied add-ons. Both untreated and 1% CMCS have residual 6 and 10 %, respectively, whereas 3% and 5% CMCS treated samples have 50 and 60% respectively. So that we found from TGA data that, the residual percentage of samples decreased when the presence of CMCS on fibers is reduced as shown in Figure 6.

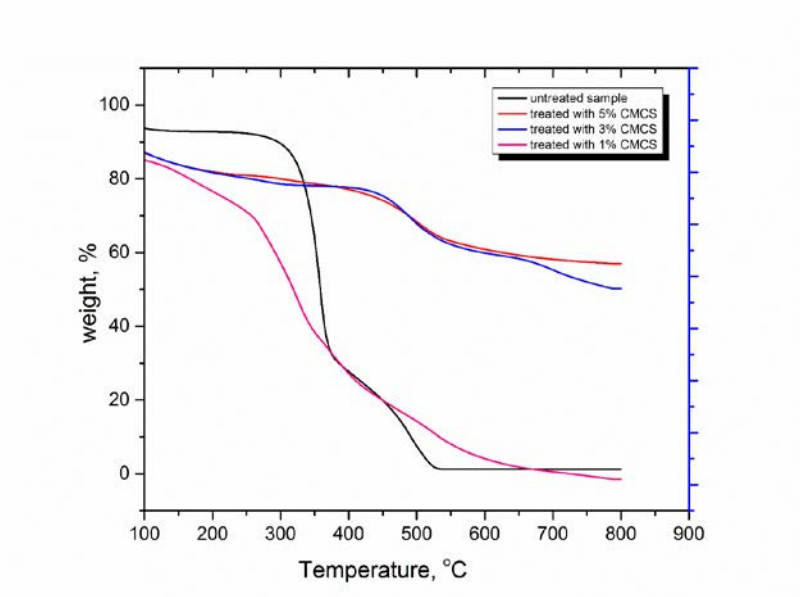


Figure 6. TGA analysis of the prepared samples with different CMCS add-on and untreated samples

3.6. Antibacterial Activity:

The antibacterial activity of 1%, 3% and 3% CMCS treated samples were evaluated towards S. *aureus* as gram-positive bacteria and E. *coli* as gram-negative bacteria according to bacterial count method [21].

Table 2. Antibacterial activity of 1%, 3% and 3% CMCS treated cotton gauze samples by bacterial count method after maintenance for 24 h before evaluation (Static method):

Sample	Bacterial Reduction, [%]	
	S. *aureus*	E. *coli*
1 % CMCS treated sample	92.0	79.0
3 % CMCS treated sample	100	87.0
5 % CMCS treated sample	100	95.0

The results reported in Table 2. Indicate that CMCS add-on resulted in the retention of strong antibacterial properties even at low concentrations of CMCS on the fibers. In addition, results showed that the antibacterial activity increased as the amount of CMCS add-on increases[13, 14].

Table 3. Continuous flow test of carboxymethylchitosan coated cotton gauze against S. aureus and E. coli (Dynamic method):

Sample	Bacterial Reduction, [%]											
	S. *aureus*						E. *coli*					
Contact time; S	0	4	8	12	16	20	0	4	8	12	16	20
1 % CMCS treated sample	0	92.0	98.0	100	100	100	0	52.0	79.0	79.0	79.0	79.0
3 % CMCS treated sample	0	98.0	100	100	100	100	0	78.0	87.0	87.0	87.0	87.0
5 % CMCS treated sample	0	99.2	100	100	100	100	0	85.0	95.0	95.0	95.0	95.0

Continues flow results indicate promising real application of carboxymethylchitosan coated cotton gauze as bacterial filter (Table 3). A contact time of few seconds was enough to produce the total bacterial reduction on *S. aureus* and *E. coli.* *As in static testing the bacterial reduction of S. aureus* is more than that for *E. coli,* this may be due to bacterial structure [27-29]. The reduction of bacteria for *S. aureus* and *E. coli* show a rise in the final part, suggesting that prolonged contact times has been improved

its filter efficacy. These results confirm that carboxymethylchitosan coated cotton gauze is suitable for continuous filtration.

4. Conclusion:

A cotton gauze was treated with carboxymethyl chitosan (CMCS) by pad-cure-method, at 1%, 3% and 5% CMCS add-ons and tested as antibacterial medium to be used as water filters. All the samples showed antibacterial activity against both gram-positive and gram-negative bacteria in two latter samples showed antibacterial reduction of gram-positive bacteria of 100% and gram-negative bacteria 87.0 and 95.0%. The antibacterial activity increased as the amount of CMCS add-on increases from 1%, 3% and 5% CMCS. Based on these resulted from FI-IR spectra, roughness, TGA analysis and antibacterial activity, we can have concluded that carboxymethylchitosan coated cotton gauze is suitable for continuous filtration.

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