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Cotton Fabric Functionalization with Cyclodextrins

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Abstract
Cyclodextrins are cyclic oligosaccharides obtained by enzymatic degradation of starch.They have been used in recent years to functionalize textile substrates. In this paper, a reactive cyclodextrin derivative, monochlorotriazinyl-β-cyclodextrin, was covalently bonded to cellulose in cotton fabric. The grafted amount was determined by gravimetric method and the treated fabrics were analyzed by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Inclusion compounds with phenolphthalein and the cyclodextrins grafted to the cotton fabric were made in order to verify that the cavities were available for inclusion compounds. Triclosan was used to test the inclusion and the release capabilities of the obtained material. Antibacterial tests of the cotton fabric treated with cyclodextrins and triclosan were performed and the treated fabrics showed excellent performance.
Keywords: Cotton, Cyclodextrin, FTIR, Cellulose, Triclosan.

1. Introduction

There is a continued interest in finding new ways to functionalize textile surfaces in order to impart diverse properties such as water repellency (1,2), self-cleaning (3), UV protection (4) and antibacterial (5). Water repellency and self cleaning properties prevent the stains from adhering to clothes or eliminating them; therefore, reducing the frequency of laundry, time and detergent required to remove the stains. Textiles with ultraviolet protection and antibacterial properties could help reduce the risk of skin cancer cases and reduce the spread of infectious diseases respectively. Recently, there has been an increasing interest in using cyclodextrins as a finishing agents on textile surfaces (6-8).

Cyclodextrins are cyclic oligosaccharides obtained as byproducts of the enzymatic degradation of starch. They consist of glucopyranose units linked by α-(1-4) bonds (9). The most common and industrially available types of cyclodextrins are α, β and γ-cyclodextrin with 6, 7 and 8 glucose units respectively. Cyclodextrins have a cone shaped structure with the primary and secondary hydroxyl groups on the outside. This characteristic shape give them a unique property, the exterior is hydrophilic while the interior of the cavity is less hydrophilic. Therefore, cyclodextrins are capable of forming inclusion compounds with hydrophobic substances (10).

In the textile area, cyclodextrins have been used for imparting properties such as: UV protection (11,12), slow release of fragrances (13), insecticide delivery (14) and antibacterial (15). Triclosan

($C_{12}H_7Cl_3O_2$) is broad spectrum antibacterial and antifungal. Its chemical name is 5-chloro-2-(2,4-dichlorophenoxy)phenol. It is widely used in consumer products and its complexation with β-cyclodextrin has been previously studied (16,17). Triclosan is used in this study as the antibacterial inclusion compound.

There are several methods to attach the cyclodextrins to textile surfaces (6). Physical methods consist of dissolving cyclodextrin derivatives with hydrophobic chains in the polymer solution prior to the formation of the fibers. After the fibers are spun, cyclodextrins tend to migrate to the surface, making the cavities available for inclusions (6,18). Chemical methods include: (1) synthesis of cyclodextrinderivatives with an ionic pendant group, which interacts with an ionic group attached to the fibers(18), (2) synthesis of a reactive cyclodextrin derivative, which is then grafted to textiles with the aid of a binder (19-21).

Several papers have been published using monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) on textile materials (10,12,14,15,22-27). These monochlorotriazinyl groups are able to form covalent bonds with nucleophilic groups, such as hydroxyl groups in cellulose (26). These reactive groups are widely used in the textile dyeing area as reactive anchors for reactive dyes (28). The advantage of using monochlorotriazinyl-β-cyclodextrin(MCT-β-CD) over other methods of grafting is that it is easily applied to the fabric under relatively mild conditions and to the fact that it is the first reactive cyclodextrins derivative produced on an industrial scale (29,30).

In this work, a reactive cyclodextrin derivative (MCT-β-CD) was covalently bonded to the cellulose macromolecules of cotton fabric. Techniques such as thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the functionalized cotton fabrics. Afterwards, inclusion compounds with phenolphthalein and the cyclodextrin grafted to the cotton fabric were made in order to correlate the amount of phenolphthalein in the solution with the amount of grafted cyclodextrins. The release capabilities of the functionalized fabric were tested with triclosan. Antibacterial test of the cotton fabric treated with cyclodextrins and triclosan were performed.

2. Experimental

Materials

Monochlorotriazinyl-*β*-Cyclodextrin (MCT-β-CD) was obtained from Wacker Chemical (Germany). The analysis for MCT-β-CD shows that it has a degree of substitution of 0.3 to 0.5 and an average molecular weight of 1560 (Information provided by Wacker Chemical). Chemicals used in the preparation of solution were purchased from Fisher Scientific: Sodium Carbonate (Na_2CO_3) ACS grade was used as catalyst, phenolphthalein was USP grade and ethanol was ACS grade. Triclosan (>97% HPLC) was purchased from Sigma-Aldrich Co. (St. Louis, Mo). All chemical reagents were used as received. The fabric used in this study was purchased from TestFabrics. It was desized, scoured, and bleached 100% cotton. The cotton fabric characteristics were: warp density of 39 yarns/cm, weft density of 22 yarns/cm, yarn count of 21.9 x 13 tex and a weight of 229.06 g/m^2 (6.8 oz/yd^2).

Fabric Treatment

MCT-β-CD was grafted to the cotton fabrics following a previously reported method (29). Different MCT-β-CD concentrations in water (5, 10, 15, 20, 25, 30 w/w %) were prepared and stirred for 5 min. Then, Sodium Carbonate (Na_2CO_3) was added to the solution (x/4, x is the amount of MCT-β-CD). The solution was stirred for 5 min. The pH of the solution was around 11.5. Cotton fabric samples were dipped into the solution, soaked for 5 min, and passed through a two roller laboratory padder (BTM 6-20-190) at a speed of 365 cm/min and an air pressure of 41 kPa. The wet pick-up was around 100%. The padded fabric samples were dried at 50^{o}C for 10 min by passing them

through a Ben Dry-Cure Thermosol Oven and then curedat 150°C in the same oven for 10 min. Samples were thoroughly rinsed with water and dried.

Weight Measurements

Samples were conditioned for at least 72 hours at 65 ± 2% relative humidity and 21 ± 1°C before and after treatment and weighted. These are standard conditions for textile testing from ASTM method D1776-98. The amount of MCT-β-CD grafted on cellulose macromolecules was determined by a modified calculation based on the AATCC Test method 20A-2000 for nonfibrous content on samples. The amount of MCT-β-CD grafted to the fabric is expressed as percent of weight increase (% weight increase=$((m-m_0)/m_0)*100$, where m_0 is the initial weight of the conditioned fabric, and m is the weight of the treated fabric after rinsing, drying, and conditioning). Three specimens were treated independently from each concentration.

Thermogravimetric Analysis

Thermogravimetric analysis was used to quantify the amount of grafted cyclodextrins and thermal stability of the fabric by measuring the weight change as a function of temperature. Thermogravimetric analysis of the cotton fabrics was performed using the Pyris1TGA equipped with an autosampler for automatic testing of 20 samples (PerkinElmer Shelton, CT). The thermograms were recorded between 100 and 600ºC with a heating rate of 10ºC/min in a flow of nitrogen at 20 ml/min. The cotton fabric samples were cut into small pieces (between 1.5 and 2 mg) and placed in the sample pan. Three measurements were performed from each concentration. The Pyris software was used to calculate the first derivatives of the thermograms (DTG).

FTIR measurements

In this work, we used universal attenuated total reflectance Fourier Transform Infrared Spectrophotometer (UATR-FTIR) to monitor the changes in the infrared spectra of the samples resulting from the treatment (31). Spectrum-One equipped with an UATR accessory (PerkinElmer, USA) was used to record the FTIR spectra of the cotton fabrics in an environmentally-controlled laboratory maintained at 65 ± 2% relative humidity and 21 ± 1^{o}C. The UATR-FTIR is equipped with a ZnSe-Diamond crystal composite that allows collection of the FTIR spectra directly from a sample without any special preparation. The instrument is equipped with a “pressure arm” which is used to apply a constant pressure to the samples positioned on top of the ZnSe-Diamond crystal. The amount of pressure applied is monitored by the Perkin-Elmer FTIR software. This ensures a good contact between the sample and the UATR crystal.

Thirty FTIR spectra per sample were acquired for each sample to produce a total of 540 spectra (30 spectra x 3 replications x 6 concentrations). All FTIR spectra were collected at a spectrum resolution of 4 cm^{-1}, with 32 co-added scans over the range from 4000 to 650 cm^{-1}. A background scan of clean ZnSe-Diamond crystal was acquired before scanning the samples.

The Perkin-Elmer software was used to perform baseline corrections, normalization and peak integration of the spectra. The spectra were subjected to Principal Component Analysis (PCA) with leverage correction and mean-center cross validation boxes checked using Unscrambler V. 9.6 Camo Software AS (CAMO Software AS, Norway).

Phenolphthalein method

Phenolphthalein method is based on the decrease in absorbance of the phenolphthalein molecule in alkaline pH solution due to the presence of cyclodextrins. Phenolphthalein can form a complex with cyclodextrins and the resulting change in color is measured with a spectrophotometer at 552 nm. A 4 mM solution of phenolphthalein in ethanol was prepared and a 125 mM Sodium carbonate in

distilled water was also prepared (32). To 200 ml of the sodium carbonate solution, 2 ml of phenolphthalein solution and 8 ml of ethanol were added. The solution was mixed and 10 ml of the prepared solution were added to a flask with known amount of MCT-β-CD powder or cotton fabrics (cut in circular form with 3.8 cm in diameter). After mixing for 5 min, a portion of each flask was placed in a cuvette and the absorbance of the solution was determined with a UV-VIS spectrophotometer (Lambda 650, Perkin Elmer). Three independent measurements were made from each concentration.

Triclosan inclusion:

Triclosan was used to perform inclusions with MCT-β-CD grafted on the cotton fabrics (Figure 1).

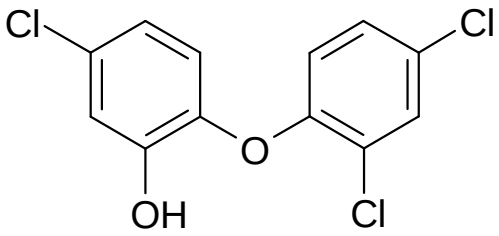

Figure 1. Chemical structure of triclosan.

Triclosan inclusion was performed as follows: A 0.01 mol/l solution of triclosan in ethanol was prepared. Cyclodextrin-grafted cotton samples were cut in small circles (3.8 cmin diameter) and placed in 20 ml of triclosan solution for 24 hrs. The samples were removed, dried in an oven at 40°C for 30 minutes, rinsed in distilled water and in 50% ethanol-water solution and then dried again in an oven at 40°C for 30 min. The 50% ethanolic solution was used due to the low solubility of triclosan in water. There are some triclosan molecules adsorbed on the fabric surface that are not forming inclusion compounds with cyclodextrins. These molecules could interfere with the spectroscopic quantification of the included compounds. Other researchers have used efficiently alcoholic solutions for the removal of the adsorbed molecules on the textile surfaces (33). Then each sample was placed in a beaker with 10 ml of ethanol for 24 hrs. The solution of each flask was placed in cuvettes and the UV-VIS spectra were acquired. The maximum absorbance of triclosan was at 282 nm. A calibration curve was made in order to calculate the amount of triclosan in the solutions.

Antimicrobial testing:

Antimicrobial tests were performed by determining the colony-forming unit (CFU) of *S. aureus*, which is a measure of viable bacteria numbers as described in previous work (34). Briefly, a solution of 2.5 µl/ml of bacteria was made and 20 µl of this solution was deposited on the cotton fabric surface. Cotton samples were placed on LB plates in an oven at 37^{o}C. Cotton fabrics with the highest MCT-β-CDconcentration in solution (30%) were cut in 1.6 cm diameter circles and the same procedure for inclusion of triclosan was followed. Three replications for each concentration of cyclodextrin grafted to the fabric were made.

3. Results and discussion

Weight Measurements

Figure 2 illustrates the reaction mechanism between cellulose macromolecules and MCT-β-CD. The cyclodextrin derivative is fixed to the cotton by a nucleophilic substitution reaction between the

hydroxyl groups of the cellulose chain and the chlorotriazine ring. Hydrochloric acid is released as a byproduct of the reaction.

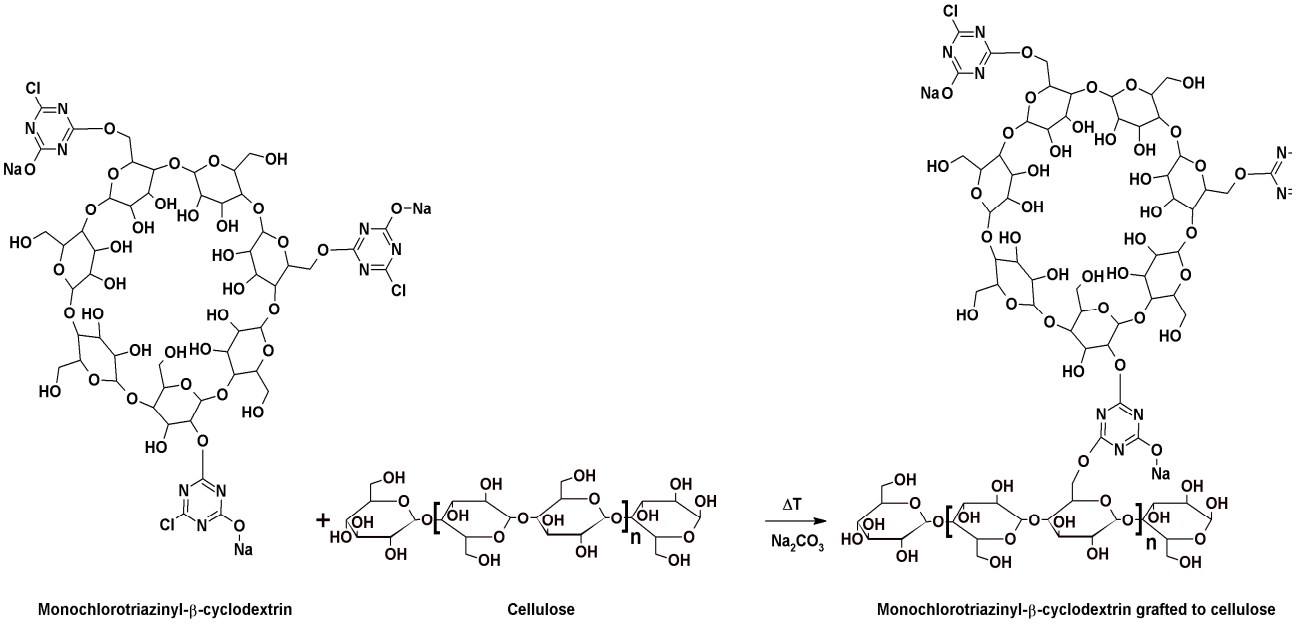

Figure 2. Reaction between MCT-β-CD and cellulose.

The relationship between the amount of MCT-β-CD grafted to the cotton fabric and the MCT-β-CD concentration in the solution is shown in figure 3. The non-linear increase of the percent add-on with increasing MCT-β-CD concentration in the solution is attributed to the saturation of cellulosic OH groups at higher MCT-β-CD concentrations.

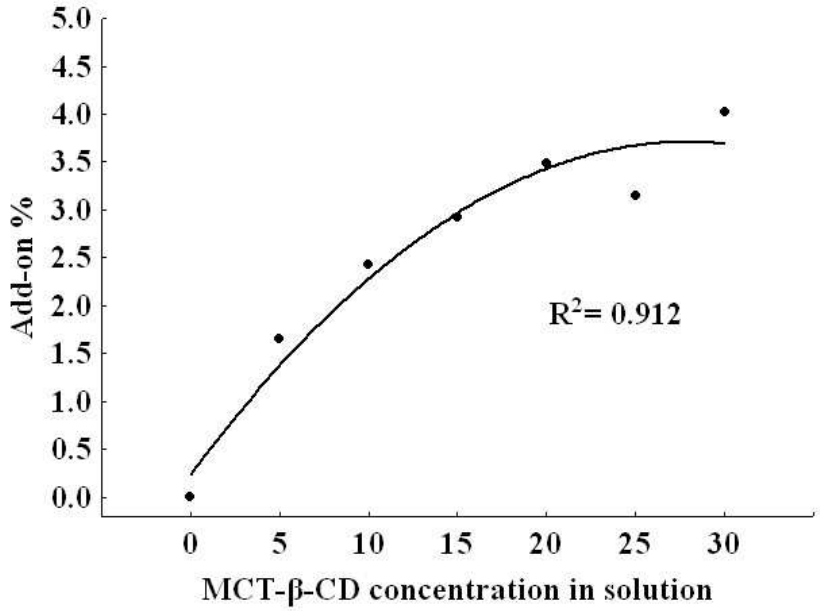

Figure 3. Percent Add-on expressed in % as a function of MCT-β-CD concentration in the solution expressed in w/w %.

FTIR measurements

Figure 4 shows representative FTIR spectra of untreated cotton fabric and MCT-β-CD-30% (cotton treated with 30% MCT-β-CD concentration in the solution).

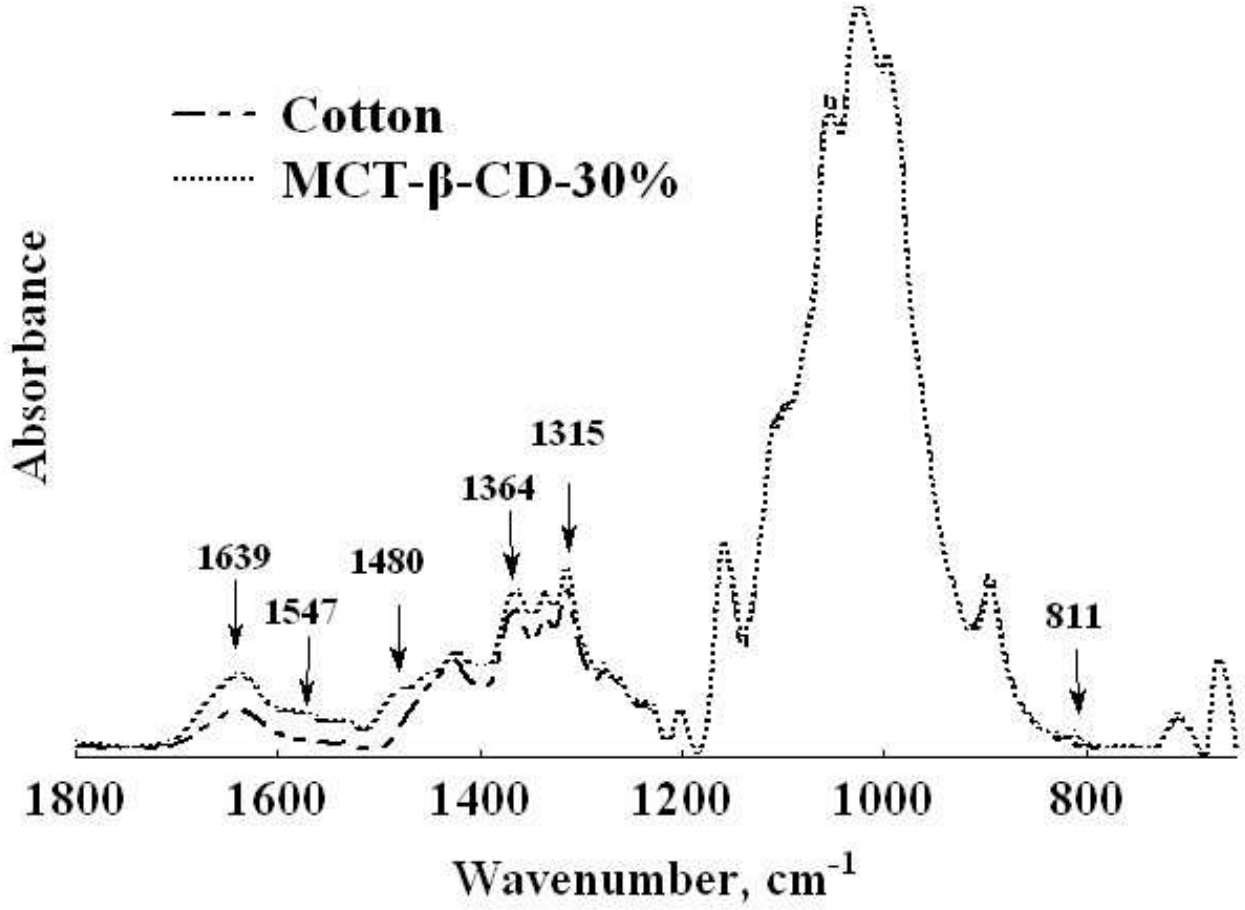

Figure 4. FTIR spectra of control (cotton) and sample treated with 30% MCT-β-CD concentration in solution (MCT-β-CD-30%).

Principal components analysis was performed on the FTIR spectra of the control (untreated fabric) and the treated fabric MCT-β-CD-30% in order to identify different groups of spectra. PCA is a multivariate technique which involves a mathematical procedure that transforms a matrix of the FTIR spectra to a matrix of mutually uncorrelated variables called principal components. Most of the variability in the data is accounted in the first principal component (PC1). The second principal component (PC2) accounts for most of the remaining variability in the data (35). The plot of PC1 and PC2 scores, depicted in figure 5, shows two distinct groups of spectra corresponding to the control fabric and the treated fabric MCT-β-CD-30%. One major component (PC1) explained 88% of the variability and it distinguished the non-treated fabric from the treated cotton fabric.

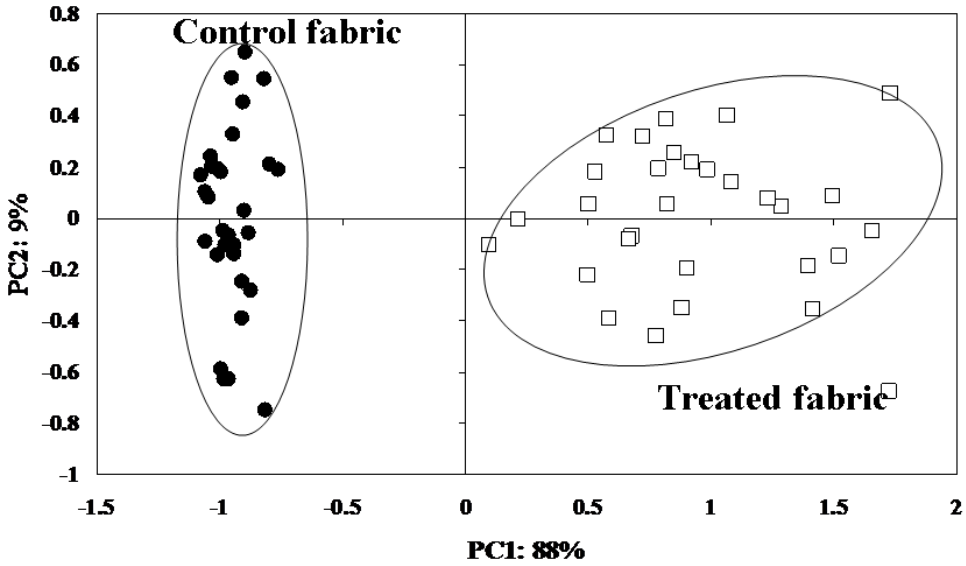

Figure 5: Principal components analysis of the FTIR spectra of the control and the treated fabric MCT-β-CD-30%.

Figure 6 shows the plot of PC1 scores as function of wavenumbers. Several vibrations are present mainly in the region from 1784 to1183 cm^{-1}. The integrated intensity in this region ($I_{1784-1183}$) was calculated and was correlated with the MCT-β-CD concentration in the solution (Figure 7). Table 1 reveals statistically significant effect of the MCT-β-CD concentration in the solution on the integrated intensity in the range 1784-1183 cm^{-1}.

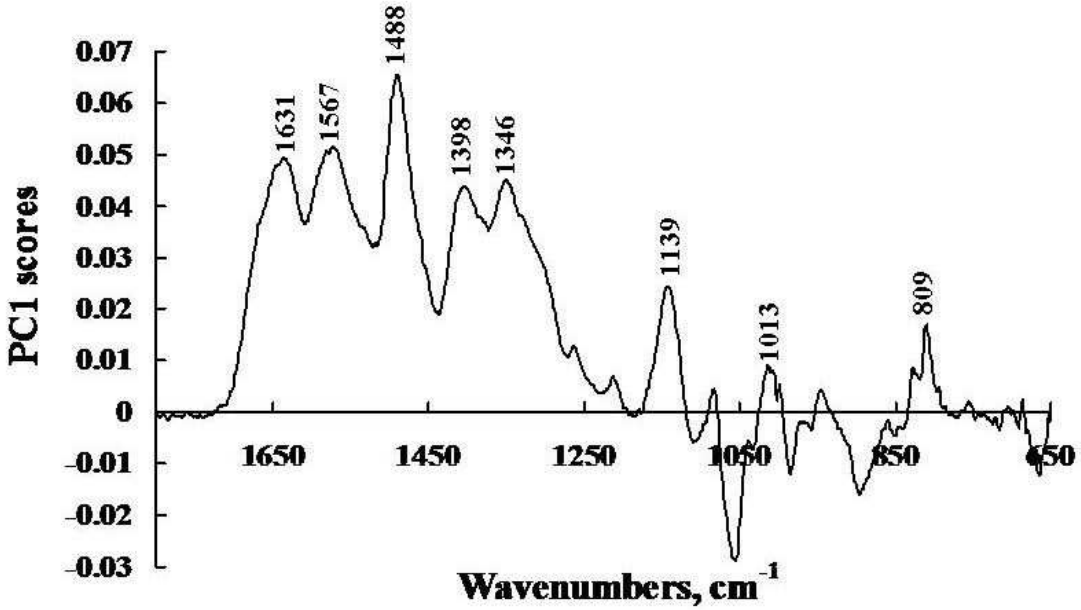

Figure 6: PC1 scores versus wavenumbers.

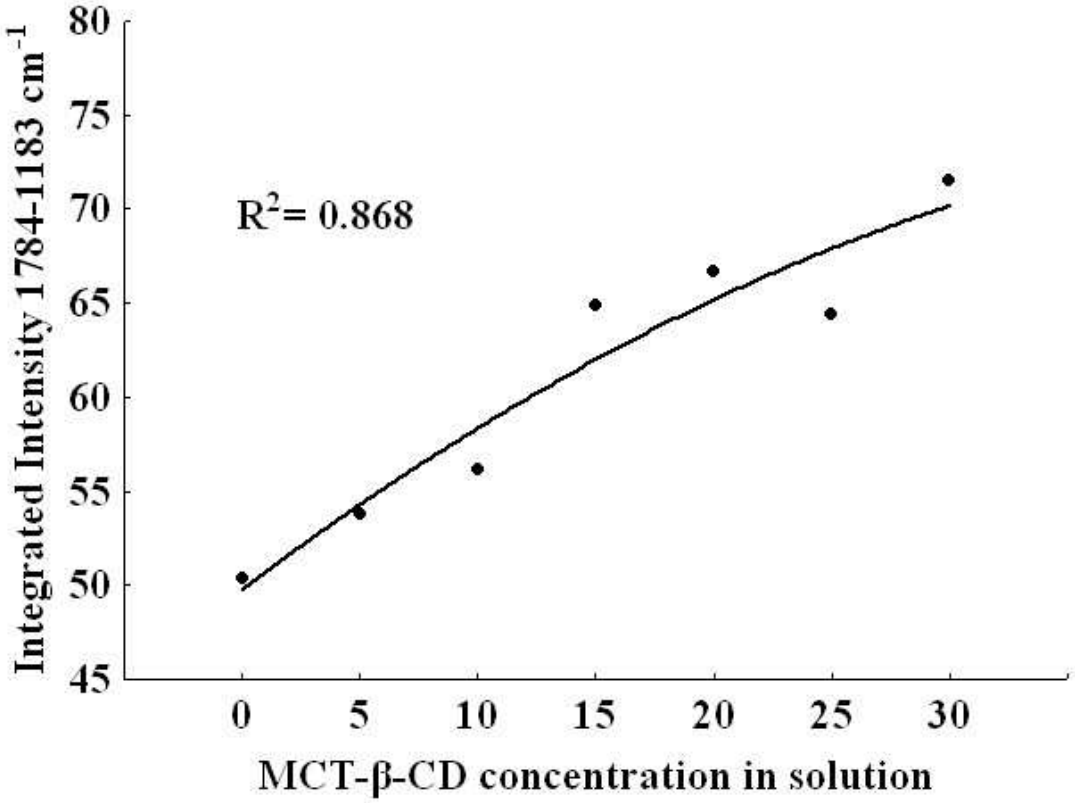

Figure 7. FTIR integrated intensity from 1784-1183 cm^{-1} as a function of MCT-β-CD concentration in the solution expressed in w/w %.

Table 1. Variance analysis: effect of the MCT-β-CD concentration in the solution on the integrated intensity $I_{1784-1183}$.

Parameter	*df*	*F*	Probability	$I_{1784-1183}$
Intercept	1	69099.47	0.000001	
MCT-β-CD concentration	6	157.64	0.000001	
0				50.3 a
5				53.8b
10				56.2c
15				64.9d
20				66.8e
25				64.4d
30				71.5 f
Error	623			

df, degrees of freedom; *F*, variance ratio, [a] Values not followed by the same letter are significantly different with α=5% (according to Newman-Keuls tests).

Thermogravimetric Analysis

TGA measurements were performed in order to correlate the thermal properties of the treated samples with the amount of grafted cyclodextrins. To compare the thermograms, the average

inflection point (peak temperature) of the first derivative was obtained for each concentration. The peak temperature is the temperature of the maximum thermal decomposition rate. Figure 8 shows the plot of the average peak temperature as a function of the MCT-β-CD concentration in the solution. The increase of the amount of grafted cyclodextrins leads to a decrease of the peak temperature. This is due to lower peak temperature of MCT-β-CD compared to cotton and to the decomposition byproducts of the grafted MCT-β-CD, affecting the thermochemical pathway of the cellulose decomposition. The peak temperature of MCT-β-CD is around 305ºC, while for cotton this peak temperature is around 390ºC (experimental data). Thus, as the amount of MCT-β-CD on the fabric increases the maximum decomposition rate gets shifted to lower temperature. The trigger temperature of each thermogram was also obtained by calculating the temperature at which a weight percentage changes more than 0.5%. Figure 9 shows the average trigger temperature plotted as a function of MCT-β-CD concentration in the solution. The trigger temperature decreases as the MCT-β-CD concentration in the solution increases. This is due to the fact that MCT-β-CD-crosslinked has a lower trigger temperature (around 220ºC) when compared to the trigger temperature of cotton fabric (around 290ºC).

In figure 10, the average weight percentage residue after reaching 600ºC is plotted against MCT-β-CD concentration in solution. There is a good non-linear relationship between the amount of grafted MCT-β-CD and the amount of char produced after thermal decomposition. It has been reported that impurities in cellulose, such as salts, could cause the char yield to change (36,37). Thus, it is reasonable to hypothesize that the by-products of the decomposition of MCT-β-CD react with the cellulose substrate and cellulose degradation by-products to produce a higher amount of char.

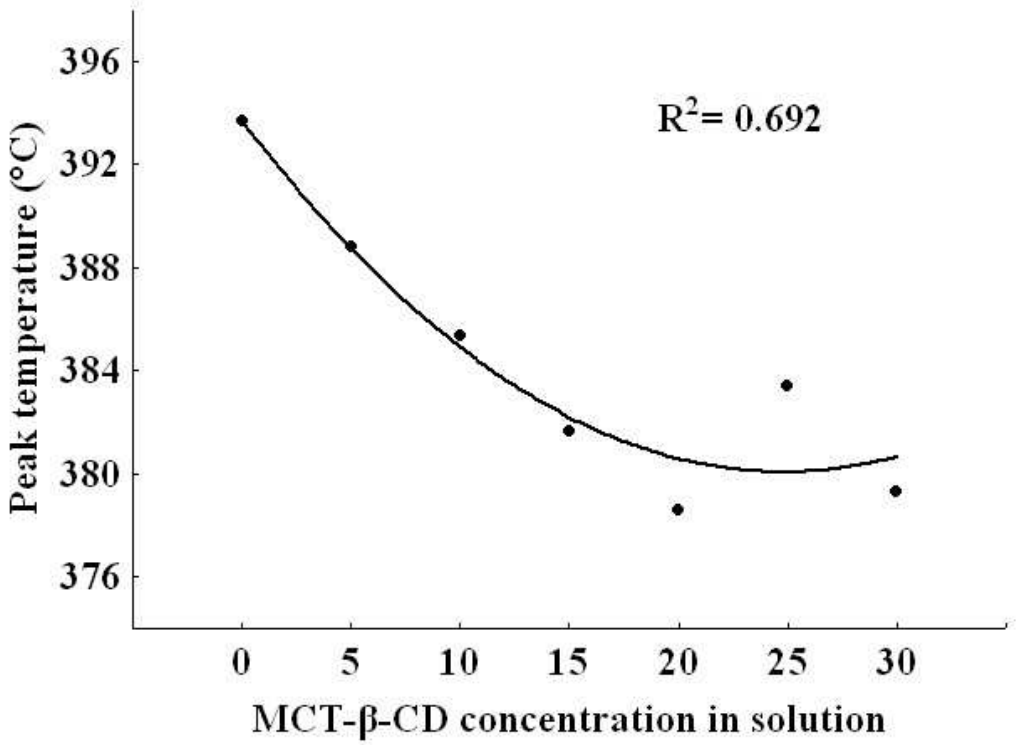

Figure 8. Peak temperature as a function of MCT-β-CD concentration in the solution expressed in w/w %.

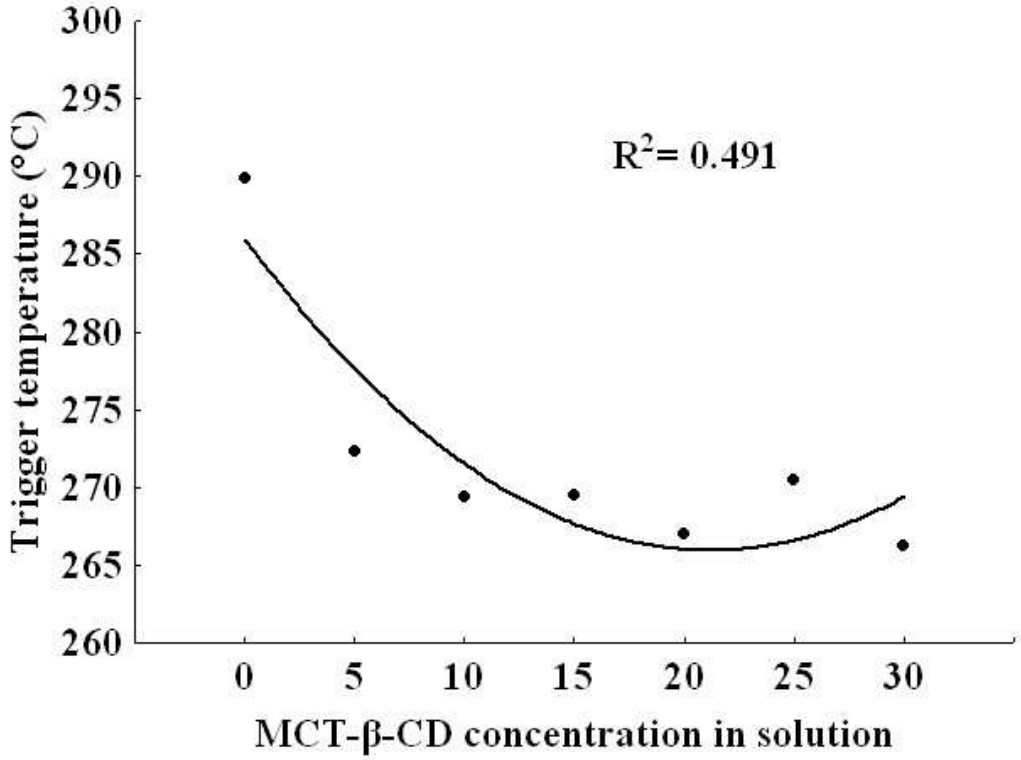

Figure 9. Trigger temperature as a function of the MCT-β-CD concentration in the solution expressed in w/w %.

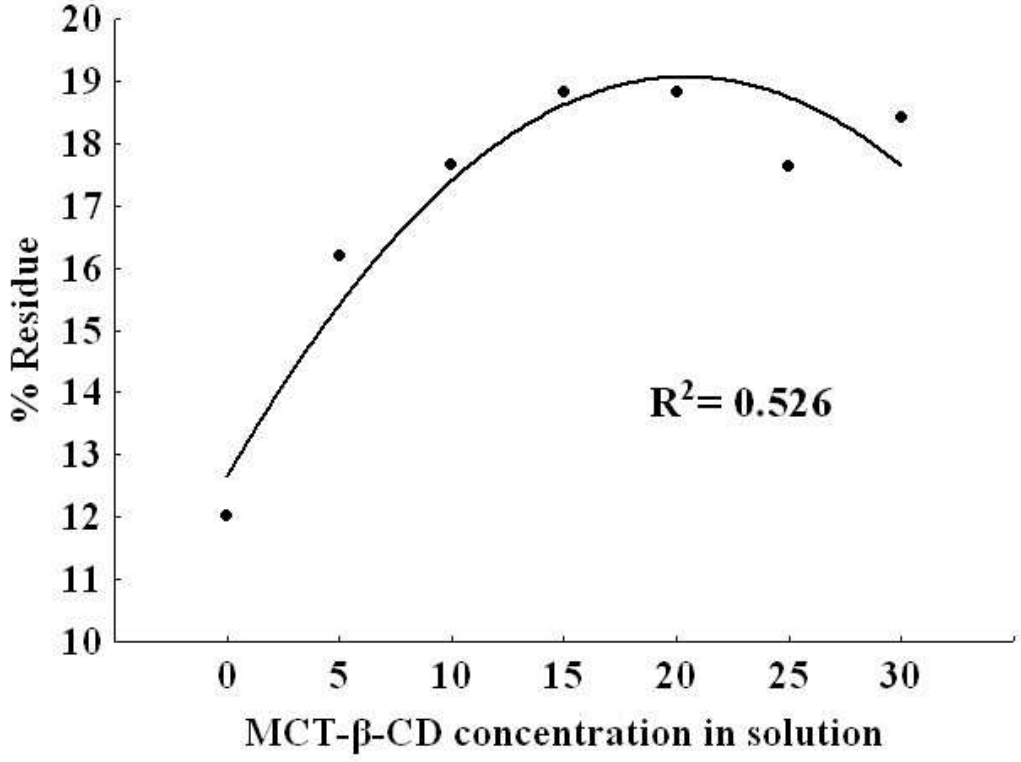

Figure 10. Residue percentage as a function of the MCT-β-CD concentration in the solution expressed in w/w %.

Phenolphthalein method

Phenolphthalein forms inclusion compounds with cyclodextrin. When the phenolphthalein is included in the CD cavity in alkaline solutions, it is transformed from the red colored dianion form to its colorless lactonoiddianion (38). This characteristic makes phenolphthalein a very effective colorimetric indicator to prove that the cyclodextrins cavities are available for forming inclusion compounds. The control and treated samples were immersed in a solution containing phenolphthalein as described in the experimental section. The maximum absorbance of phenolphthalein in an alkaline solution is at 552 nm. As shown in figure 11, when the amount of grafted MCT-β-CD on the fabric is increased the absorbance at 552 nm is decreased.

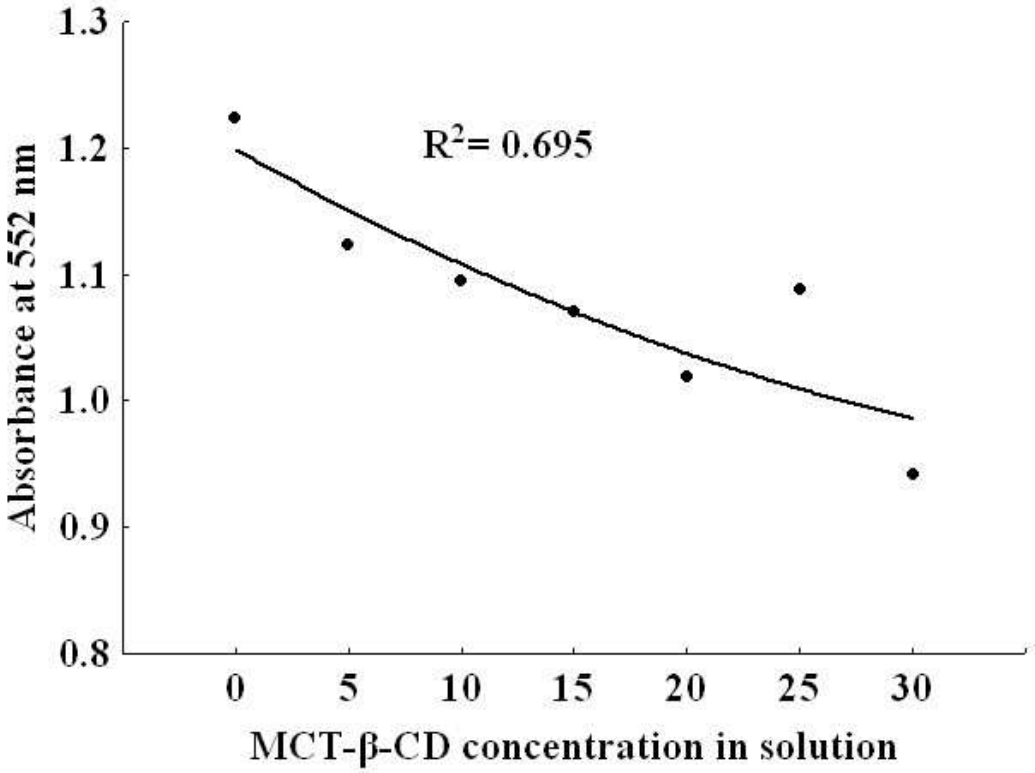

Figure 11. Phenolphthalein inclusion: absorbance at 552 nm as a function of the MCT-β-CD concentration in the solution expressed in w/w %.

Triclosan inclusion:

The measurement of the released amount of triclosan was performed as follows: first, triclosan was included in the cavities, and then the amount of molecules released in ethanolwas monitored by the UV absorbance of the solution.

Figure 12 shows the results of the release of triclosan in ethanol by measuring the absorbance at 282 nm as a function of MCT-β-CD concentration in the solution. The results show that triclosan molecules are present in the control after rinsing. This is due to the low solubility of triclosan in water and ethanol-water solution. It is important to point out that the amount of triclosan released by MCT-β-CD treated samples is higher than the untreated sample. For example, the average amount of triclosan released in ethanol by the samples treated with 30% MCT-β-CD concentration in solution is enough to achieve a molar concentration 3.5 times higher than the control.

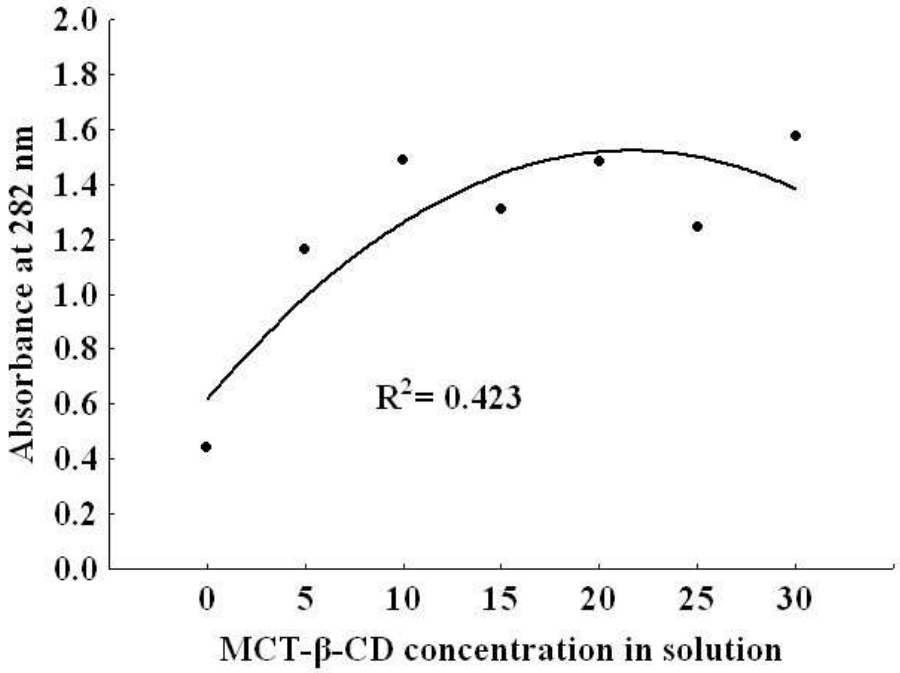

Figure 12. Triclosan release: absorbance at 282 nm as a function of the MCT-β-CD concentration in the solution expressed in w/w%.

Antimicrobial testing:

It has been reported that triclosan has very powerful antimicrobial properties. Therefore, MCT-β-CD treated cotton fabrics were immersed in triclosan solutions and rinsed as described in the experimental section. To test the ability to remove triclosam that is included in the cavities, the samples were washed in ethanol. Figure 13 shows the Colony Forming Unit of *S. aureus* of the control and treated cotton fabrics. Untreated cotton fabric (sample A) does not exhibit any antimicrobial properties. However, treated cotton fabric with MCT-β-CD and loaded with triclosan molecules (sample B), has very strong antimicrobial activity against *S. aureaus*. When the fabric is washed with ethanol to remove triclosan (sample C), the fabric does not retain its antimicrobial performance. This indicates that triclosan can be easily removed from the cavity, which allows the cavities to be available for other guest compounds.

4. Conclusions

In this investigation MCT-β-CD was grafted to cotton fabric surfaces. The amount of MCT-β-CD grafted to the fabric was correlated by gravimetric measurements, FTIR, and TGA. Good correlation between the concentration in solution of MCT-β-CD and the integrated spectra in the IR region from 1784 to1183 cm^{-1} ($I_{1784-1183}$) was obtained. Thus, proving that FTIR with an UATR accessory is an excellent tool to quantify the amount of cyclodextrins grafted to the surface. The values of the peak temperature, the trigger temperature and the weight remaining at 600ºC obtained from TGA were correlated to the amount of grafted cyclodextrins as well. Phenolphthalein was used to determine if the cavities of MCT-β cyclodextrin were available for inclusions. The maximum absorbance of phenolphthalein in alkaline solution (552 nm) was correlated to the amount of cyclodextrins grafted to the fabric. The higher the amount of cyclodextrins grafted to the textile surface the lower the measured absorbance. This is due to the fact that phenolphthalein forms inclusion compounds with the cyclodextrins. Furthermore, one inclusion compound was used to test the release capacity of the

treated samples. Triclosan included in the cyclodextrins cavities and released in ethanol was measured by the absorbance at 282 nm. The amount of triclosan released by the treated samples was higher than the amount released by the non-treated samples. Moreover, the antibacterial test performed on the samples showed that MCT-β-CD treated samples with triclosan included in the cavities had excellent antibacterial properties. Additionally, it was shown that the included triclosan could be removed from the cavities; therefore the cavities were available to form inclusion compounds with other molecules.

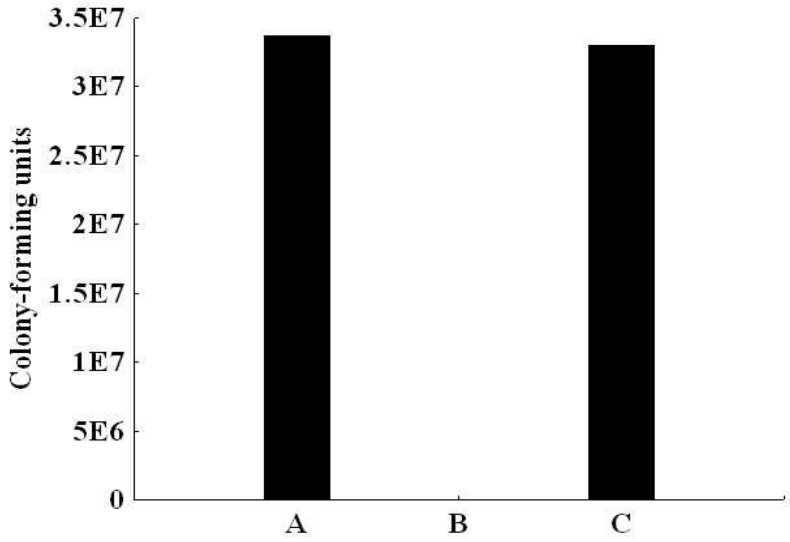

Figure 13. Antibacterial test of (A) untreated cotton (control), (B) MCT-β-CD-30% treated samples with triclosan included, and (C) MCT-β-CD-30% treated with triclosan and washed with ethanol.

Acknowledgments

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