Preparation of chitosan based antibacterial agent CS-g-DMC and its long-effective antibacterial finishing for cotton fabric

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Abstract

In this study, a chitosan-based high polymer antibacterial agent CS-g-DMC was synthesized through grafting copolymerization with an environmentally friendly initiator system of H_2O_2 and ascorbic acid (Vc). The CS-g-DMC was used for the long-effective antibacterial finishing of cotton fabric. The SEM, EDS, FTIR, XPS, and XRD were conducted for the characterization of the fabric. Result showed CS-g-DMC combined with cellulose macro-molecule chemical bond, and had uniformly distributed on surface of cotton fiber. After finishing, the cotton fabric had antibacterial rates against S. aureus and E. coli above 99.9% after 10 times of standard washing. The finished cotton fabric had significantly improved hydrophily, its contact angle decreased from 107° to 104°. Its breaking force significantly increased from 173.38 N to 219.33 N, and its breaking elongation and moisture transmission rate had not dropped obviously. In general, the cotton fabric finished by CS-g-DMC obtained long-effective antibacterial and increased mechanical properties, at meantime kept its comfortable capability to a great extent.

Introduction

The cellulose fiber products represented by cotton are widely used in textiles due to their excellent properties, such as hygroscopicity, breathability and softness. These properties also provide a suitable environment for microorganisms to survive and multiply (Cheng et al. 2022; Verma et al. 2021; Zhou et al. 2019). The attachment of microorganisms affects the performance of the fabric, for instance discoloration and loss in mechanical strength, even has many negative effects on public health. It is important to improve the anti-microbial properties of cellulosic fabrics (Ibrahim et al. 2021; Kostic et al. 2014; Li et al. 2021).

To date, many antimicrobial technologies have been successfully applied to fabrics. Compared to organic antimicrobial agents represented by phenols or vanillin and inorganic antimicrobial agents synthesized using metals such as silver, copper and zinc, natural antimicrobial agents are safer and have a non-toxic active antimicrobial component (Yu et al. 2021; Zhou et al. 2021). Chitosan is a natural cationic polysaccharide ang have a variety of active functional groups that also formed chemical bonds with cellulose molecules, providing cellulose fibers with a long-lasting antibacterial effect (Bakshi et al. 2020; Khan et al. 2020; Kumar et al. 2016; Valle et al. 2021). However, chitosan is poorly water soluble and only dissolves when the amino groups in the molecule is protonated to form ammonium ions in an acidic environment (Doan et al. 2021; Li et al. 2015). Meanwhile, the bioactivity of chitosan (e. g. antibacterial, antioxidant, cytotoxic) are limited by water solubility, so the antibacterial properties of chitosan are very limited and modifying it was a necessary way (Andreica et al. 2020; Li et al. 2020; Zeng et al. 2021).

Graft-copolymerized is an ideal method to modify chitosan (Branca et al. 2016; Hassan 2018; Yue et al. 2021), which molecular chains are rich in active functional groups - amino and hydroxyl groups - that can be easily chemically modified (Choi et al. 2016; Liu et al. 2018; Hussein et al. 2020; Sadeghi-Kiakhani et al. 2018). It has been known that the antibacterial activity of chitosan is influenced by the strength of the positive charge in its macromolecular chains. An increase in the density of the positive charge can

change the cell permeability causing the bacterium to rupture and denature proteins, resulting in the inactivity of certain enzymes in the bacterium, thus killing or inhibiting the bacteria (Kritchenkov et al. 2021; Li et al. 2020). Chitosan derivatives obtained by grafting quaternary ammonium compounds (Wang et al. 2021), such as ammonium bromide, polyacryloyloxyethyl trimethyl ammonium chloride and 2-(acryloyloxy)ethyltrimethyl ammonium chloride (Chen et al. 2017; Wang et al. 2016), onto the chitosan molecular chain not only have better physicochemical properties (solubility, crystallinity, thermal stability, etc.) (Kumar et al. 2020; Mohamed et al. 2019; Xiao et al. 2021), but also can significantly increase the positive charge density of chitosan and thus enhance its antibacterial activity (Yin et al. 2021).

In contrast, the hydrogen peroxide/ascorbic acid reduction pair initiation system, with its high reaction rate and low activation energy, can initiate polymerization at lower temperatures and also boasts simplicity, safety, non-toxicity and low cost (Hu et al. 2016; Moreno-Vásquez et al. 2017; Zheng et al. 2022).Based on this, the initiation system is ideal for the synthesis of polyphenol-g-chitosan, which is widely used in food and health applications such as caffeic and ferulic acids, gallic acid, protocatechuic acid, p-hydroxybenzoic acid and vanillic acid (Hong et al. 2019; Liu et al. 2014; Negm et al. 2020; Wang et al. 2019).However, very little research has been carried out on the synthesis of quaternary ammonium polymer-g-chitosan as a means of improving the properties of chitosan and its application in antimicrobial finishing of textiles.

In this paper, methacryloxyethyltrimethyl ammonium chloride grafted chitosan (CS-g-DMC) was prepared by free radical graft copolymerization, and its physicochemical properties and antibacterial activity were characterized. CS-g-DMC was covalently grafted onto cellulose fibers using a chemical finishing of butane tetracarboxylic acid with sodium hypophosphite. The cross-linked finishing process gives cellulose fibers long-lasting and effective anti-bacterial properties while avoiding the risks to human health and the environment posed by aldehyde finishing. Morphological analysis and structural characterization of CS-g-DMC grafted with cellulose fibers to evaluate the antibacterial and washing resistance of the modified fibers.

Experimental

Materials

Chitosan (deacetylation degree 80 ~ 90%, Viscosity:50 ~ 800 mPa·s) was purchased from Sinopharm Chemical Reagent Co., Methacryloxyethyltrimethyl ammonium chloride (DMC) was obtained from Aladdin reagent company. Acetic acid, Hydrogen peroxide (H_2O_2), ascorbic acid, 1,2,3,4-Butane tetracarboxylic acid (BTCA), sodium hypophosphite was purchased from JIANGTIAN CHEMICALS CO., LTD. Staphylococcus aureus and were procured from Beijing Microbiological Culture Collection Center. Plain woven cotton fabrics. All other reagents were of analytical grade.

Synthesis of CS-g-DMC

Chitosan (2 g) was dissolved in 40 ml of 1% acetic acid solution and stirred for 30 min at 40°C until the chitosan was completely dissolved. Then 2.5 ml of cationic monomer DMC, and green initiator (consisted of 1 ml of H_2O_2, and 0.86 g of ascorbic acid) were successive added, for 1.5 h of graft polymerization reaction under continuous stirring. Equal amounts of H_2O_2 and ascorbic acid were added and the reaction was continued for another 1.5 h. After the reaction, the product obtained was rotary evaporated and then lyophilized to obtain the CS-g-DMC.

Modification of cotton

Scheme.1 Scheme of chemical binding of CS-g-DMC to the cotton fabric

0.05 g of CS-g-DMC, with catalyst sodium hypophosphite 0.2 g, cross-linking agent BTCA 0.2 g, penetrant JFC 0.2 ml were dissolved in 100 ml deionized water, diluted and configured into a 0.1% antimicrobial agent aqueous solution. Immerse 1g cotton fabric (washed with anhydrous ethanol and deionized water and then dried) into the above solution, a “double immersion - double mangle” two-bath finishing process was adopted, using a liquid entrainment rate of 200%. After padding, the fabric was pre-drying at 80℃ for 5min, baking at 140℃ for 10min. Then fully washed with flowing deionized water and dried at room temperature to get modified cotton fabric. The synthesis of antibiotic finishing of cotton is depicted in Scheme 1. The esterification reaction of -COOH on CS-g-DMC and cellulose with -OH on BTCA take place under the catalytic influence of sodium hypophosphite, and the antimicrobial agent binds to cotton fiber in the form of covalent bonds, giving cotton fabric long-lasting and effective antimicrobial properties.

Characterizations

Surface morphologies of cotton fabrics were observed using SEM set (Phenom XL, Holland). Surface element content of cotton fabrics were measured by an energy dispersive spectrometer-scanning electron microscope (EDS-Hitachi S-4800, Hitachi Crop, Tokyo, Japan). Infrared spectra of cotton fabrics were obtained with a Nicolet iS50 fourier transform infrared spectrometer. The XPS analysis was performed by X-ray photoelectron spectroscopy (NEXSA, America). Crystalline structure of cotton fabrics determined by X-ray diffractometer (BRUKER, Germany) with scanning speed 11.8°/min from 10° to 80°.

Solubility test

0.025 g of dry CS and CS-g-DMC sample were dissolved in 9 ml 10% HCl solution. Then 0.5 M NaOH solution was dropwise added to adjust the aqueous solution to different pH value of 2 ~ 12. The pH values were determined by pH meter and a spectrophotometer was used to measure the transmittance of the solution at 600nm in the range of pH = 2 ~ 12. the solubility of the sample in this study was represented by the transmittance. The graph was plotted with pH as the X-axis and transmittance as the Y-axis.

Antibacterial property test

The antibacterial performance of cotton fabrics (0.75 g, 5×5 mm pieces) against E. coli and S. aureus was determined by the oscillation method. The principle was to load the fabrics into 70ml of test solution

(containing live bacteria 2×10^4 CFU/ml ~ 2.5×10^4 CFU/ml) in a flask, shaking at 37 ℃ for 18 h. To the specified time, with 10 times dilution method series dilution to the appropriate dilution, took 0.1 ml of sample solution from the flask and spread it evenly on the agar plate. The number of colonies on the agar plates was recorded after incubation at 37℃ for 24 ~ 48 h. The inhibition rate is calculated as follows:

$$inhibitionrate = \frac{A-B}{A} \times 100\backslash\%$$

A, B are the number of live cells before and after shaking the bottle.

Physical and mechanical property test

The water contact angle was measured by a contact angle measuring instrument. Shooting for 0.5 seconds a frame, a total of 30 frames.

The elongation at break and breaking strength were measured on a universal strength machine (Instron-3369. America) in accordance with the standard method of GB/T 3923.1–2013. The specimen size was 50×250 mm, the maximum force and elongation at maximum force of the specimens were determined by using the universal strength machine, the gauge length was set to 200 mm, the stretching rate was 100 mm/min, the preload tension was 2 N, and the results were expressed as the average of five experiments.

The moisture permeability was measured in accordance with the evaporation method in the standard GB/T 12704.2–2009. The specimen was a circle with a diameter of 70 mm, and the test conditions were 23°C and 50% relative humidity. Inject 34 ml of distilled water precisely into the moisture permeability cup. After placing the specimen on the moisture permeability cup, placed it horizontally in the fabric moisture permeability meter, balanced 1 hour after weighing, then weighed again 1 h after the test time, accurate to 0.001 g, and the test results are expressed as the average of three tests. The formula is used to calculate the moisture permeability of the specimen:

$$WVT = \frac{\Delta m}{A \bullet t}$$

WVT is the moisture permeability (g/m^2/h), Δm is the difference between two weighs of the same test combination (g), A is the effective test area (0.00283 m^2), and t is the test time (h).

Result And Discussion

Quaternization of CS-g-DMC

The graft copolymerization of chitosan with DMC is confirmed by comparing the FTIR spectra of CS-g-DMC and chitosan with two different grafting rates (CS-g-DMC-1-40%, CS-g-DMC-2-33%). As shown in Fig. 1a, the unmodified CS shows characteristic spectral bands of glucosamine. On the one hand, the IR spectra of CS-g-DMC shows new bands at 1735 cm^{-1}, 1480 cm^{-1}, and 1200 cm^{-1}. The formation of a sharp new band at 1735 cm^{-1} is attributed to the C = O stretching vibration present in the grafted DMC constitutional units (Gao et al. 2021). The band at 1480 cm^{-1} is attributed to the bending vibration of C-H

on the methyl of quaternary ammonium groups. The band at 1200 cm^{-1} is attributed to the stretching vibration of C-N in quaternary ammonium groups. Furthermore, the C-H stretching vibration of CS-g-DMC at 2850 ~ 3000 cm^{-1} is found enhanced, that is because the introduced DMC units on grafted chains contains a large number of -CH_3 and -CH_2 structures. Meanwhile, the peak of hydroxyl group v_{O-H} at 3400 cm^{-1} is weaken, indicating that the grafting reaction occurs mainly on the hydroxyl groups that located in the outside of glucosamine rings. All the above characteristic peaks indicate that after grafting polymerization, a certain number of positively charged polymer chain segments have been introduced to the CS macromolecules.

Since the water solubility is considered as a key factor to the polymer antibacterial finishing agent, a solubility test is conducted on CS-g-DMC and CS. Figure 1b shows that CS-g-DMC samples have a significantly higher dissolution rate than CS over a relatively wide pH range of 2 to 8, implying that CS-g-DMC can maintain good water solubility properties from acidic to neutral and alkaline environments. That is considered because of the introduced positively charged polymer chains on CS-g-DMC, which can weaken the intra-intermolecular hydrogen bonds of CS macromolecules via the homocharge repulsion and steric hindrance effects, thus promote the protonation and hydration of the amidogen groups, and consequently improve the solubility. The solubility is found to increase with the increase of at pH = 7, the solubility of CS, CS-g-DMC-1, and CS-g-DMC-2 are respectively 28.6%, 95.3% and 75.0%, since the antibiotic finishing of cotton weaves are often conducted at acid to neutral environments, the CS-g-DMC is supposed to have more advantages than CS.

Characterization of cotton fabrics

Morphological Study

Figure 2 show the SEM images of the surface of cotton and modified cotton. Compared with cotton (Fig. 2a, c), modified cotton (Fig. 2b, d) has a thick film attached to the surface and localized agglomeration, which makes the fiber surface rougher. The polymer film has a certain protective effect to the fiber, and can not only improve the antibacterial property but also the mechanical property for the yarn.

Figure 3 shows the elemental distribution in the modified cotton was determined by EDS mapping. The N and O elements were discovered to have relatively uniform distribution on the weave, implying that the antibacterial agent CS-g-DMC is immobilized uniformly on the weave surface due to its enhanced water solubility and permeability. Because the Cl element comes from the quaternary ammonium groups on DMC units, the new element distribution of Cl in the EDS spectra is also evidence for the immobilization of CS-g-DMC on cotton fibers.

FTIR spectroscopic characterization

The characteristic peaks of cellulose appeared in the cotton fabrics before and after modification:(1) at 3433 cm^{-1} are the stretching vibrations of -OH;(2) around 2916 ~ 2849 cm^{-1} suggest the stretching

vibrations of methyl and methylene C-H;(3) at 1165 cm^{-1} is attributed to the asymmetric stretching vibrations of C-O-C and the peak at 1057 cm^{-1} was related to the vibrations of pyranose ring skeleton (Xin et al. 2020). In addition, three new peaks appear in the spectrum of the modified cotton fabric. A peak group appears around 1740 ~ 1700 cm^{-1}, attributes to the C = O stretching vibration, including acyl groups in DMC grafted monomer chain units and ester groups formed by cross-linking agent butane tetracarboxylic acid. 1456 cm^{-1} is assigned to the stretching vibration of methyl in N^{+}-CH_3 (Duan et al. 2020). The peak at 1206 cm^{-1} is attributed to the C-N stretching vibration from aliphatic amine group. Peak at 816 cm^{-1} is attributed to plane-bending vibration of methylene groups in the backbone grafted polymer chains. The cellulose macromolecules are chemically bonded to chitosan after finishing, and a certain number of positively charged polymer chain segments are introduced, which is responsible for the cotton fabric's antibacterial properties.

XPS spectroscopic characterization

Figure 5 is the XPS spectrum of cotton fabrics before and after modification. Cotton fabrics after modification were further characterized by XPS spectra. The full wave survey in Fig. 5a shows in modified cotton fabric new photoelectron peak of N1s appeared. The signal peak of Cl2p was not found due to the limitation of the grafting rate of DMC-g-CS with cotton. In Fig. 5b, the binding energy of N1s spectrum of modified cotton from different chemical environments at chemical shift value pf 399.95ev(C-N), 401.26ev(-NH_2), 402.38ev(C-N^{+}) are found (Barbosa et al. 2019; Chen et al. 2016; Yan et al. 2020). Figure 5c and d show the C1s high-resolution XPS spectra of cotton before and after modification respectively. In Fig. 5d, the modified cotton shows a new peak of O-C = O at 289.66ev, this is assigned to ester groups formed by cross-linking reaction of BTCA. The C-O-C and C = O peaks overlap at 288.17ev, giving an enhanced signal there (Gu et al. 2018). This is due to the introduced DMC chain units contains acyl groups. At mean time, since the H-atoms of some hydroxyl groups in cotton are replaced by branched carbon chains, to form C-O-C etheric structures. In addition, the -OH signal peak of modified cotton was retained to some extent, which is the joint result of the cross-linker butane tetracarboxylic acid and the un-reacted hydroxyl groups of the cotton fabric. the XPS results show that DMC-g-CS is successfully grafted onto the cotton fiber by carboxylic acid finishing.

XRD analysis

The XRD spectra of cotton fabrics were shown in Fig. 6. The peaks at 2θ of 14.8°,16.5°,20.4°,22.7°,34.3° showed agreement between the two (Ding et al. 2019; French 2017). The results shows that the crystal form shape and crystallinity of modified cotton basically keeps its original structure, indicating that the chemical modification occurred primarily on the surface of cotton fiber and did not affect its crystalline region. For this reason, the modified cotton weave can maintain most of its mechanical properties, since the strength of fiber to a large extent depend on its crystalline structure.

Antibacterial properties of modified cotton

As shown in Fig. 7, the finished cotton fabric showed excellent antibacterial activity against *E. coli* and *S. aureus* with an antibacterial rate of more than 99.9%. A washing resistance experiment is conducted in order to examine the long effective antibacterial activity of finished cotton fabric. The bacterial inhibition rates of the original and finished cotton fabrics are measured after 5 and 10 washes. Figure 8 illustrates that after five washes, the finished cotton fabric had an inhibition rate of 96.8% for *S. aureus* and 98.1%for *E. coli*. After 10 washes, *S. aureus* and *E. coli* have an inhibition rate of 95.3% and 94.3%, respectively. It demonstrates the long-lasting and effective antibacterial performance of CS-g-DMC to cotton fabric.

S. aureus is a Gram-positive bacterium with an isoelectric point at pH = 2 ~ 3. Therefore, when in a neutral environment, its surface is negative charged (Ganewatta et al. 2015). When they contact to the finished cotton fabric, the positive charged amidogen and quaternary amine groups on cotton fibers will adhere to the cell via electrostatic attraction, forming an impermeable layer around the bacteria, which inhibits the exchange of substances and thus kills the bacteria (Li et al. 2019; Adhikari et al. 2018; Ganan et al. 2009). For *E. coli*, one of the Gram-negative bacteria, the isoelectric point is higher at pH = 3 ~ 5, so the positive charge on the surface of the bacteria is less. Hence the binding force between fiber and *E. coli* cell is considered not only electrostatic attraction, but also include van der Waals force and hydrogen bonding, which causes CS-g-DMC to wrap around the surface of *E. coli*, causing cell damage and death (Kenawy et al. 2002; Sun et al. 2006; Dai et al. 2011).

Hydrophilicity of modified cotton fabrics

Figure 10 Water contact angles of cotton fabrics (each picture is four frames apart). **a** raw cotton fabric; **b** modified cotton fabric

The water contact angle was measured for the cotton fabrics before and after modification. Compared to the initial water contact angle of 107° for the original cotton (Fig. 10a), the initial contact angle of the finished cotton fabric is smaller-104° (Fig. 10b), and decreased rapidly to 0°.

Meanwhile, by assessing the fabric's capillary effect, the hydrophilic qualities experiments on finished and unfinished cotton fabric are conducted. Figure 11 illustrates how the initial cotton fabric's liquid core wicking height changed gradually, virtually to zero. In contrast, the core wicking height of finished cotton fabric grew quickly to 7.2 cm with 90 min, and reaches its maximum value of 8.6 cm before gaining. The results show after modification the hydrophily of cotton fabric significantly improves, that is because the introduction of quaternary ammonium groups and carboxy groups from the DMC chain units and BTCA molecules. An improved hydrophilicity is considered not only benefit to improve antibacterial property but also comfort of the fabric.

Wearing performance measurements

Figure 12a shows the mechanical properties of cotton fabric have a significant improvement after finishing. The breaking force increases from 173.38 N to 219.33 N, this is because after the cross linking

of BTCA, an enhanced network structure forms among the cellulose macro-molecules, which increases the strength of fibers. And after finishing a polymer layer of CS-g-DMC coats on the surface of cotton fibers, it can also protect the fiber and thus increase the strength of fabric. On the other hand, the breaking elongation after finishing has not dropped significantly, it means the fabric maintains its flexibility.

Water-vapor transmission rate (WVT) is the performance of water passing through the fabric as vapor. In general, the greater moisture permeability a fabric has, the better its ability to let perspiration from physical activity travel through it and transfer to the outside as water vapor, and the more comfortable it will be to wear (Bhuiyan et al. 2022). The passage of water vapor through the fabric is divided into two major pathways. The first way is the water vapor directly through the gap between the fibers. The second way relies on the fabric's inherent ability to absorb moisture. when the fabric's surface comes into contact with a high-water vapor pressure environment, water vapor is absorbed and passes through the fabric's interior until it reaches the opposite side, where it then evaporates into a low water vapor pressure environment (Mohammed et al. 2021).

Figure 12b shows the WVT of finished cotton fabric decreased from 232.16 to 225.79 g/m^2/h. From the analysis of the morphological study of the fabrics, it can be seen that amount of CS-g-DMC graft on the cotton fabric, but did not completely wrap the fiber, so the gap between the fibers is slightly reduced, and the moisture permeability is not significantly decreased. Additionally, the finished cotton fabric's improved hydrophilicity and capillary effect prevent water vapor from entirely evaporating to the outside of the fabric, which also results in a slight decline in moisture permeability. In fact, because the effect on water vapor in route one is much greater than that in route two (Le et al. 1995), the moisture permeability of the finished fabric only decreased by 6.37 g/(m^2h), which has little effect on the fabric's wearing comfort.

Conclusion

In this study, a natural polymer antibacterial agent CS-g-DMC was prepared. The CS-g-DMC was used for the antibiotic finish of cotton fabric. CS-g-DMC has increased water solubility and has better permeability to cotton fibers. EDS shows the CS-g-DMC uniformly distributes on the surface of fabric.

Cotton fabric after CS-g-DMC finishing obtains long effective antibacterial property. The inhibition rate of modified cotton fabric for *E. coli* and *S. aureus* was over 99.9%, and it remained greater than 90% after 10 washings. The water solubility of finished cotton fabric was significantly improved. The finished cotton fabric has significantly increased breaking elongation, and basically maintains its elongation and moisture transmission rate.

Declarations

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Statements and Declarations

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Competing interests

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Authors' contributions

Reviewing and Editing: Hao Zhang, Yanli Hu, Fengyan Li; Conceptualization, Writing-Original draft preparation and Methodology: Shiqi He; Supervision and Funding: Baoming Zhou.

Compliance with Ethical Standards

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Scheme

Scheme 1 is available in supplementary section.

Figures

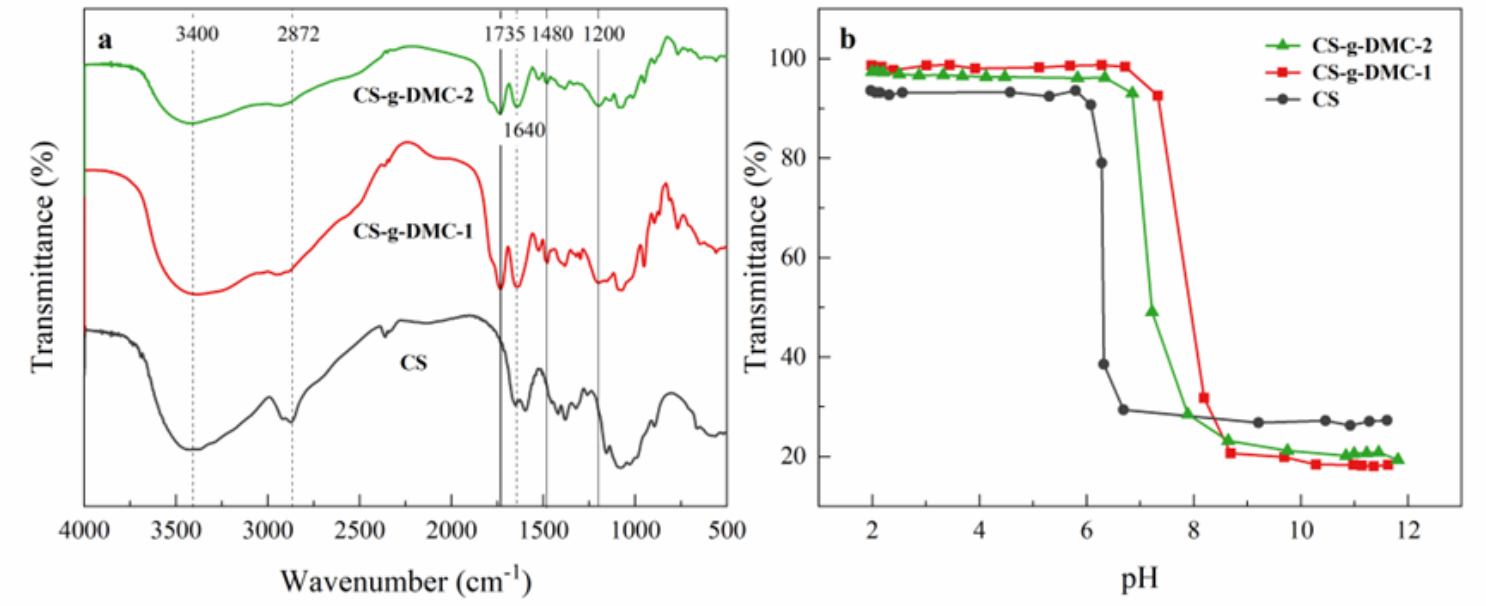

Figure 1

aFTIR spectra of the CS-g-DMC and CS; **b** Solubility of CS-g-DMC and CS

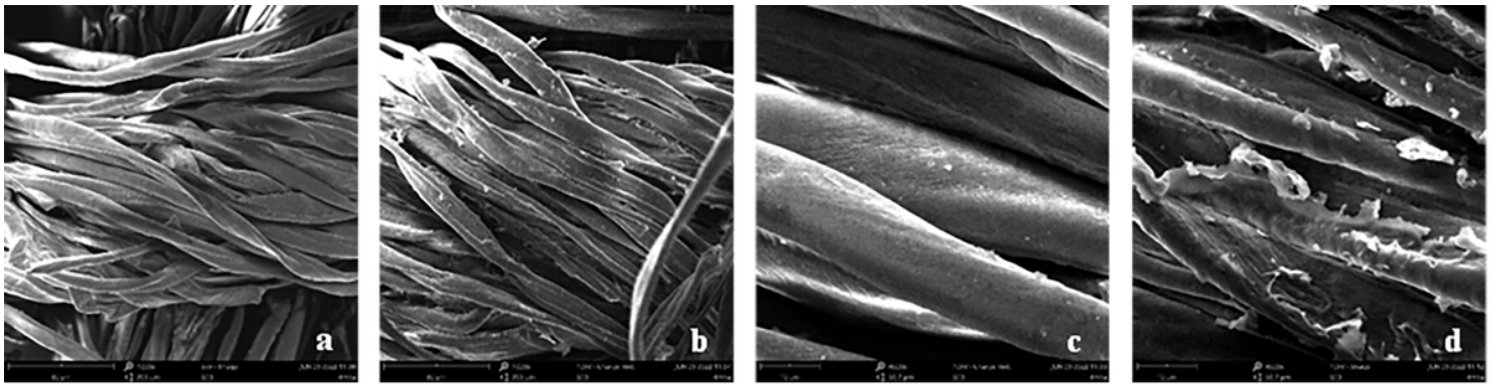

Figure 2

SEM images of the fabric surface. raw cotton fabric **a, c**; modified cotton fabric **b, d**

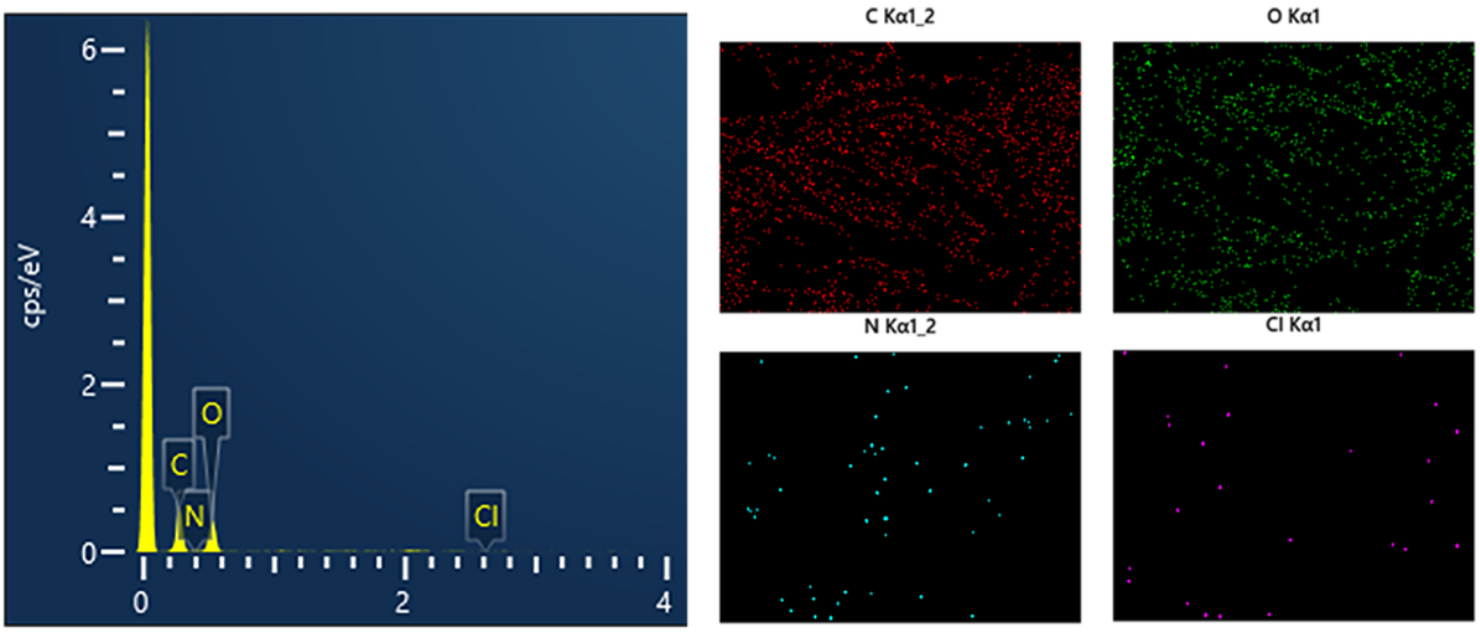

Figure 3

EDS images of the modified cotton fabric

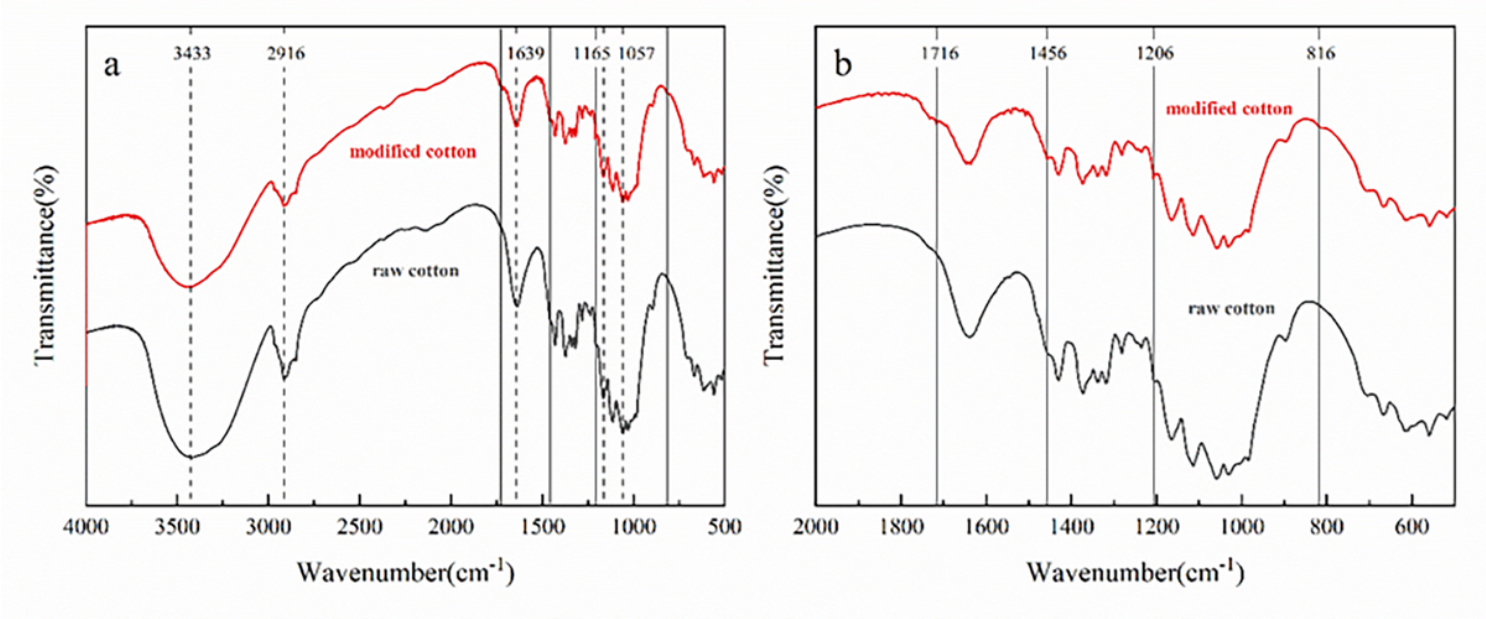

Figure 4

FTIR of the raw cotton fabric and modified cotton fabric

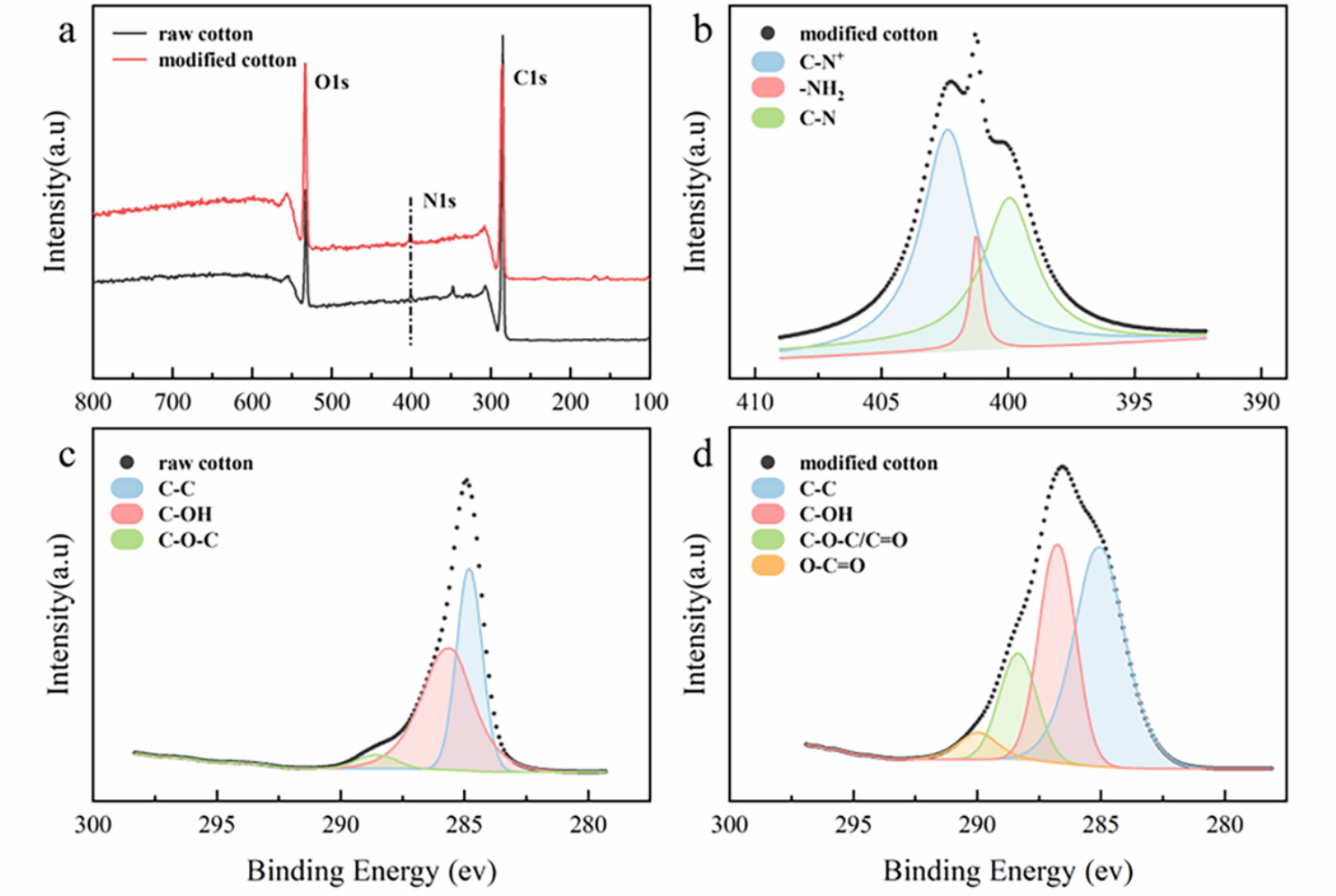

Figure 5

aXPS spectra of cotton fabrics; **b** N1s XPS spectra of the modified cotton fabric; **c** C1s XPS of the raw cotton fabric; **d** C1s XPS of the modified cotton fabric

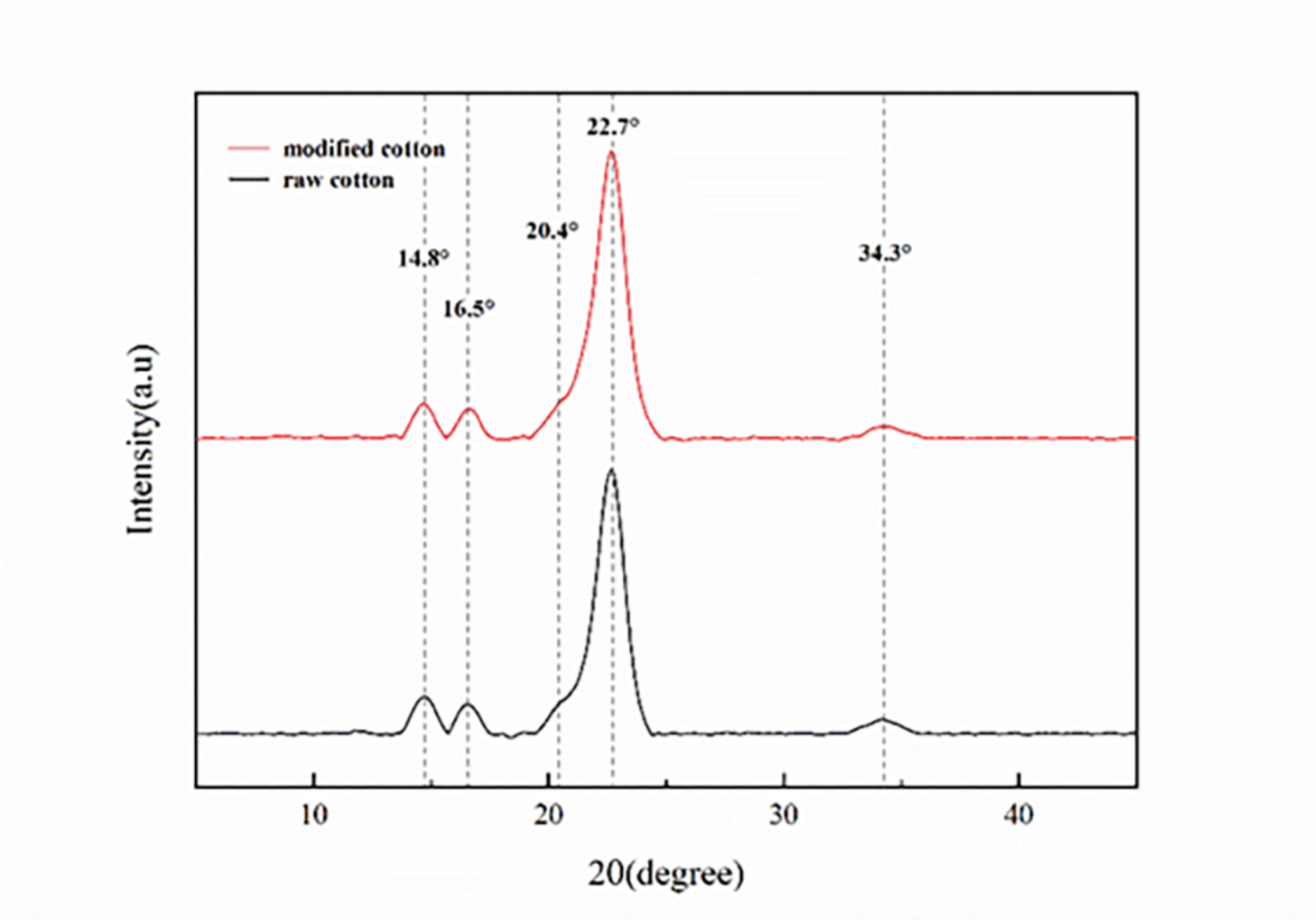

Figure 6

XRD spectra pf raw cotton and modified cotton fabric

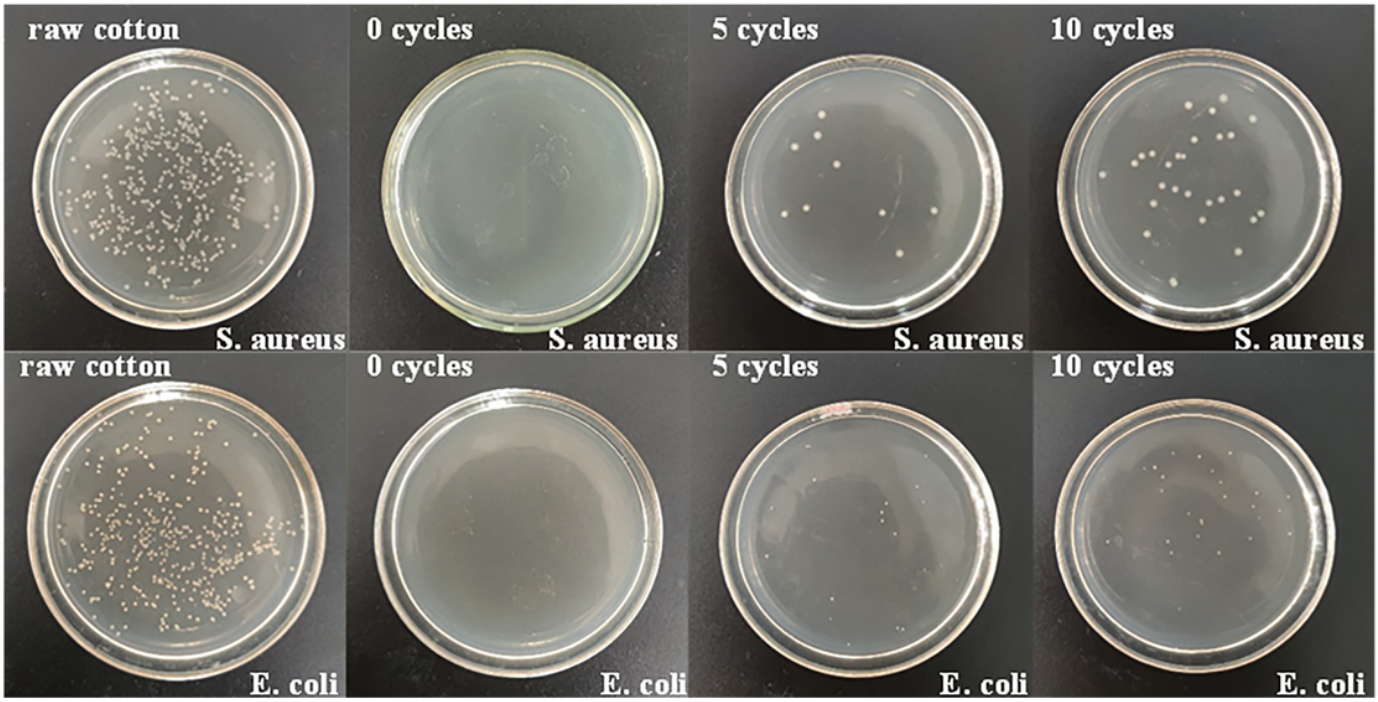

Figure 7

Antimicrobial activities of cotton fabrics against *E. coli* and *S. aureus* after washing 0, 5, 10 times

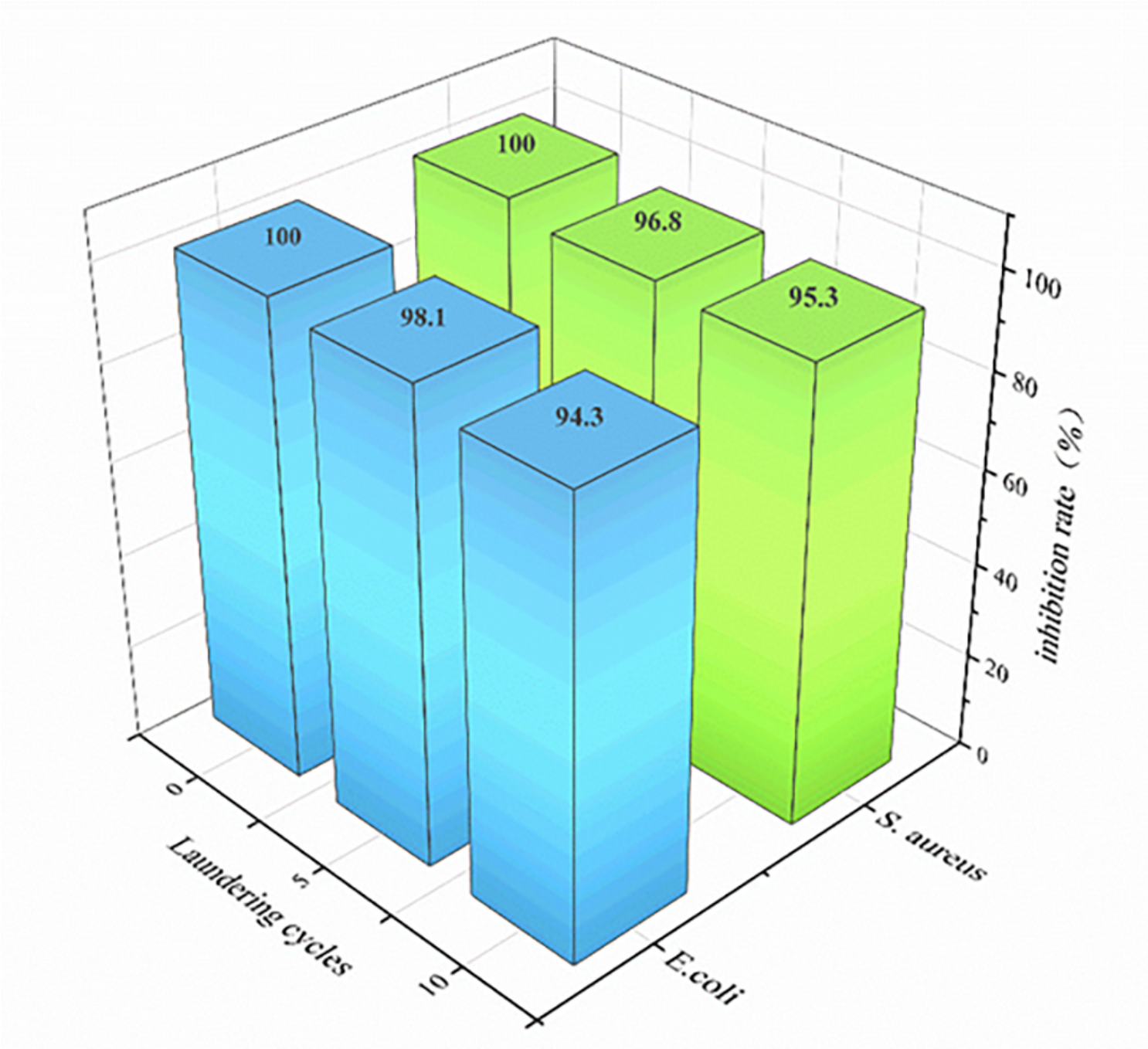

Figure 8

Statistical results of cotton fabrics against *E. coli*and *S. aureus*

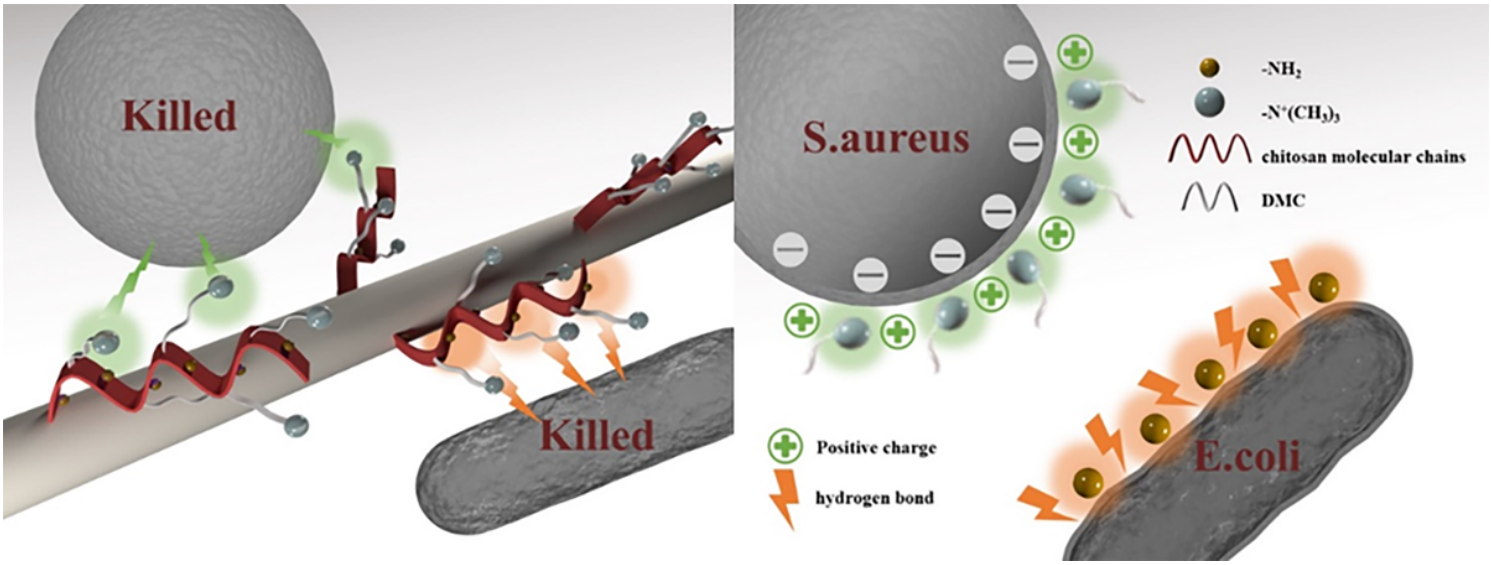

Figure 9

The major interaction between the *S. aureus* / *E. coli* and the CS-g-DMC

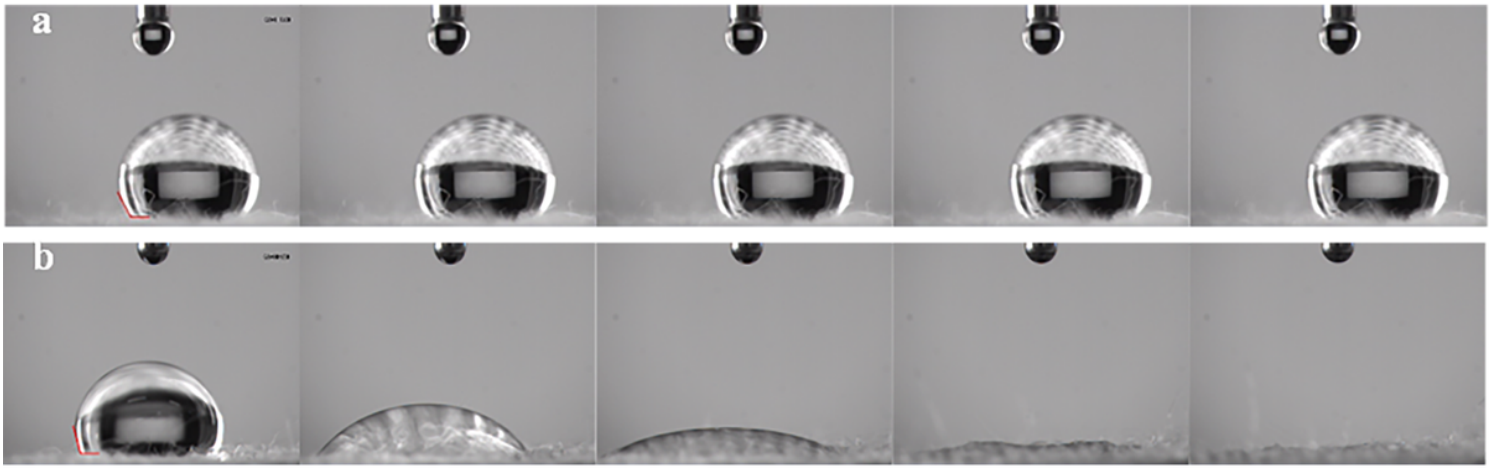

Figure 10

Water contact angles of cotton fabrics (each picture is four frames apart). **a** raw cotton fabric; **b** modified cotton fabric

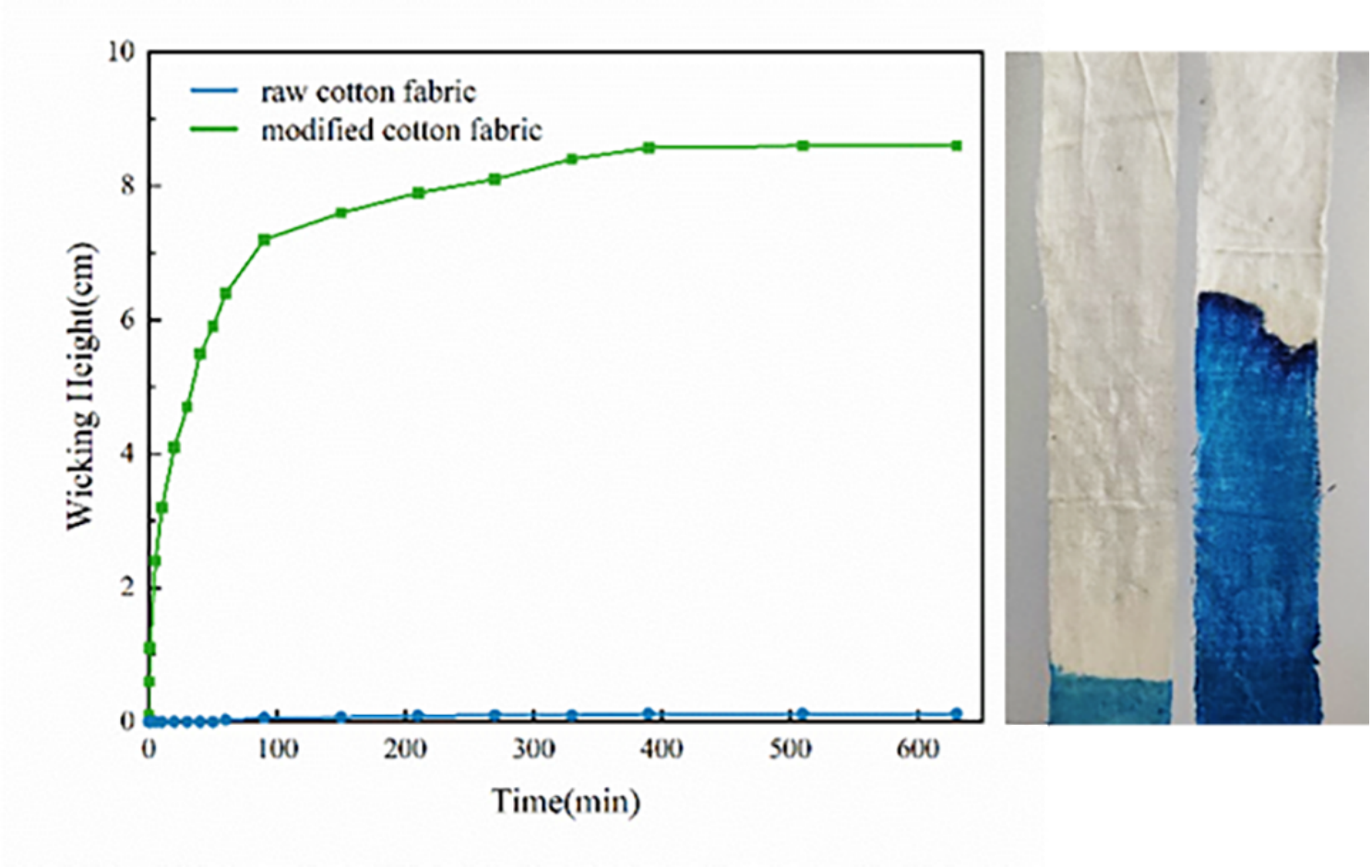

Figure 11

capillary effect of raw cotton fabric and modified cotton fabric

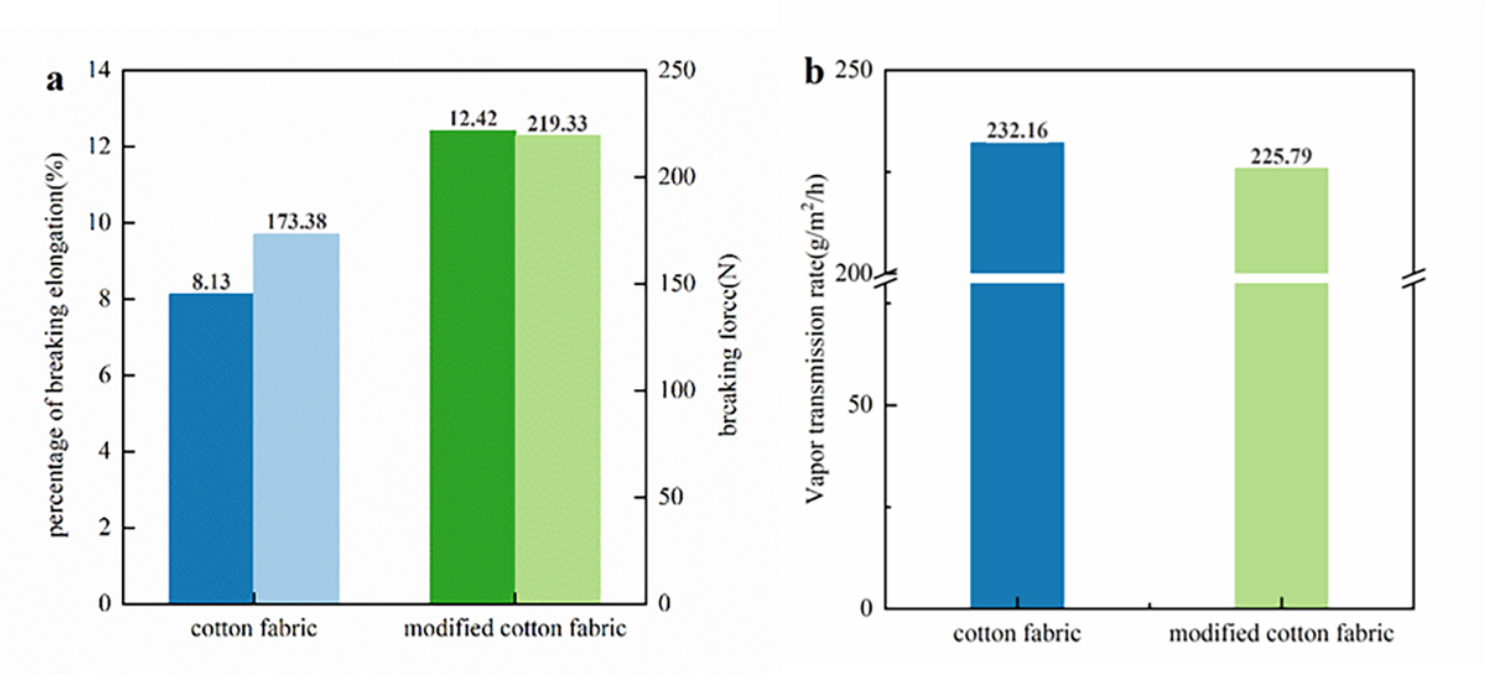

Figure 12

abreaking elongation and strength of cotton fabrics; **b** moisture transmission rate of cotton fabrics

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- scheme1.tif