Maintaining the antibacterial durability of chitosan-added cotton fabric to *E-coli* bacteria after many washing cycles

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ABSTRACT – REZUMAT

Maintaining the antibacterial durability of chitosan-added cotton fabric to *E-coli* bacteria after many washing cycles

In countries with hot and humid climates like Vietnam, textile products made from natural fibres will have limitations in resisting the attack and destruction of bacteria, microorganisms and mould. However, this is an opportunity to develop textile products with antibacterial properties to protect consumers under certain conditions. Furthermore, polluted air combined with Vietnam's hot and humid climate are causes of increased epidemics. These are the reasons why antibacterial textile products will increase in type, quantity, and quality to satisfy consumer needs. Antibacterial treatment of textile materials using chitosan is ecologically significant and has many advantages. Chitosan is a natural biopolymer with many chemical characteristics including its ability to convert to natural cations. This article develops a technological process for antibacterial finishing treatment for cotton fabrics with antibacterial durability maintaining after 20 washing cycles with chitosan produced in Vietnam. This study combines three methods, microbial method, infrared spectroscopy (FTIR) analysis method, and scanning electron microscope (SEM) method to evaluate the antibacterial ability and antibacterial durability of cotton fabric after complete treatment with chitosan. The results showed that after washing up to 20 cycles, chitosan bonded to cellulose stably and the antibacterial performance reached 56.62%. This indicated that chitosan-treated cotton fabric exhibits notable antibacterial properties, enhancing its suitability for antimicrobial products.

Keywords: *chitosan, cotton fabric, antibacterial treatment, fibre surface, textile product*

Menținerea proprietăților antibacteriene ale țesăturii din bumbac cu adaos de chitosan față de bacteria *E. coli* după numeroase cicluri de spălare

În țările cu climă caldă și umedă, precum Vietnamul, produsele textile fabricate din fibre naturale vor avea limitări în ceea ce privește rezistența la atacul și distrugerea bacteriilor, microorganismelor și mucegaiului. Cu toate acestea, există oportunitatea de a dezvolta produse textile cu proprietăți antibacteriene pentru a proteja consumatorii în anumite condiții. În plus, aerul poluat, combinat cu clima caldă și umedă din Vietnam, sunt cauze ale dezvoltării epidemiilor. Acestea sunt motivele pentru care produsele textile antibacteriene vor crește ca tip, cantitate și calitate pentru a satisface nevoile consumatorilor. Tratamentul antibacterian al materialelor textile cu ajutorul chitosanului este important din punct de vedere ecologic și prezintă multe avantaje. Chitosanul este un biopolimer natural cu multe caracteristici chimice, inclusiv prin capacitatea sa de a se transforma în cationi naturali. Acest articol dezvoltă un proces tehnologic pentru tratamentul antibacterian de finisare a țesăturilor din bumbac, cu menținerea durabilității antibacteriene după 20 de cicluri de spălare cu chitosan produs în Vietnam. Acest studiu combină trei metode: metoda microbiană, metoda de analiză prin spectroscopie în infraroșu (FTIR) și metoda microscopului electronic de baleiaj (SEM) pentru a evalua capacitatea antibacteriană și durabilitatea antibacteriană a țesăturii din bumbac după tratamentul complet cu chitosan. Rezultatele au arătat că, după 20 de cicluri de spălare, chitosanul s-a legat stabil de celuloză, iar performanța antibacteriană a atins 56,62%. Acest lucru indică faptul că țesătura din bumbac tratată cu chitosan prezintă proprietăți antibacteriene remarcabile, sporind utilizarea acesteia pentru fabricarea produselor antimicrobiene.

Cuvinte-cheie*: chitosan, țesătură din bumbac, tratament antibacterian, suprafața fibrelor, produs textil*

INTRODUCTION

Owing to the increase in industrialization in the 20th century, protective clothing made of natural, environmentally friendly synthetic fibres was researched and developed, and is considered promising in the future because of its comparative advantages in terms of technology, environment, economics, and legality [1]. Other research on low-profile, wearable textile antennas for Wireless Body Area Network applications in the 5.8 GHz ISM band was designed to protect the body from back radiation [2]. However, clothes of natural fibres are a very favourable environment for bacteria to grow because the surface area of the textile is large and has the ability to retain moisture. In recent years, consumer demand for antibacterial textile products has been increasing because, as living standards improve, people's need for protection is becoming increasingly important. Research on antibacterial treatment of fabrics with chitosan is increasing because of the many advantages of this product. Evaluating the quality of fabrics after many washing cycles is an effective measure in the textile industry. The chemical resistance of the fabric after different washing periods was evaluated according to the ISO 6530:2005 test method [3]. Colour fastness and antibacterial ability after adding chitosan were also evaluated after many washing cycles [4–8]. Chitosan treatment reduces *Staphylococcus aureus* (*S. aureus*) bacteria by 99% and improves washing durability through ionic bonding with wool keratin, particularly with chitosan of molecular weights (MW) 100,000–400,000. In another study, hinokitiol-grafted-chitosan (HTCS) was synthesized and applied to cotton fabric as an antibacterial agent. Compared with chitosan (CS) and hinokitiol (HT), HTCS showed a lower minimum inhibitory concentration (MIC) and significantly improved antibacterial efficacy against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). After 25 wash cycles, the HTCS-treated fabric maintained its antibacterial properties, hydrophilicity, and strength, indicating its potential for textile applications [9]. Chitosan was added to jute-cotton-blended denim to enhance its antimicrobial properties. The presence of chitosan in the blended fabric was verified by Fourier transform infrared spectroscopy [10]. The skin-dyed cotton fabric treated with chitosan exhibited a significant reduction in *E. coli* and *S. aureus* bacterial growth by 97.20% and 98.03%, respectively. Additionally, the chitosan-treated fabric displayed a higher Ultraviolet Protection Factor (UPF) value of 84.80% compared to the alum-treated fabric 66.70%), indicating superior ultraviolet protection [11]. A novel antibacterial agent (AgNPs@HTCS) was synthesized by grafting hinokitiol (HT) onto chitosan (CS) and incorporating nanosilver (AgNPs). When applied to fabrics, AgNPs@HTCS exhibited low minimum inhibitory concentrations against *S. aureus* and *E. coli*, maintaining high antibacterial efficacy after 25 wash cycles [12]. The melamine salt of chitosan phosphate (MCHP) was synthesized and combined with polyvinyl alcohol (PVA) to coat the cotton fabric. Coatings of PVA/nCH/MP and PVA/MCHP significantly elevated the Limiting Oxygen Index (LOI) of cotton fabric, from 17.2% to 57.9% and 58.2%, respectively. Moreover, the treated samples exhibited substantial antibacterial efficacy against both gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria, as evidenced by the larger inhibition zone diameters (IZD) compared to the control sample [13].

A simple and eco-friendly method was employed to create superhydrophobic cotton fabrics using chitosan-based composite coatings. The treated fabric exhibited outstanding super hydrophobicity with a water contact angle of 154.4° and demonstrated excellent antibacterial activity against both Gram-positive and Gram-negative bacteria, with inhibition zones of 16 and 22 mm, respectively, in disk diffusion tests. Additionally, chitosan-PAni-ZnO-STA-coated cotton effectively inhibited bacterial growth in shake-flask tests. Moreover, tests on self-cleaning, blood repellency, and oil-water separation performance confirmed the potential of modified cotton for environmental and clinical applications [14].

In general, antibacterial treatment of fabric using chitosan and chitosan derivatives has been mentioned a lot in research [9, 15–17]. The antibacterial properties of fabrics treated with chitosan, especially with its derivatives, provide high antibacterial ability and wash durability up to 20 cycles [18, 19]. A review paper has shown chitosan fibres and the synthesis of chitosan nanofibers, which have antibacterial properties [20]. Studies using chitosan have shown that the antibacterial ability of the fabric is quite high; however, its antibacterial durability is limited. If a chemical bond is not created between chitosan and the fabric, antibacterial durability will only be maintained after 1–2 washing cycles. When creating a chemical bond between chitosan and fabric, the antibacterial durability of the treated fabric is improved, and the antibacterial properties can be maintained after 10 washes. However, no author has clearly stated the mechanism of the connection between cellulose and chitosan or demonstrated this connection. Some points to note when treating emergency resistance using chitosan are as follows:

- The antibacterial ability of fabrics treated with chitosan depends on three factors: degree deacetylation (DD), MW, and concentration of chitosan used. When DD increases from 0.65 to 0.95, the antibacterial ability gradually increases and, in most studies, it has been shown that the DD must be above 0.85, to ensure the antibacterial ability of the fabric after treatment. The MW of chitosan in the studies is also very rich from 1,800 to 480,000. Studies show that as MW increases, the antibacterial ability of the fabric also increases when the chitosan concentration used is low. However, the antibacterial ability decreases for certain high MW. When using high chitosan concentrations (about 1%), the effect of MW on antibacterial ability is not clear.
- To put chitosan on fabric, researchers often use the pad-dry-cure method. To dissolve chitosan, most studies use a weak acid, acetic acid, and, as a result, the treated fabric does not have antibacterial durability after washing.
- To ensure antibacterial durability of the fabric after washing, a chemical bond was created between chitosan and cellulose. Substances such as 1,3-dimethyllol-4,5-dihydrocyethylenne urea (DMDHEU), citric acid (CA), (2-hydroxy)propyl-3trimethylamommnium)propyl)chitosan chloride) (HTCC), and cyanuric chloride (CNC) have been used as cross-linking agents between chitosan and cellulose in many studies.
- The method of evaluating antibacterial properties in most studies used the shaking method according to the ASTM E2149-01 standard, and a few studies used the AATCC100 standard.

MATERIALS AND METHODS

Material

- Fabric: The 100% cotton fabric was supplied by Nam Dinh Textile Garment J.S. CORP (Natexco), Viet Nam. The fabrics were then desized, scoured, bleached, and mercerized. The technical characteristics of the fabric are presented in table 1.

- Chitosan with the MW of 200,000 Dalton, DD of 90% was supplied by Institute of Chemistry-Vietnam Academy of Science and Technology
- Citric acid – CA ($C_6H_8O_7$) and Sodium Hypophosphite – SHP (NaH_2PO_2) supplied by Johnson Matthey Co., Ltd

Table 1

TECHNICAL CHARACTERISTICS OF THE FABRIC					
Construction	**Yarn count (Ne)**		**Fabric density (yarn/100 mm)**		**Weight of fabric (g/m^2)**
	warp	**weft**	**warp**	**weft**	
Plain weave	24	24	268	237	140

Methods

Preparation for a chitosan solution

Through general research and laboratory experiments, it was found that for treated cotton fabric to have good antibacterial properties, the chitosan concentration must be between 0.8 and 1%. Therefore, to ensure the best amount of chitosan on cotton fabric after treatment, the study will use a chitosan concentration of 1% relative to the fabric (o.w.f). The CA concentration used also ranges from 3–7%. However, through research and surveys, it has been found that with a CA concentration of 3–5%, chitosan is difficult to dissolve completely and takes more time to prepare the solution. If the CA concentration is greater than 7%, the durability of cotton fabric will be greatly reduced. Therefore, the study chose a CA concentration of 7% in solution (o.w.b). SHP and CA were mixed in a 1:1 mol ratio.

Fabric treatment

The fabric was prepared using distilled water, CA concentration 7%, chitosan 1%, SHP and CA in a mole ratio of 1:1, Erkatel NR impregnation agent: 0.1%, following the pad-dry-cure technique.

Subsequent experiments compared the untreated fabrics with the treated fabrics.

This study employed a one-bath, pad-dry-cure technique for fabric treatment. First, the fabric was impregnated with the finishing solution, then padded, dried, and cured. The antibacterial treatment of cotton fabric with the antibacterial agent was carried out in nine steps, as shown in figure 1. The fabric samples, containing dissolved chitosan, were soaked in the solution (previously mixed with the soaking agent). The soaking process ensured that the solution was evenly and thoroughly absorbed by the fabric sample. The sample was then padded, dried at the selected temperature and time, washed with distilled water, and allowed to air dry at room temperature. Finally, the sample was transferred to a standard conditioning chamber for 24 hours. The device for standard conditions: Climatest, Model M250-RH from Mesdan-Italy.

This experimental process was carried out at the Textile Chemistry Laboratory, School of Materials Science and Engineering, Hanoi University of Science and Technology (HUST).

Washing process

To determine the antibacterial durability of the fabric after treatment, the treated samples were washed in accordance with ISO 6330 standard clause 6A, using ECE non phosphate reference detergent (A). An Electrolux EW 1290 W (Italy) front-load washing machine was used. The washed samples were stored after 15 and 20 wash cycles to test their antibacterial ability. The experiments were performed at the Textile Materials Laboratory, School of Materials Science and Engineering of Hanoi University of Science and Technology (HUST).

The washing parameters were as follows: temperature of 25°C, spin speed 900 rpm with extra rinse and extra dry. Greige knitted interlock fabric with mass per unit area of 300 g/m^2 and size of 200 x 200 mm was used as ballasts.

Assessment of treated fabric's properties

• Antibacterial ability

The antibacterial ability of the samples was tested with *Escherichia coli* (*E. coli*), according to the AATCC 11303 standards after antibacterial treatment and after 15 and 20 washing cycles according to the ASTM E 2149-01 standard. Prepare all the equipment needed for the process were sterilized at 121°C for 20 minutes. The bacterial strain was activated and examined with LB medium. Measuring OD density and determining CFU/ml to analyse the antibacterial ability. The results were obtained after 3 repetitions of the experiment at 0 h, 1 h. The entire experimental process was carried out at the Proteomics laboratory – Centre for Biotechnology Research and Development, School of Chemistry and Life Sciences, Hanoi University of Science and Technology (HUST).

• Breaking force and elongation at break

The standard ISO 13934-1 was used to determine the breaking force and elongation before and after treatment. The experimental was conducted using AND multi-purpose testing equipment (Japan) at the Textile Materials Laboratory, School of Materials Science and Engineering, Hanoi University of Science and Technology (HUST).

Tensile equipment: Universal Testing machine 5000N from AND Japan, Model RTC 1250A.

• Comfort characteristic

Comfort characteristics of fabric were investigated through the air-permeability and water vapor permeability.

Air-permeability: The standard ISO 9237:1995 was used to determine the breathability of fabric before and after treatment. The experiment was carried out using M021A, Air permeability Tester (SDL-Atlas, England).

Water vapor permeability (WVP): The water vapor permeability of the fabric allows sweat to drain easily

for the user in hot weather conditions, bringing comfort to the wearer. The greater the WVP of the fabric, the better the vapor exchange capacity of the fabric, which means that the higher the WVP capacity of the fabric, the better the comfort of the fabric. On the contrary, the smaller the water vapor permeability speed of the fabric, the less comfortable the fabric. This experiment was followed by the standard UNI 4818-26. The experiment was carried out using Water vapor permeability Tester code 3122 of Mesdan – Italy.
These experiments were conducted at the Textile Materials Laboratory, School of Materials Science and Engineering of Hanoi University of Science and Technology (HUST).

• Kawabata characteristic

Examine the Kawabata properties to assess the effects of the Chitosan treatment process on cotton fabrics, focusing on the treated fabrics surface characteristics (friction and roughness), tensile deformation, slip deformation (form stability and the tendency for wrinkles); and compression deformation (fullness, softness, smoothness, anti-drape stiffness). Test samples, prepared with a size of 200 x 200 mm before and after treatment with chitosan, were tested using the Kawabata equipment system in the following order of modules:
KES-FB4-A (Surface friction and roughness): Surface friction and roughness characteristic data is useful for determining fullness and softness, smoothness, crispness
KES-FB3-A: (Compression tester): Data is useful for determining fullness and softness, smoothness, anti-drape stiffness
KES-FB1-A: (Tensile & Shear tester): Data is useful for determining stiffness and anti-drape stiffness. These properties often influence stability and the tendency for wrinkles.
These experiments were conducted at the Textile Materials Laboratory of School of Materials Science and Engineering of Hanoi University of Science and Technology (HUST).

• FTIR analysis

Infrared spectra of the fabric samples before, after antibacterial treatment, and after washing were obtained using a Nicolet 6700 FT-IR Spectrometer (Nicolet, Japan), at Petrochemical Research Institute, School of Chemistry and Life Sciences, of Hanoi University of Science and Technology (HUST).

• SEM analysis

SEM images of the samples were taken using the device JEOL 6360 (Japan), at Polymer Composite Key Laboratory, School of Materials Science and Engineering of Hanoi University of Science and Technology (HUST).

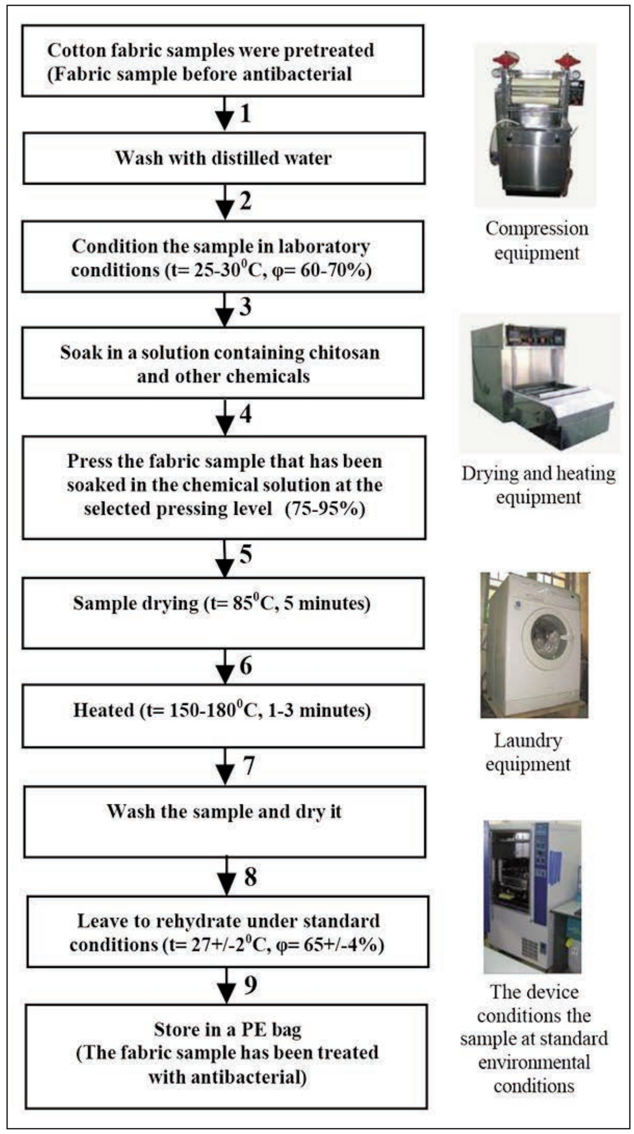

Fig. 1. Process of attaching chitosan to cotton fabric

RESULTS AND DISCUSSION

Table 2 shows the antibacterial ability of cotton fabric samples treated with chitosan after 15 and 20 washing cycles. Cotton fabric treated with chitosan still retained its antibacterial properties, although the antibacterial ability has decreased significantly, with the corresponding decrease in bacteria rate being 63.63% and 56.52%.
The properties of untreated and chitosan-treated fabrics are shown in tables 3–5, showing that after chitosan- treatment, the technical properties are better.
The analysis using FTIR infrared spectroscopy also proves that fabric samples after 20 washing cycles retain their antibacterial properties through the appearance of new peaks at wavelengths of 1730 cm^{-1} and 1582 cm^{-1} (figures 2 and 3).
The influence of 20 washing cycles on the antibacterial properties of the cotton fabric was evaluated through image analysis of the cotton fibre surface of fabric samples treated with chitosan using scanning electron microscopy (SEM) (figure 4).

Table 2

RESULTS OF RESEARCH ON ANTIBACTERIAL PROPERTIES OF FABRICS WITH CHITOSAN AFTER 15 AND 20 WASHING CYCLES								
Fabric samples	**Curing temperature (°C)**	**Curing time (minutes)**	**Pick-up level (%)**	**Initial number of *E. coli* bacteria ($x10^5$)**	**Number of *E. coli* bacteria remaining after contact with fabric ($x10^5$)**		**The rate of bacteria decreases after time of contact with the fabric R (%)**	
					2 minutes	**60 minutes**	**2 minutes**	**60 minutes**
Control	-	-	-	41	51	51	-	-
Treated sample (TS) after 15 washings cycles	170	2	80	55	34	20	38.18	63.63
Control	-	-	-	59	61	64	-	-
Treated sample (TS) after 20 washings cycles	170	2	80	46	31	20	48.33	56.52

Table 3

STRENGTH AND ELONGATION OF UNTREATED AND TREATED COTTON FABRIC								
Fabric samples	**Tensile strength (N) ISO 13934-1**		**The ratio decreases in the warp yarn direction (%)**	**The ratio decreases in the weft yarn direction (%)**	**Breaking elongation (mm) ISO 13934-1**		**The ratio decreases in the warp yarn direction (%)**	**The ratio decreases in the weft yarn direction (%)**
	warp yarn direction	**weft yarn direction**			**warp yarn direction**	**weft yarn direction**		
Untreated	537.09	477.84	-	-	32.50	53.62	-	-
Chitosan treated	336.18	289.07	37.40	39.50	23.43	41.59	27.90	22.43

Table 4

COMFORT CHARACTERISTICS OF UNTREATED AND TREATED COTTON FABRIC				
Fabric samples	**Air permeability ($l/m^2 \cdot s$) ISO 9237**	**Water vapor permeability ($g/dm^2.24h$) UNI 4818-26**	**Drape (%) NF G07-109**	**Wrinkle recovery angle (WRA) (Degree) ISO 2313**
Untreated	141	1.2776	43.26	58
Chitosan treated	161	1.3837	67.26	126

As shown in figure 4, *e*, after 20 washing cycles, the cotton fibre surface was significantly damaged quite a lot, showing that the cotton fibres were loose, and the fibre surface was no longer flat and smooth before washing. It is assumed that the chitosan membrane surrounding the cotton fibre was broken, and the amount of chitosan was lost, as shown by the rate of decreased bacteria after contact with the fabric declined after 20 washings cycles (table 5). However, some chitosan may form a strong bond with cellulose, which still exists on the fabric after 20 washing cycles. Therefore, the fabric still exhibited antibacterial resistance even after 20 washing cycles, as shown in table 5. From the results of this study can conclude that:

- The antibacterial treatment conditions for cotton fabric with chitosan allow the treated fabric to have very high antibacterial ability, Cheng et al. [15] also found that chitosan-modified cotton fabrics have similar antimicrobial performance and antibacterial durability even up to 20 washing cycles.
- Antibacterial treatment of the cotton fabric with chitosan bonded a certain amount of chitosan to the cotton fabric. The amount of chitosan in cotton gives the fabric its antibacterial ability and durability after many washing cycles.

After many washing cycles, some bonds between chitosan and cellulose gradually broke, leading to a gradual decrease in the antibacterial ability of the fabric (table 2). After 20 washing cycles, the cotton fabric treated with chitosan retained its antibacterial properties, proving that a certain amount of chitosan was firmly bonded to cellulose and was not lost. Thus, the fabric still exhibited antibacterial properties.

Table 5

KAWABATA CHARACTERISTICS AND TEARING STRENGTH OF UNTREATED AND TREATED COTTON FABRIC			
Characteristics		**Untreated fabrics**	**Chitosan treated fabrics**
Surface properties	MIU	0.179	0.155
	MMD	0.019	0.016
	SMD	6.237	4.615
Tensile properties	LT	0.612	0.585
	WT	15.00	11.78
	RT	31.07	43.52
Shear properties	G	1.27	5.79
	2HG	2.92	5.99
	2HG5	5.73	6.34
Compression properties	LC	0.224	0.288
	WC	0.230	0.282
	RC	27.39	42.91
Tearing strength	Warp (N)	14.95	9.72
	Weft (N)	9.21	6.13

Note: MIU, mean frictional coefficient; MMD: Fluctuation of mean frictional coefficient; SMD: Surface mean roughness (µm); LT: Tensile rigidity; WT: Tensile energy (cN/cm^2); RT: Tensile recoverability (%); G: Shear rigidity (gl/cm. degree); 2HG: elasticity for minute shear (gl/cm); 2HG5: elasticity for large shear (gl/cm); LC: compressive linearity; WC: compressive energy (cN/cm^2); RC: compressive recoverability (%).

On the other hand, the appearance of NH groups on cotton fabric is shown by the appearance of a new peak at 1582 cm^{-1} in the FTIR infrared spectrum of fabric samples treated with chitosan after 20 washing cycles (figure 2). The image results of the FTIR spectrum (figure 3) show that, compared to the untreated sample, the cotton fabric sample treated only with CA also appeared at a wavelength of 1730 cm^{-1}, proving that there was a CA molecule esterifying the cellulose molecule. The cotton fabric sample treated with chitosan in the presence of CA, in addition to the new peak at 1730 cm^{-1} corresponding to the carbonyl group of the ester, also has a new peak at 1588 cm^{-1} (corresponding to the imine group NH), proving that the CA molecule not only esterifies the cellulose molecule (peak at 1733 cm^{-1}), but also esterifies the chitosan molecule (peak at 1588 cm^{-1}) to create a new NH bond. Ultimately, the FTIR (Fourier-transform infrared spectroscopy) results of figures 2 and 3 both showed a peak at 1588 cm^{-1} which corresponds to NH group (secondary amine group), which explains for the antibacterial ability of fabric after treatment with chitosan solution.

To clarify the assertion that there is a chitosan film on the surface of the cotton fibres, SEM images of the fabric samples were compared. The figure 4 are SEM images of untreated cotton fabric, fabric treated with chitosan, fabric treated with chitosan after 10 washing cycles, 15 washing cycles, and 20 washing cycles Observation of SEM image results shows that with untreated cotton fabric sample, fabric treated with chitosan and fabric treated with chitosan after 10 washing cycles, the fibre surface has changed little, however, after 20 washing cycles, the fibre surface has been damaged, the microfibrils are separated,

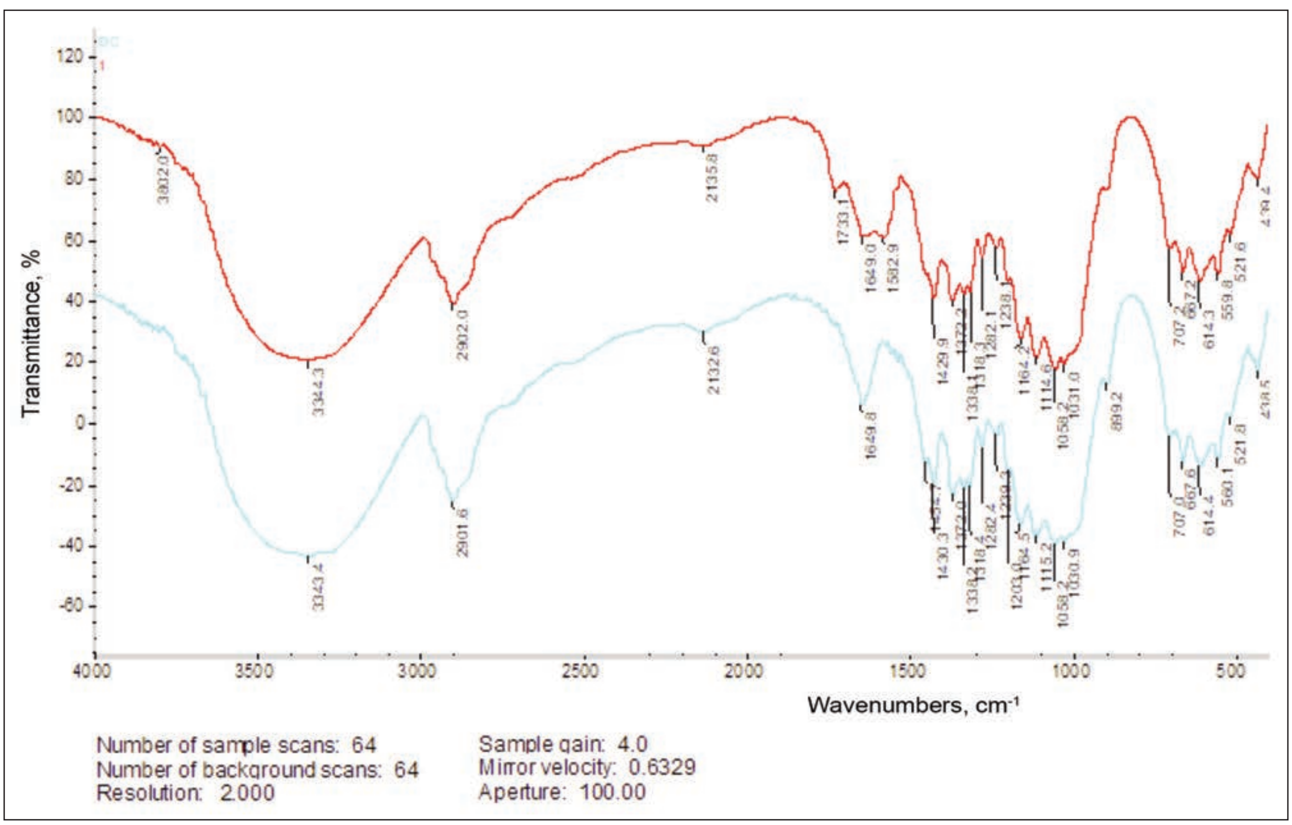

Fig. 2. FTIR of fabric treated with chitosan (red line) and fabric without treatment (green line) after 20 washing cycles

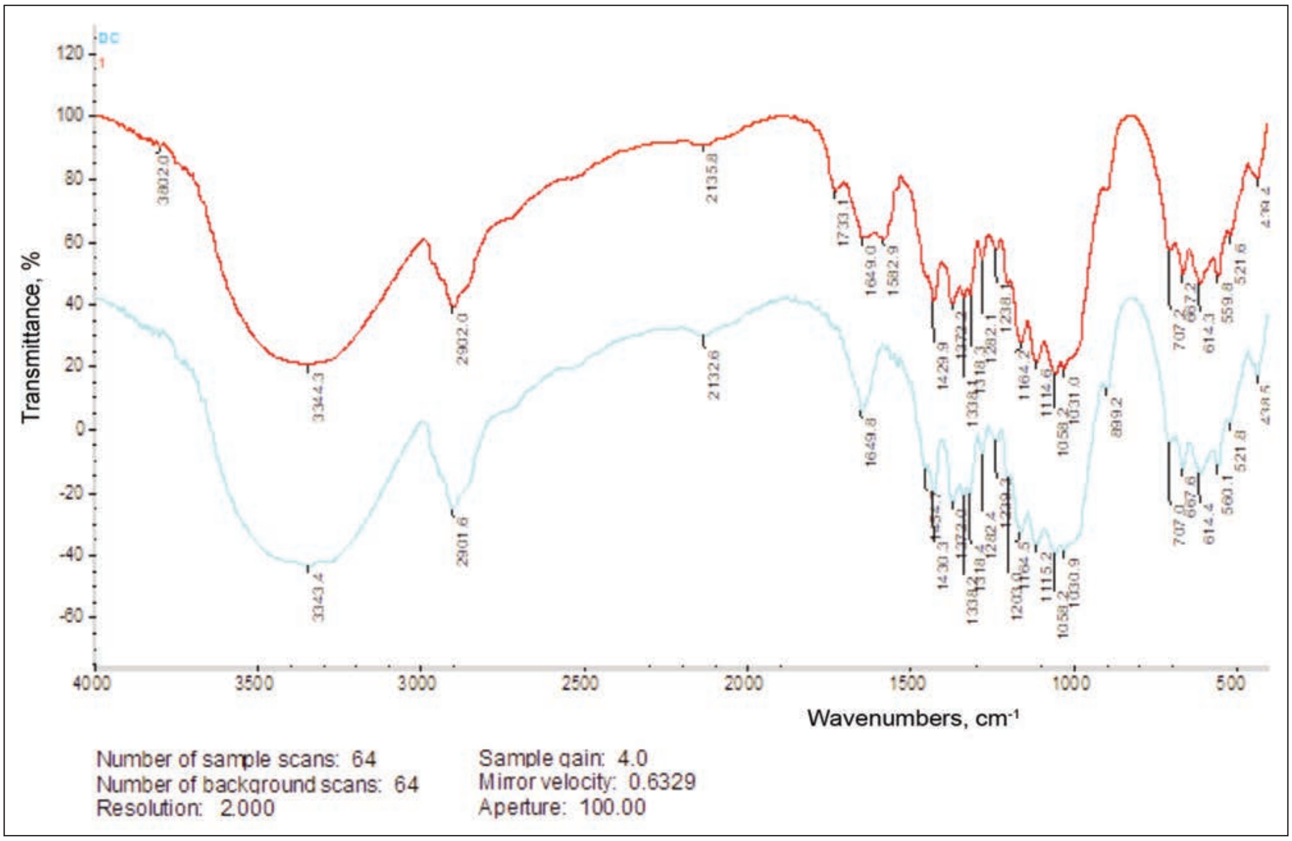

Fig. 3. FTIR of fabric without treatment (red line), fabric treated with CA (blue line), and fabric treated with chitosan (green line)

forming small frays. For fabric samples treated with chitosan, after washing cycles, there are more changes. The chitosan film on the fibre surface seems to be damaged with increasing level after washing cycles and peels off to form very thin films, most clearly in the sample treated after 20 washing cycles (figure 4, *e*).

From the analysis of the FTIR spectrum results, SEM images, and chemical reactions mentioned above, combined with the results of testing the antibacterial properties of fabrics after treatment with chitosan, the antibacterial properties of treated fabrics after control washing cycles. This shows that an ester reaction occurred during the process of fixing chitosan attached to the cotton fabric, and the bond created between chitosan and cotton fabric was quite stable. Therefore, this study proposes the following bonding mechanisms between chitosan and cotton fabric:

- If the ester reaction only occurs between chitosan and CA or between cellulose and CA, then the bond between chitosan and cellulose on the cotton fabric will give the cotton fabric treated with chitosan antibacterial durability after 20 washing cycles is just a physical and chemical bond. The physicochemical bond here is understood to be a hydrogen bond and Van der Waals bonds between chitosan molecules and cellulose molecules in the macromolecules of chitosan and cellulose. In other words, the existence of chitosan on cotton fabric after treatment and washing to give cotton fabric antibacterial properties is due to intramolecular and extra-molecular bonds between cellulose macromolecules and macromolecules created by chitosan molecules; however, these bonds are all weak and unstable. It is very difficult to maintain bond strength after 20 washing cycles, so the ability to bond chitosan and cellulose is purely a physical and chemical bond, which is unlikely.
- If the esterification reaction occurs simultaneously between chitosan and CA, and between CA and cellulose, the bond between chitosan and cellulose on the cotton fabric will make the cotton fabric treated with chitosan-resistant bacteria and antibacterial durability after washing cycles is a combination of both physicochemical bonds and chemical bonds. Therefore, the hypothesis that chitosan is bound to cotton fabric by both physical and chemical bonding mechanisms is the most scientifically based approach. The chemical bond was stable so that the fabric treated with chitosan retained its antibacterial properties after washing cycles.
- The pad-dry-cure treatment technique of fixing chitosan attached to the cotton fabric in this study may have created a chitosan film on the fibre surface. This chitosan film created covalent bonds, Van der Waals bonds, and hydrogen bonds with the cotton fabric. However, after washing cycles, a certain amount of chitosan can only create Van der Waals bonds, and the hydrogen bond with the fabric is gradually lost. Only chitosan molecules chemically bonded to cotton fabric were stable after 20 washing cycles, demonstrating that the antibacterial

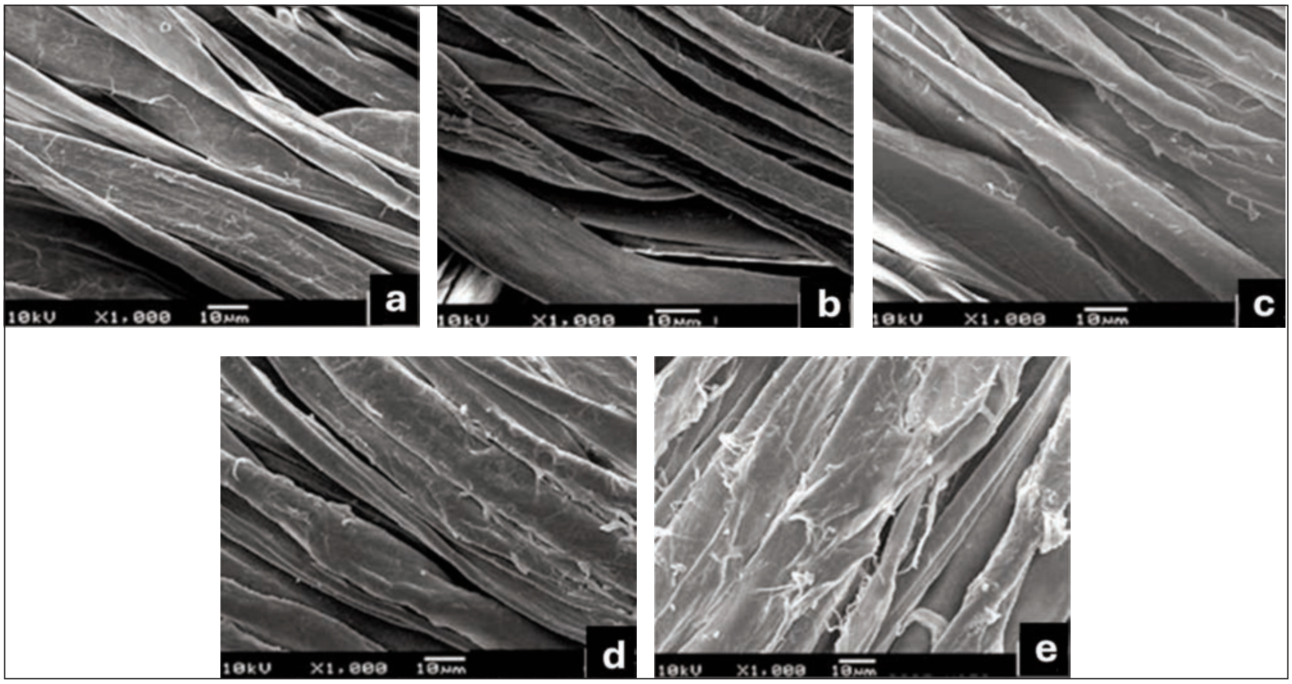

Fig. 4. SEM images of: *a* – untreated cotton fabric; *b* – fabric treated with chitosan; *c* – fabric treated with chitosan after 10 washing cycles; *d* – 15 washing cycles; *e* – 20 washing cycles

properties of cotton fabric treated with chitosan after 20 washing cycles reached 56.62%. The FTIR infrared spectrum (figures 2 and 3) still shows that picks containing imine group NH at wavelength 1588 cm^{-1} are also consistent with this proposal.

CONCLUSIONS

Research results with chitosan have shown that:

- Technological factors such as curing heating temperature, curing heating time, and pick-up level clearly affect the antibacterial properties and durability of cotton fabric treated with chitosan. The optimal technological parameters for treating antibacterial cotton fabric with chitosan has been found to ensure the antibacterial durability of the fabric after 20 washing cycles: curing temperature 170ºC, curing time 2 min, pick-up level 80%.
- Combining SEM images of the fibre surfaces, the results of studying fibre surface characteristics on the Kawabata device, and the results of measuring the air permeability of fabric samples after treatment allowed us to determine that chitosan was present on the cotton fibre surface.
- After washing up to 20 washing cycles, chitosan was bonded to cellulose quite stably. From this, the antibacterial nature of the fabric after treatment, as well as after washing, is the presence of chitosan on the cotton fabric with the antibacterial bactericidal mechanism clarified.
- The mechanical strength and drape of the fabric after treatment with chitosan were reduced, but the comfort properties were improved. After treatment, the air permeability of the fabric increased, the ability to recover from creases increased, the friction coefficient decreased, and the fabric surface became smoother.
- Antibacterial cotton fabric with chitosan is suitable for use as a garment fabric because of its high antibacterial durability, good thermo-physiological comfort, high wrinkle resistance, and smooth fabric surface. Although the mechanical strength of the fabric is reduced, it still satisfies the requirements for garment fabrics. Furthermore, in terms of the ecological environment and user safety, cotton fabric treated with chitosan is even more suitable.

Our research investigated the durability of cotton fabric treated with chitosan as an antibacterial agent, specifically targeting the gram-negative bacterium Escherichia coli, and showed promising results. In future studies, we will further explore the antibacterial properties of this treated fabric after multiple washing cycles, focusing on gram-positive bacteria, such as *Staphylococcus aureus* (*S. aureus*) to assess the fabric's overall antibacterial performance after washing.

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