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β-Cyclodextrin- grafted cotton loaded with limonene: a spectroscopically validated strategy for durable antibacterial textiles

Ayiramuthu Rukmani [a], Alagappan Kavitha [b], Meyyappan Revathi [c,*], Jagadeesan Manjunathan [d], Rasheed Ahmed Mohamed Hisam [e], Murugan Pavithra [f]

[a] Department of Chemistry, Seethalakshmi Achi College for Women, Pallathur, Affiliated to Alagappa University, India
[b] Department of Chemistry, Sree Sevugan Annamalai College, Devakottai, Affiliated to Alagappa University, Karaikudi, India
[c] Department of Chemistry, Vels Institute of Science, Technology and Advanced Studies (VISTAS), Pallavaram, Chennai, India
[d] Department of Biotechnology, Vels Institute of Science, Technology and Advanced Studies (VISTAS), Pallavaram, Chennai, India
[e] Department of Physics, Vels Institute of Science, Technology and Advanced Studies (VISTAS), Pallavaram, Chennai, India
[f] Department of Condensed Matter Physics, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences (SIMATS), Chennai, 602105, Tamil Nadu, India

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ABSTRACT

This study presents a novel, sustainable approach to enhance the antibacterial properties and wash durability of organic cotton through β-Cyclodextrin (β-CD) and monochlorotriazinyl-β-cyclodextrin (MCT-β-CD) grafting followed by limonene incorporation. Using citric acid as a cross linker and eco-friendly enzymatic bio polishing conditions, β-CD was effectively anchored onto cotton fibers, facilitating the encapsulation of limonene, a naturally derived antimicrobial terpene. SEM surface morphology indicated consistent grafting of β-CD/MCT-β-CD on cotton without fiber damage. Fluorescence spectroscopy confirmed effective incorporation of limonene within the cyclodextrin cavities. Spectroscopic techniques such as UV–Visible, FTIR, XRD and thermogravimetric analysis (TGA) confirmed the successful grating and structural integrity of the modified textiles. The experimental data was analyzed using pseudo-first order and second order kinetic models. The pseudo-second order provided the best match for the kinetic investigations, indicating that the chemisorption process limits the adsorption of Maxilon Blue GRL (MB) and Direct Yellow 12 (DY 12). HPLC Measurements demonstrated that grafted and bio-polished textiles exhibited significantly higher limonene loading and retention compared to their ungrafted counter parts. Antibacterial tests against *Escherichia coli* and Staphylococcus aureus showed significant and long-lasting inhibition, notably in biopolished β-CD and MCT-β-CD grafted samples, even after 10 wash cycles. Negative controls (untreated, biopolished-only and cyclodextrin-grafted textiles without limonene) showed no inhibition, indicating that limonene release is responsible for long term action. All experiments were done in triplicate ($n = 3$) and statistically analyzed using mean ± SD. The work reveals that cyclodextrin-based inclusion complexes function as controlled- release reservoirs for limonene indicating a possible pathway for producing high-performance, long lasting antibacterial textiles utilizing ecologically friendly approaches.

1. Introduction

Natural fibers like cotton are more prone to microbial attack than synthetic fibers, since they have porous texture capable to retain moisture and supplies nutrients necessary for the growth of microbes. Antimicrobial finishing of textile materials is needed to avoid cross infection by pathogenic microorganism, to control infestation by microbes and to safeguard the textile materials from staining, odour formation and deterioration. Surface modification of fibers can change the characteristics of fabric by imparting new functionalities. Cyclodextrins are suitable auxiliaries in textile finishing because of their toxicological and ecological advantages [1].

Cyclodextrins are produced by the enzymatic degradation by means of enzyme cyclodextrin glucosyl transferase on starch [2].They are classified as α-(six), β-(seven), and γ-(eight) cyclodextrins, based on the number of glucopyranose units present in their ring and have cavities of approximately 0.6, 0.8, and 1.0 nm in diameter respectively [3].They play a significant role in textile industry and might be used in number of

* Corresponding author.
E-mail addresses: mrev80@gmail.com, dr.revathichem.sbs@vistas.ac.in (M. Revathi).

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applications such as removal of surfactants from washed textiles, chemically bound to fibers to provide enhanced hydrophilicity and inclusion complex forming ability to immobilize perfumes, insect repellents, antimicrobial agents etc., [4]. d-limonene (1-methyl-4-(1-me thylethenyl) cyclohexene) is a monocyclic monoterpene with a lemon-like odor and is a major constituent in several citrus oils (orange, lemon, and grapefruits). It is widely used as a flavor and fragrance additive in perfumes, soaps, foods, chewing gum, and beverages because of its pleasant citrus fragrance. d-limonene is listed in the Code of Federal Regulation as generally recognized as safe (GRAS) flavoring agent and well established as a chemo preventive agent against many types of cancer [5]. Microcapsules of limonene were applied in textile and food industry for fragrance release property [6,7]. It was first registered in USA as an antimicrobial in 1971, as a dog and cat repellent in 1983 and as an insecticide in 1985. Durable insect repellent cotton is also synthesized using limonene [8]. Anti-fungal mortar and concrete are developed using microencapsulated fungus-resisting material d-Limonene [9]. The limonene in encapsulated state is used to improve the stability and aroma quality of limonene in food products [10]. Limonene as one of the constituent of essential oil has shown antibacterial activity against wide range of microorganism and is used as antimicrobial agent in food material [11,12]. Our approach replaces toxic or short-lived antibacterial finishes with eco-friendly β-CD/MCT-β-CD (β-Cyclodextrin and monochlorotriazinyl-β-cyclodextrin) host cavities that stably encapsulate limonene and release it in a controlled manner, ensuring durable and safe antimicrobial action. In this study limonene is incorporated into biopolished and β-CD and MCT-β-CD grafted organic cotton in order to enhance the durability of antibacterial activity on fabric. Cotton textiles that are antibacterial and washable without the use of artificial chemicals. As a result, carvacrol, thyme, and thymol were chosen as natural active ingredients. The kneading method, a straightforward and repeatable technique for encapsulating with a high manufacturing yield, was used to produce the inclusion complexes with β-cyclodextrin [13].

An alternate method for producing medical materials is the use of cyclodextrins in textiles to create biofunctional fabrics. A nanostructured surface with functional qualities was produced by the nanoscale integration of cyclodextrin molecules onto the cotton fiber surface. Drugs and dyes are examples of active compounds that cyclodextrins can combine with before being released. According to the study, the production of singlet oxygen by the Maxilon Blue GRL (MB) dye significantly lowers bacterial viability, especially when light is present. The presence of MB dye has antimicrobial effects even when there is no exposure to direct light. When used as a photosensitizer in cutaneous antimicrobial treatments, MB dye seems to be a promising option. This study fills the gap by combining enzymatic biopolishing with cyclodextrin grafting to achieve durable and eco-friendly antibacterial textiles [14]. [β -Cyclodextrin-Modified Cotton Fabric for Medical and Hospital Applications with Photodynamic Antibacterial Activity Using Methylene Blue, [15]. This study uses β-CD and MCT-β-CD grafting to entrap limonene in cotton, allowing for controlled diffusion-based release and long antibacterial performance. SEM and fluorescence analyses confirm uniform grafting and inclusion of limonene.

2. Experimental details

2.1. Materials and methods

Plain bleached knitted organic cotton was purchased from Tirupur textile Industries, India. Cellulase enzyme, sodium acetate, acetic acid, trisodium citrate, sodium carbonate, β- cyclodextrin, citric acid, sodium hypophosphite, limonene, agar, E.coli (ATCC 10,536) & S.aureus (ATCC 11,632) were purchased from Himedia, India. Monochlorotriazinyl-β-cyclodextrin [MCT-β-CD (CAVASOL W7 MCT)] was obtained from Wacker & Chemie Ltd., Bangalore. UV–Visible spectrophotometer (Perkin Elmer make model Lambda 35 (Range 190–1100 nm) analysis to identify the components from their absorption maximum peak. XRD analysis of samples was performed with PANalytical X'Pert PRO X-ray Diffractometer. FTIR analysis was carried out by Perkin Elmer make Model Spectrum RX1. Thermogravimetric Analysis (TGA) was performed at the heating rate of 10 °C/min in nitrogen atmosphere with computer-controlled TA Instruments Model SDT Q 600 with maximum temperature 1500 °C. The HPLC analysis of sample was analyzed by Shimadzu LC-20AD model.

2.2. Wash durability test

The wash durability of the treated textiles was assessed using a modified AATCC 61–2006 (2A) technique. Fabric samples (4 × 4 cm) were washed in 150 ml of normal detergent solution (0.37 % w/v) using stainless steel balls to imitate mechanical agitation. A laundrometer was used to wash at 40 ± 2 °C for 30 min, with a liquor-to-material ratio of 50:1. After each wash cycle, the samples were thoroughly washed with distilled water before air drying. One accelerated cycle is equivalent to about five domestic washes; so, two cycles equal 10 washes. Antibacterial activity was determined after 0 and 10 comparable wash cycles.

2.3. Biopolished β-CD limonene fabric for antibacterial activity

The unbiopolished, biopolished, unbiopolished β-CD and biopolished β-CD fabrics are loaded with limonene. The UV–Visible and FTIR analysis are performed for confirmation of β-CD and limonene on fabric. The crystalline nature and thermal stability of the modified fabrics are analyzed by XRD and TGA method. Limonene content of the various categories of fabrics is estimated from the HPLC analysis of the alcoholic extract from the respective fabrics. The antibacterial efficacy and the durability of the activity to repeated washing cycles are tested.

2.4. Inclusion of limonene into β-CD fabric

The grafting yield for β-cyclodextrin fixation on unbiopolished and biopolished fabric was assessed from the weight gain of fabric and the effect of reaction parameters on the yield is discussed below.

Mechanism of β-CD grafting

The fabrics are modified by crosslinking with β-cyclodextrin using citric acid as crosslinker in presence of sodium hypophosphite. Citric acid forms a five member cyclic anhydride on heating in presence of sodium hypophosphite. The five member cyclic anhydride of citric acid links with hydroxyl group of cellulose; subsequently the neighboring carboxylic acid groups on adjacent carbon atom undergo dehydration to form cyclic anhydride. Finally the second cyclic anhydride cleaves to form ester more preferentially with primary alcoholic group of β-cyclodextrin. The schematic representation of the reaction is given in Fig. 1.

The grafting of β-CD and inclusion of limonene into cyclodextrin cavity occurred as per the schematic representation given in Fig. 1a.

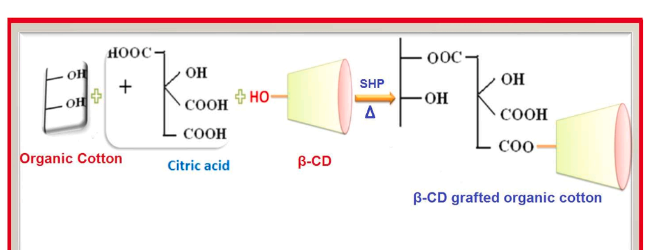

Fig. 1. Schematic representation of β-CD grafting on fabric.

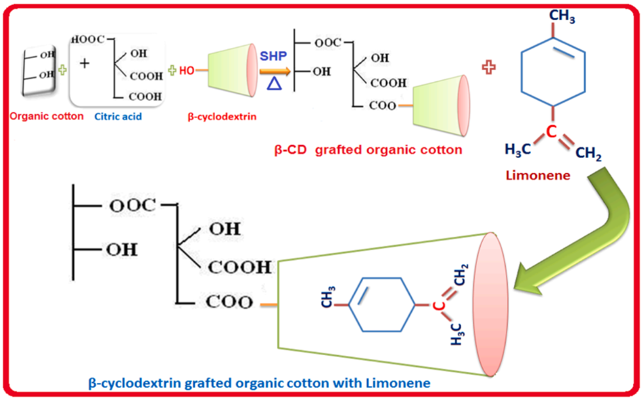

Fig. 1a. Schematic representation of limonene inclusion into β-CD fabric.

2.5. Kinetic experiments

Dye adsorption tests on β-cyclodextrin loaded fabric were conducted in a thermostated shaker water bath. Stock color solutions were made in distilled water. In each run, 50 mg of β-CD loaded fabric was agitated with 100 mL of Maxilon Blue GRL (MB) and Direct Yellow 12 (DY 12) dye solution with a constant starting concentration at 20 °C and natural pH at a swirling speed of 120 rpm. Preliminary studies showed that equilibrium may be reached in 120 min under these conditions. Two-milliliter aliquots were withdrawn at predetermined time intervals, centrifuged for 15 min at 5000 rpm, and the remaining dye concentration in the supernatant was determined by UV–Vis spectroscopy at the wavelengths of maximum absorbance (λ_{max} = 599 nm for Maxilon Blue GRL and 403 nm for Direct Yellow DY 12). Calibration curves were created by plotting absorbance against dye solution concentration. Quantification was performed using calibration curves of absorbance vs dye concentration. We studied how contact duration and starting concentration affect the elimination of Maxilon Blue GRL and Direct Yellow DY 12 with β-CD.

2.6. UV–Visible analysis

The UV–Visible spectrum of a) unbiopolished fabric (F_1), b) unbiopolished β- CD fabrics (F_3), are given in Fig. 2. Fabrics (F_1 and F_3) do not show any absorption in the region 200 – 400 nm due to absence of chromophore characteristic of $\pi - \pi^*$ or n- π^* transition in fabric.

UV–Visible spectrum of (a) limonene and (b) unbiopolished-β-CD limonene fabric (L_3) is depicted in Fig. 2a. Limonene shows absorption maximum (λ_{max}) at 241 nm corresponding to the $\pi - \pi^*$ of exocyclic and endocyclic double bond in limonene. This distinct absorption pattern suggests the existence of conjugated unsaturation, which is a frequent characteristic of limonene. The UV–Vis spectra of L_3 fabric also shows an absorption peak at 241 nm, indicating that limonene has been collected and stuck to the surface of the β-CD- loaded fabric. The constant absorption maximum suggests that limonene's molecular environment remains stable when interacting with the β-CD host structure and fabric matrix.

2.7. Fluorescence analysis

The fluorescence emission spectra of free limonene and the β-CD/limonene inclusion combination were obtained at 280 nm excitation. There was no observable fluorescence in free limonene, which can be attributed to the absence of an extended conjugated system. The inclusion complex, on the other hand, showed a unique emission maximum at 317 nm (Fig. 3). Encapsulation creates a stiffer and hydrophobic milieu that suppresses non-radiative pathways and boosts fluorescence response. This study verifies the effective trapping of limonene within the β-CD cavity and indicates how complexation alters its photo physical characteristics. Fluorescence spectroscopy helps stabilize the β-CD limonene inclusion complex in the changed fabrics.

2.8. FTIR analysis

The spectrum of a) unbiopolished fabric (F_1), b) β-CD, c) unbiopolished β-CD fabric (F_3) are represented in Fig. 4. Spectrum of fabric F_1 shows a broad peak for -OH stretching of cellulosic hydroxyl group at 3357 $cm^{-1}$and a complex band in the range 1000 –1420 cm^{-1} due to -OH in plane bending of cotton. A symmetric stretching of C—H is observed at 2890 cm^{-1}. β- Cyclodextrin depicts peaks characteristic of -OH stretching at 3347 cm^{-1} and strong complexed band at 1025, 1103, 1178, 1360 and 1420 cm^{-1} corresponding to characteristic-C-O stretching and-OH in plane bending vibration of β-CD. The spectra of unbiopolished β-CD fabric (F_3) produces a broad peak between 3300–3500 cm^{-1} characteristic of -OH stretching of cellulose and-OH in plane bending is shifted from 1000 - 1420 cm^{-1} to1000 - 1200 cm^{-1} due to the attachment of cyclodextrin with the -OH group of cellulose.

FTIR spectrum of a) limonene and b) unbiopolished β-CD limonene fabric (L_3) are given Fig. 4a. Limonene exhibits the stretching vibration of –CH in alkane at 2953 cm^{-1} and =CH at 3066 cm^{-1} as broad and small bands respectively. The stretching vibrations in –C—C and $C = C$ are ascribe to the sharp peak at 1196 cm^{-1} and 1659 cm^{-1}. The bending vibration of methylene (-CH_2-) and methyl groups (-CH_3) are represented at 1470 cm^{-1} and 1380 cm^{-1}. The out of plane bending of endocyclic and exocyclic double bonded carbon (CH=C) are attributed at 840 and 932 cm^{-1} confirming the presence of substituted alkanes.

Unbiopolished β-CD limonene fabric (L_3) exhibits the C—O

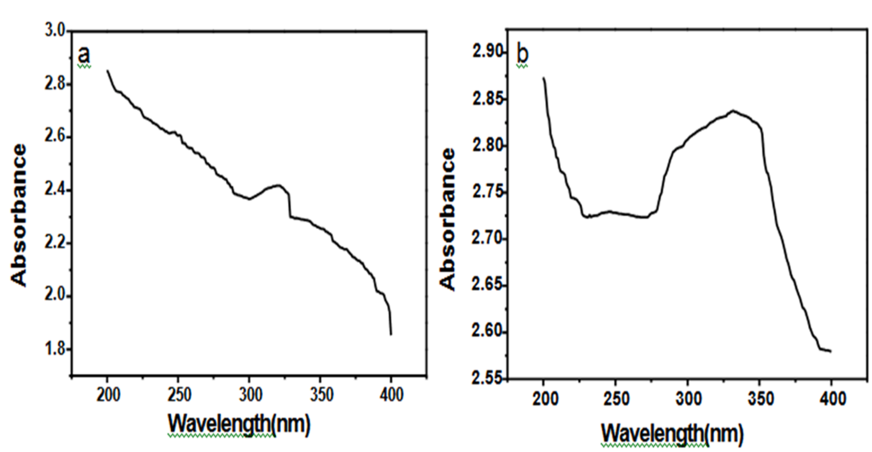

Fig. 2. UV–Visible spectra of a) unbiopolished (F_1), b) unbiopolished β-CD (F_3).

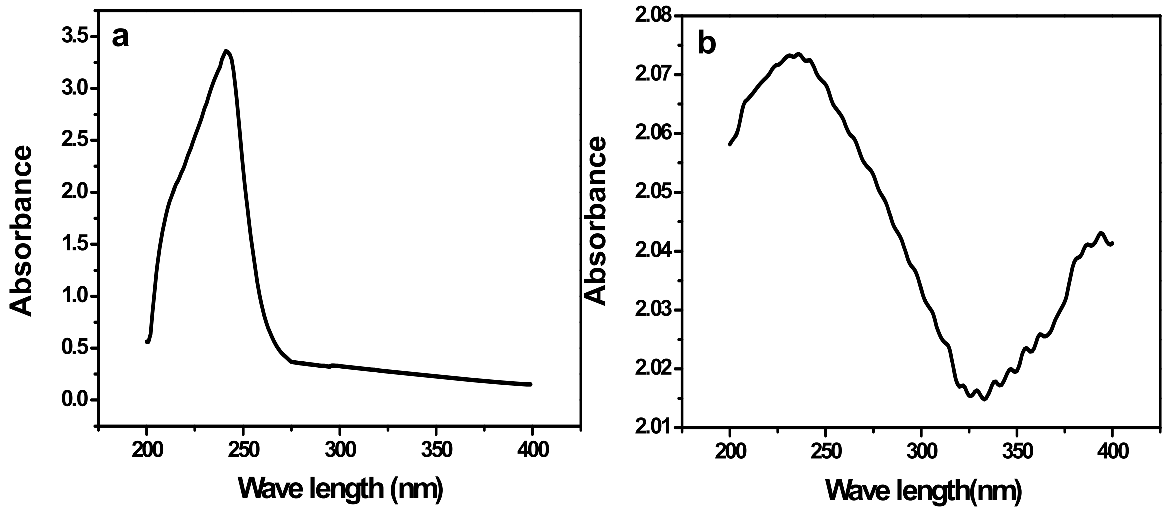

Fig. 2a. UV spectra of a) Limonene and b) unbiopolished β-CD limonene fabric (L_3).

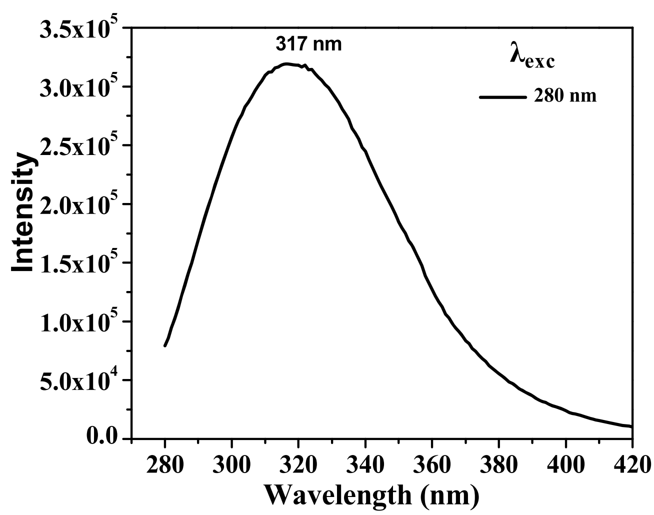

Fig. 3. Fluorescence emission spectrum of the limonene inclusion complex (λ_{exc} = 280 nm) showing an emission maximum at 317 nm. Free limonene did not display detectable fluorescence under the same conditions.

stretching and OH in plane bending as small peaks between 1033 and 1415 cm^{-1}. The stretching vibration of -OH of cellulose occurs at 3357 cm^{-1}. The alkenyl group ($C = C$) of limonene exhibits the stretching vibration of $C = C$ at 1685 cm^{-1}, this peak stays in the treated fabric, indicating that limonene was effectively trapped inside the β-CD- cellulose system.

2.9. HPLC analysis

The limonene content of fabrics (L_1, L_2, L_3 & L_4) is obtained from High Performance Liquid Chromatography analysis and the chromatogram is represented in Fig. 5. The limonene peaks are identified from their retention time obtained for limonene in separate HPLC. The response factor was calculated by running the co-chromatography with benzoic acid as internal standard. The limonene concentration of the fabrics L_1, L_2, L_3 and L_4 is estimated as 0.0174 %, 0.0227 %, 0.416 % and 0.468 % respectively. The results show that enzymatic treatment and β-cyclodextrin (β-CD) grafting significantly improve limonene loading efficiency. Fabric L_1, with no surface changes has the lowest limonene concentration. This is most likely owing to its compact fiber structure, which reduces surface accessibility and lacks the functional groups or cavities required to capture limonene molecules. In contrast, L_2 was cleaned using an environmentally friendly enzymatic biopolishing technique. This process is recognized for selectively breaking down cellulose amorphous areas, eliminating superficial microfibrils and increasing the fiber's surface roughness and porosity. Adding β-CD molecules to the fiber matrix without biopolishing significantly improved the L_3 fabric. The L_4 fabric had the highest limonene concentration of all tests. The fabric underwent enzymatic biopolishing and β-CD grafting. Biopolishing improved fiber surface accessibility by increasing pore size and exposing more cellulose hydroxyl groups, allowing for better β-CD grafting. Hence the eco-friendly bio-polishing has played a significant role for the improvement of limonene concentration in fabrics similar to the enhancement of dye ability of reactive dyes in biopolished fabric [15].

2.10. XRD

The XRD pattern of unbiopolished fabric (F_1), unbiopolished β-CD fabric (F_3) are shown in Fig. 6. The unbiopolished fabric (F_1) and unbiopolished β-CD fabric (F_3) represents peaks characteristic of 101, 10ī, 002 and 040 planes at 2θ equal to14.8°, 16.5°, 22.8° and 34.5° with slight variation in angle (± 0.2°) of reflection. It indicates that during the chemical modification the cellulose is retaining its native cellulose form I. While comparing the fabrics crystallinity before and after treatment, the β-CD grafting via cross linker citric acid has improved the crystallinity of fabric to 92.8 %. When cross linking occur in the more accessible amorphous regions of the fabric, the more reactive hydroxyl groups are cross linked with citric acid and then grafted with β-CD through a five member cyclic anhydride intermediate with the aid of sodium hypophosphite. The crosslinking remarkably attacked the amorphous region most effectively there by the relative proportion of crystalline region increases in one hand and also on the other hand the crosslinker is competitively used by the hydroxyl groups of cellulose chain and β-CD, therefore there is no acidic erosion occurs in crystalline region of cellulose as occurred in the case of cross linking of 1,2,3,4 Butane tetracarboxylic acid studied by Xu [16]. Parikh et al., studies on cross linking of cotton with dimethylol dihydroxy ethylene urea (DMDHEU) and citric acid (CA) supported the increase of crystallinity index of cotton [17].

The XRD pattern of unbiopolished limonene fabric (L_3) is shown in Fig. 6a.The crystalline reflections of fabric L_3 are more or less same as that of the reflections of native cotton (2θ = 14.8°, 16.5°, 22.8° and 34.5° for planes 101,10ī, 002 and 040 of cellulose form I [18]. The surface modification of cellulose using β-cyclodextrin (β-CD) and limonene does not alter its basic crystalline structure. The intensity peak at

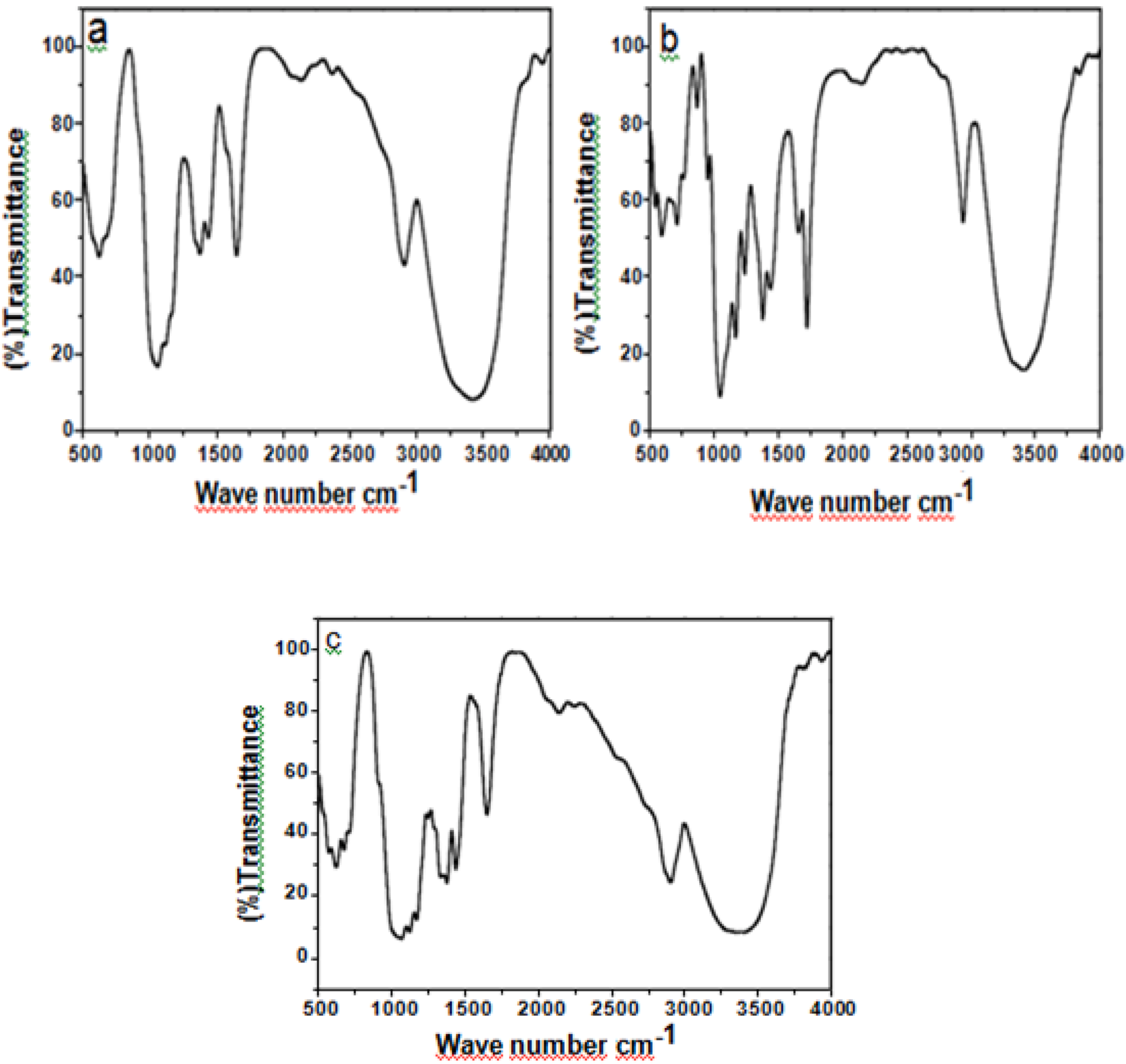

Fig. 4. FTIR spectra of a) unbiopolished (F_1), b) β-CD, c) unbiopolished β-CD fabric (F_3).

$2\theta = 22.8^\circ$ corresponding to the (002) plane indicates a high amount of crystallinity in the cellulose chains. This is often associated with the tightly packed portions of cellulose microfibrils. The existence of prominent and sharp peaks indicates that the material retains its solid crystalline structure even after chemical treatments. The prominent reflections for the planes 101, $10\bar{1}$, 002 and 040 of all the three fabrics suggested that the grafting of β-CD and inclusion of limonene onto the toroid cavity of cyclodextrin has not changed cellulose to their different allomorphs such as cellulose II, III and IV form [19]. The fabrics retained their cellulose I form after grafting and inclusion of limonene. The crystallinity index of the modified fabrics (L_3) is 93.2 % and there is no tremendous raise in crystallinity on inclusion of limonene, specifies that limonene is not chemically bonded with cellulose chain of cotton. The XRD investigations demonstrates that surface modification with β-CD grafting and limonene inclusion preserves the native structure of cellulose without disrupting its crystalline domains.

2.11. *TGA*

Thermogravimetric analysis of unbiopolished fabric (F_1) unbiopolished β-CD fabric (F_3) and unbiopolished β-CD limonene fabric (L_3) are represented in Fig. 7. It provides quantitative information on weight change during heating process [20]. The recorded thermogravimetric plots for all cotton samples show three degradation steps which suggest the co-existence of more than one degradation process. In accordance with the literature [21] it has been established that there is no degradation taking place until 200 °C. The lower temperature loss (first step) may correspond to the breaking of water linkage, and the second stage represents the degradation of the whole polymer cotton, where weight loss percentage and rate of weight loss are very high. Char pyrolysis commences above 430 °C and leaves residue after complete burning process.

The thermogram of unbiopolished fabric (F_1) represents the weight loss of 20 % in the initial stage of pyrolysis up to 200 °C. The onset of the

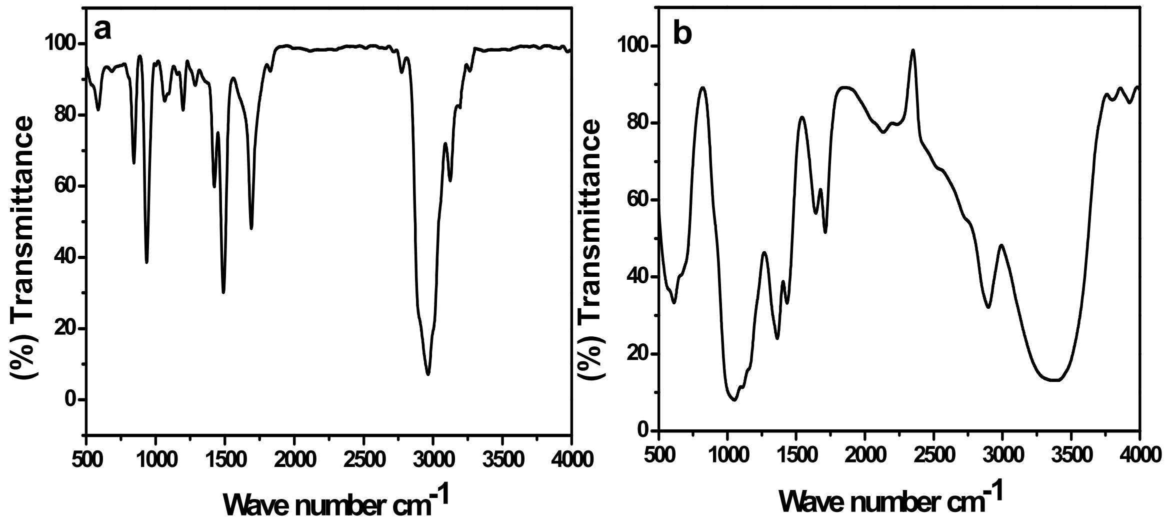

Fig. 4a. FTIR spectra of a) Limonene and b) unbiopolished β-CD limonene fabric (L_3).

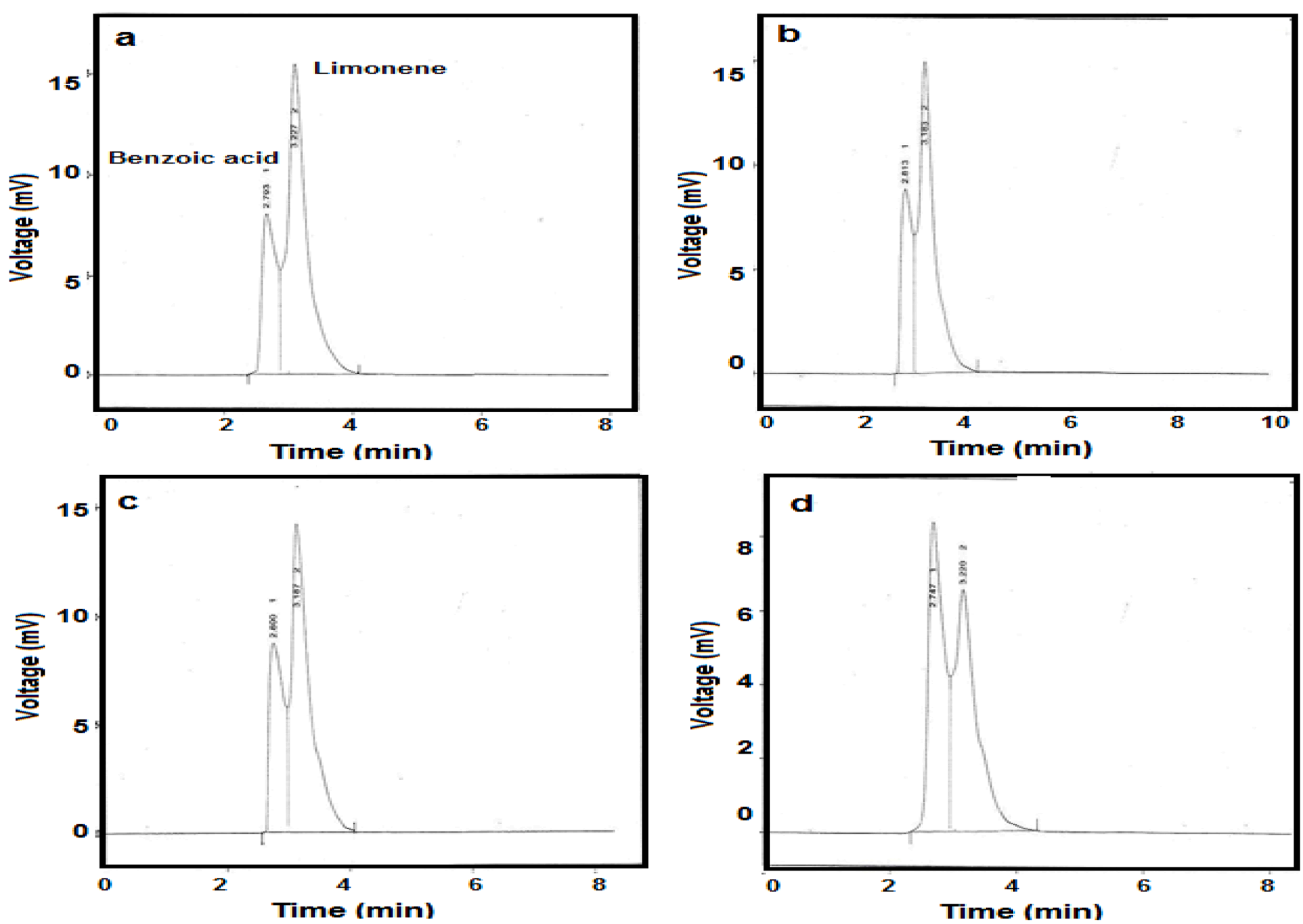

Fig. 5. HPLC chromatogram for alcoholic extract of limonene a) unbiopolished limonene fabric (L_1), b) biopolished limonene fabric (L_2), c) unbiopolished β-CD limonene fabric (L_3) and d) biopolished β-CD limonene fabric (L_4).

cellulose depolymerization has started at 320 °C. The major decomposition of cellulose polymer has occurred between the temperature range 320–380 °C and a weight loss 60 % was obtained. The final decomposition of cellulose occurred at 543 °C with 99 % weight loss as in earlier reports [22]. The thermogravimetric analysis of unbiopolished β-CD fabric (F_3) shows the same three stages in cotton fabric with slight deviation of depolymerization temperature and decomposition temperature. The previous reports on crystallinity of citric acid treated cotton states that there is an increase in crystallinity, therefore the final decomposition temperature increases to 561 °C with 95 % weight loss. The onset depolymerization has started at 315 °C slightly at lower temperature than that of pure cotton which may be due to

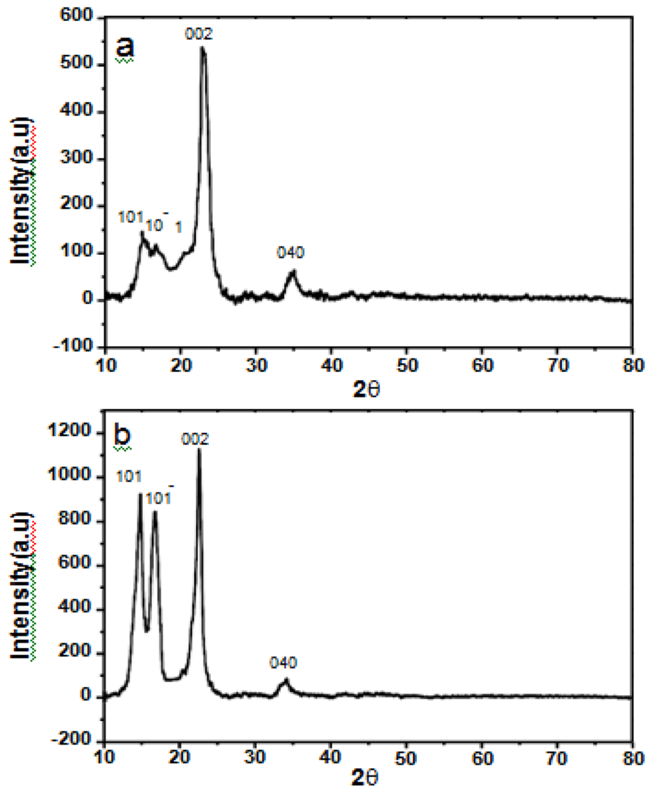

Fig. 6. XRD spectra of a) unbiopolished fabric (F_1), b) unbiopolished β-CD fabric.

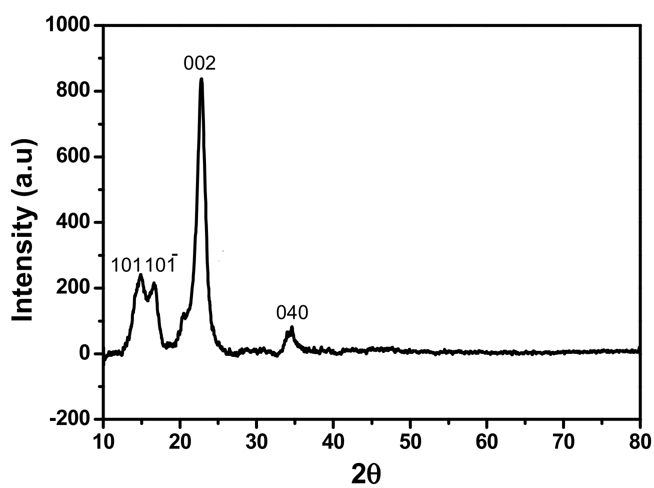

Fig. 6a. XRD spectra of unbiopolished β-CD limonene fabric (L_3).

decomposition of cyclodextrin started at 270 °C. But the percentage of weight loss is comparatively lower in all stages of decomposition process indicates that higher crystallinity in fabric (F_3) increased the thermal stability of the fabric.

The fabric (L_3) has the three major stages of weight loss and the decomposition starts 282 °C with 9 % weight loss because of the evaporation of absorbed moisture and low molecular weight components. The onset depolymerisation begins at 322 °C and completes at 388 °C. The higher crystallinity of fabric (L_3) increased the thermal stability of the fabric [23]. The relative weight loss proportion is less in fabric F_3 and L_3 in all stages of pyrolysis as compared with the reference fabric (F_1), which could be the result of the presence of cyclodextrin and limonene on fabric. Crystalline patches in cellulose degrade at higher temperatures due to stronger hydrogen interactions between molecules. Limonene is a volatile chemical that evaporates/decomposes at significantly lower temperatures. However, the heat breakdown products may interfere with cotton's degradation route. These secondary interactions are likely responsible for the small rise in the ultimate breakdown temperature (571 °C) and the greater char residue seen in limonene-loaded fabrics. The final residue content is higher than that of the other two fabrics indicates that the decomposition products of limonene have interfered with the decomposition of cotton. TGA research indicates that grafting β-CD and limonene improves the fabric's structure and heat resistance. This modification delays thermal deterioration and enhances char formation, thereby increasing the thermal stability of the fabrics.

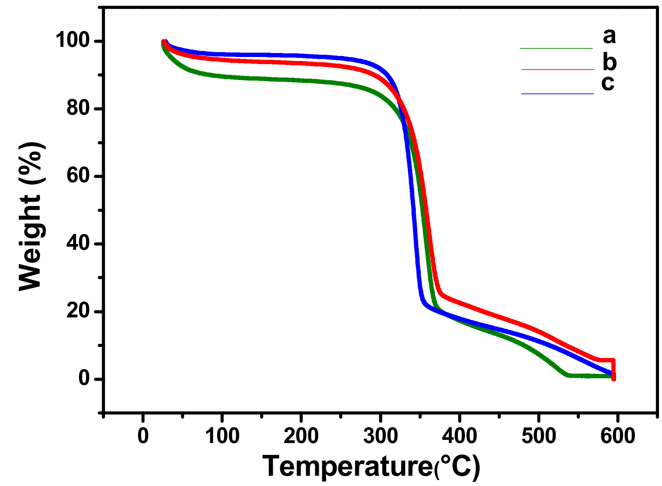

Fig. 7. TGA curves of a) unbiopolished fabric (F_1), b) unbiopolished β-CD Fabric (F_3) and c) unbiopolished β-CD limonene fabric (L_3).

2.12. *Evaluation of antibacterial activity*

The antibacterial property of fabrics (L_1, L_2, L_3 & L_4) is measured from the zone of inhibition developed in and around the fabric on nutrient agar plate and represented in Fig. 8 for E.coli and S.aureus. The

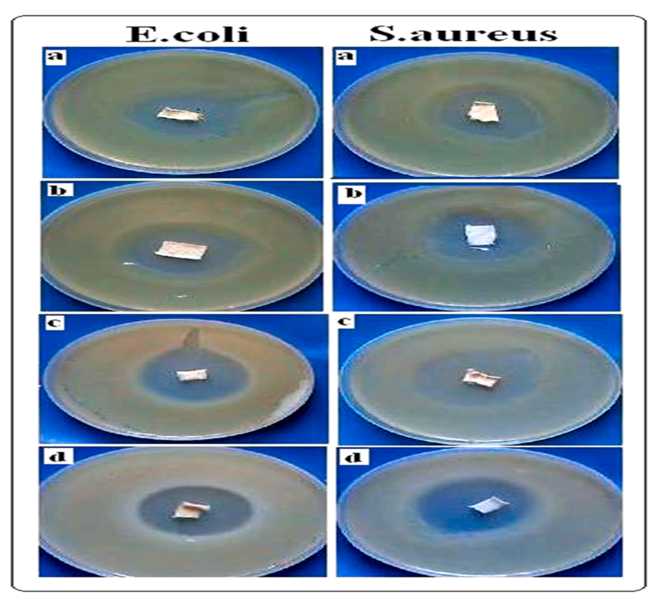

Fig. 8. Antibacterial activity of a) unbiopolished limonene fabric (L_1), b) biopolished limonene fabric (L_2), c) unbiopolishedβ-CD limonene fabric (L_3) and d) biopolishedβ-CD limonene fabric (L_4) against E.coli and S.aureus.

zones of inhibition developed in unwashed fabric and after ten cycles of washing are given in Table 1. Citrus products contain a wide variety of oils that are toxic to bacteria [24,25]. Limonene is the major constituent of the citrus essential oil [26]. They contain 85-99% volatile component (limonene) and 1-15% nonvolatile component. It is well known that monoterpenes develop their antimicrobial inhibitory effects through the interaction with membrane structure and function. This is in fact due to their lipophilic and solubility properties. These interactions include membrane expansion, increase membrane fluidity and permeability, disturbance of membrane-embedded proteins, inhibition of respiration and alteration of ion transport processes [27–32].

The limonene loaded fabrics (L_1, L_2, L_3 & L_4) shows inhibition against the growth of E.coli and S.aureus. The exclusive nature of the fabric which has been modified with enzyme and cyclodextrin shows the highest inhibition in both bacteria compared with the all other fabrics. The gram negative bacteria is less susceptible to attack than gram positive S.aureus. Limonene as lipophilic compound is capable to attack the cell membrane (lipo polysaccharide membrane) and alter cell permeability. The presence of unsaturation in limonene has influenced the antibacterial activity. The unbiopolished and biopolished limonene fabrics exhibited antibacterial activity as a result of the absorption of limonene into void space available in fabric but their washing durability is poor. The unbiopolished and biopolished β-CD limonene fabrics developed more inhibition, but the latter one has showed pronounced effect even after repeated washing process. The presence of limonene as inclusion complex into the cavity of cyclodextrin and their controlled release are the reason for the durability of the antibacterial activity in fabric L_3 andL_5.In addition to that biopolishing boosts the grafting of β-CD and positively increased the concentration and antibacterial activity of limonene. Bactericidal experiments were carried out in triplicate ($n = 3$), with randomized plating and independent evaluation to reduce bias. Untreated cotton, biopolished-only, and β-CD grafted fabrics without limonene showed no inhibition against *Escherichia coli* or S. aureus, showing that the observed activity in L_1 - L_4 textiles is primarily due to limonene.

2.13. Biopolished MCT-β-CD limonene fabric for antibacterial activity

The unbiopolished, biopolished, unbiopolished MCT-β-CD and biopolished MCT-β-CD fabrics are loaded with limonene. The UV–Visible and FTIR, analysis are performed for confirmation of β-CD and limonene on fabric. The crystalline nature and thermal stability of the modified fabrics are analyzed by XRD and TGA. Limonene content of the various categories of fabrics is estimated from the HPLC analysis of the alcoholic extract from the respective fabrics. The antibacterial efficacy and the durability of the activity to repeated washing cycles are tested.

3. Inclusion of limonene into MCT-β-CD fabric

The grafting of MCT-β-CD and inclusion of limonene into cyclodextrin cavity occurred as per the schematic representation given in Fig. 9.

Table 1
Antibacterial activity of limonene-loaded fabrics against *E. coli* and *S. aureus* (mean ± SD, $n = 3$).

Micro organism	Zone of inhibition (mm)							
	Washing cycles							
	L_1		L_2		L_3		L_4	
	0	10	0	10	0	10	0	10
E.coli	19	3	23	5	27	25	30	27
S.aureus	22	3	26	6	28	26	32	29

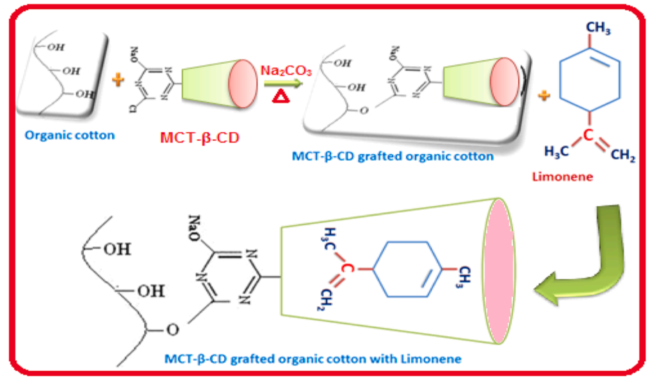

Fig. 9. . Schematic representation of limonene inclusion into MCT-β-CD fabric.

3.1. UV–Visible analysis

UV- Visible spectrum of a) limonene and b) unbiopolished MCT-β-CD limonene fabric (L_5) is depicted in Fig. 10. Alcoholic solution of limonene exhibits significant absorption at 241 nm characteristic of $\pi - \pi^*$ in exo and endo cyclic double bond. Unbiopolished MCT-β-CD limonene fabric (L_5) represents absorption maximum between 230–240 nm characteristic of the triazine and limonene moiety.

3.2. FTIR analysis

FTIR spectrum of a) limonene and b) unbiopolished MCT-β-CD limonene fabric (L_5) are depicted in Fig. 11. Limonene exhibits the stretching vibration of –CH in alkane at 2953 cm^{-1} and =CH at 3066 cm^{-1} as broad and small bands respectively. The stretching vibrations in –C—C and $C = C$ are ascribe to the sharp peak at 1196 cm^{-1} and 1659 cm^{-1}. The bending vibration (-CH) of methylene and ethyl groups are represented at 1470 cm^{-1} and 1380 cm^{-1}. The out of plane bending of endo and exo cyclic double bonded carbon (-CH═C) are attributed at 840 and 932 cm^{-1}. The spectrum of unbiopolished MCT-β-CD limonene fabric (L_5) exhibits stretching vibration of -OH group of cotton at 3372 cm^{-1} and asymmetric stretching of –CH at 2876 cm^{-1}. The stretching vibration of alkenyl bond (-$C = C$) occurs at 1689cm^{-1} and the bending vibrations of methylene and methyl groups of limonene at 1369 cm^{-1}

3.3. Adsorption kinetics

The principle behind the adsorption kinetics of dyes on the fabric involves the search for a best model that well represents the experimental data. The kinetic data were analyzed using two commonly used models to describe the adsorption behavior and illuminate the regulating mechanism: the pseudo-first-order and pseudo-second-order kinetic models. Lagergren [33] presented a pseudo-first-order model.

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

Where q_e is the amount of dye adsorbed (mg/g) at equilibrium, q_t (mg/g) the amount at time t (min), and k_1 (mg/g) at time t (min) and k_1 is the pseudo-first order rate constant of adsorption. The first order rate constant (k_1) and q_e were determined from the slopes and intercepts of plots of log ($q_e - q$) versus t at different adsorbent dosages.

The kinetics of adsorption can also be described by pseudo-second order equation and it is given by [34]:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

The second order rate constant (k_2) and q_e were determined from the slope and intercepts of the plots (Fig. 12a) obtained by plotting t/q_t versus time t. The value of q determined experimentally $q_{e(exp)}$,

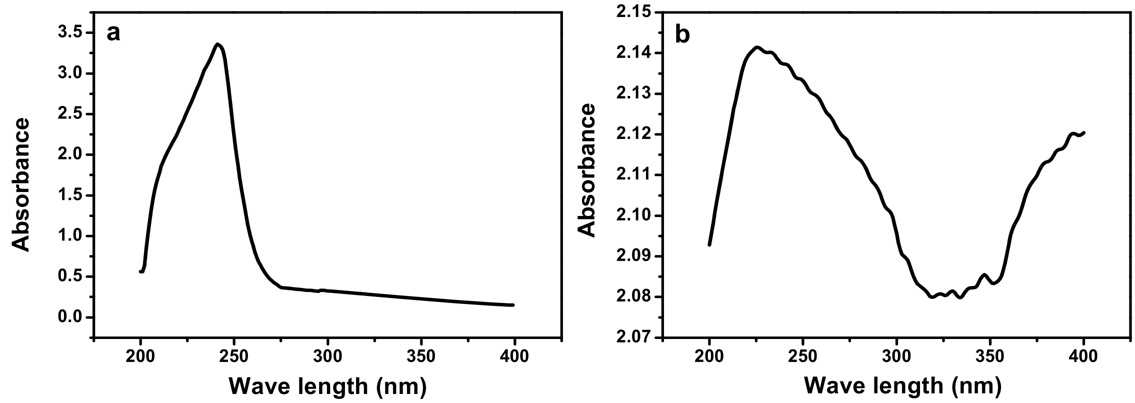

Fig. 10. UV spectra of a) Limonene and b) unbiopolished MCT-β-CD limonene fabric (L_5).

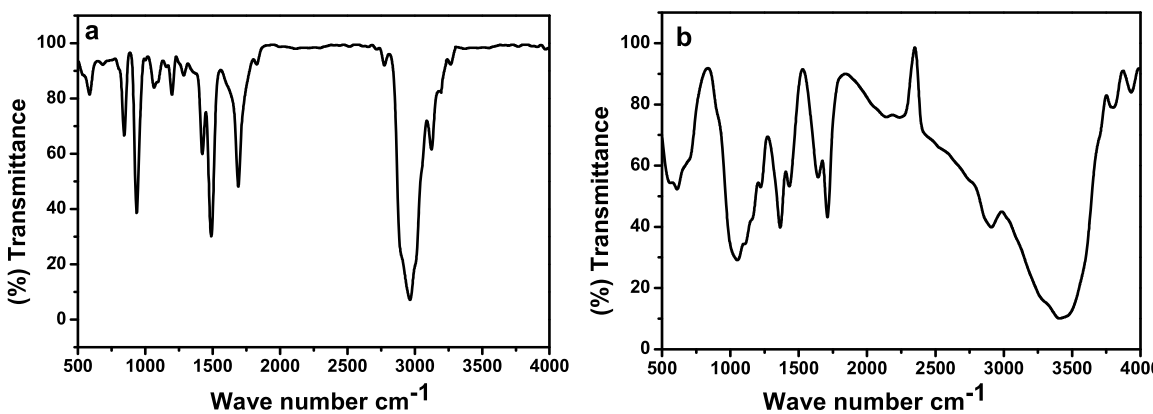

Fig. 11. FTIR spectra of a) Limonene and b) unbiopolished MCT-β-CD Limonene fabric (L_5).

calculated $q_{e(cal)}$, correlation coefficient together with the adsorption rates k_1 and k_2 are shown in Table 2.

Pseudo-second-order kinetics better describes dye adsorption on β-cyclodextrin, as evidenced by consistently higher correlation coefficients compared to the pseudo-first-order model (Fig. 12). The pseudo-second-order kinetic model is supported by the linearity of the t/q_t against *t* graphs (Fig. 12a), as well as the close agreement between experimental and predicted q_e values.

3.4. SEM

The scanning electron microscopic images of unbiopolished fabric (F_1) and unbiopolished MCT-β-CD fabrics (F_5) are shown in Fig. 13. The surface of unbiopolished MCT-β-CD fabric (F_5) appears laminated as which is attributed to the reactivity of the MCT-β-CD with the fabric.

3.4.1. EDAX

Energy dispersive X-ray analysis is used to analyze near surface elements and estimate their proportion at different position, thus giving an overall mapping of the sample. This technique is used in conjunction with SEM. The EDAX image is shown in Fig. 13a. When the electron beam (10–20 keV) strikes the surface of the fabric (made conductive by gold sputtering) X-rays are emitted from the material. The energy of the X-rays emitted depends on the material under investigation. The EDAX analysis of unbiopolished MCT-β-CD grafted fabrics (F_5) confirmed the existence of nitrogen element on the fabric and it implies that MCT-β-CD is fixed permanently on the fabric

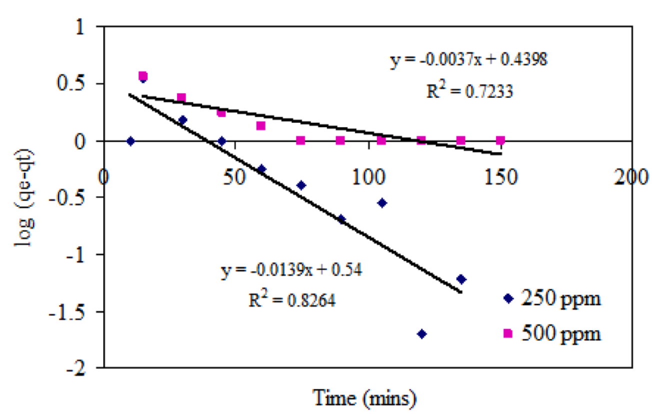

Fig. 12. Pseudo-first-order kinetic plots for the adsorption of dye on β-cyclodextrin at two initial concentrations (250 ppm and 500 ppm).

Table 2
Kinetic parameters for dye adsorption onto β-cyclodextrin.

Dye (initial concentration, mg L^{-1})	Initial Concentration	q_e exp	Pseudo first order			Pseudo second order		
			k_1	$q_{e\ (Cal)}$	R^2	k_2	$q_{e\ (cal)}$	R^2
Maxilon Blue GRL	250 500	24.36 14.93	0.036 0.012	5.36 3.31	0.8775 0.8312	0.015 0.008	24.81 16.03	1 0.998
Direct Dye 12	250 500	23.21 11.98	0.022 0.010	4.98 3.04	0.8678 0.8215	0.012 0.006	23.21 15.06	0.992 0.991

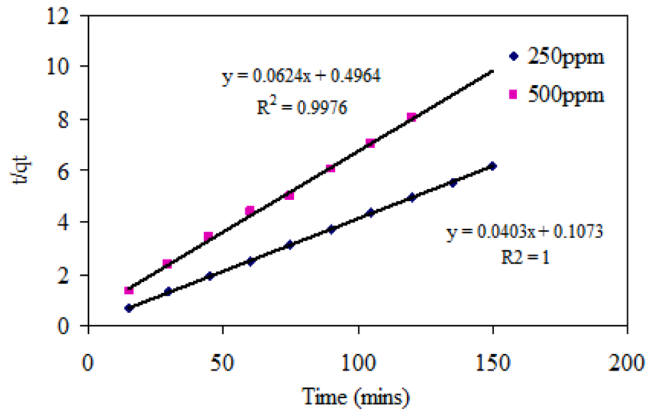

Fig. 12a. Pseudo-second-order kinetic plots for the adsorption of dye on β-cyclodextrin at two initial concentrations (250 ppm and 500 ppm).

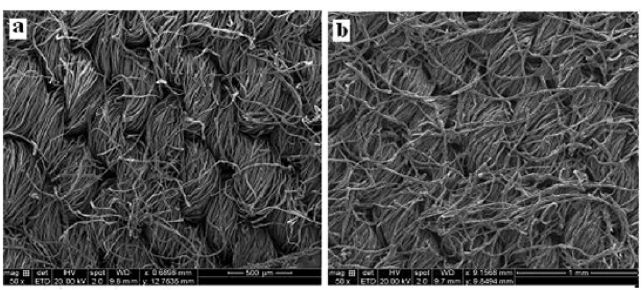

Fig. 13. SEM images of a) unbiopolished (F_1), b) unbiopolished MCT-β-CD (F_5) fabrics.

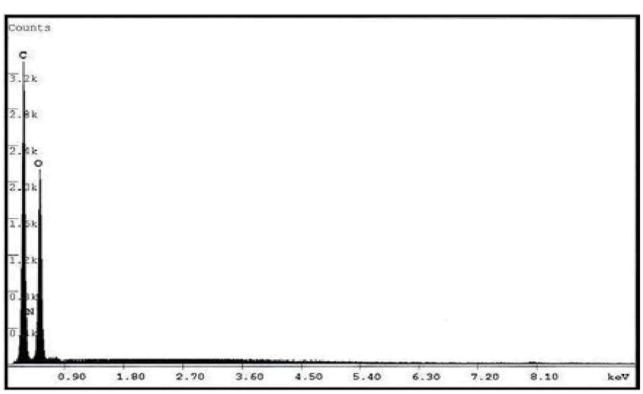

Fig. 13a. EDAX of unbiopolished MCT-β-CD (F_5) fabric.

3.5. HPLC analysis

HPLC chromatogram of the alcoholic extract obtained from fabrics (L_1, L_2, L_5 & L_6) are depicted in Fig. 14.The limonene content was evaluated from the peaks area of the sample (limonene) and the standard benzoic acid using response factor derived from the co-chromatography run with standard compound benzoic acid. The limonene content in fabrics ($L_1 = 0.0174$ %, L_2=0.0227 %, $L_5 = 0.489$ %, L_6= 0.537 % w/w) showed that enzyme treatment has improved more penetration of limonene into the interstitial sites and also more grafting of MCT-β-CD on fabric. MCT-β-CD enriched fabric accommodated more quantity of limonene into their cavity. The unbiopolished and biopolished limonene fabric (L_1 & L_2) has lower percentage of the core material limonene as it is held by weak Vander Waals forces with cellulose chain of cotton and it can be washed out from the fabric surface. The higher content of limonene in other two fabrics (L_5 & L_6) is as result of presence as inclusion complex into cyclodextrin cavity, which could not washed out easily from the fabric. limonene fabric (L_1), b) biopolished limonene fabric (L_2), c) unbiopolished MCT-β-CD limonene fabric (L_5) and d) biopolished MCT-β-CD limonene fabric (L_6).

3.6. XRD

XRD pattern of unbiopolished MCT-β-CD limonene fabric (L_5) are represented in Fig. 15. Unbiopolished MCT-β-CD limonene fabric (L_5) shows 94.4 % crystallinity and it is very close to the crystallinity of unbiopolished MCT- β-CD fabric (F_5). The limonene moiety is included into the toroid cavity of cyclodextrin and it is not involved in bonding with the cellulosic hydroxyl group. Since the grafting of MCT- β-CD and the inclusion of limonene into cyclodextrin cavity has no way hindered crystallite dimension of cellulose form I, therefore their reflection occurs only with minor deviation (±0.2°) as reported earlier [15].

3.7. TGA

The thermal analysis of the a) unbiopolished fabric (F_1), b) unbiopolished MCT-β-CD fabric (F_5) and c) unbiopolished MCT- β-CD limonene fabric (L_5) are represented in Fig. 16. The thermogram of above said fabrics shows slight variation as a result of modification.

The onset inflexion of unbiopolished MCT-β-CD limonene fabric (L_5) begins at 316 °C with a weight loss of 15 % which is lower than that of unmodified fabric with a weight loss of 20 % at 320 °C. The thermal stability of fabrics F_5 and L_5 are in close association. The increase of crystallinity and decomposition products of MCT-β-CD and limonene lowered the depolymerisation temperature and percentage of weight loss. The char pyrolysis starts at 380 °C and completes at 571 °C with 95 % weight loss of fabric. The reduction in weight loss percentage and higher content of residue (5 %) proved that the decomposition product of MCT-β-CD and limonene lowered the decomposition rate of cotton.

3.8. Evaluation of antibacterial activity

The agar diffusion test conducted on fabrics (L_1, L_2, L_5 & L_6) shows positive results on all fabrics towards gram negative and positive bacteria with deviation in their efficacy of the antibacterial activity represented in Fig. 17. The zones of inhibition developed by fabrics are given in Table 3 for E.coli and S.aureus. Amongst all the fabrics the enzyme treated MCT-β-CD limonene fabric (L_6) developed more inhibition compared with the other three fabrics. This may be due to their higher limonene content within the toroid cavity of cyclodextrin. Another fact is that the fabrics grafted with MCT-β-CD retain nearly 60–70 % of the antibacterial activity even after 10 cycles of washing, as limonene occupies hydrophobic cavity of cyclodextrin and not the interstitial site of fabric. The biopolishing has improved the antibacterial efficacy of fabricL$_2$ but it couldn't help to retain the effect during washing. The antibacterial characteristics of fabrics (L_5 and L_6) have been improved and also durable as it has the limonene in protected form. Biopolishing has played a prominent role in well establishing the grafting yield of MCT-β-CD and indirectly paved way to accommodate more percentage of limonene into the fabrics. Limonene as the major compounds of essential oils, have the ability to disrupt and penetrate the lipid structure of the cell wall of bacteria, leading to denaturation of proteins and destruction of the cell membrane [35,36].When considering the antibacterial activity of limonene towards the two bacteria E.coli and S.aureus, the latter has been destroyed more compared to the former. Mostly gram negative bacteria like E.coli are less susceptible to antimicrobial agent, but limonene is capable to attack the lipopolysaccharide cell wall easily as a result of their hydrophobic or lipophilic nature. Therefore the inhibition developed in both bacteria is in close association with each other. It has been reported that the presence of alkenyl group in limonene showed more activity than p-cymene since the latter has alkyl

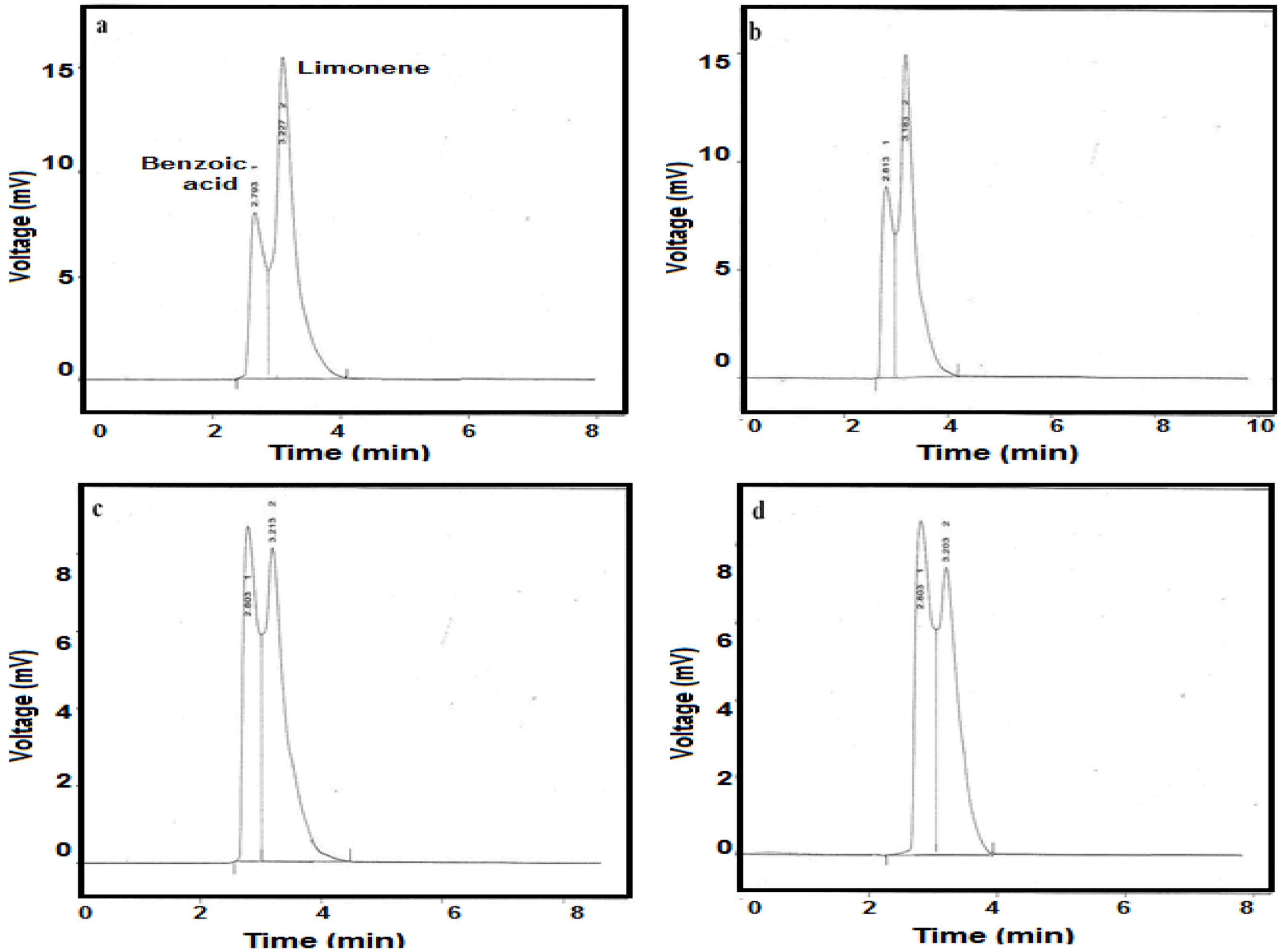

Fig. 14. HPLC chromatogram for alcoholic extract of limonene a) unbiopolished.

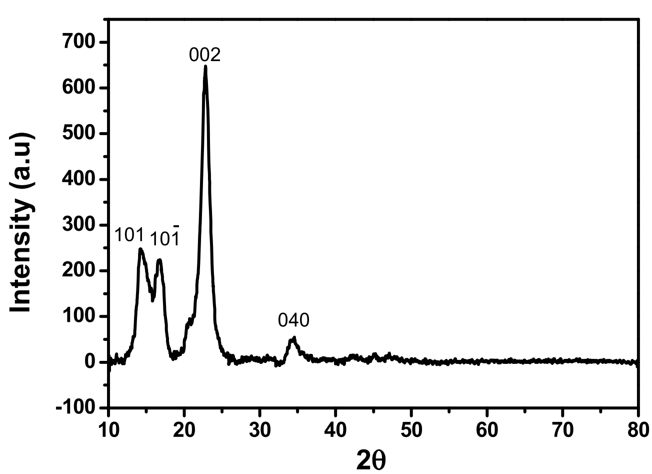

Fig. 15. XRD spectra of unbiopolished MCT-β-CD limonene fabric (L_5).

group in their ring. The alkenyl group of limonene upon air oxidation produces ions, which disturbs the cell wall and adversely causes the leakage of ions and other cell contents [37,38]. Only MCT-β-CD/limonene textiles shown long-term antibacterial efficacy, reducing S. aureus by 3 - 3.4 $\log_{10}$ and *E. coli* by 2.2 - 2.8 $\log_{10}$. This demonstrates that host-guest encapsulation maintains limonene, providing persistent and wash-resistant effectiveness.

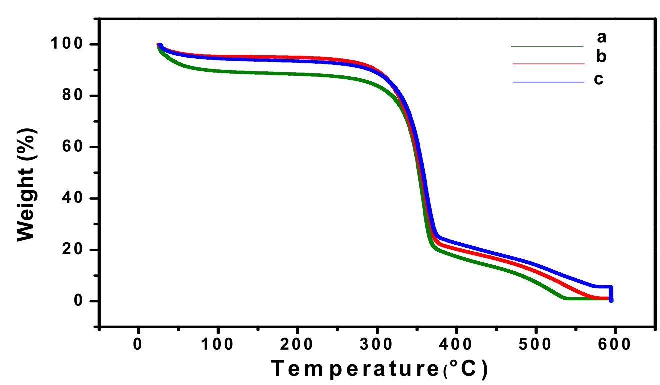

Fig. 16. TGA curves of a) unbiopolished fabric (F_1), b) unbiopolished MCT-β-CD Fabric (F_5) and c) unbiopolished β-CD limonene fabric (L_5).

Biopolished limonene 1 fabric (L_2), c) unbiopolished MCT-β-CD limonenefabric (E_5) and d) biopolished MCT-β-CD limonene fabric (E_5) against E.coli and S.aureus.

4. Conclusion

Eco-friendly enzymatic biopolishing increased the fixation yield of β-CD and MCT-β-CD on cotton. Limonene, a biodegradable and non-toxic terpene, was effectively integrated and it's loading verified by

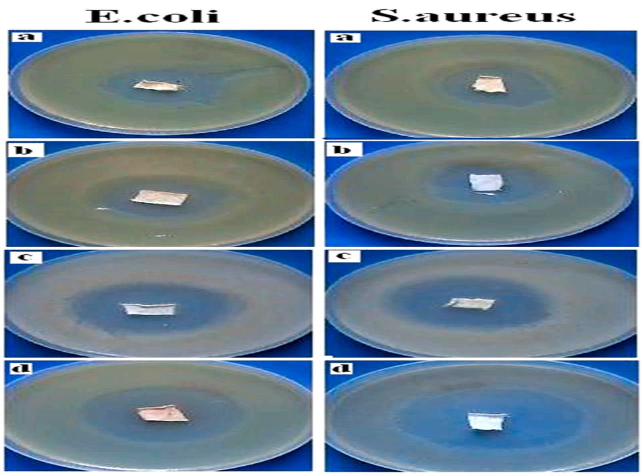

Fig. 17. Antibacterial activity of a) unbiopolished limonene fabric (L_1), b).

Table 3
Antibacterial activity of MCT-β-CD limonene fabrics against *E. coli* and *S. aureus* (mean ± SD, $n = 3$).

Micro organism	Zone of inhibition (mm)							
	Washing cycles							
	L_1		L_2		L_5		L_6	
	0	10	0	10	0	10	0	10
E.coli	19	3	23	5	30	27	35	30
S.aureus	22	3	26	6	34	29	36	31

HPLC. UV–Vis and FTIR confirmed the grafting and inclusion, whereas XRD revealed higher crystallinity and TGA demonstrated improved thermal stability. Negative controls (untreated, biopolished-only, and β-CD/MCT-β-CD without limonene) showed no bactericidal impact, indicating that long-lasting action is primarily due to limonene release. Limonene-loaded β-CD and MCT-β-CD textiles inhibited S. aureus more effectively than *E. coli*, and remained active after ten wash cycles. Statistical analysis revealed that these improvements were extremely significant. Fluorescence spectroscopy and SEM revealed homogenous grafting of β-CD and MCT-β-CD on cotton, with effective limonene inclusion inside the cyclodextrin cavities. Controlled-release testing revealed a distinct biphasic release pattern, which explains the material's outstanding wash durability and long lasting antibacterial efficacy. This work demonstrates that enzymatic biopolishing coupled with cyclodextrin grafting produces a green and long-lasting platform for regulated release of natural antimicrobials, overcoming the constraints of traditional synthetic finishes and offering sustainable antibacterial textiles.

CRediT authorship contribution statement

Ayiramuthu Rukmani: Writing – review & editing. **Alagappan Kavitha:** Methodology. **Meyyappan Revathi:** Writing – original draft. **Jagadeesan Manjunathan:** Investigation. **Rasheed Ahmed Mohamed Hisam:** Software. **Murugan Pavithra:** Resources.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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