Egypt. J. Chem. **Vol. 65**, No. 5 pp. 377 - 389 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Environmentally Sound Approach for Fabrication of Antibacterial/Anti-UV/Anti-crease and Fragrant Denim Fabrics

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Abstract

A green approach for imparting multifunctional properties namely antibacterial, anti-UV, anti-crease and fragrance property to indigo dyed cotton denim fabrics using environmentally benign finishing, hosting and bioactive agents was investigated. In the current work, pre-loading of MCT-βCD, as a hosting agent, via ester-cross linking using CA/SHP, as formaldehyde-free cross linking system using pad-dry-cure method, followed by post-treatment with selected bio-active agents namely Clove oil, Lavender oil, Tulsi oil and Vanillin AR were carried out to add new, durable and desirable functional properties. The obtained results demonstrated that the variation in the efficacy and durability of the imparted functional properties is governed by extent of loading the modified βCD, number and availability of hydrophobic hosting-cavities, type and chemical constituents of the guest molecule and its extent of inclusion into the created cavities via formation of host-guest complex, as well as its retention or release during the washing process. The remarkable improvement in antibacterial activity against the pathogenic bacteria followed the decreasing order: Tulsi≥Clove>Vanillin>Lavender>>None. The obtained results also demonstrated that, the imparted anti-UV capability of post-loaded denim samples follows the descending order: Vanillin>Tulsi>Clove>Lavender>>None. The imparted functional properties showed a high durability even after 15 washes.

Keywords: MCT-βCD-loading; Denim fabric; Bioactive agents; Inclusion complexes; Green multi-functional finish.

1. Introduction

Monochlorotriazinyl-β cyclodextrin, MCT-βCD, is a reactive cyclodextrin derivative having the ability to form covalent bonds with cellulose active sites under proper treatment conditions and capability to form inclusion compounds inside its interior host cavities with numerous hydrophobic guest substances [1-4]. Recently, there have been an increasing efforts in utilization and potential application of MCT-βCD for increasing the extent of loading and holding capacity of many active ingredients for imparting a wide ranges of functional properties to the βCD-loaded substrate like antibacterial [5-8], UV-protection [9-11], controlled release of fragrances [12-15], insecticides delivery [16, 17] as well as improving coloration quality [18, 19].

On the other hand, there is an ever growing interests in using environmentally benign-green bioactive substances and essential oils for replacement of non-ecofriendly functional chemicals currently used along with implementation of sustainable emerging finishing techniques for development of high value-added, durable and multifunctional protective textiles for health care and hygiene potential applications [1, 20-23].

Additionally, many attempts have been carried out recently to improve the mechanical and softness properties [24, 25], crinkle appearances and tensile

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Receive Date: 31 October 2021, Revise Date: 13 November 2021, Accept Date: 14 November 2021

DOI: 10.21608/ejchem.2021.103592.4792

properties [26], wettability and fastness properties using nanometal and metal oxides [27] as well as to enhance antibacterial efficacy using essential oils and nano-metal oxides [28], medicinal herbs [29],or by green surface modification followed by nano-multifunctionalization [30] of denim, the favourite fabric for young generation, to satisfy the customer needs for health, hygienic and fashionable textile products.

More R&D efforts are still needed to develop high value-added denim fabrics with multifunctional properties taking in consideration the product and environment quality as well as health and hygiene concerns. Therefore, the main task of the present work was to develop a new facile-green finishing application method for imparting durable multifunction properties namely anti-bacterial, anti-UV, anti-crease, and fragrance property to denim fabric using: an eco-friendly hosting agent, MCT-βCD, selected bioactive functional agents namely Clove oil, Lavender oil, Tulsi oil and Vanillin AR, as hydrophobic guest molecules, along with citric acid/Na-hypophosphite, as non-formaldehyde cross-linking/binding system. The imparted functional properties were evaluated. Mode of interactions among the used active materials and the denim substrate was also suggested.

2. Experimental

2.1. Materials

Mill-desized indigo dyed cotton denim fabric (240 g/m^2, twill weave, indigo-dyed warp and white weft yarns) was used in this research work.

Citric acid (CA, $C_6H_8O_7$), sodium hypophosphite monohydrate (SHP, $NaH_2PO_2.H_2O$), and ethanol were of laboratory reagent grade.

Clove oil, Lavender oil, and Tulsi oil, natural bio-active compounds were of commercial grade kindly supplied by Kalamina® Co. Egypt. Vanillin AR ($C_8H_8O_3$, molecular weight: 152.15) from SDFCL®-India, was used as a multifunctional agent. Monochlorotriazinyl β-cyclodextrin, (MCT-βCD), Cavasol® W7MCT, average molecular weight ~ 1560, degree of substitution (0.3-0.6 per anhydroglucose unit, Wacker, Germany), was used as a hosting agent for formation of inclusion complexes with the nominated bio-active substances. Leomin® W (a nonionic wetting/detergent agent, BASF, Germany) was used for after washing treatment.

2.2. Methods

2.2.1. βCD-grafted fabric samples

Pre-loading of βCD onto the cotton denim fabric samples was carried out by the pad-dry-cure method. The denim fabric samples were padded twice in a finishing bath containing CA (50 g/L), SHP (30 g/L), MCT-βCD (25 and 50 g/L) at a room temperature to wet pick-up of 85% followed by drying at 100℃ for 5 min and curing at 160℃ for 3 min. The treated denim samples were then thoroughly washed with hot water and nonionic wetting agent (2 g/L), rinsed with cold water and finally dried at 100℃ for 3 min.

2.2.2. Post-loading of the nominated active-substances

Portion of βCD-grafted denim fabric samples were kept immersed in the alcoholic solutions of the nominated essential oils (10 and 20 g/L), material to liquor (ML) ratio (1:20) for 45 min at 90℃ using IR dyeing machine cups. After loading the nominated essential oils, guests, into the host cavities of the grafted βCD, the fabric samples were removed, squeezed, to wet pick-up 80% and dried at 100℃ for 5 min.

Another portion of the grafted βCD-denim fabric samples were kept immersed in the aqueous solution of Vanillin (10 and 20 g/L), ML: (1/20) for 45 min at 90℃ using IR dyeing machine cups. After finishing, the treated fabric samples were removed, squeezed, to wet pick-up 80% and finally dried at 100℃ for 5 min.

2.3. Testing and Analysis

- Nitrogen content of the treated fabric samples were determined by Vogel-1975 [31].
- The color strength, expressed as (K/S) value, of both untreated and treated denim fabric samples were calculated according to the Kubelka–Munk equation: $K/S = (I - R)^2/2R$, where K/S is the ratio of absorption and scattering coefficient, and R is the reflectance measurement at the wavelength of maximum absorbance of the used indigo dye [32].

- Antibacterial efficacy of untreated and post-treated fabric samples against the Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) pathogenic bacteria was evaluated quantitatively according to the AATCC TM100-2019, expressed as bacterial reduction percent[33].
- UV-protection factor (UPF), of both untreated and treated denim fabric samples were evaluated according to the Australian/New Zealand Standard method AS/NZS 4399:1996, and classified as follows: good (UPF: 15–24), very good (UPF: 25–39) and excellent UV-protection (UPF > 40). The higher the UPF value, the better the UV-protecting ability [34].
- Dry wrinkle recovery angle (DWRA) of untreated and finished denim fabric samples was evaluated according to AATCC-TM66-2017e[35].
- The sensorial evaluation of scent intensity of the post-treated denim fabric samples was evaluated according to the method reported in the literature [14, 36] by a group of fine well-trained test-panel at different intervals.
- Wettability of untreated and treated denim swatches was assessed according to AATCC TM27-1952e8 (2018)e. The shorter the wetting time, the better the water absorbency is.
- Durability of some functionalized denim fabric samples was evaluated according to AATCC Test methodTM61-2013e2, using a nonionic detergent (2 g/L).
- The FTIR spectroscopic analysis was performed for both untreated and treated fabric samples using Nexus 670 FT-IR Spectrometer, Nicolet Co., USA.
- SEM images were observed using model Quanta SEM 250 FEG (Field Emission Gun) attached with an Energy Disperse X-ray spectroscopy (EDX) with accelerating voltage-30 kV FELKO Netherland, for determining both the surface morphology and the elemental composition of the selected fabrics surface respectively.
- All tests have been performed in triplicate and presented as mean values.

3. Results and discussion

The present study aimed at developing an eco-friendly multifunctional cotton denim fabrics by using a non-formaldehyde ester-cross linking and binding agent, CA, a biocompatible hosting agent, MCT-βCD, and selected functional agents namely Clove, Tulsi, and Lavender essential oils and Vanillin.

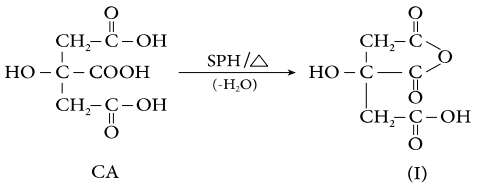
3.1. Tentative mechanism

Multifunctionalization of denim fabric swatches was carried out according to the following two steps:

i- Ester cross linking of cellulose structure as well as pre-loading of MCT-βCD molecules, with their hosting cavities, to facilitate formation of inclusion complexes with the nominated active agents in the next step as follow [30, 37-39].

- Ester-cross linking of cellulose structure

- Grafting of MCT-βCD [2, 40]



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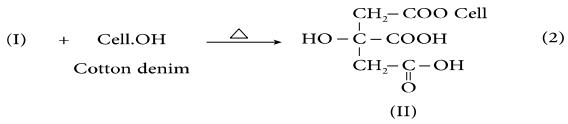

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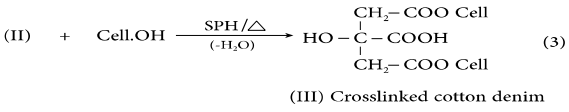

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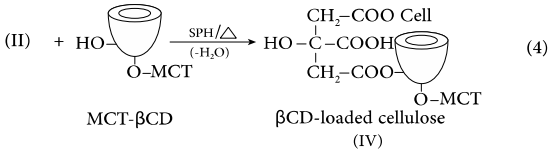
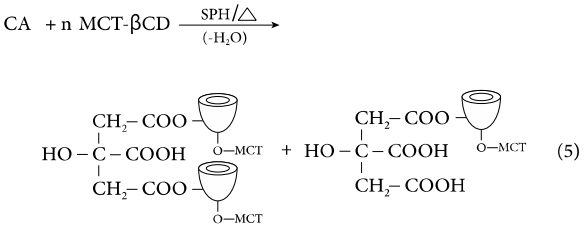


(4)

- Formation of MCT-βCD -CA adducts



, and

ii- Post-loading of the nominated guest substances individually via formation of inclusion complexes between the host-cavities of βCD-loaded substrate and the guest molecules to create and add new and innovative functional properties to the pre-modified denim swatches as follow [1, 3, 5, 36]**:**

βCD-loaded substrate host cavities
+
lipophilic constituents of guest active material
↓↑
Host-guest inclusion complex
(functionalized denim fabric)(6)

3.2. Loading of MCT-βCD onto denim fabric

As far as the change in some performance and functional properties of the treated cotton denim fabric samples as function of finishing formulation constituents, Fig 1(a) shows that inclusion of MCT-βCD, with its hydrophobic cavity and exterior hydroxyl groups, into the finishing formulation along with CA, as non-formaldehyde crosslinker, and SHP, as esterification catalyst, brings about a remarkable increase in the % nitrogen of the ester- crosslinked fabric samples. The extent of increase in the % N is governed by the presence of MCT- βCD, its concentration as well as its degree of fixation and immobilization onto and/or within the treated fabric samples under the given thermofixation conditions, and follows the decreasing order:

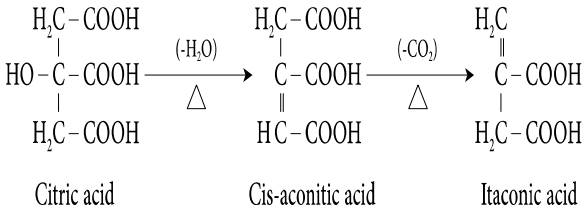
IV>III>II>I, keeping other parameters constant.

The increase in the %N reflects the positive role of eco-friendly ester-cross linking system, CA/SHP, in loading and grafting of MCT-βCD onto/within the cotton denim structure via formation ester-bonds among the hydroxyl groups of cellulose and the exterior hydroxyl groups of MCT-βCD [Eq's 1-4], as well as formation of βCD-CA adducts [Eq. 5], to create functionalized cotton denim fabrics having more hydrophobic host cavities for the anchorage of the functional guest molecules [38, 41].

Fig 1(b) illustrates that the imparted antibacterial efficacy of the treated cotton denim fabric samples is affected by type of finishing formulation and follows the decreasing order:

IV>III>II>I, as well as kind of the pathogenic bacteria, i.e. Gram-positive (*S. aureus*)> Gram negative (*E. coli*), keeping other parameters constant.

The reasonable improvement in the imparted antibacterial property, expressed as % bacteria reduction, could be discussed in terms of the positive impact of loaded CA [38, 42], the formed aconitic and itaconic acid at high thermofixation temperature [42, 43] as follows [Eq. 7]:



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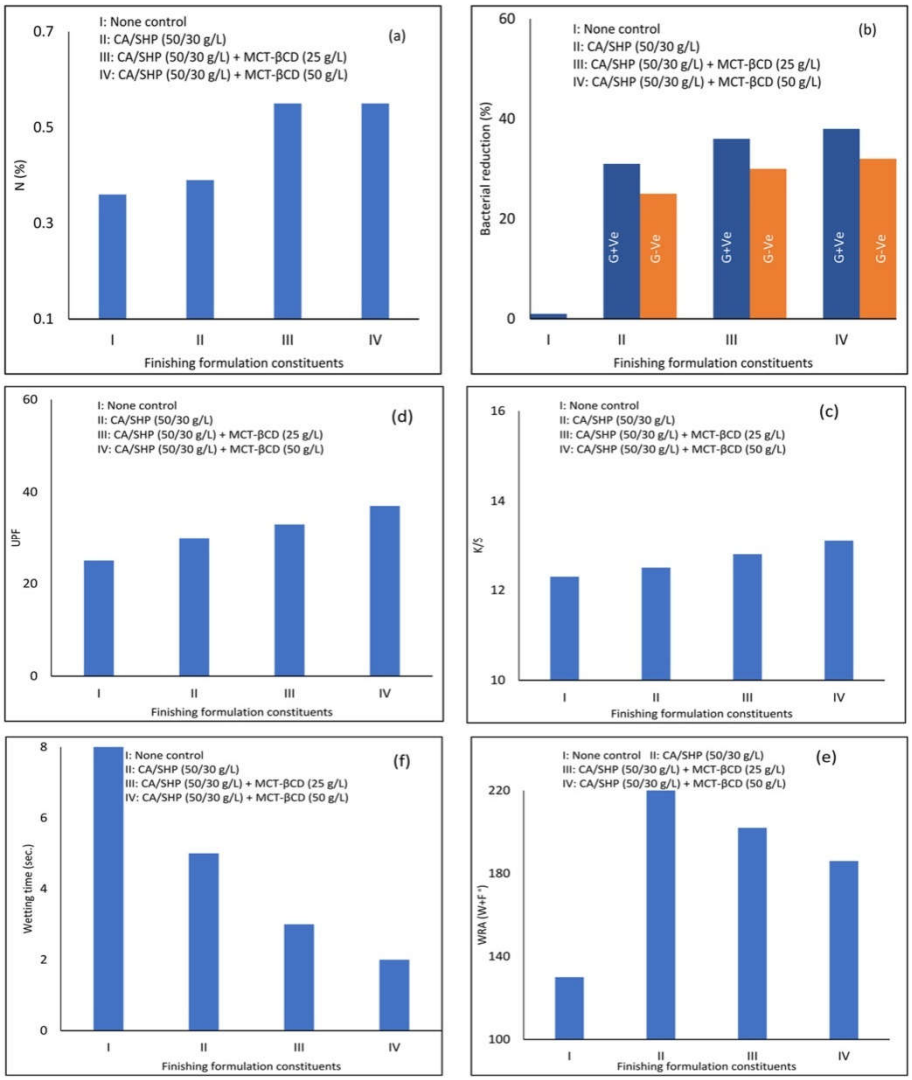

Figure 1 (a-f) Effect of finishing formulation constituents on N % (a), and bacterial reduction % of *S.aureus* (G+ve) and *E. coli* (G-ve) bacteria, K/S (c), UPF (d), WRA (e), and wetting time (f) Wet-pickup (85%), drying at 100℃ / 5 min, curing at 160℃ / 3 min

as well as the partial hydrolysis of MCT moiety and subsequent splitting of chlorine atom [44]on depressing the internal pH of the microbial cell, altering the cell membrane permeability damaging and disrupting the bacterial cell thereby inhibiting the growth of pathogenic bacteria or even killing the hazardous ones [38, 42, 43].

On the other hand, the variation in the % of bacteria reduction against the tested pathogenic bacteria is attributed to their differences in cell wall constituents, their arrangement as well as subsequent amenability to inhibition and/or killing [5].

As far as the change in the color strength, expressed as K/S value, of the untreated and treated fabric samples as a function of finishing bath constituents, Fig 1(c) shows that inclusion of MCT-βCD into the finishing bath along with other ingredients results in a slight increase in the K/S values which could be discussed in terms of better fixation of the indigo dye onto the denim fabric via its-NH group [30, 45], deposition of coating film and/or cross linked network onto the desized denim fabric thereby enhancing the extent of fixation and entrapping of the indigo dye molecules, decreasing the fabric lightness, increasing the fabric darkness and minimizing the effect of after washing step, i.e. high K/S values.

On the other hand, the variations in finishing bath constituent result in a slight improve in the extent of protection against the harmful UV-radiation (Fig. 1 (d)). It is clear that, incorporation of CA/SHP alone

and in combination with MCT-βCD results in an improvement in the imparted UV-protection property, expressed as UPF value, which follows the decreasing order: IV>III>II>I

The enhancement in UPF value reflects the positive role of the indigo dye in UV-absorption as well as the positive impact of surface modification and ester crosslinking on minimization of the free zones within the fabric structure thereby minimizing the transmission of harmful UV-radiation, i.e. better UV-protecting capacity [30, 41, 46].

Fig.1 (e) illustrates that the dry wrinkle recovery angle, WRA, of the treated fabric samples is determined by the finishing bath constituents and follows the decreasing order: II>III>IV>I.

The enhancement in WRA of treated samples is a direct consequence of ester-crosslinking of cellulose structure [Eq's 1-3]. On the other hand, the decrease in fabric resiliency by increasing MCT-βCD concentration most probably is attributed to the negative effect of MCT-βCD on hindering the accessibility of cellulose hydroxyl groups as well as the mobility of CA for ester-crosslinking along with its fixation onto the finish/fabric matrix via its exterior hydroxyl groups [Eq.s 4,5], i.e. lower fabric resiliency [30, 47].

Fig. 1(f) shows the effect of ester-crosslinking of cotton denim fabric samples in absence and presence of CA/SHP and MCT-βCD constituents on the hydrophilic property, expressed as wetting time. For a given set of treatment conditions, it is clear that ester-crosslinking of fabric samples in absence and presence of MCT-βCD results in decreasing the wetting time from 8 sec. (desized samples) down to 2 sec. for CA/SHP/MCT-βCD finished sample reflecting the positive impact of ester-crosslinking on creating more carboxyl groups at fabric surface as well as superficial deposition fixation of MCT-βCD moieties onto treated fabric samples thereby increasing the accessible hydrophilic hydroxyl groups at the loaded fabric surface, i.e. shorter wetting time.

In conclusion, our results, in Fig. 1, clearly demonstrate that the optimal finishing bath constituents for obtaining better performance and functional properties were CA/SHP (50/30 g/L) and MCT-βCD (50 g/L), as compared to other finishing formulations.

3.3. Multifunctional properties of denim fabrics

Table 1 demonstrates that post-treatment of the host hydrophobic cavities of MCT-βCD grafted indigo dyed denim swatches with the selected functional guests namely Lavender, Clove, Tulsi and Vanillin is accompanied by the formation of inclusion complexes, i.e. host-guest complexes, which in turn affect the variation in the imparted functional properties of finished denim fabrics [Eq. 6]. It is clear that inclusion of any of the nominated guest substance results in a reasonable increase in the %N as follows: Clove> Vanillin> Tulsi> Lavender> None. The higher the guest concentration, the higher is the %N. The variation in the increase in %N of treated samples is attributed to the differences in chemical constituents of the included guest as well as its positive role in enhancing the extent of indigo dye and MCT-βCD fixation, i.e. better durability to wash [36].

On the other hand, the change in in color strength, K/S, of the finished denim swatches follows the decreasing order: Tulsi> Lavender> Clove> None> Vanillin, keeping other parameters constant. This increase or decrease in K/S values is governed by the positive or negative role of the formed inclusion complex as well as the chemical constituents and film-forming properties of the post-loaded guest substance on increasing the finished fabric darkness or lightness as well as facilitating the indigo dye fixation or discoloration [30, 45].

As far as variation in the imparted antibacterial efficacy of the fabricated denim samples, the data in Table 1 signify that increasing the functional guest concentration up to 20 g/L brings about a significant increase in the % bacterial reduction, irrespective of the loaded functional guest. Antibacterial activity against the tested Gram positive and Gram-negative pathogenic bacteria follows the decreasing orders:

Tulsi≥ Clove> Vanillin> Lavender>>None, and

S. aureus (G+ve)>*E. coli* (G-ve), keeping other variables constant.

The variation in imparted antibacterial functionality by using the above nominated bio-active guests reflects their differences in i) chemical constituents, ii) bio-active ingredients such as caryophyllene, phytol and germacrene (in Tulsi oil) high content of eugenol constituent (in Clove oil), and linalool, linalyl acetate, 1,8-cinole, β-ocimene,

camphore and terpinen-4-01 (in Lavender oil), as well as phenolic aldehyde (Vanillin) [36, 46-49], iii) synergetic effect of their constituents iv) extent of inclusion and entrapment of guest constituent into the grafted hydrophobic host-cavities via forming host-guest inclusion complex, as well as v) in their extent of leaching out and controlled release [3, 5, 36, 50-52].

On the other hand, the data in Table 1 demonstrate an higher antibacterial activity against gram-positive than gram-negative bacterial pathogens, which reflects these differences in cell wall structure, outer membrane, extent of diffusion of bio-active constituents within their structure, antibacterial action, extent of damage and inhibition of enzymes function, inactivation of DNA replication, and hence subsequent disruption in cell metabolism and bacterial death [5].

Additionally, the results in Table 1 clearly signify that, increasing the guest substance concentration from zero up to 20 g/L results in a significant improvement in the imparted anti-UV capability of post-loaded denim swatches.

The remarkable improvement in the UV protective performance, UPF value> 50, of treated denim fabric swatches is governed by type of the loaded functional agent and its chemical constituents and follows the decreasing order:

Vanillin> Tulsi> Clove> Lavender>> None.

Table 1. Effect of post-loading of MCT-βCD grafted denim fabric samples with selected functional guests

Post-loaded functional agent	Conc. (g/L)	N (%)	K/S	Bacterial reduction (%)		UPF	WRA (w+f°)	W.T (sec.)
				S. aureus	*E. coli*			
Non	0	0.626	13.10	38	32	35	188	2
Lavender	10	0.650	14.77	87	84	53	182	>180
	20	0.688	15.65	92	88	66	180	>180
Clove	10	0.821	13.58	94	90	64	184	7
	20	1.037	14.90	98	95	77	180	12
Tulsi	10	0.712	15.41	96	90	72	185	50
	20	0.754	16.30	99	97	89	182	160
Vanillin	10	0.801	12.36	90	85	82	190	<1
	20	0.837	11.43	95	91	98	187	<1

Pre-modification conditions: CA/SHP (50/30 g/L), MCT-βCD (50 g/L), wet pick-up 85% drying at 100℃ for 5 min, curing at 160℃ for 3 min. Post-loading of functional agents: alcoholic solution of essential oil (10, 20 g/L), aqueous solution of Vanillin (10, 20 g/L) ML (1/20), treatment at 90°C for 45 min, then squeezed and dried. %N: nitrogen content; K/S: color strength; UPF: UV-protection factor; WRA: dry wrinkle recovery angle; WT: wetting time.

The positive role of ester-cross linking in the presence of MCT-βCD along with host-guest complex formation onto the treated denim surface on reducing the treated fabrics porosity as well as deposition of phytochemical constituents of the nominated functional guests results in better UV-absorbing, shielding and blocking its transmission and passage of the harmful UV-radiation through the modified fabric structure, i.e.-excellent UV-protective denim fabrics, compared with the non-modified counterpart [39, 47, 53].

Table 1 also reveals that inclusion of the aforementioned functional agents into MCT-βCD-grafted denim cavities has practically a marginal or no effect on the fabric resiliency, expressed as WRA, irrespective of type and concentration of guest substance.

The effect of type of loaded-guest substance on water absorbency of treated denim fabrics is shown in Table 1. For a given set of treatment conditions, it is clear that i) inclusion of Vanillin into the hydrophobic cavity of grafted fabric samples

enhances the wetting performance, ii) post-treatment with Clove results in an increase in wetting time, iii) incorporation of Lavender or Tulsi oil into the loaded hydrophobic cavities brings about a remarkable increase in wetting time, regardless of the used concentration and follows the decreasing order Lavender>Tulsi>>None.

This remarkable increase in wetting time reflects the hydrophobic nature of Lavender and Tulsi oils which in turn creates a hydrophobic-thin cavity film onto the fabric surface and lowers the surface energy thereby prolonging the wetting time [49, 54].

3.4. Durability to wash

The results of durability of the imparted functional properties as well as the color strength values of the finished denim fabric samples in Table 2 revealed that i) increasing the number of washing cycles up to 15 results in a marginal or slight decrease in the imparted antibacterial, UV-protection properties, a reasonable decrease in the K/S values along with an improvement in wetting time, regardless of the used functional agent, ii) the extent of variation of the aforementioned properties is governed by kind of functional agent, its chemical constituents, extent of interaction among other ingredients as well as the denim fabrics during the thermofixation step, along with the subsequent fixation of active ingredients, iii) both the retained functional properties as well as the K/S values of post-treated indigo-dyed denim fabric samples were still very promising even after 15 washings which confirms the durability of functional finishes, and iv) the slight decrease in antibacterial activity, UV-protection ability, as well as in depth of denim fabrics along with an improvement in fabrics wettability are ascribed to the removal of surface deposits, unfixed functional agents as well as physically entrapped or attached bi-products onto/within the finish/ fabric matrix [5, 30, 55].

Table 2. Durability of the imparted functional properties to wash

Functional agent (20 g/L)	Wash-cycle	Bacterial reduction (%)		UPF	WT (sec.)	K/S	SI
		S. aureus	*E. coli*				
None	1	38	32	35	2	13.10	0
	15	31	26	29	1	11.65	0
Lavender	1	92	88	66	>180	15.65	5
	15	85	80	60	160	14.15	4
Clove	1	98	95	77	12	14.90	5
	15	93	89	70	8	13.52	3
Tulsi	1	99	97	89	160	16.30	5
	15	95	91	81	130	14.87	3
Vanillin	1	95	91	98	<1	11.43	5
	15	90	85	91	<1	10.15	5

Pre – modification conditions: CA/SHP (50/30/ g/L), MCT-βCD (50 g/L), wet pick-up (85%) drying at 100℃ / 5 min, curing at 160℃ / 3 min
Post – loading of functional agents: functional agent (20 g/L), ML ratio (1/20) at 90℃ for 45 min, then squeezed and dried
SI: scent intensity, 5: most intense fragrance, 3: common, 0: no fragrance

On the other hand, the functionalized denim fabric samples were scented even after 15 washings. The extent of fragrance retention, expressed as scent intensity, follows the decreasing order:

Vanillin> Lavender> Tulsi= Clove,

Keeping other parameters constant, which could be discussed in the differences among the hosted fragrant in: extent of retention and fixation, complex formation between host cavity of grafted β-CD andthe guest molecule, and the % release of active ingredients from the anchored cavities during the washing process [36, 49, 56]. The washed fabric

samples can be recharged after certain washing cycles.

3.5. FTIR analysis

The FITR spectra of untreated, βCD-loaded and post treated denim fabrics with Lavender, Clove, Tulsi, or Vanillin are shown in Fig. 2.

• In the spectrum of untreated denim, the bands record at 3277 cm^{-1}, 2900 cm^{-1}, 1625 cm^{-1}, 1315 cm^{-1} and 1024cm^{-1} were related to (OH and N–H),(C–H aromatics), (N–H), (C–N), (C–O) respectively [57].

• The spectrum of MCT-βCD grafted denim fabric with using CA/SHP as ester- crosslinking system showed an additional peak at 1718 cm^{-1} which attributed to the (C=O) stretching and confirmed ester-crosslinking of cotton cellulose and fixation of modified βCD onto denim fabric. Other characteristic peaks related to βCD were overlapped by the peak of denim cellulose [58].

On the other hand, FTIR spectra for post-treated βCD grafted denim fabric with the nominated active agents demonstrate that:

- Post-treatment with Lavender and Clove oil is accompanied by a remarkable increase in the intensity of the peak at 1720 cm^{-1} related to C=O stretching. the peak at 2850 cm^{-1} related to C-H stretch and corresponds to methylene group in case of using Clove oil as bio-active agent for post-treatment of βCD-grafted samples [59].
- The Tulsi loaded denim fabric showed a band at 3000 cm^{-1} representing asymmetric C-H stretching of CH_3 alkane group and band at around 2920 cm^{-1} which was ascribed to asymmetric C-H stretching of CH_2 of alkane group. The strong recorded band at 2860 cm^{-1} representing the symmetric C-H stretching of CH_2 of alkane group. The peak of C=O stretching of aromatic ester was shifted to 1739 cm^{-1}. Another band recorded at 1620 cm^{-1} assigned to C=O stretching vibration of amide overlapped with the exited peak in untreated denim fabric. The band located at 1315 cm^{-1} represented the stretching vibration of C=N [60].
- Additionally, the IR spectrum of Vanillin loaded substrate showed a characteristic peaks at 1520 cm^{-1}, 1590 cm^{-1} and 1665 cm^{-1}, with small intensity, are attributed to stretching absorption of benzene ring and C=O of the aldehyde group. After loading of Vanillin into the hydrophobic surface cavities, the peak around 1720 cm^{-1} disappeared from IR pattern [61].

The aforementioned evidences confirmed the pre-modification of cotton denim cellulose with MCT- βCD along with subsequent functionalization by loading the nominated active agents into the introduced hydrophobic cavities of grafted βCD.

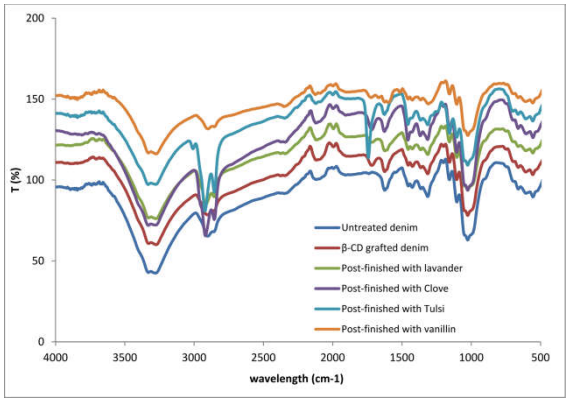

Figure 2. FTIR Spectra of untreated denim, βCD grafted denim, and post-treated denim with bioactive ingredients

3.6. SEM & EDX analysis

The changes in surface morphology and elemental composition before and after loading of Lavender or Tulsi oil onto the βCD-grafted denim fabric samples are shown in Fig. 3.

The SEM images demonstrate:

i. a ribbon shaped of cotton fibers in denim fabric along with some surface deposits due to grafted βCD onto denim (Fig. 3a)

ii. a change in surface morphology with more surface deposits as a direct consequence of loading Lavender oil into the hydrophobic cavity of preloaded βCD (Fig.3c), and

iii. a homogenous, uniform and smooth surface coat reflecting the positive coating ability of the post-loaded Tulsi oil (Fig.3e).

Additionally, EDX spectra (Fig. 3b,d and f) confirm i) grafting of MCT- βCD onto cotton denim during pre-modification step, expressed as N-element. Fig. 3b, ii) the existence of Ni- element a direct consequence of encapsulation of Lavender oil into the hydrophobic cavity of grafted MCT- βCD

(Fig. 3d), as well as the presence of Zn-, Cu-, Mn-, and S- elements which again confirm the successful loading of Tulsi oil into the hydrophobic host cavities of preloaded MCT- βCD onto denim fabric surface (Fig. 3f).

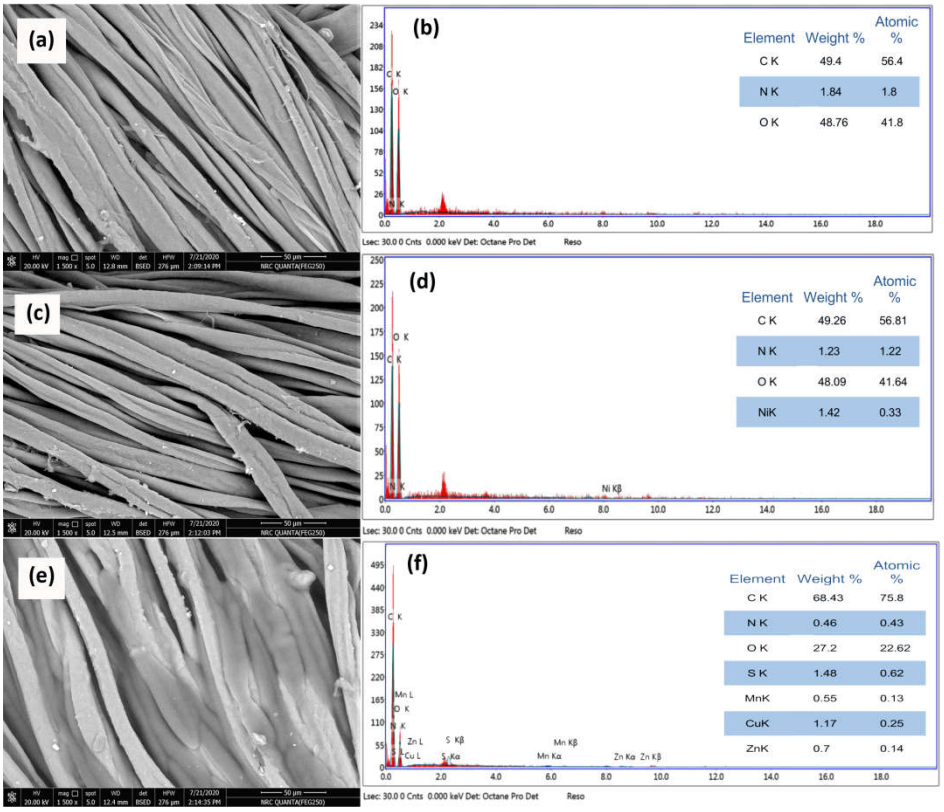

Fig. 3 SEM images & EDX spectra of grafted denim fabric with β-CD alone (a & b), and post-treated Lavender oil (c & d), and post-treated Tulsi oil (e & f)

4. Conclusion

An eco-friendly approach for upgrading the functional properties of denim fabrics was carried out using MCT-βCD, as a green hosting agent, along with CA/SHP, as an environmentally-sound formaldehyde-free cross linking system to create hydrophobic hosting cavities onto/within the cross linked denim fabric structure, followed by post-loading of the selected bio-active agents namely Clove oil, Lavender oil, Tulsi oil, and Vanillin AR to impart durable and multifunctional properties via forming host-guest inclusion complexes with the hosting cavities. The obtained experimental results demonstrated that:

- Inclusion of MCT-βCD (25 g/L) into the ester cross linking formulations brings about a remarkable modification of the denim cotton structure via creation of new hydrophobic hosting sites, i.e. cavities, an improvement in wettability along with a reasonable increase in UPF, antibacterial efficacy, WRA as well as in K/S values of the finished substrates compared with the untreated one.
- Post-treatment of βCD-loaded fabric samples with the nominated functional agents (up to 20 g/L) results in a slight increase in the %N and K/S value (except Vanillin), a remarkable improvement in antibacterial activity agent the tested G+ve (*S. aureus*) and G-ve (*E. coli*) bacteria, a significant enhancement in UV-protection functionality without adversely affecting the WRA values.

- The variation in the imparted functional properties as well as in wetting time of the functionalized denim fabric samples is governed by type and chemical constituents of the used active agent as well as the number of washes.
- The imparted functional properties, i.e. antibacterial, anti-UV as well as fragrance retention are noticeably maintained even after 15 washes.
- Increasing washing cycles up to 15 resulted in an improvement in wettability of the treated fabric samples along with a reasonable decrease in their K/S values.
- FTIR, SEM and EDX analysis of selected samples confirmed surface modification and deposition of some constituents of the used guest molecules onto the fabricated denim samples.

5. Conflict of interest

All authors have no Conflict of interest

6. Formatting of funding sources

There is no significant financial support for this work.

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