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Optimization of monochlorotriazine β -cyclodextrin grafting on cotton and assessment of release behavior of essential oils from functionalized fabric

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Abstract

Monochlorotriazinyl β -cyclodextrin (MCT β -CD) was employed for the inclusion complexation with oils of cedarwood, clove, eucalyptus and peppermint to assess their release behavior from functionalized cotton. The process of MCT β -CD grafting was optimized using response surface methodology with three independent factors including MCT β -CD concentration, pH and curing temperature and effect of their second order interactions on dependent variables as % nitrogen content, % graft yield, tensile strength and wash durability was examined. The interaction of MCT β -CD concentration and pH had the decisive effect on the investigated dependent variables. FTIR and % retained nitrogen confirmed the substantial retention of modified host on functionalized cotton after five vigorous wash cycles. ^1H NMR characterized the full entrapment of oils within MCT β -CD cavity on cotton. All the oils were substantially retained in the inclusion complexes with the MCT β -CD before and after wash than when present uncomplexed on the treated cotton. Peppermint was the slowest to fade off and cedarwood was rapid in sublimation from the cyclodextrin moieties.

Keywords: Monochlorotriazine, Grafting, % nitrogen content, % retained nitrogen, Cyclodextrin moieties

Introduction

The presence of chemical hosts in the form of native β -cyclodextrin on cotton facilitates the suppression of essential oil's release from the finished surfaces to a greater extent but their adherence to any of the treated substrates is not long lasting as only weak Vanderwaal and Hydrogen interactions prevail between cotton and β -cyclodextrin. This is due to the non existence of permanent interactions between the substrate and the anchoring host.

A temporary textile finishing of textiles is easily achieved, but is easy to wash off (Nelson 2002). It is evident that β -CD cannot form direct covalent bonds with any textile fiber but it is capable of forming only hydrogen bonds with the cellulose based materials. Their lack of durability on textile substrates severely limits their effective use as fabric finishing agents. Instead, the modified monomolecular containers are postulated

to form van der Waal bonds, ionic bonds or even covalent bonds with suitable textile surfaces such as cotton. There is currently an increasing demand for improved reactive β -CD derivatives with better stability after storage under different conditions and processes without cleavage or the production of toxic or harmful subsidiary products (Wen et al. 2010). Durable finishing is generally achieved by the slow-release method, in which the treated fabrics slowly release the oil molecules for a long duration of time (Halim et al. 2011). Monochlorotriazinyl- β -cyclodextrin (MCT- β -CD) is the first reactive cyclodextrin derivative and can be used to permanently bind β -CD to cotton with the conventional reactive dyeing method (Bhaskara-Amrit et al. 2011; Bereck 2010). The reactive chlorine atom of triazinyl group of MCT- β -CD can react with nucleophilic residues such as ^-OH to form covalent bonds (Halim et al. 2010; Sricharussin et al. 2009). It can work as a universal anchor for a wide horizon of textile materials as cotton; fabric or yarns (Halim et al. 2011; Boonsod 2007; Cabrales et al. 2012; Hauser and Jianshuo 2000; Peila et al. 2012; Shown and Murthy 2008; Marwa et al. 2013; Sricharussin et al. 2009). Mixed fiber materials like cotton/polyurethane, cotton/polyamide or even silk can be finished with MCT β -CD in good yields (Bendak et al. 2010; Ibrahim et al. 2007; Bergamasco et al. 2007; Boonsod 2007), cotton/wool, viscose/wool blends, filter papers & polyester along with its blends (Anitha et al. 2011; Shahba 2008; Popescu et al. 2011). The application of MCT- β -CD on textiles is influenced by a number of process parameters viz concentration of MCT β -CD, time of reaction of MCT β -CD with the textile substrate, temperature of curing of MCT β -CD, pH of reaction and presence of moisture in substrate (Moldenhauer and Reuscher 1999; Rehmann et al. 2003). Some studies have been carried out to assess the impact of independent process variables for the fixation of MCT β -CD on cotton to assess its antimicrobial activity (Halim et al. 2011), polyester and cotton/polyester blends for imparting antistatic property (Halim et al. 2010) and on thin polyester films after their saponification for the activation of the surface (Popescu et al. 2011). But the interactions of the process variables of MCT β -CD grafting on textile substrate holds incredible importance as physical properties of the treated substrates are immensely affected. Also, the durability of the reactive host is adjudged based upon its adherence on to the textile surfaces for the anchorage of guests as essential oils. But due to lack of scientific and systematic approach for the elucidation of impact of interactive process variables in any of the previous works, present work was carried out for the process optimization of MCT β -CD grafting on cotton with the exploitation of the key variables. The stability analysis of essential oils for aroma sustained textiles in presence of the reactive host was investigated for characterized inclusion complexes.

Methods

Materials

Thoroughly pre-treated plain woven cotton fabric possessing epi (76), ppi (70), warp (42.8 Ne^s), weft (38 Ne^s) and GSM (136) was used for finishing with four categories of essential oils, viz. clove (CO; Assay-eugenol ~85%), cedarwood (CdO; Assay-cedrol ~70%), eucalyptus (EO; Assay-cineole ~60%) and peppermint (PO; Assay-menthol ~44%). All the analytical grade chemicals, viz. β -cyclodextrin (β -CD-M.W.1134.98 and minimum assay ~98%), cyanuric chloride (M.W. 184), sodium carbonate, sodium hydroxide, ethanol, oils and phenolphthalein were supplied by SDFL (*Mumbai, India*). UV-Vis-210

spectrophotometer (*Lab India analytical UV 3000+*), FTIR-spectroscope (*Perkin Elmer, US*), Elemental Analyzer (*EuroVector EA 3000; CSIR-Central Drug Research Institute: Saif, Lucknow, India*), Bruker Avance II NMR Spectrometer (*Saif, PU, Chandigarh, India*), Thermogravimetric analyzer (*SDT Q600 V20.9 Build 20; NITRA, Gaziabad, India*), Water bath (*Laboratory glassware co., Ambala*), Electronic pH meter PH-009 (I), Electronic weighing balance (*CAS Model MW -11 series*), Drying oven (*Kaypee Udyog, Ambala, India*), Orbital shaker (*Bio-Technology Lab, M.D.U Rohtak, India*), Padding Mangle (*Electronic and Engg. Company*), Laundrometer (*RBE, Mumbai*) and Tensile tester (*Globe Tex Industries*) were the equipment used to evaluate the physical properties of the functionalized cotton and stability of the inclusion complex on cotton.

Synthesis and characterization of MCT β -CD

The synthesis of MCT β -CD was carried out according to the procedure described previously without any major process modifications with the use of reactants viz. β -cyclodextrin and cyanuric chloride in presence of alkaline medium (Khanna et al. 2015). *FTIR spectroscopy* (for micro structural analysis with FTIR-spectroscope), *elemental analysis* (for compositional analysis with elemental analyser), *Thermogravimetric Analysis* (TGA with Thermogravimetric Analyzer) and *$^1\text{H-NMR spectra}$* (for host-guest investigation with NMR spectrometer) were used for the characterization of MCT β -CD powder.

Solubility analysis of MCT β -CD in water

The solubility of MCT β -CD was analyzed in water to assess the modification in native β -CD in terms of its improvement in aqueous solubility.

Optimization of process parameters of MCT β -CD application on cotton

The process optimization of MCT β -CD grafting on cotton was carried out by the response surface methodology using 3^3 Box and Behnken factorial design i.e. MCT β -CD concentration (60, 70, 80 gpl), Temperature of curing (100, 125, 150 °C) and pH (6, 8, 10) as independent variables. Treated cotton was assessed for Graft yield%, Nitrogen content% and change in physical properties of treated cotton explicitly tensile strength and wash durability (up to five washes). Statistical analysis was done using Design Expert software version 7.1.2 (State-ease Inc., Minneapolis, USA). The statistical significance of regression co-efficient and model-fit was checked. Model equations for all responses were also determined (Fischer's test).

Graft yield% (GY) was measured by the analysis of the weight difference of the treated cotton with MCT β -CD from the untreated one according to Eq. 1. *Nitrogen content%* (N_2) was assessed for the determination of the amount of MCT β -CD fixed on cotton according to standard Kjeldahl method. *Tensile strength* was measured according to the ASTM D5034-1995 (strip method) by using digital tensile strength tester. *Wash durability* was evaluated as follows—4 cm \times 10 cm strips of MCT β -CD treated cotton and further, oil treated cotton samples were washed according to ISO 105-C03:1989 with 5 gpl of soap and 3 gpl of Na_2CO_3 with a material to liquor ratio of 50:1. The treated samples were then laundered at 60 ± 2 °C for 30 min. The washed samples were rinsed with tap water for 10 min and dried at room temperature after each wash cycle. The durability to

wash was determined with FTIR and % retained nitrogen for 5 subsequent washes. Also, the effect of wash treatments on the % retention of oils on treated fabrics was investigated for 30 vigorous washes.

$$\text{Graft yield \%} = \frac{\text{Final weight of treated cotton} - \text{Weight of untreated cotton}}{\text{Weight of untreated cotton}} \times 100 \quad (1)$$

Characterization, application and stability analysis of inclusion complexes of MCT β -CD-oils on functionalized cotton

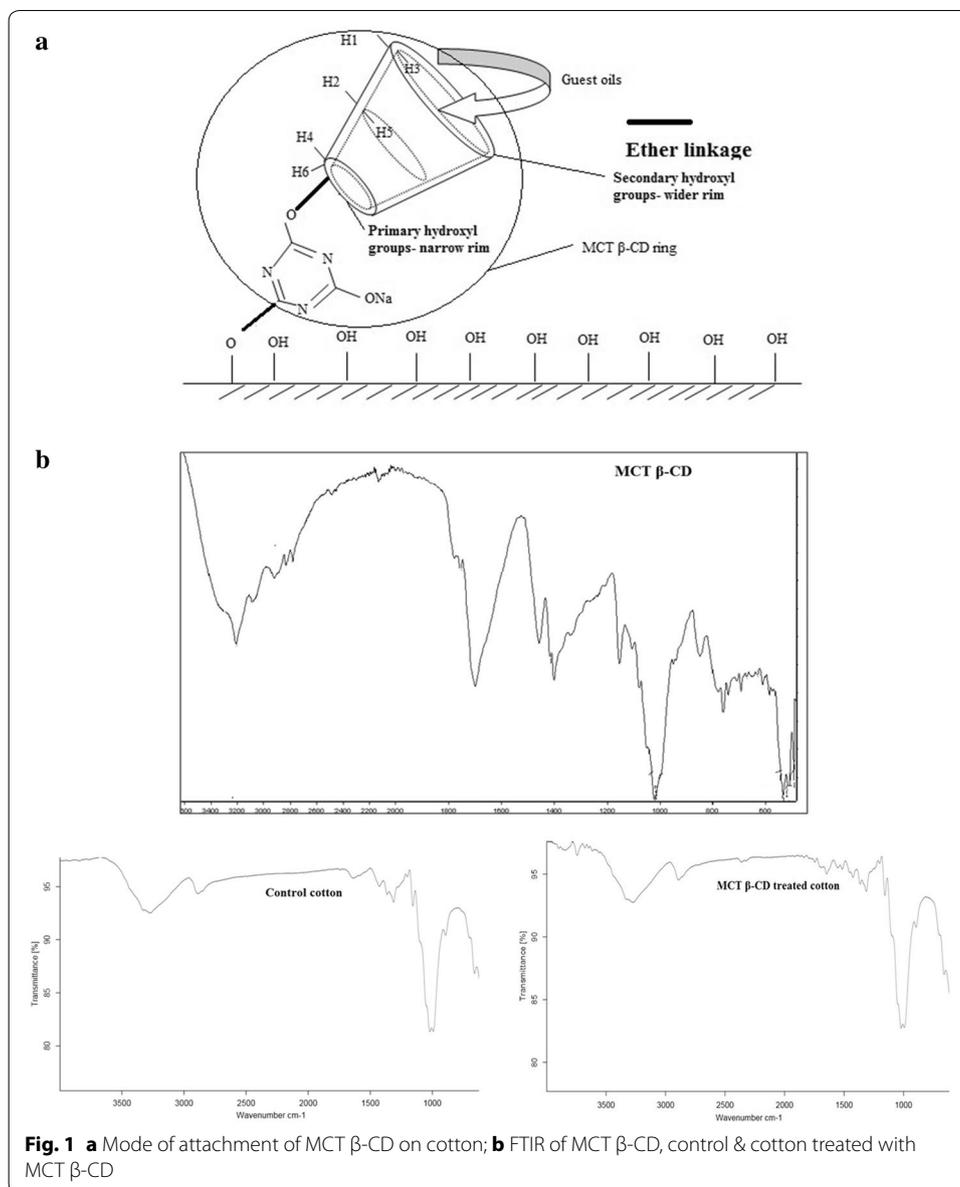
$^1\text{H-NMR}$ was used to characterize the inclusion complexes of MCT β -CD and essential oils in D_2O (solvent) at room temperature and all chemical shifts were measured relative to Trimethylsilane (TMS) as reference. The stoichiometry of MCT β -CD: oils were assumed to be 1:1. The solutions of MCT β -CD-oils were prepared at 10 mM in free state (without complex) and at 5 mM:5 mM (host: guests) for the complex. The precalculated amount of host and guest oils in uncomplexed and complexed states as 1.6 ml oil (free state), 14 g host (free state) and 0.8 ml oil and 7 g host (for inclusion complex). Dry mixing technique was used for complexation with magnetic stirring at 4000 rpm for 25 min to achieve a uniform and stable complex of MCT β -CD and oils. Further, MCT β -CD functionalized cotton was treated with essential oils at 10% concentration to achieve a dynamic yet a stable inclusion complex. Fragrance stability of oils on functionalized cotton was investigated by estimation of their release rate after extraction in ethanol solution from treated cotton at stipulated time intervals at respective λ_{max} CO (282 nm), CdO (306 nm), EO (270 nm) and PO (240 nm) according to Eq. 2. The impact of wash down treatments was analyzed by the estimation of % retained oils on cotton after 30 subsequent wash cycles as mentioned in "[Optimization of process parameters of MCT \$\beta\$ -CD application on cotton](#)" section.

$$\begin{aligned} &\text{Rate of release of oil at stipulated time gap (\%)} \\ &= \frac{\text{Conc. at 0 h} - \text{Conc. at stipulated time interval}}{\text{Conc. at 0 h}} \times 100 \end{aligned} \quad (2)$$

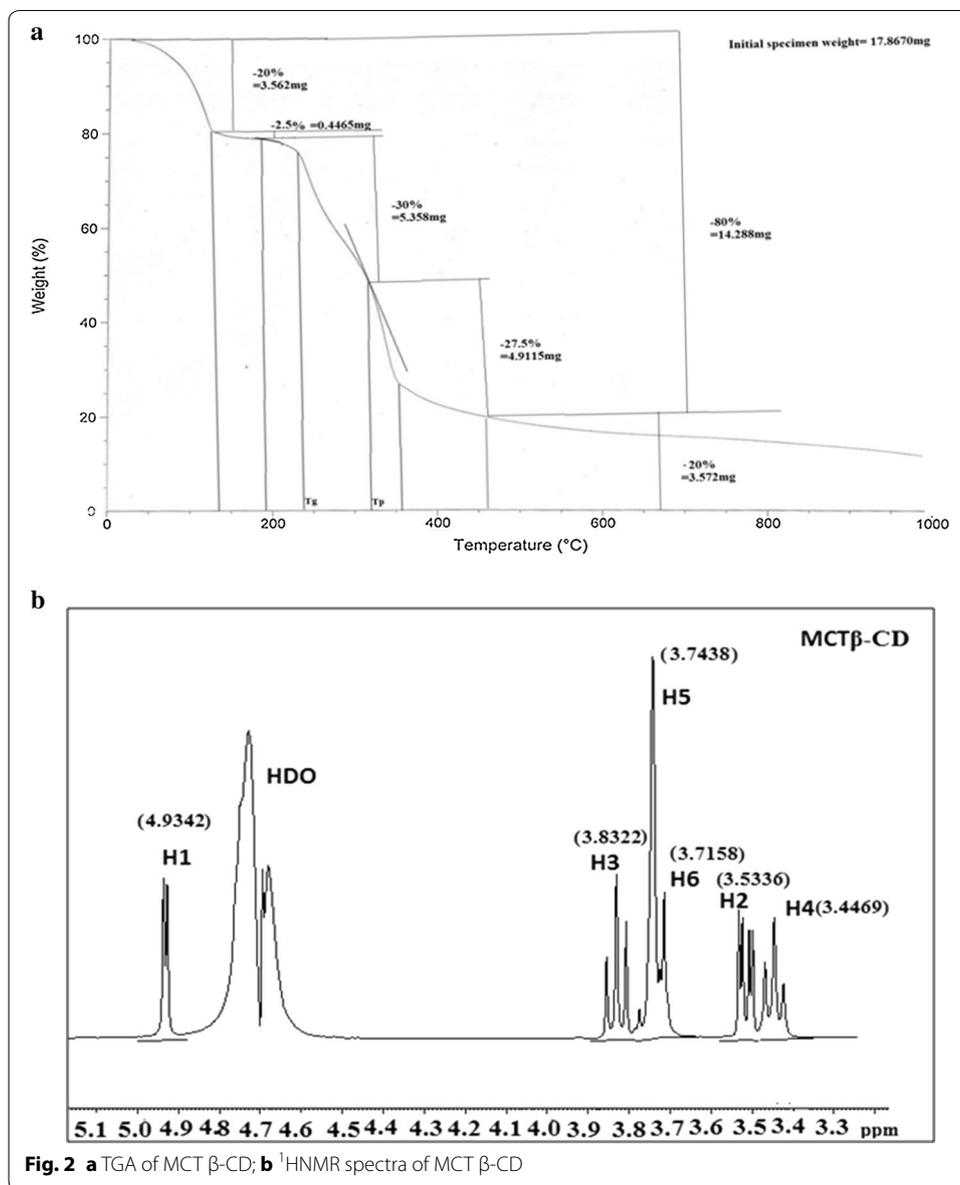
Results and discussion

Synthesis and characterization of MCT β -CD

The yield % of the reaction mechanism between β -CD and cyanuric chloride in alkaline medium was satisfactory enough at 63.34% with the peripheral structure of synthesized MCT β -CD as depicted in Fig. 1a. The degree of substitution was found to be 0.3 to 0.5 with molecular weight of 1560. *Elemental analysis* of MCT β -CD powder had shown about 3.7% N_2 present in MCT β -CD, whereas, 0% was available in native β -CD; that confirmed the modification of β -CD with monochlorotriazine group. *FTIR* revealed the appearance of bands at 2920, 2778 cm^{-1} for the presence of C-H bonds in the synthesized MCT- β -CD. The presence of strong bands at 1753, 759 and 1150 cm^{-1} characterized C=N, C-Cl and C-O groups. Further, the identification of a band at 1018 cm^{-1} accounted for carbon atoms in cyclic ring. The characteristic bands in the IR- spectra of the MCT- β -CD treated cotton were recorded at 2890 (C-H), 1745 (C=N stretching) and 1157 (C-O) in comparison to control. Also, a strong band at 759 cm^{-1} (C-Cl) was absent in the IR spectra of MCT- β -CD treated cotton that indicated the involvement



of chlorine atom in the grafting process of MCT- β -CD on cotton (Fig. 1b) as discussed in an elaborated manner in our previous publication (Khanna et al. 2015). MCT β -CD had shown thermal decomposition as a measure of % weight reduction in TGA results (Fig. 2a). At the initial stage, 20% (~3.52 mg) weight loss occurred in MCT β -CD powder as H₂O molecules are lost at 128 °C, remnant traces of moisture were lost at 195 °C resulting in about 2.5% (~0.447 mg) weight loss. The transition from solid to liquid phase took place at 310 °C resulting in about 30% fall in weight and finally, second stage thermal degradation of char resulted in about 27.5% weight loss at higher temperature of 460 °C. Figure 2b depicted ¹H-NMR spectra that characterized MCT β -CD in terms of respective chemical shifts relative to Trimethylsilane (TMS) as reference in D₂O as solvent at room temperature. The spectra had revealed that the nucleophilic substitution of β -CD takes place at the primary hydroxyl groups present at the narrower rim by the



chlorotriazine moiety (Pessine et al. 2012; Levy et al. 2001; Medronho et al. 2012). The ¹H-NMR spectra of MCT β-CD is used as a reference to adjudge the extent of chemical shifts of free and complexed states of the modified host and guests.

Solubility of MCT β-CD

MCT β-CD had shown improved solubility in water as compared to native β-CD due to the reduced ring strain of β-CD frame. The % solubility was estimated in the range of 95% (for 10 gpl) up to 65% (for 100 gpl). The scarce solubility of β-CD is due the formation of intramolecular hydrogen bonds between the hydroxyl group at carbon atom 2 (C2) and the hydroxyl group at carbon atom 3 (C3) of the adjacent glucose unit on

the cyclodextrin periphery, that prevents the β -CD from being soluble in most of the media, whereas, MCT β -CD is produced by the substitution of primary C6 -OH groups from the smaller rim of β -CD (which are the most susceptible to substitution). Thus, the substitution had helped in the relaxation of the boat-skew structure of unmodified β -cyclodextrin, and also, the intramolecular H-bond belt is prevented to form, thereby increasing its solubility in water.

Optimization of process parameters for MCT β -CD application on cotton

The desirability function (DF) = $f\{N_2, GY, TS, \text{ and } WD\}$ was formulated as:

$N_2\%$ is % nitrogen targeted to 'maximum', GY% is % Graft yield targeted to 'maximum', TS is % change in Tensile strength targeted to '1.82' (maximum on the +ve scale, experimental data), WD is wash durability in terms of % retained weight gain after 5th wash is targeted to 'maximum'. The optimum DF was achieved at 0.912 at the optimized process variables. The overall DF analysis and formulated model equations are shown in Table 1.

Nitrogen content (N_2)%

The increase in MCT β -CD concentration had shown an increase in $N_2\%$ on cotton due to the availability of more MCT β -CD molecules from the solution for attachment on the substrate. On the other hand, the increase in pH of MCT β -CD solution had resulted in $N_2\%$ increase from 0.179 to 0.56% at pH 6-8 and then decreased up to 0.263% at pH 10. MCT β -CD was unstable in acidic pH of 6 and got stabilized at pH 8 (near to neutral), finally got hydrolyzed at pH 10; thereby reducing the extent of $N_2\%$ on cotton. The minimum of N_2 (0.169%) was found at 60 gpl, 8 pH and 100 °C and maximum of N_2 was observed at 70 gpl, 8 pH and 125 °C. The interaction of concentration and pH had resulted in the achievement of the highest $N_2\%$ at 70 gpl and pH ~8 as shown in Fig. 3a. With the increase in concentration and temperature, $N_2\%$ decreased substantially due to the hydrolysis of chlorotriazine moiety that prevented its fixation on cotton as shown in Fig. 3b, c.

Graft yield (GY)%

Graft yield% is dependent on the concentration of MCT β -CD and pH as in Fig. 4a. With the increase in concentration and pH from (60 gpl and 6 pH) to (80 gpl and 10 pH), GY% had increased from 9.5% up to 13.43% due to the favorable conditions for the MCT β -CD moiety adherence on cotton; higher MCT β -CD concentration and alkaline pH ~10 had facilitated add on % for cotton but temperature had little or no impact as the interaction of concentration and pH had the decisive affect on the fixation of MCT β -CD as shown in Fig. 4b, c. The difference in the trends of $N_2\%$ and GY% was observed, attributed to the reason that $N_2\%$ on substrate is the actual indicator of the MCT β -CD presence rather, GY% is an indirect mode. The hydrolysis of chlorotriazine moiety at high temperatures directly indicated lesser adherence of cyclodextrin cavities on cotton via monochlorotriazine bridge, while higher GY% at higher temperatures could be due to free and unmodified cyclodextrin cavities present in the synthesized MCT β -CD powder attached superficially on the cotton; mostly susceptible to removal during washing.

Table 1 Experimental responses of MCT β-CD treatment on cotton

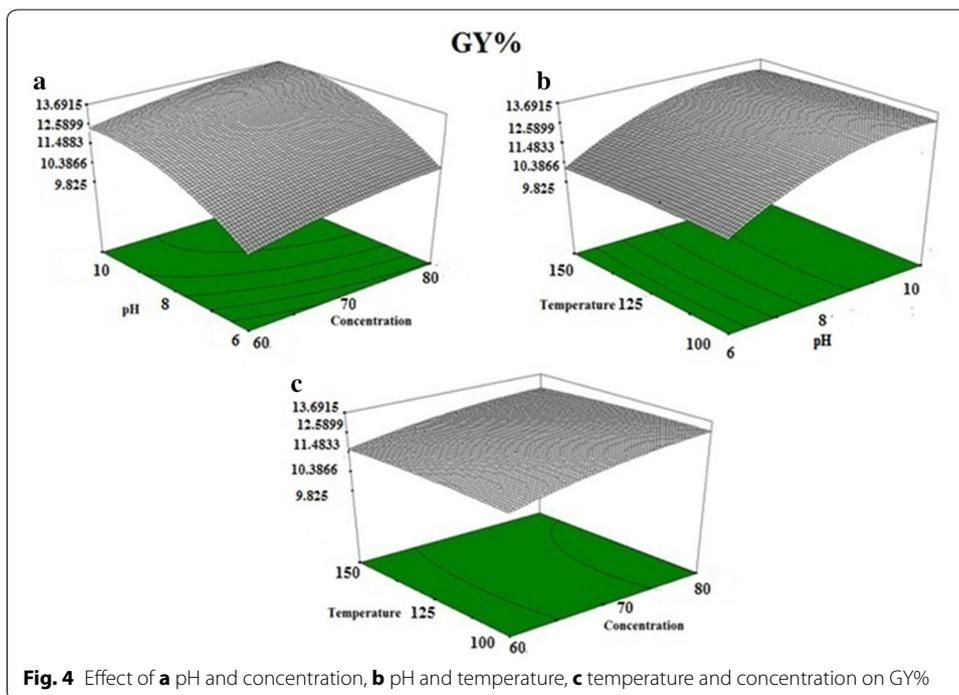
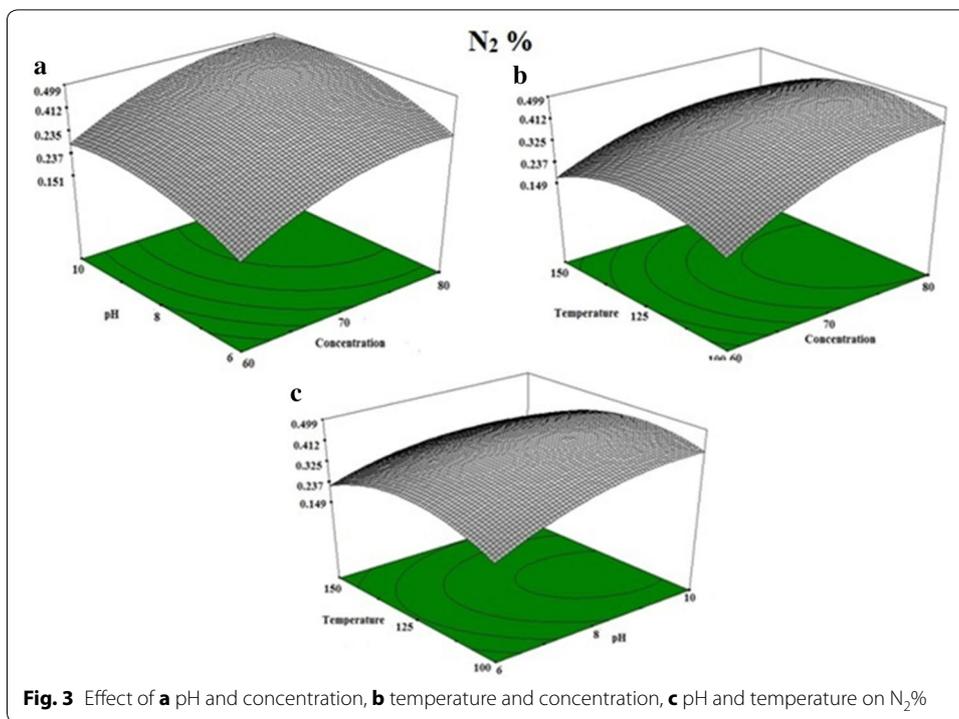
Run no.	Independent variables				Responses					Quantified MCT β-CD on cotton (g/100 g fabric)		
	Concentration (gpl)	pH	Temperature of curing (°C)	GY%	N ₂ %	TS%	WD					
								1st	2nd		3rd	4th
1	70	6	150	10.12	0.202	-3.56	10.1	10.05	10.01	9.95	9.96	2.89
2	70	8	125	12.90	0.46	-2.15	12.87	12.84	12.76	12.43	12.36	6.57
3	70	8	125	12.85	0.432	-2.19	12.81	12.78	12.67	12.56	12.34	6.17
4	60	10	125	12.56	0.263	-6.03	12.48	12.41	12.31	12.17	12.02	3.76
5	80	6	125	10.51	0.368	1.48	10.38	10.14	10.02	9.78	9.52	5.26
6	70	8	125	12.40	0.422	-2.21	12.36	12.31	12.22	12.19	12.15	6.03
7	80	8	100	13.41	0.448	1.82	13.28	13.14	13.02	12.87	12.78	6.4
8	70	10	100	13.20	0.432	-5.85	13.11	13.02	12.93	12.82	12.78	6.17
9	70	10	150	13.15	0.312	-6.45	13.07	13.01	12.97	12.89	12.82	4.46
10	70	8	125	12.81	0.441	-2.24	12.76	12.69	12.52	12.37	12.19	6.3
11	60	6	125	9.50	0.179	-2.34	9.41	9.22	9.02	8.91	8.86	2.55
12	60	8	100	11.53	0.169	-3.29	11.23	11.11	10.97	10.82	10.74	2.41
13	80	8	150	13.00	0.334	1.18	12.94	12.86	12.65	12.51	12.45	4.77
14	60	8	150	11.43	0.165	-3.11	11.25	11.08	10.78	10.65	10.44	2.36
15	70	8	125	12.54	0.422	-2.21	12.46	12.32	12.21	12.21	12.01	6.02
16	80	10	125	13.43	0.458	-0.32	13.12	13.02	12.92	12.83	12.77	6.54
17	70	6	100	10.10	0.198	-3.09	10.02	9.89	9.74	9.63	9.55	2.82

Table 1 Continued

Response	Statistical analysis of DF (model equations)	R ²	Adjusted R ²	Predicted R ²	Lack of fit (Prob > F)
Y1, GY%	Model equations				
Y2, N ₂ %	$-31.86 + 0.47X_1 + 4.72X_2 + 0.06X_3 - 0.237X_2^2$	0.980	0.954	0.786	0.210; not significant
Y3, T5%	$0.44 + 0.10 X_1 + 0.065X_2 - 0.03X_3 - 0.065X_1^2 - 0.0058 X_2^2$	0.9773	0.9481	0.690	0.0459; not significant
Y4, WD	$50.42 - 2.849X_1 + 4.71X_2 + 0.37X_3 + 0.02X_1^2 - 0.44X_2^2 + 0.024X_1 * X_2$	0.999	0.998	0.991	0.011; not significant
	$41.46 + 0.799X_1 + 4.4X_2 + 0.04X_3 - 0.53X_2^2$	0.962	0.914	0.441	0.012; not significant

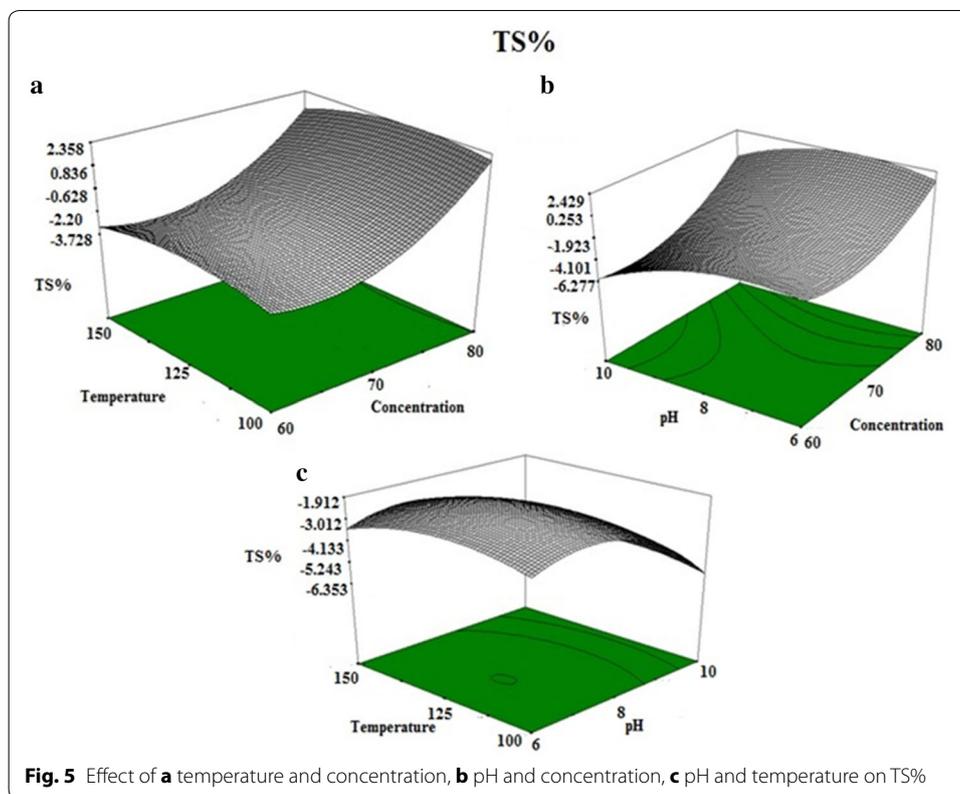
G% graft yield, N₂% nitrogen, T5% change in tensile strength, WD wash durability up to 1, 2, 3, 4, ** 5th washes (% retained weight gain), X₁ concentration of MCT β-CD solution, X₂ pH of MCT β-CD solution, X₃ temperature of curing (°C)

**WD after 5th wash considered for the analysis



Change in tensile strength (TS)%

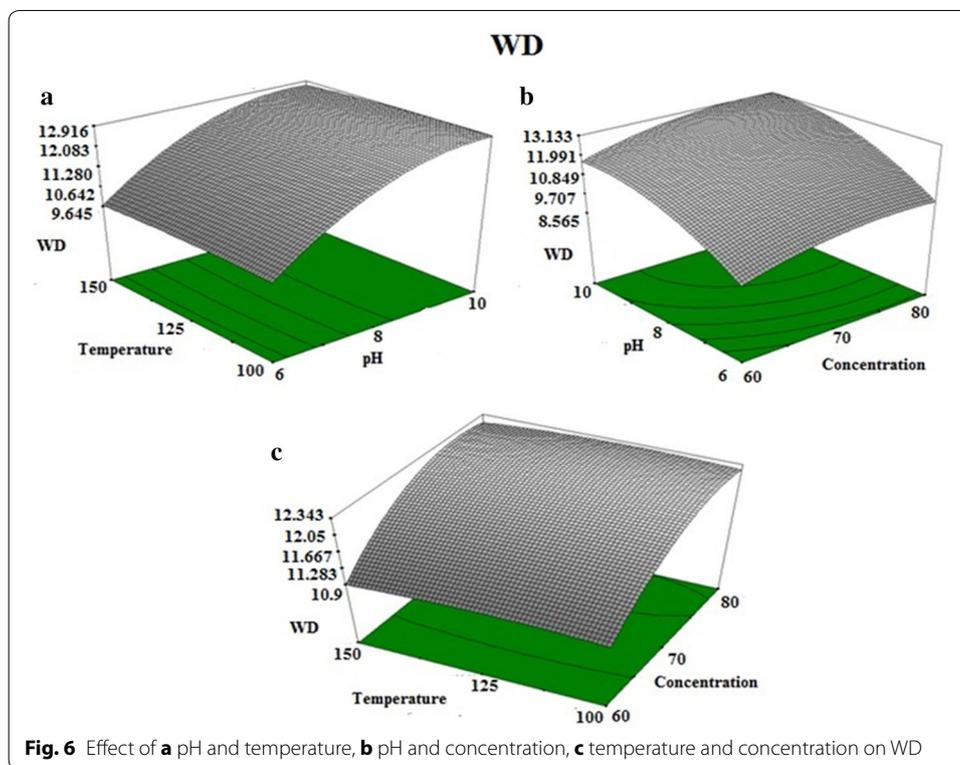
With the increase in MCT β -CD concentration from 60 to 80 gpl at pH 6 and 125 °C, the change was from -2.34 to -3.56% up to +1.48%. At pH ~10 and 125 °C, TS% was -6.03 to -5.85% up to -0.32%. This indicated that with the increase in the concentration of MCT β -CD, less loss is exhibited in TS%. But with the interaction of pH with



concentration, strength loss was encountered up to 70 gpl followed by an increase at 80 gpl; might be due to the plasticizing effect of MCT β -CD at higher concentrations that seemed to lessen the restriction of segmental movement of the cellulose chains in the cotton fibre. On the other hand, at pH 10, strength loss reduced from 60 to 80 gpl but the affect of high pH had overpowered the concentration increase to keep the variable on the negative side as shown in Fig. 5a. Thus, the interaction between pH and concentration was the main influence behind the strength loss. Degradation of cotton was observed at higher alkaline pH due to the formation of intermolecular and intramolecular crosslinks that reduces the possibility of equalizing the stress distribution, causing reduction in the capacity to withstand load. Increase in temperature from 100 to 150 °C at 70 gpl and increasing pH (6–10), –3.09 to –6.45% was the observed change (Fig. 5b). The major change was seen at pH 10 with increasing temperature from 100 to 150 °C (–5.85 to –6.85%), due to cotton tendering at higher temperatures in presence of alkaline pH (above 125 °C) (Fig. 5c).

Wash durability (WD) as % retained weight gain

The highest WD of 12.77% (with GY% of 13.43-without wash) at 80 gpl and pH ~10 with a minimum of 8.86% (with GY% of 9.5-without wash) was observed at 60 gpl and pH ~6. It followed the similar trend as GY% i.e. with the increase in the levels of both concentration and pH, WD was improved as MCT β -CD was affixed in a durable manner and thus, better retention of the host cavities on cotton (Fig. 6 b). Temperature had a little role to play as an independent factor but its interaction with either pH or concentration,



especially at their higher levels of (pH 10 and 150 °C) or (80 gpl and 150 °C) had shown a fall in WD due to the intervention of high temperature despite high initial GY% and superficial deposition of cyclodextrin cavities on cotton; which is further supported by N₂%. Thus, subsequent washing had resulted in the removal of the apparent MCT moieties from the cotton surface at higher temperature (Fig. 6a, c).

The cotton was treated at optimized process variables viz. MCT β-CD concentration (79.01 gpl), pH (7.57) and curing temperature (112.37 °C). Then, this functionalized cotton was given 5 subsequent wash down treatments and comparative FTIR was recorded that assured the presence of MCT β-CD-cellulose grafting intact even after wash treatments as apparent in the unwashed treated cotton at 1157 cm⁻¹ (ether group) as seen in Fig. 7. Residual % N₂ was analyzed for functionalized cotton (with and without wash) as -0.489 (Without wash), 0.252 (1st wash), 0.235 (2nd wash), 0.205 (3rd wash), 0.201 (4th wash) and 0.2 (5th wash) that evinced the presence of the reactive host even after washing of cotton. This also ascribed the initial % N₂ loss during first two washes was due to the inadequate cross linking of MCT β-CD with cotton resulting in washing off MCT β-CD but with further washes, the % retained N₂ content had stabilized.

Inclusion complexation of MCT β-CD and oils on cotton

¹H-NMR was consummated for inclusion complexation analysis of MCT β-CD-oils on cotton (Table 2; Figs. 8, 9). The chemical 'δ' and induced chemical shifts 'Δ δ' of the MCT β-CD and oils in free as well as in compounded state had revealed evident shifts ensuring the formation of dynamic complexes between anchor and guests. Δ δ (H5 > H3) had revealed significant entrapment of oil molecules into the cavities for both oils confirming

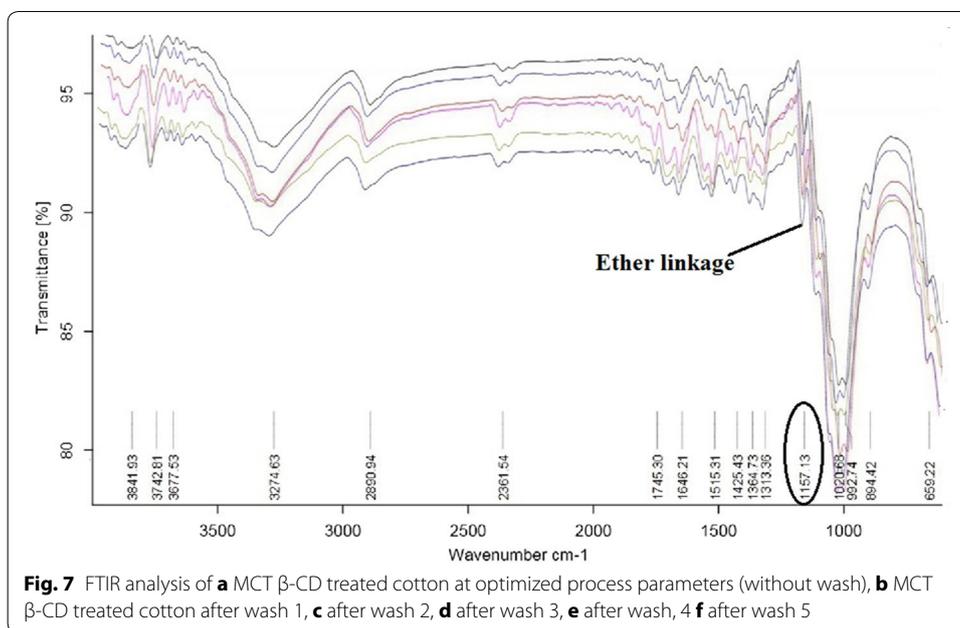
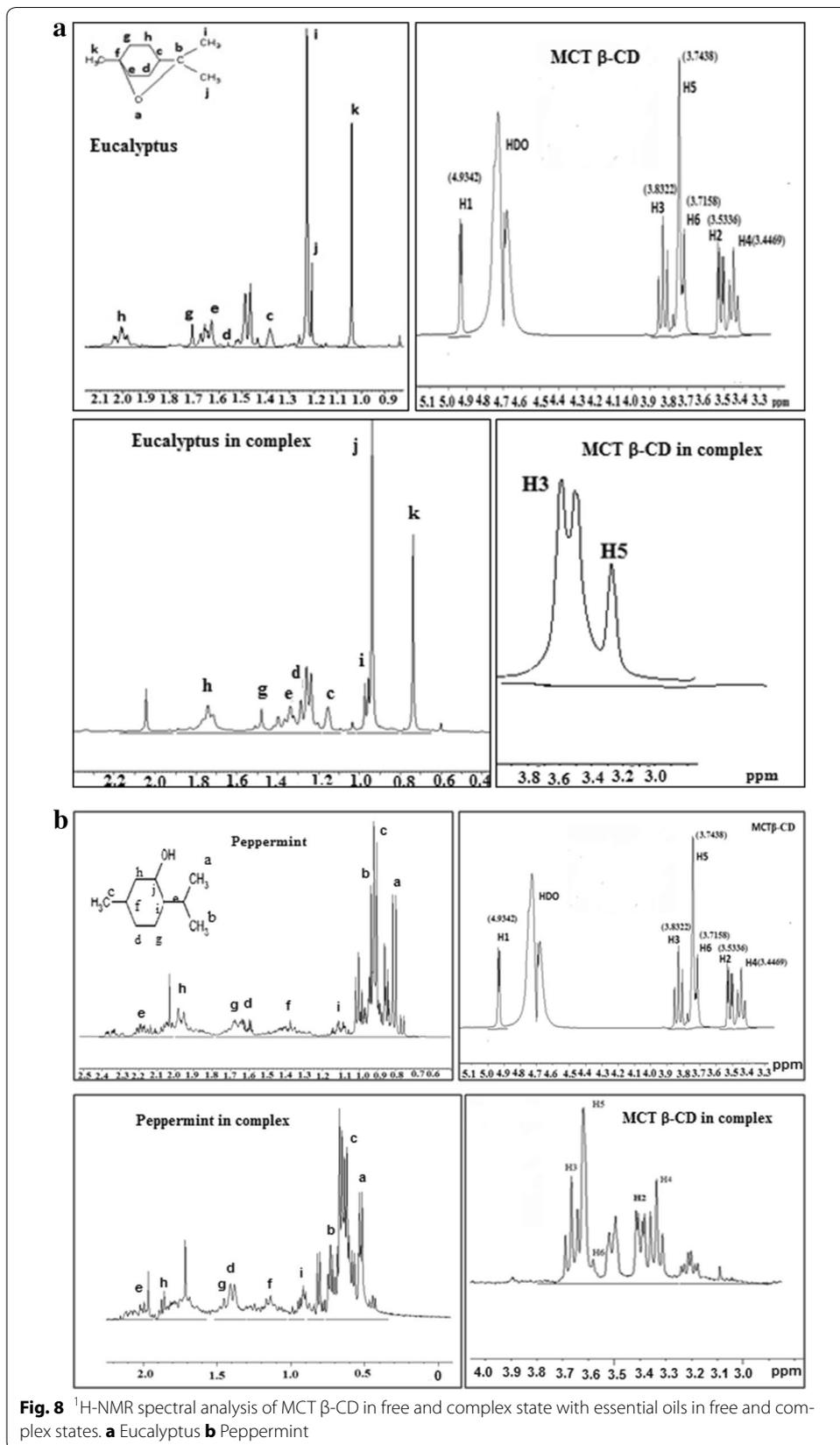


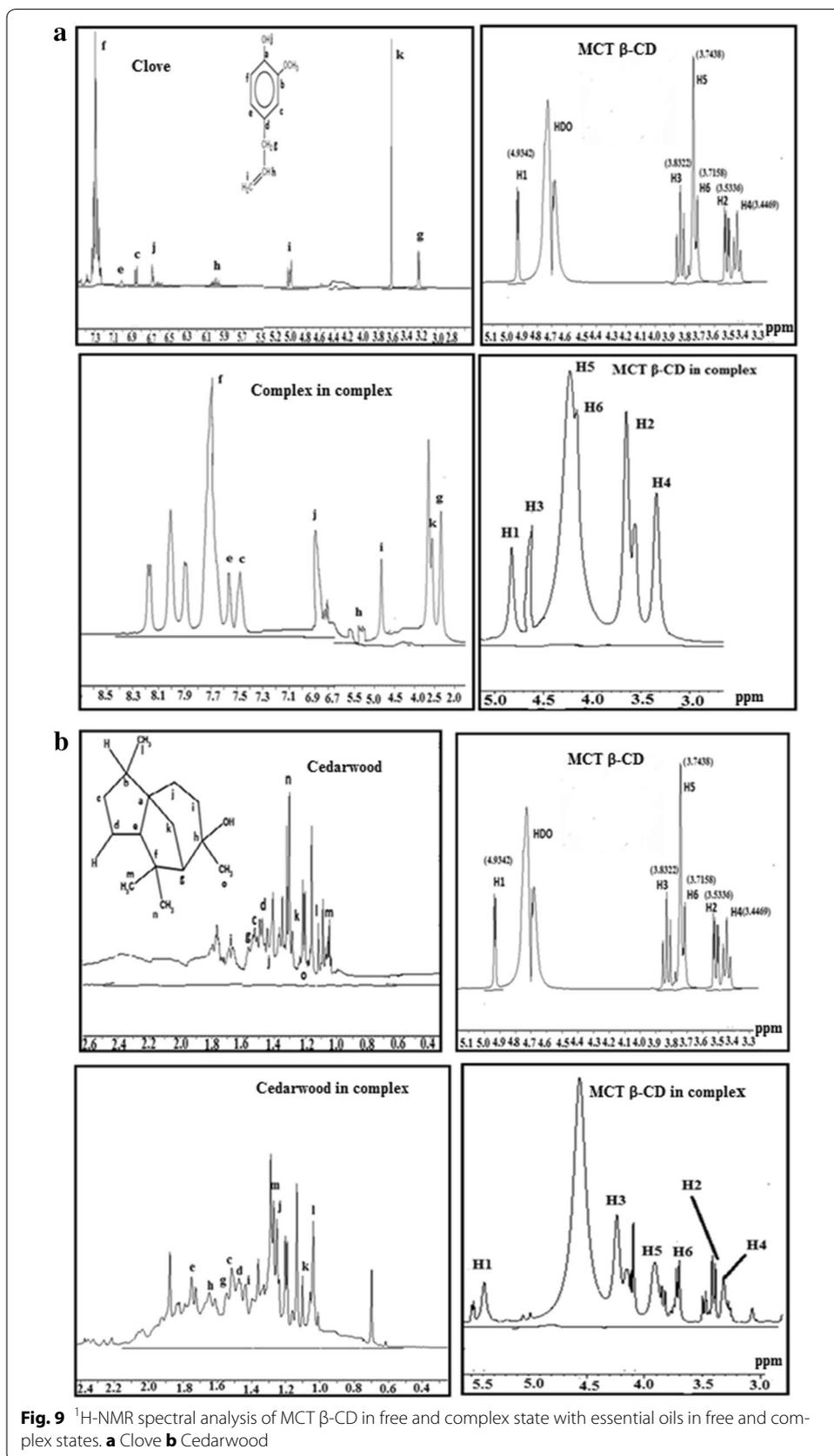
Table 2 Induced shift analysis of MCT β -CD-oil complexes in free and complex states

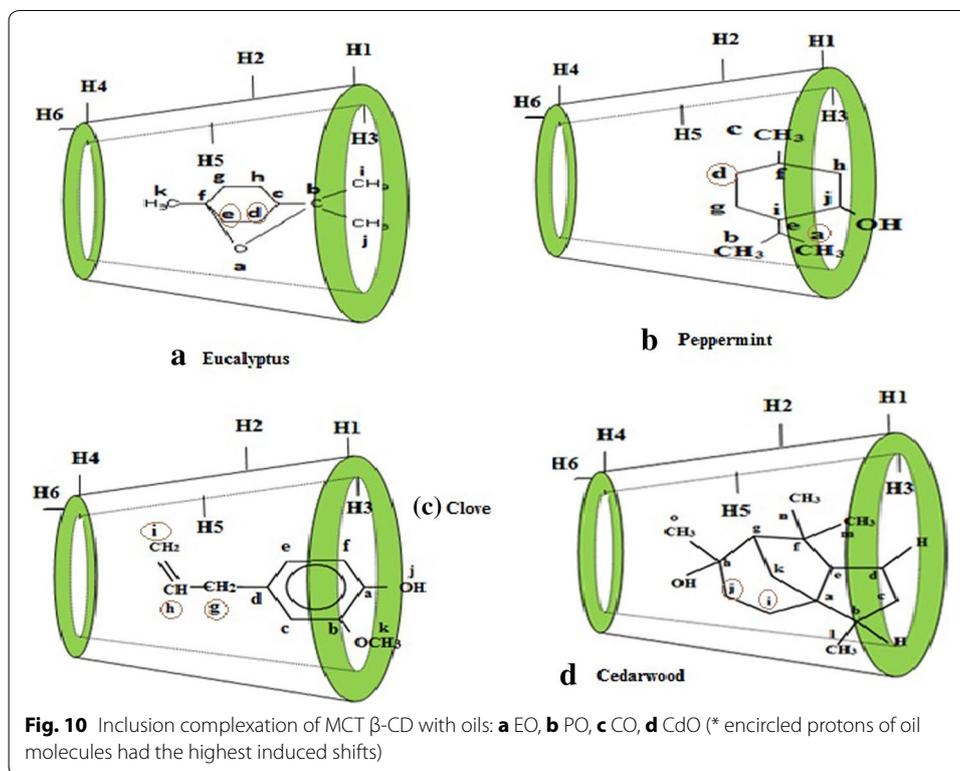
Proton (MCT β -CD)	$\delta^1_{\text{MCT } \beta\text{-CD (free)}}$	$\delta^{*2}_{\text{MCT } \beta\text{-CD (complex)}}$	$\Delta \delta^3_{\text{MCT } \beta\text{-CD}}$	$\delta^4_{\text{oil (free)}}$	$\delta^{*5}_{\text{oil (complex)}}$	$\Delta \delta^6_{\text{oil}}$	Proton (oil)	Oil type
H3	3.8322	3.7398	0.3446	3.2453	2.321	0.9243	H _g	
H5	3.7438	3.4124	0.3034	5.8937	5.131	0.7627	H _h	CO
				5.0256	4.823	0.2026	H _i	
H3	3.8322	4.659	-0.8268	1.5895	1.5123	0.0772	H _i	
H5	3.7438	4.269	-0.5252	1.3601	1.2966	0.0635	H _j	CdO
H3	3.8322	3.4873	0.3446	1.5592	1.2602	0.299	H _d	
H5	3.7438	3.1758	0.5681	1.6295	1.3390	0.286	H _e	EO
H3	3.8322	3.54	0.2922	0.7989	0.7357	0.0632	H _a	
H5	3.7438	3.3644	0.3794	1.6755	1.5584	0.1171	H _g	PO

$\delta^1_{\text{MCT } \beta\text{-CD (free)}}$ chemical shift of MCT β -CD in free state; $\delta^{*2}_{\text{MCT } \beta\text{-CD (complex)}}$ chemical shift of MCT β -CD in complex with oils; $\Delta \delta^3_{\text{MCT } \beta\text{-CD}}$ induced shift of MCT β -CD ($\delta^1_{\text{MCT } \beta\text{-CD (free)}} - \delta^{*2}_{\text{Complex}}$); $\delta^4_{\text{oil (free)}}$ chemical shift of oils in free state; $\delta^{*5}_{\text{oil (complex)}}$ chemical shift of oils in complex with MCT β -CD; $\Delta \delta^6_{\text{oil}}$ induced shift of oils ($\delta^4_{\text{oil free}} - \delta^{*5}_{\text{oil}}$)

the full inclusion of oils into the MCT β -CD cavity as H5 is more deeply embedded into MCT β -CD cavity than H3. ¹H-NMR spectra had shown generation of no newer peaks for any oil as complex formation was a dynamic process, the included oils being in a faster exchange between the free and bound states. The $\Delta \delta$ for oils had shown that in EO, Hk, Hd and He protons had shown more induced shifts than the other protons. This could be an indication that the oil had entered from the tail side into the cavity. Similarly, Hd and Hg for PO showed the inclusion of oil from the bottom side; Hi and Hj for CdO depicted segmental inclusion of the oil into the cavity and CO had shown the induced shift pattern as either Hk or Hg, Hh and Hi sided penetration into the cavity as shown in Fig. 10.

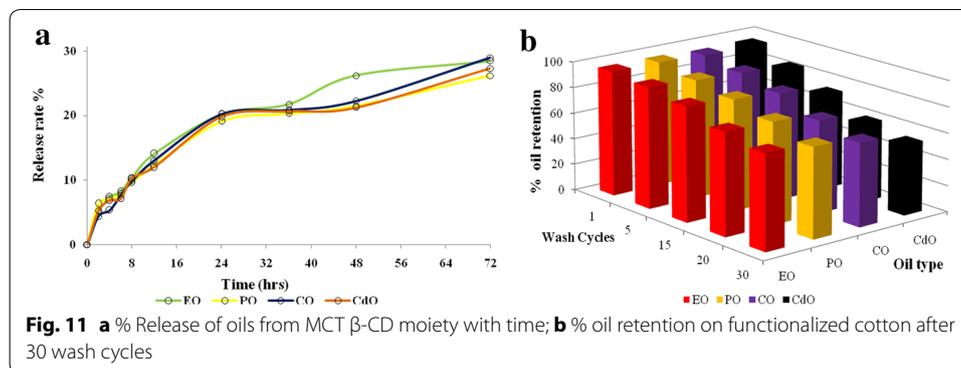






Stability analysis of oils through MCT β -CD complex—before and after wash

The application of oils on cotton was through the host compound rather than its direct application on cotton, in which, the oils are physically adsorbed on the treated surface in three subsequent phases; surface adsorption, absorption and finally the capillary action of oils into the fibrous pores of cotton that result in the development of vander-waal forces between oils and cotton at low temperature. Oils generally forms multi-molecular layer on the surface of cotton. But, covalent bonded host (MCT β -CD) tends to trap the oils into its cavities that further depends upon the compatibility between the sizes of guest and host cavity and also the thermodynamic interactions between host, guest and the solvent used (alcohol in the present case) due to the requirement of the structural conformation for either partial or full entrapment of oils into the cavities of host. The oils are hydrophobic (apolar) in nature, so these bind strongly to the hydrophobic cavities of the host. The retention of oils in the host cavities don't comply with the chemical bonding between the host and oils as the formation of inclusion complex do not exert any structural modification of the oils to be chemically bonded to the host or cotton. As if, the oils get chemically bonded to the host cavities, then to release oils on demand would require a lot of activation energy to dismantle oils from the host cavities. Thus, only non-covalent bonds (hydrophobic interactions along with vanderwaal forces) are formed in inclusion complex that allows the oils to be released on its own due to its volatile nature in a controlled manner as there is a dynamic equilibrium between the oils trapped in the host cavity and the water (moisture) present in its surroundings. Thus, all experimented oils fit well into the host cavities and had shown a curtailed release from the cotton. EO and CO were the slowest to fade off in the initial hours in comparison to the PO and CdO, with



EO being the most stable after initial 2 h, whereas, CO had shown the fastest sublimation (Fig. 11a). After the initial quick release of PO, the oil had shown a moderate release rate after 72 h. This was due to the better settlement of oil in the cyclodextrin cavities after the initial sublimation from the cotton surface during drying. This had facilitated the suppression of oil release from the cotton's surface and thus, prevented their fading off. The eugenol of CO is the middle note of the oil; on the other hand, cedrol of CdO behaves as the base note that lasted for longer time span than eugenol. In addition, monoterpenes as eugenol and thyme constitutes CO, whereas, sesquiterpenes as cedrol forms the backbone CdO. Their presence dictates the volatility of oils from cotton as monoterpenes being more volatile than the sesquiterpenes from the oil compositions.

All the oils were retained almost up to 65% even after 20 vigorous washes and substantial oil % was still present even after 30 washes. The high % aroma retention was due to the presence of anchored cavities to hold and control the release of oil from the surface of cotton. EO > PO > CO > CdO was the observed trend of % retained oils. CdO was left in the least proportion on cotton. This might be due to the reason that the retention time of cedarwood was the minimum on cotton that washed off easily after wash cycles as seen in Fig. 11 b.

Conclusions

The concentration and pH of MCT β -CD are the most influencing variables for the treated cotton as increase in concentration and pH of MCT β -CD had resulted in an increase in GY%, but TS% was tremendous ranging from low strength loss at low pH values along with some strength improvement at higher concentrations and low pH index, however, at higher pH, the strength had decreased. With the increase in concentration and temperature together, N₂% had decreased but pH played a role in the prevention of the hydrolysis of the chlorotriazine moiety for better fixation onto cotton. The inclusion complex of MCT β -CD and oils had suppressed the quicker fading off the oils from the semi-enclosed cavities.

Authors' contributions

AK and JNC planned the work. AK carried out the work and drafted the manuscript. Both authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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