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Performance assessment of fragrance finished cotton with cyclodextrin assisted anchoring hosts

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Abstract

Infusion of textiles with aromatic essential oils makes them immense value enriched for the aesthetic dominated fashion consumers to attain cosmeto-therapeutic and medicinal benefits. However, longevity of aroma on the textile with the time passage and subsequent launderings is a major concern for researchers and consumers too. In this work, essential oils of Eucalyptus, Peppermint, Lavender, Jasmine, Clove and Cedarwood were applied directly on cotton as well as with anchoring hosts as cyclodextrin in native and modified form viz. monochlorotriazine-β-cyclodextrin (MCT-βCD) to assess their stability of retention on the fabric surface. The release rate of oils, in isolation, had revealed the disappearance of fragrances rapidly with time as a result of weak physical forces between essential oils and textile surfaces in the absence of any anchoring hosts. MCT-β-CD showed enhanced fragrance stability with added advantage of exhibiting no major change in tensile strength, stiffness and air permeability of cotton.

Keywords: Aromatic essential oil, Aesthetic, Cosmeto-therapeutic, Anchoring hosts, Cyclodextrin, MCT-β-CD

Introduction

With rising global trends and changing lifestyles in terms of fashion, beauty as well as healthcare, awareness of consumers has enforced evolution of speciality value added textiles. The addition of essential oils on textiles makes the wearer afresh and relaxed by the unique aromas of oils (Eugenio et al. 2005). Though the effect is relatively short-lived, no matter how eminent the technology used to impart aroma may be employed. By using microencapsulation technique, the retention of aroma on textiles has been proved to improve (Wang and Chen 2004), offering diversified opportunities for the improvement of aesthetics through application of additional compounds as aromas, dyes, antimicrobial agents and phase changing materials through binder application with good wash durability (Chinta and Pooja 2013; Nelson 2002; Yamato et al. 1993), though some disadvantages such as non-uniformity in microcapsule distribution throughout the textile, monotonous core compounds, requirement of external stimuli, immense skill of capsule formulation and high expensive are all associated with this technique of aroma finishing. As an alternative, cyclodextrins (CDs) are a promising class of universal molecular containers.

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CDS are cyclic oligosaccharides produced with the transformation of starch by bacteria's such as Bacillus macerans (Astray et al. 2009; Jeang et al. 2005). These are capable of forming inclusion compounds with hydrophobic substances (Valle 2003) and found in different forms viz. consisting of six α-CD, seven β-CD, eight γ-CD and various other derivatives, such as δ, ζ, ξ, θ and ή-cyclodextrins or more glucopyranose units linked by α-(1, 4) bonds (Aggrawal and Warmoeskerken 2008; Lo et al. 2003; Martel 2002a, b; Ribeiro et al. 2008). The most notable feature of CDs is their ability to form solid inclusion complexes (host–guest complexes) with a very wide range of solid, liquid and gaseous compounds by molecular complexation. Complex formation between host and guest is a dimensional fit between host cavity and guest molecule in which no covalent bonds are broken or formed during formation of the inclusion complex and hydrophobic interactions might be the main driving forces for CD-based host–guest compounds (Lo et al. 2003; Ribeiro et al. 2008). Since each guest molecule is individually surrounded by a cyclodextrin (derivative) the molecule is micro-encapsulated from a microscopic point of view, this property of β-cyclodextrin can be utilized in finishing of textiles like antimicrobial finish, aroma finishing and flame retardant finishing (Eugenio et al. 2005). The purification of α- and γ-CDs increases the cost of production considerably, so that 97 % of the CDs used commercially are β-CDs (Jeang et al. 2005).

β-CD can be incorporated onto textile by means of spraying, printing, padding, grafting, surface coating, impregnation, ink jet printing and via sol gel (Aggrawal and Warmoeskerken 2008; Martel 2002a, b). Many novel techniques such as grafting with cross-linking agents and use of resin binders has been investigated to fix β-CD to fibres like cotton, wool, polyester, polyamide and polyacrylonitrile (Andreaus 2010; Cabrales et al. 2012; Ciobanu et al. 2013; Dehabadi et al. 2013; Hebeish and El-Hilw 2001; Ibrahim et al. 2007; Martel 2002a, b; Sricharussin et al. 2009; Velaz et al. 2007; Voncina and Marechal 2005). Resins such as epicholorohydrin had been used to fix β-CD to cellulose (Hebeish and El-Hilw 2001) and polyester (Ciobanu et al. 2013). The adherence of reactive cyclodextrins such as monochlorotriazinyl (MCT) chloride along with butyl acrylate to cellulose fibres has been reported too (Cabrales et al. 2012; Ibrahim et al. 2007; Sricharussin et al. 2009; Velaz et al. 2007). Dyeing and easy care finish could be achieved by using a formulation containing a reactive dye, MCT-β-CD and a resin (Bereck 2010; Crini 2003; Parlati et al. 2007; Szetjli 1998).

However, the investigation on stability of fragrant essential oils on treated substrates in the absence as well as presence of anchoring hosts has been lacking a systematic approach in the earlier reported works. Along with, the effect of employing anchors as MCT-β-cyclodextrin on to the substrate's physical and functional performance had been reported scarcely. Thus, the necessity of imparting durable fragrance finishing with the consideration of its influence on the performance of the treated cotton is immensely vital.

Thus, the present work deals with the application of a variety of essential oils on cotton in non-complexed form i.e. in free State, complexed state with β-cyclodextrin and derivative viz. MCT-β-CD, followed by the study of their post-release behaviour to assess the stability of the aroma on cotton. Performance of essential oils complexed with MCT-β-CD as well as its impact on the physical properties of finished cotton had also been investigated.

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 six categories of essential oils, viz. eucalyptus, peppermint, lavender, jasmine, clove and cedarwood. All the analytical grade chemicals, viz. β-cyclodextrin (β-CD), cyanuric chloride, sodium carbonate, sodium hydroxide, ethanol and phenolphthalein were supplied by SDFL, Mumbai. UV–Vis-210 spectrophotometer (Lab India analytical UV 3000^+), FTIR-spectroscope (Perkin Elmer, US), Elemental Analyser (EuroVector EA 3000), Bruker Avance II NMR Spectrometer, Thermogravemetric Analyser (SDT Q600 V20.9 Build 20), spray gun, 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), Orbital shaker (Bio-Technology Lab, M.D.U Rohtak), wash fastness tester (RBC Electronics, Mumbai), Laundrometer (RBE, Mumbai), Tensile tester (Globe Tex Industries), Shirley Stiffness tester and Air permeability tester (Prolific) were the equipment used to evaluate the variables of the finish and characterise the synthesised MCT-β-CD and inclusion complexes of β-CD-oils. Release rate of essential oils was also evaluated by extracting the fragrance left on to the treated fabric after stipulated time in ethanol solution as depicted in Eq. 1.

$$\text{Rate of release of oil at stipulated time gap } (\%) = \frac{\text{Conc. at 0 hours} - \text{Conc. at stipulated time interval}}{\text{Conc. at 0 hours}} \times 100 \quad (1)$$

Application of essential oils on cotton

Solutions of essential oils, viz. eucalyptus, peppermint, lavender Jasmine, clove & cedarwood (2, 4, 6, 8 and 10 %) were prepared in 100 % ethanol carrier. Cotton was treated with oil-ethanol solutions by the use of spray gun at 4 kg/cm^2 pressure followed by air drying. The content of essential oil left on cotton was extracted after stipulated time with ethanol heated at 60 °C and spectrophotometrically assessed at respective λ_{max} (lavender oil—LO, 344 nm; eucalyptus oil—EO, 270 nm; peppermint oil—PO, 240 nm; jasmine oil—JO, 264 nm; clove oil—CO, 282 nm and cedarwood oil—CdO, 306 nm) to evaluate the fragrance release rate. The use of ethanol for oil extraction is encouraged due to the ease of spectroscopic evaluation of residual oil content present in treated cotton and thereby, indirect investigation of the released aroma in air; which is otherwise difficult to account.

Solubility of β-cyclodextrin

The solubility of β-cyclodextrin (10–100 g/L) was studied in water, ethanol (100 %) and NaOH (1–10 g/L) separately at room temperature.

Optimisation of β-CD and oil concentration

Soluble β-CD was applied on cotton through padding-drying within a concentration range (10–100 g/L). The optimization of the β-CD was done with the analysis of weight gain and also through the measure of absorbance of phenolphthalein solution using UV–Vis spectroscopy at λ_{max} (553 nm), which is based on the color change intensity due to

the formation of host- guest complexation between β-CD and the indicator. Weight gain was assessed with Eq. 2.

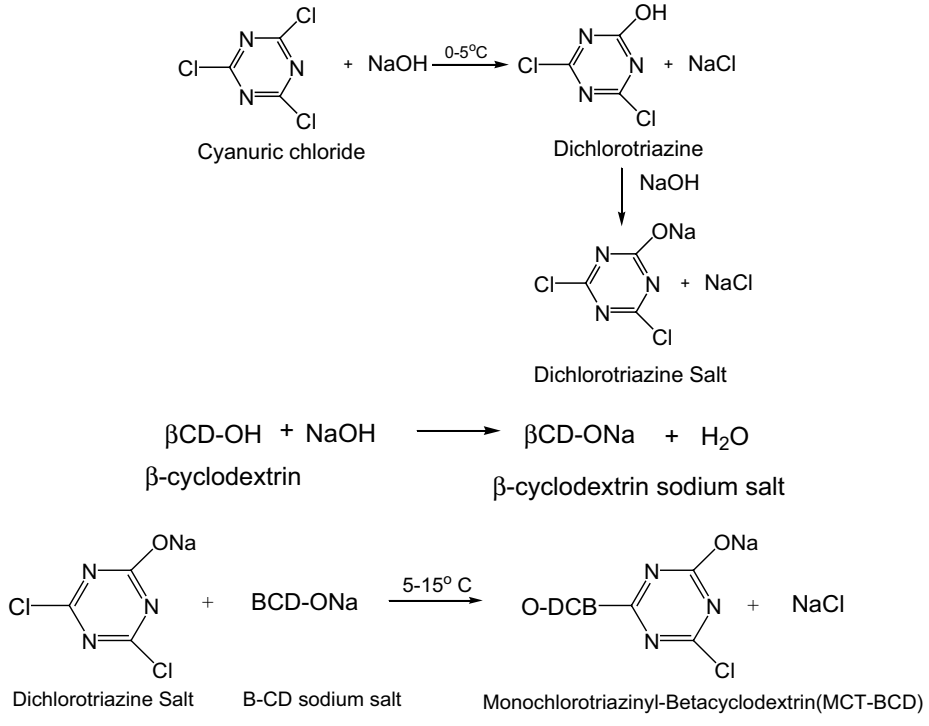
$$\text{Weight gain } (\%) = \frac{W_f - W_i}{W_i} \times 100 \tag{2}$$

where, W_f and W_i represent final and initial fabric weight respectively.

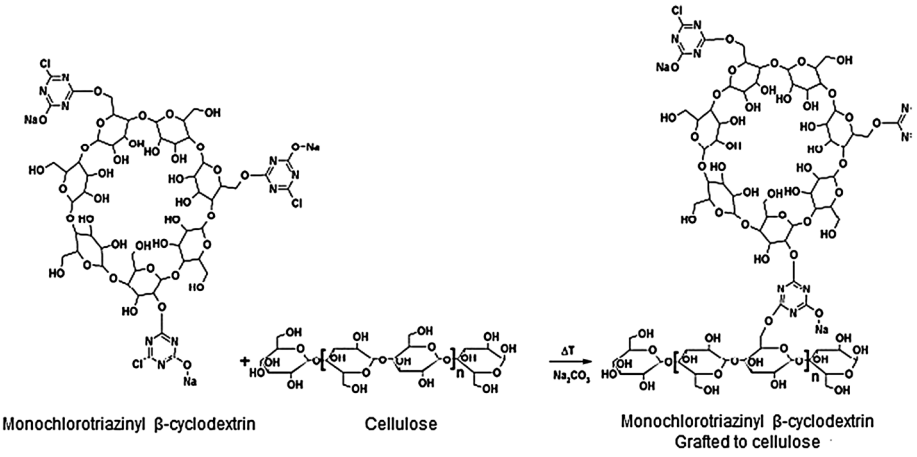
The oil concentration was optimised as- Cotton (0.1 g) previously treated with optimised concentration of β-CD, was kept in all the essential oil solutions (1–15 %, prepared in ethanol) for 1 h at room temperature, after which the treated cotton was discarded and the absorbance of each residual oil solution was checked at respective λ_{max} for the evaluation of complexed oil in the solution. The stability of oils on cotton was evaluated for specific time, viz. for 0, 1, 2, 4, 8, 12, 24, 36 and 72 h.

MCT-β-cyclodextrin (MCT β-CD): synthesis, characterisation and application

The synthesis of MCT β-CD was carried out in laboratory as per the referred literature (Sricharussin et al. 2009). The reaction mechanism of MCT β-CD synthesis is depicted in Scheme 1 and the mode of MCT β-CD attachment with cotton is shown in Scheme 2 (Cabrales et al. 2012). The synthesised MCT β-CD compound was characterised with FTIR (Fourier Transform Infrared spectroscopy), Elemental Analysis, Thermogravimetric Analysis (TGA) and Graft yield %. The yield of the reaction mechanism was satisfactory enough at 63.34 %. Also, the inclusion complex between β-CD and peppermint oil was characterized with ^{1}H-NMR analysis. Thereafter, 70 g/L of synthesised MCT β-CD was applied on cotton at five pH levels (4, 6, 8, 10 and 12)



Scheme 1 Stepwise reaction mechanism of MCT-β-CD synthesis



Scheme 2 Mode of MCT-β-CD attachment with cotton

through padding with 80 % expression followed by air drying, curing at 150 °C for 5 min, rinsing in cold water to remove any superficial MCT-β-CD, spraying of oils in optimised amounts and subsequent drying of treated cotton. The curing treatment is carried out to strengthen the ester linkage between the reactive host and cellulose to achieve wash durable functionalized cotton. Weight gain of cotton before and after wash was determined to elucidate the retention of the modified host on the substrate. Elemental Analysis, TGA and FTIR were carried out for the MCT-β-CD treated fabric to visualise the presence and retention of the reactive host. Also, the comparative effect of MCT-β-CD and β-CD on functional and physical properties of cotton had been studied.

Results and discussions

Release rate of essential oils

The release rate of the essential oils from finished cotton is shown in Fig. 1a, f. It was observed that a substantial part of essential oils was sublimated-off within a very short time limit (likely 1 min), required to just dry out the finished cotton at room temperature in open air. With progress of time, the concentration of oils extracted went on decreasing; the decrease was more in initial hours after fragrance application, beyond which the concentration decreased at a slower rate; the increased rate of release might be due to the reduced stability of essential oils on the substrate and the presence of physical Van der Waal's forces. Peppermint, Clove and Cedarwood were first to fade off from the cotton surface and on the other, Eucalyptus, Lavender and Jasmine were better retained by the fabric due to the presence of 1,8 cineole (Eucalyptus), Linalyl acetate (Lavender) and Benzyl acetate and alcohols (Jasmine) that have longer retention time than Eugenol (Clove), Menthanone (Peppermint) and pinene (Cedarwood), which are the main constituents of oils.

The order of oil release from native cotton as observed:

$$PO > CO > CdO > LO > EO > JO$$

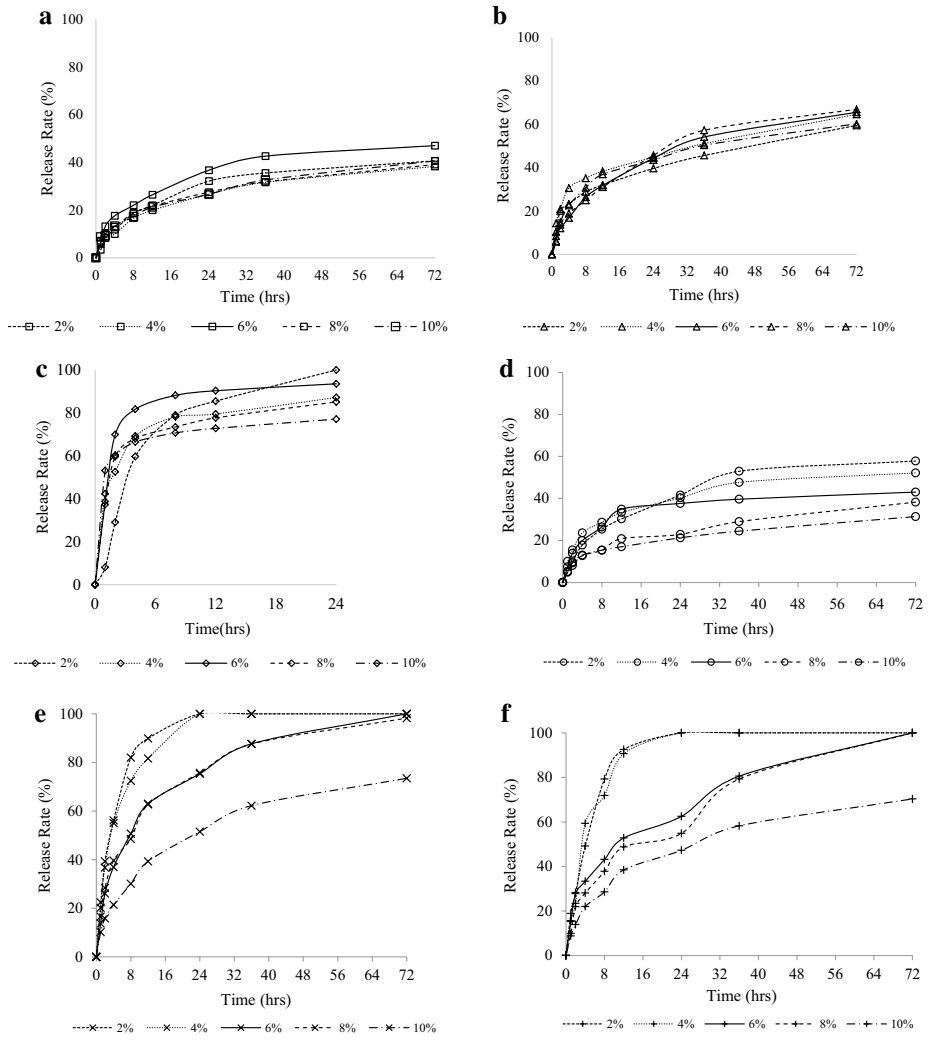


Fig. 1 Release rate of oils alone **a** lavender, **b** eucalyptus, **c** peppermint, **d** jasmine, **e** clove and **f** cedarwood from cotton

Also, clove, cedarwood & peppermint were released much faster than lavender and Jasmine from the treated surface due to their olfactory character as peppermint and cedarwood are the top-feeble notes of the oils that faded away at the fastest pace to provide initial scents but lavender and jasmine are the base note of the oil that lasted the longest.

Solubility of β-cyclodextrin

Solubility of β-CD (%) in three solvents is shown in Fig. 2. β-CD at 10 g/L was completely soluble in all solvents but as the concentration of β-CD was increased, the solubility decreased in water and ethanol as well. This may be attributed to the higher bond energy of cyclodextrin due to the intermolecular hydrogen bonding between C2 and C3 groups of adjacent glucose rings in the crystal state of cyclodextrin. This results in the formation of secondary hydrogen bond belt within the structure of cyclodextrin, making

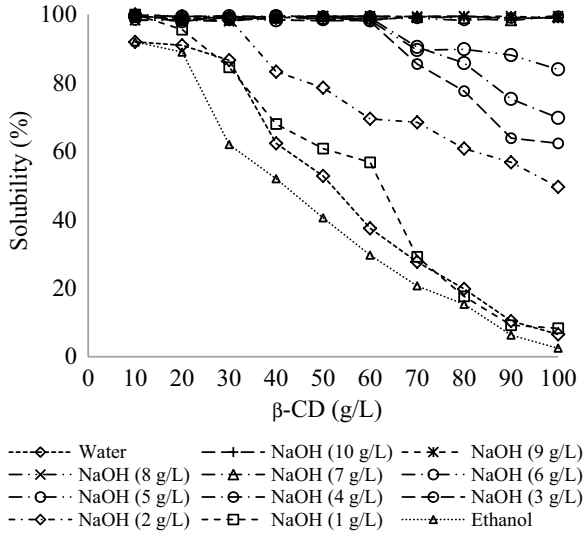


Fig. 2 Solubility (%) of β-cyclodextrin in different solvents

the structure more rigid and also, insoluble in water. Water and ethanol are polar protic solvents, whereas NaOH is a polar aprotic medium that do not participate in hydrogen bonding (no O–H or N–H bonds). The high polarity of NaOH permits dissolution of cyclodextrin in a better way than the other media. β-CD (10–100 g/L) was found to be completely soluble in NaOH (6 g/L).

Optimization of β-CD concentration

The weight of cotton increased in the array of 1.03–6.23 % with increase in applied β-CD concentration up to 70 g/L, without any substantial change at 80–100 g/L (6.42–6.83 %). The inclusion compound formation with phenolphthalein had shown maximum color change at minimum absorbance (0.027) with β-CD (70 g/L), but lesser complex formation had taken place between β-CD and phenolphthalein between 80 and 100 g/L. The minimum absorbance of β-CD (70 g/L) was related to the maximum extent of complex formation between β-CD and phenolphthalein molecules but beyond 80 g/L up to 100 g/L, the cavities were not available for more complex formation with the phenolphthalein molecules, further related to the increased absorbance of the solution. Thus, β-CD at optimized concentration, i.e. 70 g/L was taken for oil optimization.

Optimization of concentration of essential oils

The maximum complexation between β-CD and oils took place at a concentration range of 9–11 % as seen in Table 1. Reason for this can be attributed to the saturation of cavities of β-CD and no more cavities were available for the inclusion of guest molecules. The amount of oils inside the cavities might be less because some of the oil was on the surface of fabric rather than in cavities.

Table 1 Oil concentrations used for complex formation with native β-CD

Oil concentration (%)	Essential oil used (mg/ml)					
	Eucalyptus	Peppermint	Lavender	Jasmine	Clove	Cedarwood
1	0.6	0.18	0.37	0.89	0.34	0.24
2	1.62	1.57	1.50	1.72	1.23	1.17
3	1.90	1.80	1.22	2.21	1.56	1.45
4	1.81	2.19	1.43	2.52	1.78	1.63
5	1.62	2.20	1.91	3.21	2.14	1.97
6	2.04	2.35	3.43	3.67	2.56	2.13
7	2.12	2.74	3.97	4.45	2.89	2.56
8	3.2	3.02	4.23	5.31	3.13	3.04
9	*4.70*	*4.65*	*4.96*	*5.78*	*4.45*	*3.68*
10	*4.93*	*4.79*	*4.87*	*6.11*	*4.84*	*4.23*
11	*4.79*	*4.72*	*5.56*	*6.43*	*5.03*	*4.67*
12	4.77	4.68	4.97	5.28	4.78	4.45
13	4.75	4.70	4.79	5.05	4.63	4.44
14	4.76	4.69	4.65	4.98	4.54	4.37
15	4.76	4.69	4.32	4.88	4.52	4.28

Italic values indicate the maximum level of inclusion complex formation between oils and β-cyclodextrin

Stability of inclusion complex of β-CD and essential oils

The release rate of essential oils in the complex was studied with 70 g/L β-CD and two concentrations of all essential oils, i.e. 9 and 10 % (Fig. 3a, b). The β-CD-oil complexes had shown suppressed release rate of oils. With the increase in β-CD and also oil concentrations, the release rate was marginally increased for all the host-oil complexes due to the availability of more oil molecules in the oil-carrier (alcohol) solution. Around 40 % of oils were released from the treated substrates with oils of Lavender, Peppermint and Eucalyptus. On the other, Clove, Jasmine and Cedarwood were better retained by the fabric due to the presence of cavities that held the oil molecules, thereby, suppressing the oil sublimation from the textile surface. Peppermint, Clove and Cedarwood were released after 72 h in the absence of anchoring host but in their presence, substantial amount of fragrance was still present even after 72 h. Release rate of oils was somewhat lowered due to the lowering of the vapour pressure of essential oils as the oils were entrapped in the cavities of cyclodextrins. It was also evident that the fragrance release increased with time lapse as depicted in Fig. 4.

Characterisation of MCT-βCD

Graft yield

The Graft yield of MCT-βCD on cotton was measured at variable pH in terms of weight gain of cotton due to graft polymerization according to Eq. 2. It was inferred that the weight gain was more in alkaline but lesser in acidic pH due to lesser stability of MCT-βCD in the latter. In addition, a yellowing of cotton was observed with alkaline pH. A linear increase in weight of functionalised cotton had occurred up to 13.46 % (at pH 8), followed by a slight decrease at higher pH values due to the hydrolysis of excess MCT-β-CD. Sodium carbonate might have influenced the fixation of MCT-β-CD up to pH ~8, beyond which it decreased due to hydrolysis of MCT-β-CD. Also, in acidic

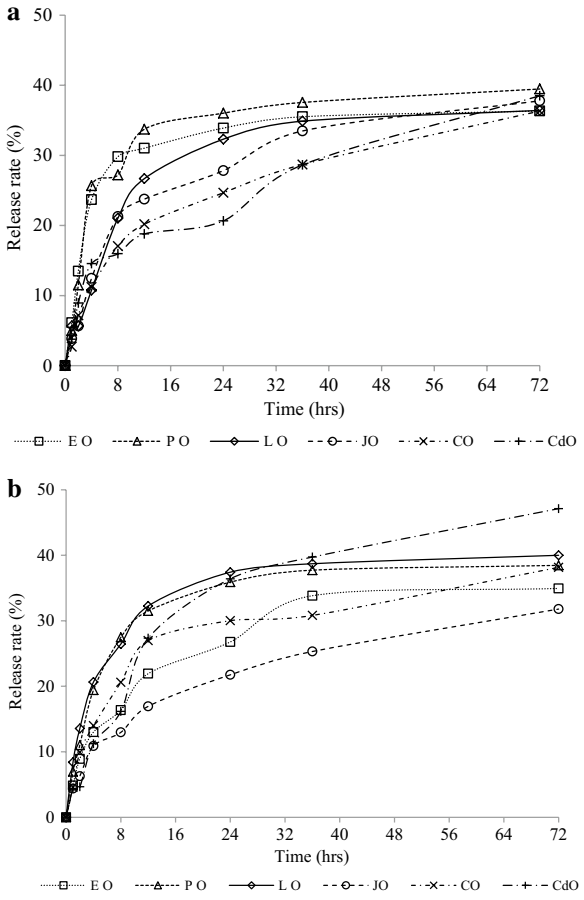


Fig. 3 Release rate of oils from β-cyclodextrin treated cotton. **a** 9 % oil concentration—70 g/L β-cyclodextrin, **b** 10 % oil concentration—70 g/L β-cyclodextrin

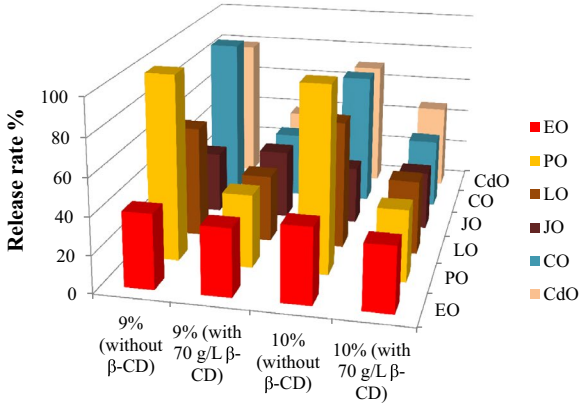


Fig. 4 Comparison of release of oils from untreated and β-CD treated cotton at 9 and 10 % oil concentrations with 70 g/L β-CD after 72 h

pH, exothermic reaction took place and after keeping solution overnight, pH might have stabilized.

Elemental analysis

The Elemental analysis of synthesised MCT-β-CD, control cotton and MCT-β-CD treated cotton was performed to analyse the composition of the samples with Elemental analyser. The results are reported in Table 2. The results of Table 2 had shown about 3.7 % (MCT-β-CD), 0 % (control) and 0.41 % (MCT-β-CD treated cotton) N_2 content in the three specimens. The presence of Nitrogen in the MCT-β-CD and MCT-β-CD treated cotton confirms the modification of native β-CD and control cotton with MCT-β-CD (Okeil and Shafie 2011; Peila et al. 2012).

Fourier transform infrared spectroscopy

The comparative FTIR analysis of MCT-β-CD with native β-CD and Cyanuric chloride and also for control and MCT-β-CD treated cotton was performed at spectral range from 400 to 4000 cm^{-1} (Fig. 5A, B). The spectrogram had shown both increase and decrease in the vibrational intensity of the bonds present. The shift was negative because of incorporation of more polar groups of cyanuric chloride with β-CD. Polarity increased the vibration corresponding to negative change; whereas, positive change in intensity was because of change of microenvironment which led to the formation of weak Van der Waal forces (ONa). From Fig. 5A, it was possible to analyse the appearance of a band at 1661 cm^{-1}, which was not found in the characteristic spectrum of β-CD and even cyanuric chloride. This band is due to the stretching of the C=O and NH_2 bonds in the synthesised MCT-β-CD. Also, the stretching of bonds as –OH had been investigated from 3388.2 to 3444.39 cm^{-1}. The shifting of ester linkages (C=O) at 1776.34 (1777.7), 1752.28 (Absence), 1724.14 (1725.1) cm^{-1} had been evinced to assure the modification of β-CD when compared with cyanuric chloride as confirmed from Fig. 5A. Also, from the Fig. 5B, MCT-β-CD treated cotton had shown an additional peak at 1718.17 cm^{-1}, that was not apparent in control. It is the characteristic of an ester carbonyl group as well as confirms the presence of a cyclic ring on treated cotton that had confirmed the anchorage of MCT-β-CD on cotton (Sricharussin et al. 2009).

^{1}H-nuclear magnetic resonance studies

The ^{1}HNMR spectroscopy is one of the most useful techniques for the investigation of host- guest complexation and determination of association constants between host and guests in the complex form. The inclusion complex was characterised in D_2O as solvent at room temperature and all chemical shifts were measured relative to Trimethylsilane (TMS). The inclusion complex of β-CD and Peppermint was investigated by the change in the chemical shift of some guest peppermint and host (β-CD) protons in the complex,

Table 2 Elemental analysis of MCT-βCD, control cotton and MCT-βCD treated cotton

	O (%)	N (%)	C (%)
MCT-βCD	50	*3.7*	35.46
Control	30	*0*	42
MCT-βCD treated cotton (70 g/L)	51	*0.41*	38.13

Italic values indicate N % which signifies the presence of monochlorotriazine in the treated samples

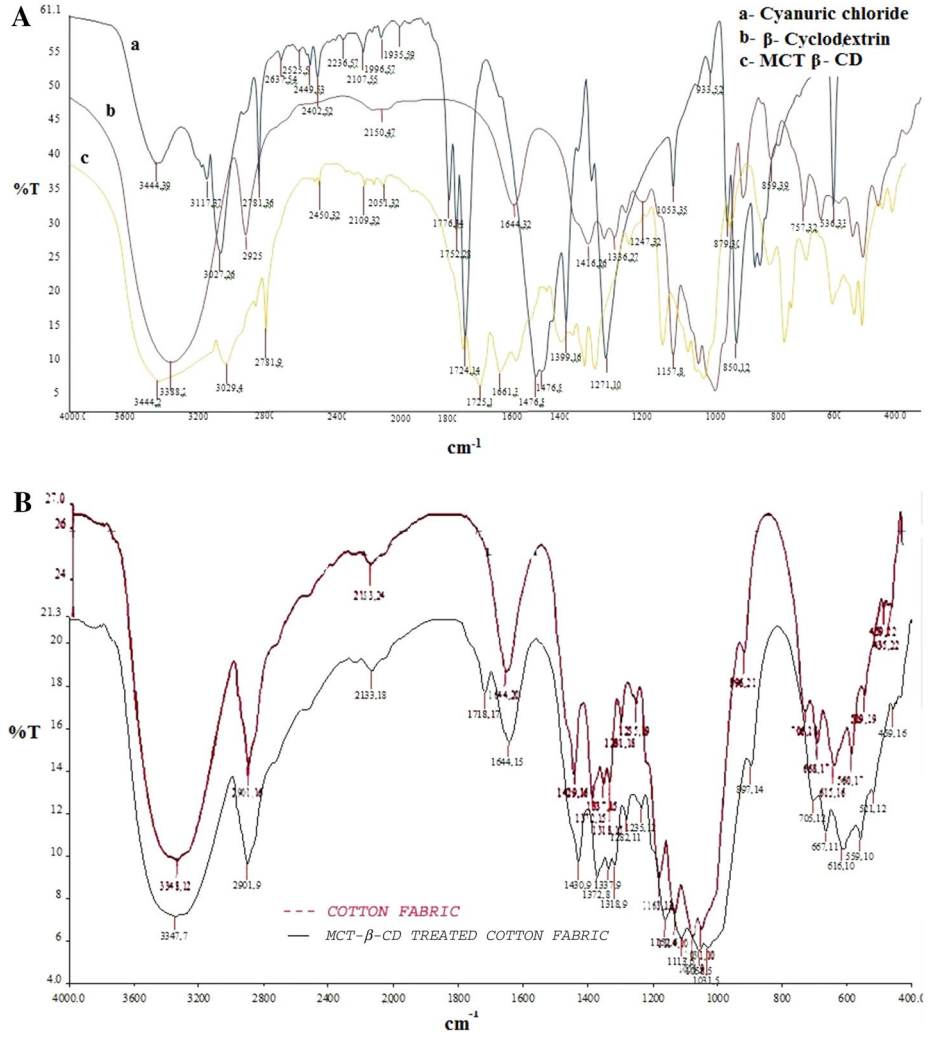


Fig. 5 Comparative FTIR of **A** Cyanuric chloride, β-Cyclodextrin and MCT β-CD; **B** Control and MCT β-CD treated cotton (70 g/L)

in comparison with the chemical shifts of the same protons in the free components (induced shift). Partial ^{1}H NMR spectra of pure β-CD and Peppermint and Peppermint: β-CD inclusion complex in a 1:1 molar ratio is presented in Fig. 6A, B. The absence of new peaks could be assigned to the fact that complexation is a dynamic process, the included peppermint being in a fast exchange between the free and bound states. The Fig. 6A, B had shown that H3, H5 and H6 of β-CD (interior cavity) had shown a significant upfield shift and H2 and H4 (exterior cavity) had exhibited marginal upfield shift. The peppermint had also shown a substantial induced shift in the presence of β-CD than in the Free State as shown in Table 3. The results had confirmed the formation of inclusion complex between the host (β-CD) and guest (peppermint).

Thermogravemetric analysis

TGA of MCT β-CD, control, MCT β-CD treated cotton and cotton treated with Inclusion complex of MCT β-CD and peppermint is shown in Fig. 7. The comparative results

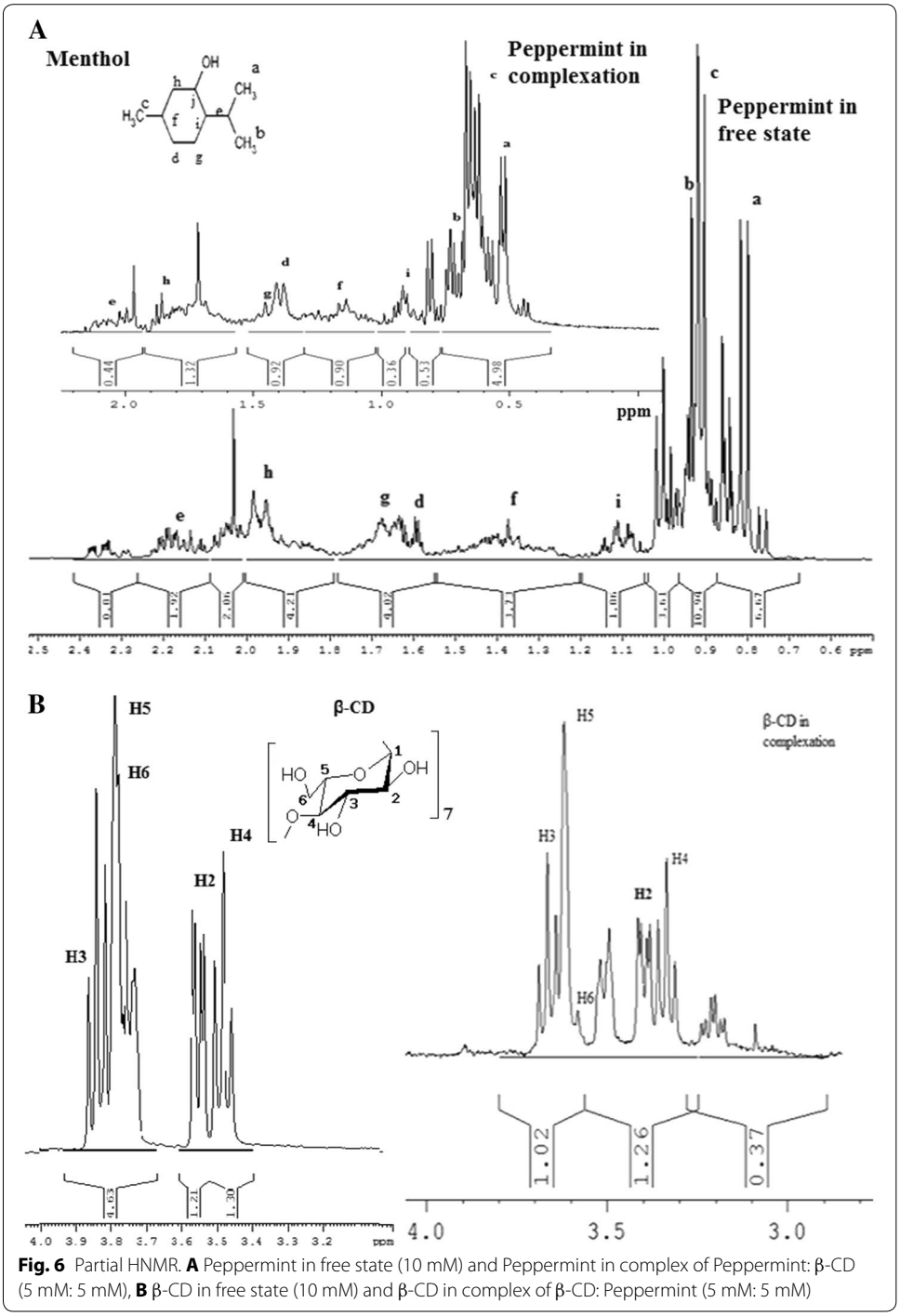


Fig. 6 Partial HNMR. **A** Peppermint in free state (10 mM) and Peppermint in complex of Peppermint: β-CD (5 mM: 5 mM), **B** β-CD in free state (10 mM) and β-CD in complex of β-CD: Peppermint (5 mM: 5 mM)

had shown that the peak temperature of control at 390 °C had shifted to 360 °C due to the treatment with the reactive host and further, cotton treated with the Inclusion complex (MCT β-CD and oil) decomposed at 350 °C. This change in the thermal behavior of treated cotton was due to the presence of MCT β-CD with lower peak temperature of 330 °C that affected the thermo chemical pathway of the cellulose decomposition. Also, the overall residual weight % had increased for the treated cotton when compared with

Table 3 Chemical and induced shifts of protons of β-CD and Peppermint in free and complexed states

Proton (β-CD)		Chemical shift $\delta_{\beta\text{-CD free}}$	Chemical shift δ^*_C	Induced shift $\Delta\delta$ $(\delta_{\beta\text{-CD free}} - \delta^*_C)$
H3	Internal Cavity	3.867	3.644	0.2233
H5		3.782	3.521	0.2614
		3.769	3.496	0.2735
H2	Exterior Cavity	3.564	3.383	0.1811
H4		3.484	3.337	0.1472
(Peppermint)		$\delta_{P\text{ free}}$	δ^*_C	$(\delta_{P\text{ free}} - \delta^*_C)$
Ha		0.789	0.569	0.22
Hb		0.926	0.734	0.1922
Hc		0.894	0.685	0.2094
Hf		1.398	1.614	0.2309
Hg		1.676	1.453	0.2221

δ^*_C = chemical shift in complex

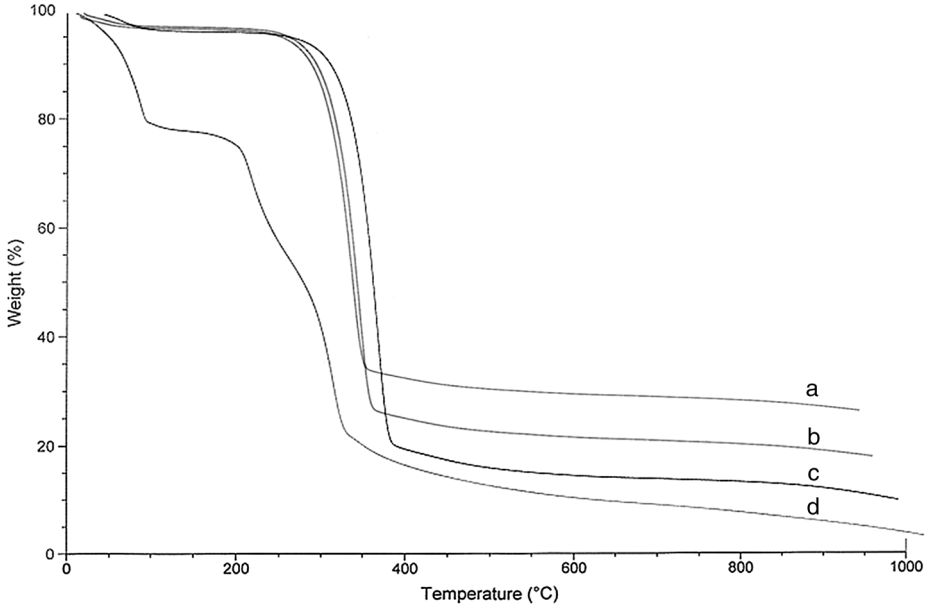


Fig. 7 Thermogravemetric analysis. *a* Cotton treated with IC of MCT β-CD (70 g/L): Peppermint (10 %), *b* cotton treated with MCT β-CD (70 g/L), *c* Control, *d* MCT β-CD

control viz. 20 % (for control), 26 % (for MCT β-CD treated cotton) and 34 % (for cotton treated with complex). This had further affirmed the presence and retention of the reactive host on cotton as compared to control.

Effect of the modified cyclodextrin and native β-CD on physical and functional performance of cotton

Wash durability

The wash durability of the functionalized cotton was assessed with the retention of weight gain (%) after subsequent wash cycles-up to five cycles (Fig. 8). The β-CD

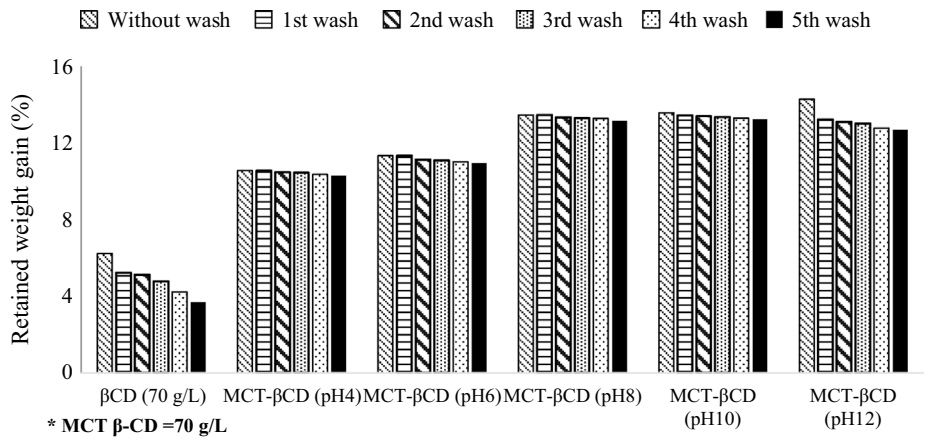


Fig. 8 Wash durability of β-CD and MCT-βCD treated cotton with retained weight gain (%)

retention on cotton was adjudged as retained weight of cotton, which reduced from 6.23 % (without wash) up to 5.23 % (1st wash), 5.12 % (2nd wash) and 3.69 % (5th subsequent wash). This was due to the presence of only weak hydrogen interactions between cotton and native cyclodextrin. On the other, no significant decrease in the weight of cotton was observed (MCT-βCD treated), due to the minimal loss of the amount of fixed MCT-βCD as this derivative of β-CD is attached to cellulosic hydroxyl groups through ether linkages offering good wash fastness similar to that between reactive dyes and cellulose. This was further confirmed by the prolonged retention of the fragrances in the treated cotton as the hosts were in a stable retention position even after washing. Thus, the modified hosts gave superior retention of oils on cotton than the unmodified β-CD.

Tensile strength

The tensile strength of cotton treated with unmodified β-CD and MCT-βCD were compared with that of control (Table 4). There was a slight increase in strength with βCD but for MCT-βCD treated cotton, the loss in tensile strength was higher at pH 4 and 12, with minimum strength at the lowest pH 4, whereas at pH 6 and 8, the strength of cotton had increased might be due to the plasticisation effect of MCT-βCD on cotton. This is due to the reason that MCT-βCD seemed to lessen the restriction of segmental movement of the cellulose chains in the fibres thereby improving tensile character and also, these pH were

Table 4 Effect of modified CD and native β-CD on physical performance of cotton

Sample	Tensile strength		Bending length		Air permeability ($cm^3/cm^2/s$)
	Warp	Weft	Warp	Weft	
Control	255.4	193.0	1.9	1.5	180
βCD	258.1	198.4	2.1	1.8	174
MCT-βCD (pH4)	212.6	154.6	2.1	2.3	170
MCT-βCD (pH6)	267.4	200.5	2.2	2.5	161.5
MCT-βCD (pH8)	268.9	205.8	2.3	2.5	155.3
MCT-βCD (pH10)	219.0	173.5	2.4	2.7	146.6
MCT-βCD (pH12)	216.6	169.7	2.5	2.9	139.5

near to neutral (pH ~7) (Sricharussin et al. 2009). At pH 4 (highly acidic) and pH 12 (highly alkaline), cotton had undergone degradation that resulted in decrease in tensile strength.

Stiffness and air permeability

The stiffness and air permeability of functionalized cotton with MCT-βCD and native β-CD were compared with those of control (Table 4). It was evident that the bending length increased for both treatments but substantial increase was found in bending rigidity of MCT treated samples than native β-CD because of the presence of monochlorotriazine derivative of cyclodextrin (containing cyanuric chloride) as a conventional cross-linking agent. On the other, at MCT (pH 12), air permeability was the minimum and for acidic pH with MCT-βCD, air permeability was least affected. The pH-8 for MCT-β-CD was chosen to study the release rate of oils from the fragranced cotton due to the increase in tensile strength along with highest weight gain retention with wash durability up to five washes.

Release rate of essential oils from the functionalised cotton and oil alone treated cotton

The oil-alone treated cotton (with Eucalyptus, Lavender and Peppermint) had shown the fastest fading of the oils from the treated surfaces as accounted in Table 5. The presence of native β-CD had shown better retention and slower release from cotton due to the cotton functionalisation with cyclodextrin cavities. The influence of MCT-β-CD on the volatility of the guests was also studied, after 3 days, the release rate was found to be only 33.47 % for eucalyptus, 35.07 % for peppermint and 32.04 % for lavender. It has also been observed that the use of modified cyclodextrin have exerted substantial impact on curtailing the release of oils from the cotton in comparison to the use of native cyclodextrin and also, oils alone treatments. This is due to the reason that more cavities were adhered to the cotton when modified hosts were used and thereby increased oil retention by cotton substrate (either before wash or after washing cycles).

Conclusions

The application of essential oils without any form of anchoring hosts lasted for only few hours due to weak forces of interaction between the oils and cotton. Application of

Table 5 Release of essential oils from functionalized cotton and oil alone treated cotton

Time (h)	Essential oils (10 %) [70 g/L βCD/70 g/L MCT-βCD]								
	EO			LO			PO		
	MCT-βCD	βCD	Oil alone	MCT-βCD	βCD	Oil alone	MCT-βCD	βCD	Oil alone
0	0	0	0	0	0	0	0	0	0
1	5.44	4.83	8.78	6.15	8.39	5.74	4.35	6.96	53.12
2	8.37	8.92	9.33	9.38	13.55	14.75	8.12	11	60.25
4	13.39	13.01	13.3	15.21	20.65	22.54	12.75	19.42	66.46
8	20.08	16.36	17.3	20.39	26.45	30.74	20.58	27.47	70.67
12	24.69	21.93	21.3	22.33	32.26	36.89	25.80	31.50	72.79
24	29.72	26.77	26.66	27.18	37.42	43.45	31.89	35.90	77.08
36	32.22	33.83	32.65	29.77	38.71	50.31	33.91	37.73	85.78
72	33.47	34.94	40.65	32.04	40	60.18	35.07	38.46	95.45

β-Cyclodextrin alone has resulted in slower but prolonged release of oils. The application of MCT-βCD had outstand with highly durable essential oil retention lasting for five or more washes and also for longer span. Thus, MCT β-CD proved to be a more valuable host for durable functionalised fabrics. The tensile strength had shown an increase with MCT β-CD (pH 6 and 8); on the other, air permeability had shown a fall and stiffness had increased but moreover, the stability of oils had increased with the modified host. Thus, new genre of novel apparel products having customised aroma can be designed and developed for the fashion savvy consumers.

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