FUNCTIONALIZATION OF OUTDOOR COTTON TEXTILES: COMBINING FRAGRANCE AND UV PROTECTION THROUGH β-CYCLODEXTRIN DERIVATIVE INCLUSION COMPLEXES INFUSED WITH PEPPERMINT AND CLOVE ESSENTIAL OILS

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The polyfunctionalization of cotton textiles for outdoor applications has been successfully achieved through the incorporation of complexes involving monochlorotriazine β-cyclodextrin (mono-CT β-CD) and essential oils of peppermint and clove, resulting in the creation of aromatic and UV protective ensembles. The β-cyclodextrin (β-CD) derivative was synthesized *in vitro*, followed by rigorous characterization and solubility testing to ensure its compatibility with water-based applications. To confirm the successful functionalization, the textiles were subjected to thorough characterization using techniques such as H-NMR and thermogravimetric analysis, verifying the attachment of inclusion complexes of mono-CT β-CD and essential oils onto the fabric. Furthermore, the release kinetics of the native aromatic oils from the cotton textiles were investigated, revealing superior retention of peppermint over that of clove. The impact of inclusion complexes on the release behavior and wash durability of essential oils was also assessed, demonstrating a significant enhancement in aroma retention, compared to unfunctionalized textiles. Additionally, the UV protection properties of the peppermint oil-treated cotton textiles exhibited improved performance against electromagnetic radiation in comparison with their untreated counterparts, further highlighting the efficacy of the polyfunctionalization process for enhancing both fragrance and UV protection in outdoor textiles.

Keywords: polyfunctionalization, inclusion complexes, monochlorotriazine β-cyclodextrin, UV protection

INTRODUCTION

For centuries, people have utilized essential oils for cosmetic reasons and to experience the oils' uplifting effects on their spiritual and emotional well-being. The potency of the purest essential oils surpasses that of the botanical sources from which they are derived. Peppermint oil has various beneficial properties, such as antimicrobial properties, fragrance, UV protection, and mosquito-repellent functions. Peppermint oil encapsulated in plant-based alginate nanocapsules was employed as an antimicrobial agent for cotton fabrics. The nanocapsules effectively reduced *E. coli* and *S. aureus* bacteria, demonstrating durability through multiple washes, while retaining their aromatic properties.[1–3] A nanoemulsion containing peppermint oil has been used on textiles through layer-by-layer techniques to obtain multifunctional properties. The findings indicated 99% antimicrobial efficacy, complete mosquito repellency, and a moderate UV protection factor (UPF 7.28). The fabric retained its multifunctional properties through 20 washing cycles.[4,5] Peppermint and garlic oil mixture finishes were applied on knitted fabric to study mosquito-repellent properties.[6,7]

Similarly, clove oil has biological attributes, such as antifungal, antibacterial, antioxidant, and insecticidal properties. It has been employed in culinary applications for centuries, serving as both a flavoring component and an antimicrobial substance.[8,9] A study reported on using clove oil in CuO/TiO_2 composites for making anti-mosquito and self-cleaning fabrics.[10]

An active lifestyle leads to increased time spent outdoors and higher skin exposure to solar

UV radiation.[11,12] Sunscreens and ordinary lightweight cotton fabrics can help protect the skin to a certain degree, however, using such fabrics alone, without sunscreen, does not provide adequate protection from solar rays, since cotton has a UPF value in the range of 5-8, which is less than the required value of 15. Therefore, there is a dire need for the development of sustainable textiles that can protect the wearer's body from detrimental exposure to UV rays, while also shielding the user from dust and polluted air by providing aroma, and maintaining breathability.[13] Lately, significant focus has been directed towards providing barrier properties to textiles designed for clothing using essential oils and other functional agents to obtain multifunctional properties in terms of UV radiations, antibacterial, fragrance, and others.[14–16]

Cyclodextrins are cyclic oligosaccharides characterized by a truncated cone shape. They possess a hydrophilic surface containing hydroxyl groups and a hydrophobic cavity, enabling the formation of reversible inclusion complexes with various compounds. Amongst the various available CDs commercially, β-cyclodextrin (β-CD) is the most widely used derivative of cyclodextrins, as it is the cheapest of all, being also non-toxic for oral use, causing no skin irritation, no skin sensitization, no mutagenic effects, no water pollution, being biodegradable.[17-18] Inclusion into β-CDs exerts a profound effect on the physico-chemical properties of the guest molecules, as they are temporarily locked or caged within the host cavity, giving rise to beneficial modifications of guest molecules, which are not achievable otherwise, such as control of volatility and sublimation.[19] β-Cyclodextrins find diverse applications in the textile sector, from finishing to filtration. They are also utilized in various other applications, including UV protection, fragrance enhancement, insecticide delivery, and antibacterial finishing.[20] However, β-CD is difficult to dissolve in water and many common solvents,[21] limiting its use and exploitation.

It is evident that β-CD cannot form a direct covalent bond with any textile fiber, but it is capable of forming only hydrogen bonds with cellulose-based materials. Their lack of durability on textile substrates severely limits their effective use as fabric finishing agents. To exploit the benefits of β-CD monomolecular containers, modified cyclodextrins are postulated to form van der Waals, ionic, or covalent bonds with suitable textile surfaces. Of these approaches, the covalently bonded cyclodextrin has been the most successful. There is 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.[22] Monochlorotriazinyl β-cyclodextrin (mono-CT β-CD) is the first reactive cyclodextrin derivative manufactured on an industrial scale. It can permanently bind β-CD to cotton with the conventional reactive dyeing method.

The present paper aims to explore the essential oils of peppermint (PO) and clove (CO) as an exceptional value addition to cotton textile substrates, with inclusion complexes of oils through derivatization of β-CD. These oils have a great potential to protect against UV radiations and microbial development when applied on outer apparel and accessories such as gloves. Also, due to their fragrance, they can have a number of different effects, such as fatigue relief, to eliminate tiredness, promote appetite, reduce anger and tension. Also, cotton fabrics possess good moisture absorbency, comfort, and satisfactory protection against UV. Fabrics featuring ultraviolet protection and antibacterial characteristics can potentially decrease the incidence of skin cancer and mitigate the transmission of infectious diseases.[23,24]

EXPERIMENTAL

Materials

The experiments in the present study utilized 100% cotton fabric obtained from Vardhman Fabrics Pvt. Ltd., located in Ludhiana, India. The composition of the procured fabric is mentioned in Table 1. The chemicals employed in this study were of analytical grade.

Procedure

The β-CD concentration was optimized by determining weight gain and phenolphthalein titration. The weight gain % (*i.e*., wet pick-up) was obtained using the initial weight of the sample before immersion and the final weight of the sample after immersing it into the β-CD solution, followed by padding. A solution of 1% phenolphthalein was formulated using ethanol (80%) to conduct phenolphthalein titration. The pH of the working solution was maintained at 10.5, using sodium hydroxide (0.5 M). The maximum wavelength of the solution, *i.e*., λ_{max} = 558 nm, was measured using a UV-visible spectrophotometer. Further, 1×1 cm β-CD treated fabrics were immersed in a 30 mL of phenolphthalein solution and shaken for 1 hour in an orbital shaker at 100 rpm at 35 °C.

Subsequently, the fabric was removed, and the absorbance of the residual phenolphthalein was assessed at a wavelength λ_{max} of 558 nm, employing a dilution factor of 4.

Table 1
Fabric structure composition

Parameters	Values
Gram per square meter (GSM)	135
Weave	1/1 Plain
Ends per inch (EPI)	76
Picks per inch (PPI)	70
Warp count	42 Ne^S
Weft count	38 Ne^S
Thickness	0.28 mm

To optimize the essential oil concentration, fifteen cotton samples were individually immersed in varying oil concentrations (1% to 15%) for 1 minute. Subsequently, padding (2 dips and 2 nips) was carried out, followed by air-drying at room temperature. The oil extraction process involved taking 0.1 g of each treated sample, immersing it in 100% ethanol with a ratio of 1:50 (oil to ethanol), and heating the test tube at 50 °C for 5 minutes. Then, the samples were removed from the solutions. The absorbance reading of each solution was measured using a spectrophotometer at their respective wavelengths (λ_{max}) for PO and CO.

Following the optimization of β-CD and essential oil concentrations, the synthesis and characterization of mono-CT β-CD were conducted. The synthesis involved mixing 5.5 g of cyanuric chloride (30 mmol) with 30 mL of cold water in a round-bottom flask fixed with a thermometer. Subsequently, 12 mL of NaOH (5 mole/L) was slowly added, and the mixture was stirred until a uniform solution of dichlorotriazine sodium salt was obtained. This solution was then reacted with 11.35 g (10 mmol) of β-CD at a temperature ranging from 5-15 °C. A resulting white precipitate was obtained using acetone, followed by desalting with DMF and re-treatment with acetone to precipitate. The powder was filtered and dried in an oven until a constant weight was achieved. The mono-CT β-CD was characterized through FTIR, elemental analysis, and TGA.

The application of mono-CT β-CD onto the acquired cotton fabric was followed by its characterization. To apply the mono-CT β-CD, the cotton fabric underwent an initial treatment in a 2% sodium carbonate aqueous solution for 2 minutes, followed by drying. Subsequently, the fabric was treated with 90 grams per liter (g/L) of mono-CT β-CD and padded through a padding mangle at a setting of 20 kg/cm^3 to achieve 70-85% wet pick-up by the weight of the fabric. The treated fabric was then dried for 2 minutes at 80 °C and cured in an oven for 3 minutes at 150 °C. Finally, the treated fabric underwent a rinsing process with water to eliminate any untreated chemicals. The fixation of mono-CT β-CD was assessed through weight gain %, FTIR, elemental analysis, and TGA.

Lastly, the application and characterization of essential oils on mono-CT β-CD pretreated cotton were undertaken. Initially, the inclusion complex formation between mono-CT β-CD and essential oils involved mixing 0.35 grams (70 g/L) of mono-CT β-CD with 5 mL (5 mM) of PO and CO. The characterization of the final inclusion compound was conducted through HNMR spectroscopy at SAIF, Punjab University, confirming the formation of the inclusion compound between the reactive host and guest compounds (essential oils). For the application process, the cotton underwent initial treatment with mono-CT β-CD, followed by immersion in 10 mL of PO and CO for 1 minute and subsequent air-drying. The characterization of essential oils on mono-CT β-CD treated cotton was performed using TGA.

Analytical methods

Fragrance release rate: a quantitative evaluation of the fragrance release rate was determined using a UV-visible spectrophotometer. The fragrance was obtained from 0.1 g of each sample immersed in 100% ethanol with a 1:50 ML ratio. Subsequently, the test tube was heated at 50 °C in a water bath for 5 minutes, then cooled, and fabric samples were removed from the solutions. The absorbance of the extracted fragrance was measured at their respective λ_{max}. To assess the fragrance release rate and intensity retained in the treated fabric, readings were taken at 2, 4, 6, 12, 24, 48, and 72 hours. The release rate was calculated using the following formula:

$$\%\ Release\ rate\ of\ fragnance = \frac{Immediate\ concentration\ at\ 0\ hour - Concentration\ after\ observed\ hour}{Immediate\ concentration\ at\ 0\ hour} \quad (1)$$

The performance evaluation of the treated fabric was done with the help of the characterization techniques described below.

Fourier transform infra-red spectroscopy (FTIR): FTIR (CIL Chandigarh, India) was carried out for β-CD, mono-CT β-CD treated sample, cyanuric chloride sample, and control and mono-CT β-CD treated cotton for a sample size of 1-2 g in the range of 400-4000 cm^{-1}.

Elemental analysis (Euro Vector, SAIF, Lucknow) was carried out for mono-CT β-CD treated sample, β-CD sample, control, and mono-CT β-CD treated cotton.

Thermogravimetric analysis (TGA) was done for mono-CT β-CD powder, control sample, mono-CT β-CD treated cotton, and the cotton sample treated with inclusion complex of mono-CT β-CD-oils at [4] 0.1 to 100 °C/min; air was introduced into the samples at a rate of 25 mL/min. TGA was performed at NITRA, Ghaziabad, India.

For *H-NMR*, the sample quantity used was between 5 and 10 mg. An Avance-II (Bruker) instrument was used to analyze the mono-CT β-CD sample, the inclusion complex formed by mono-CT β-CD and PO, CO and for pure PO, CO.

The *ultraviolet protection factor (UPF)* measurements were made as per AATCC 183-2004. The testing was carried out at NITRA, Ghaziabad.

RESULTS AND DISCUSSION

Weight gain %

Cotton was treated with varying concentrations of β-CD using the padding method. It was observed from Figure 1 that the weight of the cotton fabric was increased from 1.93 to 6.23%, as the concentration of β-CD concentration increased from 20 g/L to 70 g/L, and then became constant (6.42-6.83%) at higher concentrations from 80 g/L to 100 g/L. The change in the weight of the treated fabric was attributed to the attachment of β-CD on the fabric surface having substantial molecular weight and the availability of the moieties of the host compound on the fabric.

Assessment of inclusion compound formed by phenolphthalein and β-CD

Phenolphthalein was chosen as an indicator, because it can form a complex with β-CD and undergoes a color change inside the cavity of β-CD. At 60, 70, and 80 g/L β-CD, the lowest absorbance and concentration of phenolphthalein were obtained, indicating the maximum concentration of β-CD moieties with cavities was available for complexation (Fig. 2). This further indicated that, at 60-80 g/L of β-CD on cotton, maximum phenolphthalein molecules were enclosed in the cavities of β-CD in an alkaline solution, where the phenolphthalein dianion was transformed into phenolphthalein lactone form, which proved that at these particular concentrations, most of the cyclodextrin cavities were available and thus utilized for forming the inclusion complex with the guest.[25] Since minimum absorbance was recorded at 60, 70 and 80 g/L, these were selected as optimized concentrations for further work.

Optimization of concentration of essential oils with β-CD

For this, a 70 g/L concentration of β-CD was selected for treating cotton fabric. Table 2 shows the amount of EO used on β-CD padded fabric dipped in the respective oil-ethanol solutions. The optimal complexation occurred within a concentration range of 9-11%. This can be explained by the saturation of β-CD cavities, where no additional cavities were accessible to include guest molecules. The lower quantity of oils within the cavities may be attributed to the presence of some oil on the fabric surface rather than within the cavities.

Characterization of mono-CT β-CD

FTIR, TGA and elemental analysis were performed to characterize the mono-CT β-CD. The solubility analysis of mono-CT β-CD was also done as per the following method. Different concentrations of mono-CT β-CD (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 g/L) were dissolved in water for 30 minutes.

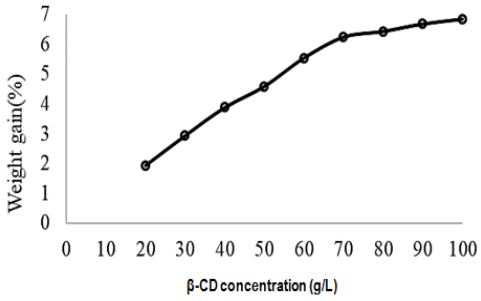

Figure 1: Effect of β-CD concentration on weight of cotton

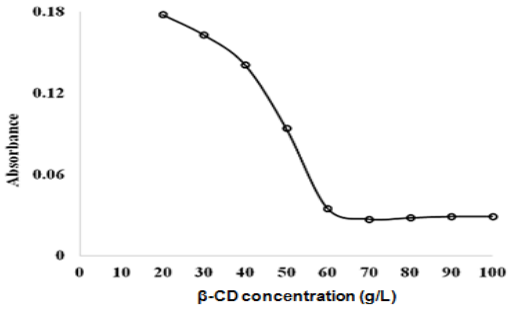

Figure 2: Phenolphthalein titration with β-CD

Table 2
Oil concentration involved in the formation of an inclusion complex with β-CD

Oil concentration (%)	Essential oil used (mg/mL)	
	Clove	Peppermint
1	0.34	0.18
2	1.23	1.57
3	1.56	1.80
4	1.78	2.19
5	2.14	2.20
6	2.56	2.35
7	2.89	2.74
8	3.13	3.02
9	4.45	4.65
10	4.84	4.79
11	5.03	4.72
12	4.78	4.68
13	4.63	4.70
14	4.54	4.69
15	4.52	4.69

Then, the solution was filtered with the help of filter paper. The filter paper was oven-dried and weighed. The filter paper was weighed before and after filtration to get accurate results.

Solubility % was determined according to Equation (2):

$$\text{Solubility \%} = \frac{\text{Initial weight of β CD} - \text{Final weight of β CD}}{\text{Initial weight of β CD}} \times 100 \quad (2)$$

FTIR analysis of mono-CT β-CD

FTIR spectroscopy was employed to analyze the powder form of mono-CT β-CD. The comparative study of FTIR has been done between cyanuric chloride, β-CD, and mono-CT β-CD in the wavelength range from 400 cm^{-1} to 4000 cm^{-1}, as shown in Figure 3. The investigation focused on stretching bonds associated with -OH, ranging from 3388.2 cm^{-1} to 3444.39 cm^{-1}. Additionally, the analysis revealed the presence of a band at 1661 cm^{-1}, a feature that is not present in the characteristic spectra of β-CD and cyanuric chloride. The origin of this band can be attributed to the stretching of the C=O and NH_2 bonds in the synthesized mono-CT-β-CD. Besides, a stretch of Cl-C=N bond at 1081 cm^{-1} in β-CD also present in mono-CT β-CD at 1027 cm^{-1}, which is not available in cyanuric chloride, which is a good indication of the formation of this derivative compound. The observed shifts in ester linkages (C=O) from 1776.3 cm^{-1} to 1777.7 cm^{-1}, and from 1724.1 cm^{-1} to 1725.1 cm^{-1} had been evinced to confirm the modification of β-CD in comparison with cyanuric chloride. Also, the N-C=N group has been observed in cyanuric chloride and mono-CT β-CD, which is not present in unmodified β-CD. Meanwhile, the bands at 948 cm^{-1}, 933 cm^{-1}, and 945 cm^{-1} of cyanuric chloride, β-CD, and mono-CT β-CD show a strong presence of C=CH.

Thermogravimetric analysis of mono-CT β-CD

TGA was performed on pure mono-CT β-CD powder in the temperature range from 50 °C to 1000 °C. The mono-CT β-CD presented three-stage weight loss. At 130 °C, a weight loss of 20% was measured due to the loss of loosely bound water molecules in mono-CT β-CD's cavities (Fig. 4). It was followed by the decomposition of macrocycles at 343 °C, which resulted in a weight loss of 15%. Relatively slow weight decomposition of 40% at 360 °C was due to the thermal degradation of char.

Elemental analysis (EA) of mono-CT β-CD

Elemental analysis was carried out by a Euro Vector instrument to analyze mono-CT β-CD quantitatively. Table 3 shows the percentage distribution of nitrogen, oxygen, and carbon in mono-CT β-CD powder. Nitrogen at 3.71% confirmed the formation of mono-CT β-CD from native β-CD. Nitrogen in the mono-CT-β-CD powder confirms the modification of native β-CD.[26-27]

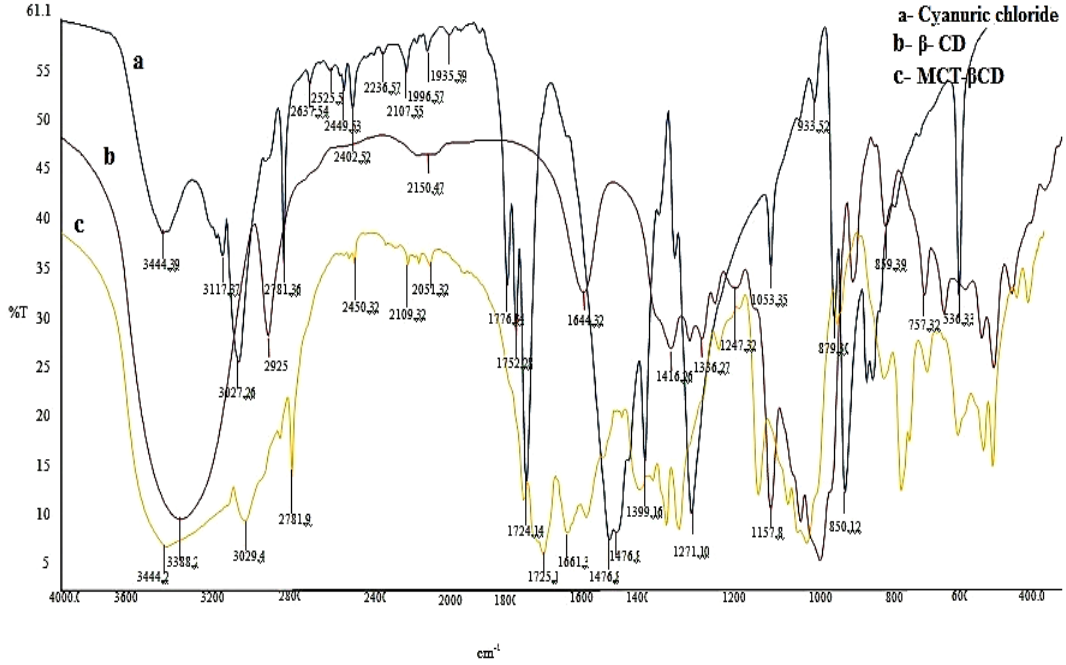

Figure 3: FTIR spectra of (a) cyanuric chloride, (b) β-CD, (c) mono-CT β-CD

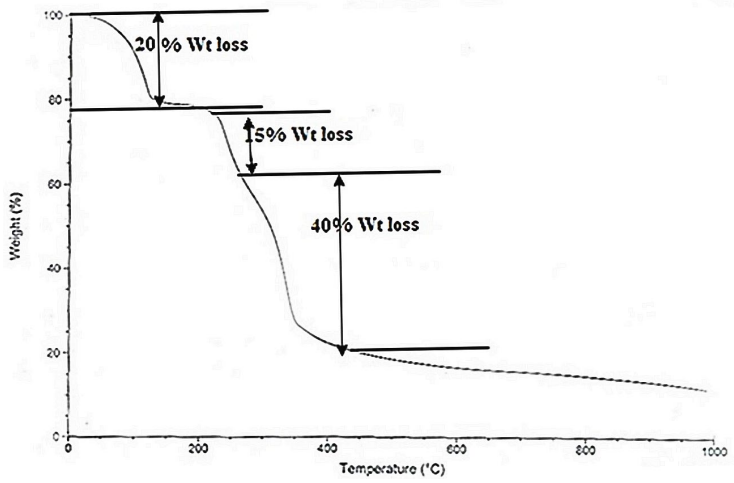

Figure 4: TGA of synthesized mono-CT β-CD

Solubility analysis of mono-CT β-CD

The solubility % of mono-CT β-CD in water is shown in Figure 5. As the concentration of mono-CT β-CD increased from 10 g/L to 100 g/L, there was a gradual decrement in the solubility of mono-CT β-CD in water. This occurs because when a developed complex is introduced to water, it undergoes dissolution, with a minimal displacement by water molecules, establishing equilibrium between the free and complexed mono-CT β-CD and between the dissolved and undissolved complex.

Table 3
Elemental analysis of mono-CT β-CD powder

S.No	Material	Nitrogen (%)	Oxygen (%)	Carbon (%)
1	mono-CT β-CD	3.71	49.93	35.46
2	β-CD	0	52.65	39.64

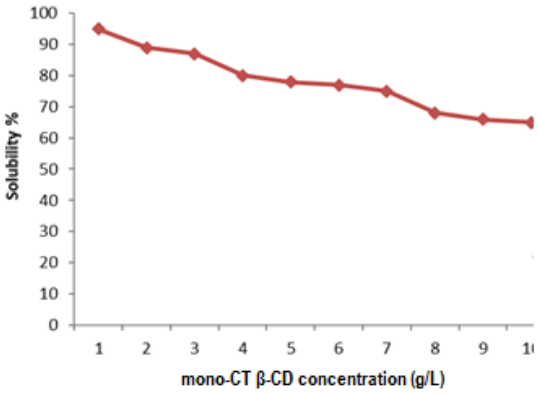

Figure 5: Solubility% of mono-CT β-CD in water

Characterization of mono-CT β-CD on cotton

FTIR analysis of mono-CT β-CD grafted cotton

The structures of the cellulose preparations with grafting were examined through comparative analysis of their IR spectra (4000–400 cm^{-1}), both before and after the integration of mono-CT β-CD. This is an established method for investigating ester cross-linking between mono-CT β-CD and cotton fabrics. The attachment of mono-CT β-CD to cotton fabrics post-curing is demonstrated in Figure 6. The emergence of an additional band at 1718 cm^{-1} suggests the presence of an ester carbonyl group, affirming the existence of a cyclic ring on treated cotton and confirming the anchoring of mono-CT-β-CD onto cotton. This indicated that this group is implicated in the grafting process, and the grafting of cellulose with mono-CT β-CD was complete. Meanwhile, the frequencies for mono-CT β-CD treated fabric were recorded at 3347 cm^{-1}, 2901 cm^{-1}, 1644 cm^{-1}, 1162 cm^{-1}, and 1031 cm^{-1} corresponding to the functional groups O-H, C-H, C=O, C-O-C and C-O stretch, respectively.

Thermogravimetric analysis of mono-CT β-CD grafted cotton

Thermogravimetric analysis was performed on the control and mono-CT β-CD treated cotton in the temperature range from 50 °C to 1000 °C, as shown in Figure 7 and Table 4. The cotton fabric starts decomposing around 150 °C and deteriorates at 250 °C. By the application of mono-CT β-CD on cotton, the net weight loss is reduced, and the decomposition temperature of mono-CT β-CD cotton increases up to 180 °C and in the last stage, it extends up to 400 °C.[9]

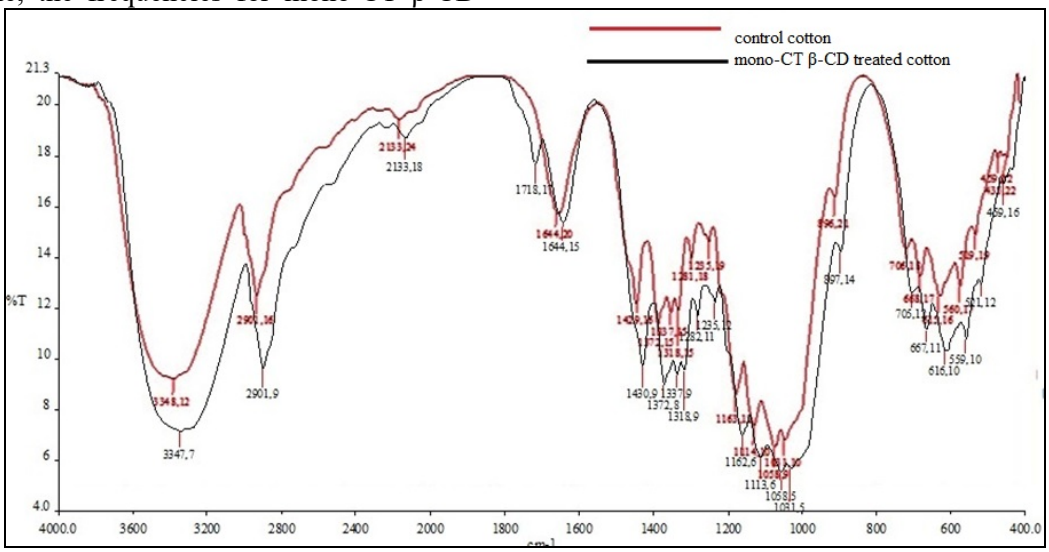

Figure 6: Comparative FTIR spectra of control cotton and mono-CT β-CD treated cotton

Elemental analysis of mono-CT β-CD grafted cotton

Elemental analysis was carried out for control and mono-CT-β-CD treated cotton to know the composition of the samples. Table 5 shows the percentage distribution of nitrogen, oxygen, and carbon in the control and mono-CT β-CD cotton. The presence of nitrogen in mono-CT β-CD treated cotton confirms the attachment of the host to cotton. The nitrogen amount was found to be nil in the control, whereas around 0.41% of the nitrogen in mono-CT β-CD treated cotton confirms the presence of mono-CT β-CD reactive group in cotton.

Table 4
Decomposition temperature and % weight loss of control and mono-CT β-CD treated cotton

Specimen	Temperature	Weight loss (%)	Change
Control	290 °C	-4.5% (0.555 mg)	Loss of absorbed moisture
	383 °C	-76.5% (9.437 mg)	Decomposition of cellulose
	600 °C (above)	-19% (2.34 mg)	Residual char
Mono-CT β-CD treated cotton	250 °C	-5% (0.452 mg)	Loss of moisture from the treated fabric
	370 °C	-75% (7.0 mg)	Decomposition of byproducts of grafted MCT-β-CD on cotton
	600 °C (above)	-20% (1.58 mg)	Char production by combination of by-products of MCT-β-CD and cellulose substrate

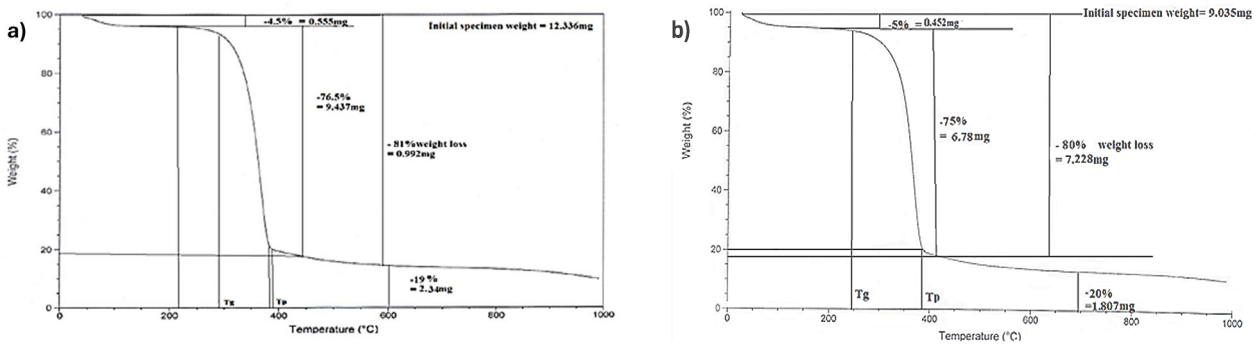

Figure 7: TGA curves of a) control b) mono-CT β-CD treated cotton

Table 5
Elemental analysis of control and mono-CT β-CD treated cotton

S.No	Material	Nitrogen (%)	Oxygen (%)	Carbon (%)
1	Control	0	30.33	42.69
2	Mono-CT β-CD treated cotton	0.41	38	53

Weight gain%

The increased weight of the treated cotton occurs due to the attachment of the cyclodextrin derivative to the cotton through a nucleophilic substitution reaction. This reaction occurs between the cellulose chains' hydroxyl groups and the chlorotriazine ring. The amount of mono-CT β-CD grafted to the fabric is expressed as % weight increase in cotton after grafting it with mono-CT β-CD. 10% weight was gained after grafting.

Application and characterization of inclusion complexes of essential oils and mono-CT β-CD on cotton fabric

The essential oils were applied to the treated cotton with the optimized variables. HNMR was used to characterize inclusion complexes of essential oils and mono-CT β-CD cavities. TGA was used to confirm the presence of inclusion complexes on treated cotton.

HNMR spectroscopy

HNMR spectroscopy stands out as a valuable method for examining host-guest complexation. It was employed to analyze the proton behavior of mono-CT β-CD, essential oils, and the inclusion compound formation of mono-CT β-CD with peppermint and clove oils, as shown in Figures 8 and 9. The investigation of the inclusion complex involving mono-CT β-CD and peppermint/clove was carried out by examining the changes in the chemical shift of both the guest peppermint and host (mono-CT β-CD) protons in the complex. This was done by comparing the chemical shifts of these protons in the complex with those in the accessible components. Introducing a guest molecule into the hydrophobic cavity of mono-CT β-CD led to observable chemical shifts in the HNMR spectra for both the guest and host molecules. Specifically, significant shifts were noted at H3 and H5, located within the inner cavity of mono-CT β-CD, resulting from the inclusion phenomenon. Peppermint and clove also exhibited notable induced shifts in the presence of mono-CT β-CD in their free states. These results confirm the formation of an inclusion complex between the host (mono-CT β-CD) and the guests (peppermint and clove).

TGA

The TGA results for mono-CT β-CD powder, control cotton, mono-CT β-CD treated cotton, and cotton treated with the inclusion complex of mono-CT β-CD and peppermint oil are depicted in Figure 10. A comparative analysis revealed that the peak temperature for the control cotton, initially at 390 °C, shifted to 360 °C after treatment with the reactive host. Furthermore, the cotton treated with the inclusion complex (mono-CT β-CD and oil) exhibited decomposition at 350 °C. This alteration in the thermal behavior of the treated cotton was attributed to the presence of mono-CT β-CD, which has a lower peak temperature of 330 °C, affecting the thermochemical pathway of cellulose decomposition. Additionally, the residual weight percentage increased for the treated cotton compared to the control, with values of 20% for control cotton, 30% for mono-CT β-CD treated cotton, and 35% for cotton treated with the complex, confirming the presence of the reactive host on the cotton.[28]

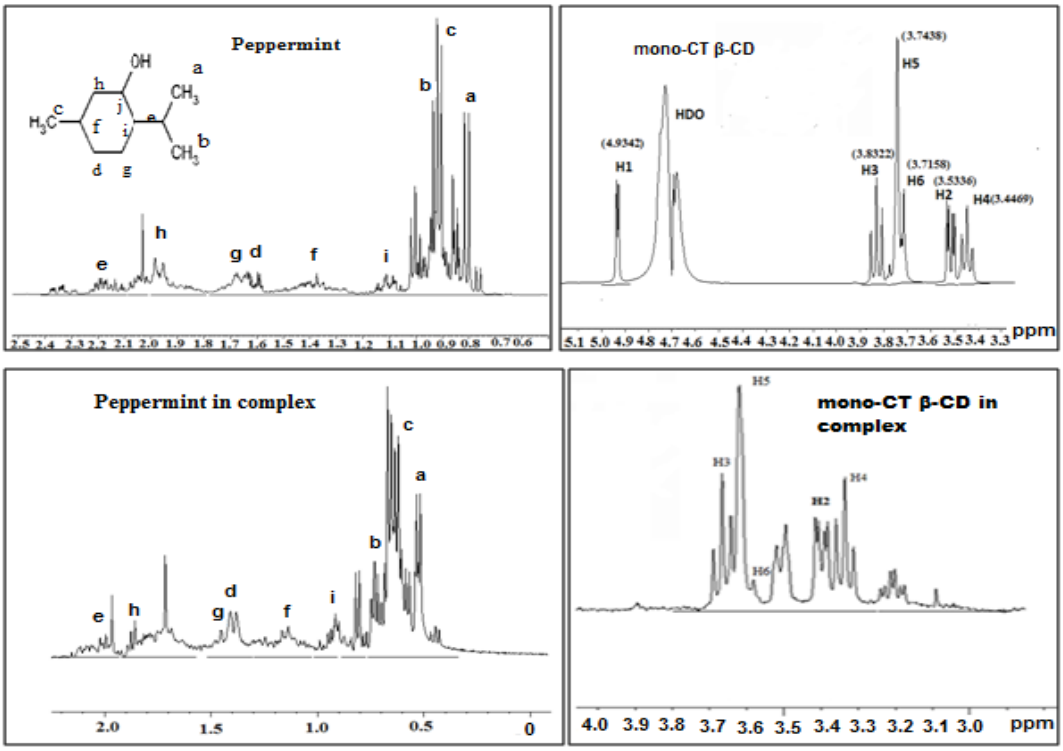

Figure 8: [1]HNMR spectra of peppermint and mono-CT β-CD in free state and complex state

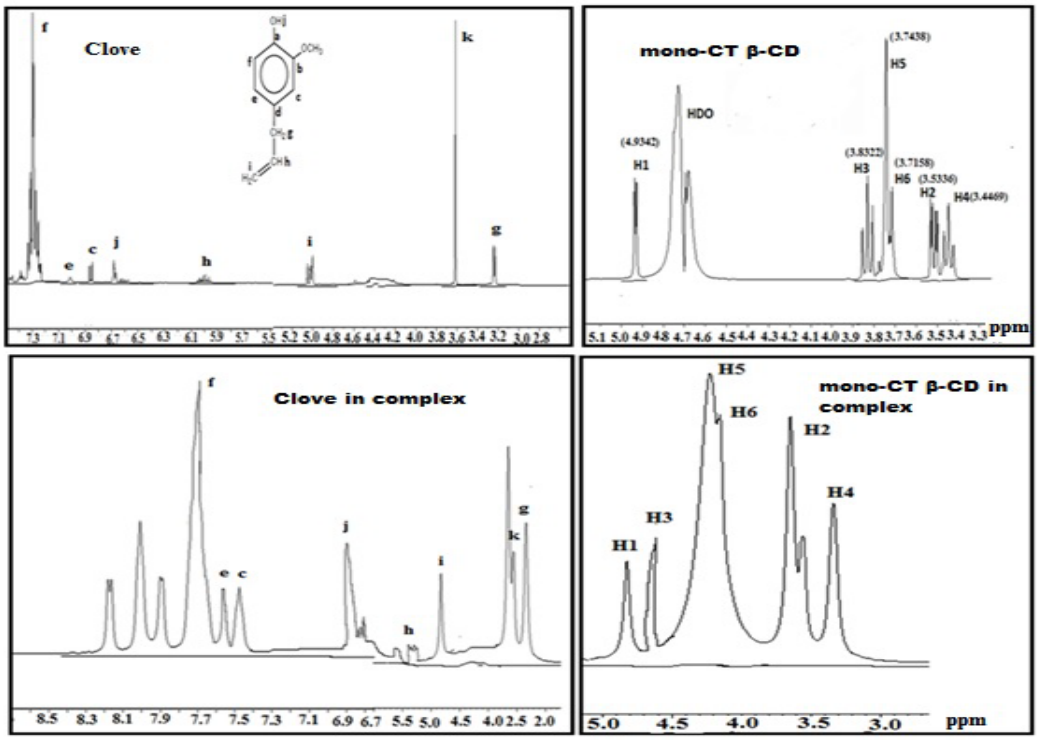

Figure 9: [1]HNMR spectra of clove and mono-CT β-CD in free state and complex state

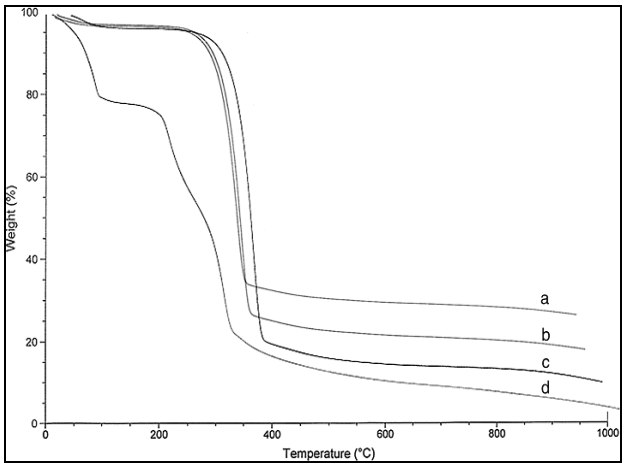

Figure 10: TGA curves for (a) cotton treated with inclusion compound of mono-CT β-CD; (b) cotton treated with mono-CT β-CD; (c) control; (d) mono-CT β-CD

Fragrance release analysis of treated cotton

Fragrance release

Fragrance evaluation of finished cotton was done quantitatively by observing the absorbance of extracted peppermint and clove in ethanol over time. The fragrance release rate (%) is shown in Figure 11. It has been observed from the data that there was an increase in the release rate of fragrance from finished cotton over a span of time. The order of fragrance release rate for both peppermint and clove was 9%>10%>11%, which means the fragrance release rate at 9% concentration of oils was higher, as compared to the other concentrations, because it was noticed that at higher concentrations, more oil adhered to the cavities of the reactive host and thereby increased the oil retention onto cotton fabric. The release rate of peppermint oil is lower, as compared to clove oil, due to a decrement in vapor pressure of peppermint oil, as compared to the clove oil, so the peppermint oil content entrapped in the cavities of mono-CT β-CD was higher than in the case of clove oil.[29]

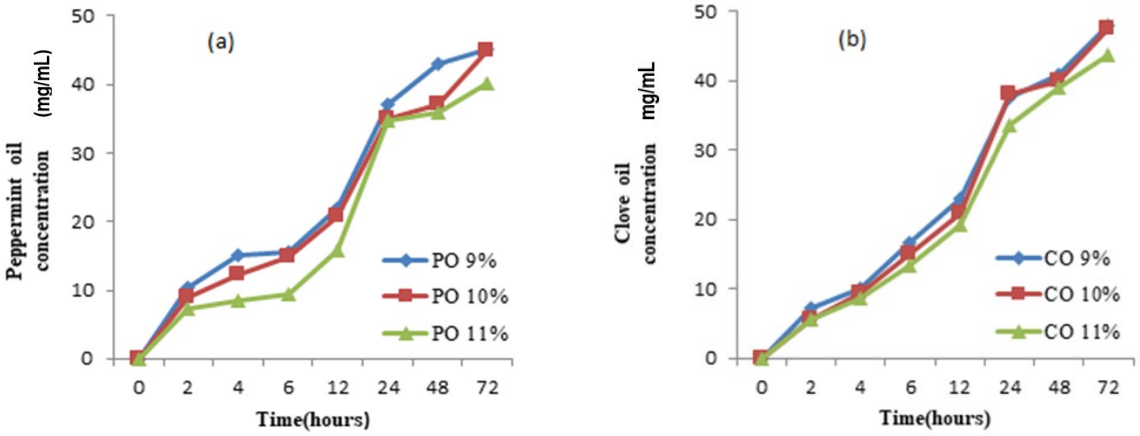

Figure 11: Fragrance release rate for (a) peppermint oil and (b) clove oil

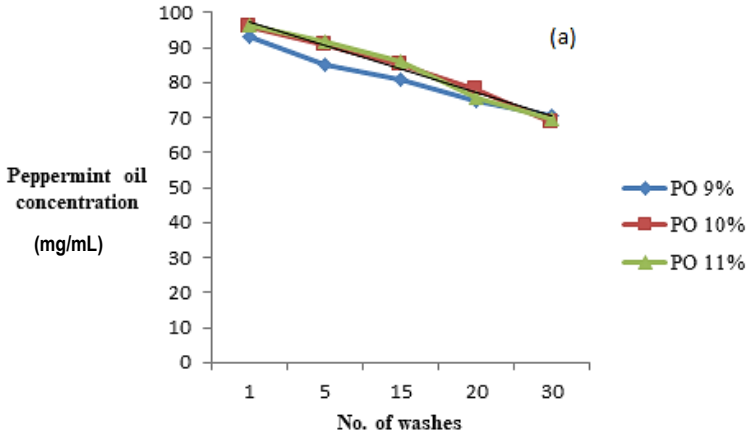

Figure 12: Fragrance retention for (a) peppermint oil and (b) clove oil

Wash durability

% Fragrance retention was taken as the wash durability of the treated cotton up to 30 washes. The fragrance retention after washing has been shown in Figure 12. It has been observed from the data that the % fragrance retention after washing was higher for the cotton treated with 11% peppermint and clove oils, which exhibited greater efficacy compared to other concentrations. This is attributed to the higher concentrations, allowing more oil to be entrapped in the cavities of the reactive host in cotton. Consequently, the fragrances were retained for an extended period in the treated cotton, as the hosts maintained a stable retention position even after washing. Also, fabrics treated with peppermint, clove, jasmine, and cedarwood and anchored using mono-CT β-CD exhibited improved oil retention after washing compared to fabrics anchored with β-CD alone.[29] The fragrance retention decreased with the number of washing cycles because, as the treated cotton was washed out, the amount of oil entrapped in the reactive host from the treated cotton decreased, resulting in a decrease in fragrance retention on treated cotton.

Ultraviolet protection factor (UPF) of treated cotton samples

The effect of incorporating inclusion complexes on the treated fabric's UV protection is expressed as UPF (Table 5). The UPF of the control was 18, which can be explained by its tight fabric structure. Also, there is a significant increase in the UPF values of treated cotton. The UPF of peppermint treated cotton was the highest, superior to both the cotton treated with clove oil and the control. This is due to the composition of PO; menthol, menthone, limonene, β-pinene and α-pinene are its primary components, and they can provide a cooling sensation to the skin against prolonged UV exposure, which is not the case of clove oil. Peppermint oil is also known to

alleviate skin irritation and itchiness and to reduce skin redness caused by inflammation resulting from exposure to UV rays. The oils had made strong complexes with mono-CT β-CD as guests that provided long-lasting ultraviolet protection. Peppermint oil and its extracts exhibited significant antioxidant activity when solar rays hit oil or skin; the antioxidants present in the oil move up and form a protective shield. Peppermint oil also acts as a skin hydrating agent that lasts on skin or clothes for a long time. It also activates melanin (the special antioxidant present in the body) that can disperse 99.9% of absorbed UV radiation as heat, thereby protecting the skin from UV damage.[30] The hydroxycarboxylic acid ester, phenols, and acetates are UV protection filters. Their presence in peppermint oil makes it more active and provides better UV protection against harmful UV rays.

Table 5
UPF activity of control and treated cotton

Samples	UPF value	Rating
Control	17.8	3
Cotton mono-CT β-CD + PO	25.5	1
Cotton mono-CT β-CD + CO	24	2

CONCLUSION

The combined FTIR spectra of mono-CT β-CD, cyanuric chloride, and β-CD confirm the formation of mono-CT β-CD, a reactive host from its reactants, and the FTIR spectra of cotton treated with mono-CT β-CD shows that there has been esterification between mono-CT β-CD and cotton by the presence of the peak at 1162 cm^{-1}. This peak indicates the formation of the carboxylic ester of mono-CT β-CD with the cellulosic hydroxyl groups of cotton. The study of the solubility % of mono-CT β-CD in water reveals that it decreases with an increase in concentration. The reason might be due to the attainment of saturation in mono-CT β-CD, due to which further solubility cannot be obtained in the solution. From the oil concetrations studied (9, 10 and 11%), that of 11% peppermint and clove made more complexes with the substrate, probably due to the fact that, at this concentration, fabric saturation with the oil was achieved. Thus, 11% was selected as the optimum concentration for the application of both peppermint and clove oils on the textiles. Mono-CT β-CD-PO shows the best results of fragrance retention (both before and after washes), compared to the other finishing formulations. The reason is the linkage of mono-CT β-CD and cotton, allowing to retain the fragrances for the longest span of time. The performance evaluation confirmed that mono-CT β-CD-PO was the best among all UV protection finishing formulations. The mono-CT β-CD-PO shows better UV protection activity, as compared to clove oil. This is because the SPF value of peppermint oil is higher than that of clove and other essential oils.

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