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Inclusion complexation of clove oil in MCT β-CD grafted cotton for enhanced stability using nanoemulsion as a sustainable alternative to solvent

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The aim of this study is to investigate the effectiveness of reactive monochlorotriazine β-cyclodextrin (MCT β-CD) in developing durable, fragrance-finished cotton fabrics using clove essential oil applied through solvent and nanoemulsion techniques. Natural essential oils offer desirable sensory and functional attributes; however, their limited durability on textiles necessitates the development of suitable microencapsulation systems. In this work, MCT β-CD is synthesised from β-CD and cyanuric chloride, characterised using FTIR, TGA, SEM, EDS and XRD, and subsequently covalently grafted onto cotton under alkaline conditions. Optimal fixation is achieved using a 70 g/L MCT β-CD solution, as determined through add-on percentage, wash durability and phenolphthalein absorbance analysis. Clove oil is applied to the MCT β-CD finished cotton using both ethanol-based solvent treatment and a sustainably formulated nanoemulsion. The retained oil content is quantified after atmospheric exposure and multiple wash cycles. Results show that MCT β-CD exhibits strong covalent bonding with cotton, resulting in significantly enhanced durability for clove oil through the formation of an inclusion complex. The nanoemulsion method performs comparably to the solvent method, offering an effective and environmentally benign alternative for essential-oil finishing. Thus, the nanoemulsion technique can be utilised efficiently as a sustainable alternative to toxic solvents in essential oil applications, resulting in MCT β-CD finished textiles with multifunctional properties.

Keywords: Cyclodextrin, Clove oil, Fragrance finish, Nanoemulsion, Solvent method, Wash fastness

1 Introduction

Functionalised textiles with fragrance[1], UV protection[2], insecticide delivery[3], antibacterial[4,] mosquito repellent properties[5-9] have great potential in the present scenario. Several microencapsulation techniques enable the utilisation of cyclodextrins (CDs) to play an important role in controlled release phenomena. CDs exhibit a truncated cone shape and are linked by a 1, 4-glucosidic bond, forming a ring structure[10]. These macromolecules are crystalline, homogeneous, water-soluble, biocompatible, and non-hygroscopic, formed by the enzymatic degradation of starch[11]. CDs are classified as α, β, and γ-CD, each containing 6, 7, and 8 glucose units, respectively. They position their primary and secondary hydroxyl groups outwardly in the cyclic structure, making the outer surface hydrophilic. Meanwhile, the inner cavity remains non-hygroscopic and forms inclusion complexes with compatible hydrophobic guest molecules[12]. Moreover, β-CD has been extensively studied and utilised in various medical, pharmaceutical, health, and personal care products to enhance their water solubility, stability, bioavailability, and biocompatibility[13]. β-CD can be attached to the textile by physical adsorption or chemical cross linking[14]. Additionally, the β-CD structure can be modified to impart affinity or reactivity toward the fibres. Several studies have been conducted on the synthesis of reactive CDs capable of forming covalent bonds with cotton through nucleophilic substitution or addition reactions[15]. In the same context, monochlorotriazine β-CD (MCT β-CD) is extensively used as reactive β-CD in the surface modification of textiles for various functional properties[16]. MCT β-CD is utilised for complexation due to its perfect cavity size, effective drug encapsulation, loading accessibility, and reasonably inexpensive cost.

Clove essential oil stands out as one of the most widely utilised and versatile among all essential oils. It contains not only 80 % eugenol, 10–13 % tannin, and different kinds of trienic acid, but also esters, tartaric acid, flavone, and other macromolecular substances. It offers various functional benefits, including antibacterial properties, mosquito repellent

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capabilities[17] and a pleasant fragrance due to the aforesaid constituents. However, at the same time, clove oil exhibits high volatility, limited aqueous solubility, and low stability, which creates a problem in providing a stable fragrance finish. The inclusion of clove oil in a complex with MCT β-CD can provide stability to clove oil against an open atmosphere and multiple wash cycles[18]. Therefore, cavities available in bound MCT β-CD to cotton can be utilised for hosting the essential clove oil for controlled release.

The application of oil on MCT β-CD finished cotton using the solvent method has several drawbacks, including inherent volatility, which increases fire risks during the application procedure and amplifies safety concerns[19]. Besides this, their toxic behaviours contribute to environmental problems such as air pollution and groundwater contamination[20]. Conversely, emulsions represent a safer and more environmentally sustainable alternative to solvents[21,22]. The water-based nanoemulsion significantly reduces the risk of fire and eliminates the need for ventilation systems when used in enclosed spaces. Thus, in contrast to the solvent method, nanoemulsion prevents the release of harmful fumes and disagreeable odours. It is essential to maintain the nanoemulsion's stability, which is achieved by combining essential oils with surfactants that possess the correct HLB values.

The present research work is focused on the synthesis of MCT β-CD from β-CD and cyanuric chloride under alkaline conditions. The synthesised MCT β-CD was characterised by various techniques, including Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy, and scanning electron microscopy analysis, for confirmation. Further, MCT β-CD has been applied to cotton to achieve maximum add-on %. The durability of the inclusion complex is dependent on the stability of MCT β-CD on cotton. Thus, the efficacy of MCT β-CD fixation on cotton is determined against consecutive wash cycles. Thereafter, the application of clove oil on cotton was performed using the solvent and emulsion method. Further, due to a limited study available in the literature on essential oil application on textiles by solvent method versus nano emulsification method, a comparative study with two methods was carried out by assessing the clove oil retention capacity on MCT β-CD treated cotton after exposing cotton samples for different time durations in the open atmospheric conditions, as well as after the consecutive wash cycles.

2 Materials and Methods

2.1 Materials

The 100% plain woven cotton fabric, with a plain weave of 29.97 Ne warp and 20.02 Ne weft yarn count, had an EPI of 85, PPI of 65, and a GSM of 155, which was used in the present investigation. AR grade β-cyclodextrin (β-CD) (MW-1134.98 g/mol), cyanuric chloride (MW-184.41 g/mol), sodium carbonate, sodium hydroxide, ethanol, acetone, dimethyl formamide (DMF), Span 80 (sorbitan oleate having HLB 4.3 and Tween 80 (polysorbate 80 having HLB 15) were procured from SRL, Mumbai, India. Natural essential clove oil (eugenol ~85 %) was procured from SDFL, Mumbai,

2.2 Methods

2.2.1 Synthesis of MCT β-CD Complex

MCT β-CD complex was synthesised using β-CD and cyanuric chloride in alkaline conditions in a two-stage reaction process, reported previously[23]. In the first stage, an aqueous solution of NaOH was added dropwise to the previously prepared cyanuric chloride solution at 5 °C, resulting in a clear solution of the dichlorotriazine sodium salt. In the second stage, dichlorotriazine sodium salt was mixed with β-CD at an alkaline pH of 15 ºC. This facilitates the potential occurrence of the coupling reaction. MCT β-CD complex produced in the reaction was washed with acetone to get the precipitates. Furthermore, desalting was performed using DMF. The produced product was passed through filter paper and dried in a vacuum oven until a constant weight was achieved.

2.2.2 Characterisation of MCT β-CD Complex

Synthesis of MCT β-CD needs controlled reaction conditions; otherwise, another by-product may form. Thus, the detailed required procedure was followed under stringent quality control parameters. The purity of synthesised MCT β-CD was confirmed through water-solubility testing, melting point determination, Fourier transform infrared spectroscopy (FTIR), Energy dispersive X-ray spectroscopy (EDS), and thermogravimetric analysis (TGA) before grafting application to cotton textiles[24].

2.2.3 Grafting of MCT β-CD Complex on Cotton

The MCT β-CD tends to react with cotton in alkaline conditions by nucleophilic substitution reaction. Thus, varying concentrations of MCT β-CD solutions, i.e., 10, 30, 50, 70, and 90 g/L, were applied to cotton to achieve its maximum fixation or add on

by covalent bond formation. Thus, cotton samples were immersed in the respective solutions of MCT β-CD for 10 min at pH 9 and material-to-liquor ratio (MLR) 1:15. Subsequently, cotton samples were taken out from the solution and passed through a padding mangle at 100% expression, followed by drying at 55 °C to avoid the hydrolysis of MCT β-CD molecules. Thereafter, curing was performed at 125 °C for effective fixation of the reactive host on the cotton samples. Furthermore, the poorly adhered hydrolysed MCT β-CD molecules were removed from the cotton fabric by a soaping treatment.

2.2.4 Determination of Bound MCT β-CD Amount on Grafted Cotton Sample

The amount of MCT β-CD bound to cotton as per the aforesaid treatment was optimised by calculating the increase in weight of the cotton samples and the phenolphthalein absorption test method[25]. MCT β-CD forms a strong covalent bond with cotton, although it may hydrolyse and form a weak hydrogen bond with cotton. Thus, the durability of MCT β-CD on cotton was evaluated by determining the amount of residual MCT β-CD present on cotton samples after multiple wash cycles on a launderometer. Washing of MCT β-CD finished cotton samples was carried out in triplicate on a launderometer using a 5g/L soap and 3 g/L Na_2CO_3 solution, with an MLR of 1:50 at 60 ºC for 30 min. The aforesaid weight gain and wash durability experiments were performed in triplicate to minimise the error.

The amount of MCT β-CD present in finished cotton can also be estimated indirectly by measuring the phenolphthalein molecules that are absorbed by the finished cotton sample[24,25]. The absorbance value of the phenolphthalein standard solution at λ_{max} (553nm) decreases with an increased MCT β-CD amount on finished cotton. Thus, the durability of bound MCT β-CD on cotton was determined by standard phenolphthalein solution after consecutive 1, 2, 3, 4, 5, and 6 wash cycles.

2.2.5 Characterisation of MCT β-CD Finished Cotton and MCT β-CD Finished Clove Oil Treated Cotton

MCT β-CD grafted cotton was characterised by FTIR, which provides structural information on the MCT β-CD complex formed and the interactions between the host and guest molecules. FTIR spectra were recorded using an FTIR Spectrometer (Bruker, Germany). Scanning electron microscopy analysis was employed to investigate the impact of grafting the MCT β-CD complex on the morphology of cotton fabric. Surface morphology was examined using SEM (ZEISS, Germany). Elemental analysis (Ametek, Germany), thermogravimetric analysis (PerkinElmer, USA), and XRD studies (D8 Advance Eco diffractometer, Bruker, Germany) were conducted to evaluate the chemical composition, thermal stability, and crystalline structure changes.

2.3 Application of Clove Oil on MCT β-CD Finished Cotton

Clove oil was loaded onto MCT β-CD-finished cotton using solvent and emulsion methods for a comparison of functional performance. In the solvent method, 4%, 8%, and 10% clove oil solutions in ethanol were applied using the pad–dry method (100 % expression), followed by drying at 25˚C for 3 min, allowing the ethanol to evaporate[26]. In the emulsion method, a 4% clove-oil nanoemulsion was applied similarly and dried at 25 ˚C for 15 min. In both cases, the amount of clove oil taken up by MCT β-CD finished cotton was determined by extracting the oil in 100% ethanol and analysed on a UV Visible spectrophotometer at 280 nm using a standard calibration curve of clove oil as mentioned in section 2.3.2.

2.3.1 Preparation of Nanoemulsion

Several emulsions with varying HLB values were prepared by varying the blend proportions of Span 80 and Tween 80[27]. Preliminary experiments revealed that a blend of Span 80 and Tween 80 in a 23/77 proportion provided a stable emulsion at an HLB value of 12.5. Thus, the same proportion was taken for further formulation. Oil-in-water (o/w) emulsions of clove oil, i.e., 1, 2, 4, 6, 8, and 10% (w/w), were prepared. After the aqueous phase reached 45 ± 5 °C, the oily phase, along with an equal amount of emulsifier, was added to the aqueous phase under magnetic stirring (REMI, Mumbai) at 750 rpm for 90 min. Final homogenisation was achieved using ultrasonication (Sonics Vibracell, USA) for 5 min. Emulsions were monitored for 7 days for phase separation, creaming, and sedimentation[28]. The mean droplet size was also determined, with the average droplet size expressed as the mean diameter.

2.3.2 Standard Calibration Curve of Clove Oil

Clove oil solutions in 100 % ethanol (0.0001, 0.0002, 0.0004, 0.0006, 0.0008, 0.001 %) were prepared, and absorbance was observed at 280 nm[29] using a UV/Visible spectrophotometer (Perkin Elmer,

United States). A calibration curve was plotted between concentration and absorbance.

2.3.3 Optimisation and Stability Analysis of Clove Oil on MCT B-CD Finished Cotton

The stability of clove oil on treated cotton was evaluated by assessing fragrance intensity and functional durability after storage at 30 °C and 65 % RH for 2, 4, 6, and 8 days, as well as after multiple washes. Fragrance was assessed using a scratch-and-sniff test by a trained panel (rating scale 1–5). In this context, a 10 cm × 10 cm-sized cotton sample treated with clove oil was observed. The clove oil exclusively held within MCT β-CD cavities was estimated by subtracting the oil uptake of untreated cotton from that of treated cotton. Samples were further characterised by SEM and FTIR.

2.3.4 Particle Size Analysis of Nanoemulsion

Particle size distribution of the nanoemulsion was measured using a dynamic light scattering device (Nano-ZS Malvern Instrument, UK). Samples were diluted 1:20 with double-distilled water to avoid multiple scattering, and the mean particle diameter (z-average) was recorded.

3 Results and Discussion

3.1 Synthesis and Characterisation of MCT β-CD Complex

The MCT β-CD complex is synthesised from β-CD and cyanuric chloride with a reaction yield of 68%. The product is characterised using the solubility test, elemental analysis, FTIR, TGA, and XRD.

β-CD exhibits low solubility in water due to its crystalline structure, which features strong molecular bonding and a high crystal lattice energy. Its secondary hydroxyl groups form intramolecular hydrogen bonds, restricting hydration and promoting aggregation, which further reduces solubility. In contrast, MCT β-CD exhibits higher solubility due to reduced ring strain and improved interaction with water.

Solubility testing of β-CD and MCT β-CD (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 g/L) shows a decrease in solubility with increasing concentration; however, MCT β-CD consistently remains more soluble, confirming successful modification.

Elemental analysis of MCT β-CD shows 3.98% nitrogen and 1.65% chlorine (Fig. 1), confirming the incorporation of the triazine ring, which is consistent with earlier reported literature[29]. Additional peaks arise from reactant, sodium ions, and other byproducts formed during the synthesis of MCT β-CD. These results agree with earlier reports[29] and validate the formation of the substituted MCT β-CD.

The FTIR spectra of MCT β-CD complex, β-CD powder, and cyanuric chloride powder are shown in Fig. 2. The spectrum of MCT β-CD complex presents strong absorption band at 1150cm^{-1} corresponding to C-O stretching, an additional absorption peak of 2913 cm^{-1} corresponding to C-H stretch, 1658 cm^{-1} peak implying to C-N stretch, express a broad peak at 3285 cm^{-1}, which impute to O–H stretch[30], and the

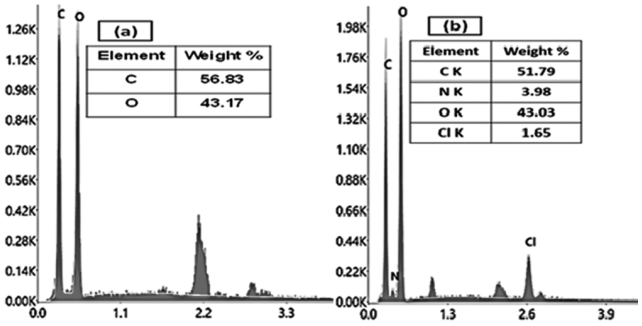

Fig. 1 — Elemental analysis of (a) β-CD and (b) MCT β-CD

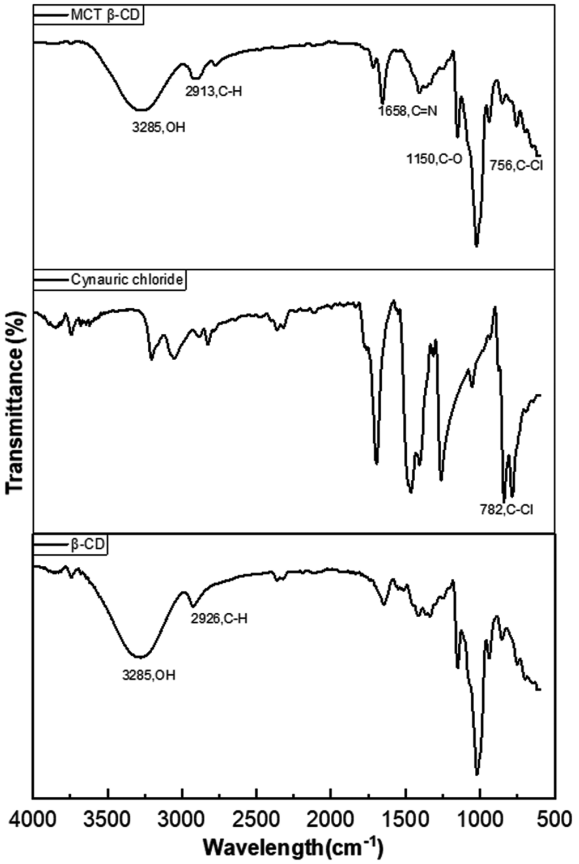

Fig. 2 — FTIR comparative spectra of β-CD, cyanuric chloride and synthesised MCT β-CD

absorption bands at 756 cm^{-1} which shows of C-Cl stretch indicating the involvement of chlorine atom[31]. Also, a strong band at 759 cm^{-1} C–Cl is absent in the IR spectra of β-CD powder, whereas O-H stretch and C-H stretch are observed in β-CD powder at 3285 cm^{-1} and 2926 cm^{-1}. The obtained FTIR curve of the synthesised MCT β-CD complex aligns with previously reported data30-32, confirming the formation of the MCT β-CD complex.

β-CD powder and synthesised MCT β-CD compound exhibit thermal decomposition as a measure of percentage weight reduction in TGA analysis (Fig. 3). The continuous loss of MCT β-CD powder up to 10 % of its weight is observed due to the approximate loss of water molecules when the temperature is raised from 29 ºC to 105 ºC. Thereafter, a weight loss of 2.5% is observed due to the loss of remaining moisture content when the temperature is raised to 220 °C. Further, up to 330 °C, a solid-to-liquid phase transition is observed, accompanied by dehydration and bond cleavage during the thermal degradation of MCT β-CD powder. The formed pyrolytic byproducts, such as H_2O, CO_2, CO, and hydrocarbons, evaporate rapidly at high temperatures, resulting in a weight loss of approximately 55%[32,33]. Then, the second stage of thermal degradation of the char results in a weight loss of approximately 10% when the temperature reaches 440 °C. Whereas β-CD displays weight loss in two regions (Fig. 3). Initially, the weight loss of β-CD occurred upon reaching approximately 71 °C due to the dehydration of water, and thereafter, major weight loss took place due to the decomposition of macrocycles at around 320 °C[34]. It can be observed from the TGA curves that the synthesised MCT β-CD exhibits less thermal stability than β-CD up to 335 °C, but thereafter it shows more thermal stability, consistent with earlier reports[29,30].

XRD analysis shows that the absorption peaks of β-CD at 9 °C, 19 °C, and 20 °C sharply diminish or disappear in the MCT β-CD (Fig. 4). In addition, the characteristic peaks of β-CD at 12 °C, 15 °C, 18 °C, and 28 °C disappear in the MCT β-CD complex. The XRD curves of MCT β-CD are significantly different from β-CD due to the presence of reactive sites in MCT β-CD. The XRD curves affirm the synthesis of MCT β-CD, consistent with earlier literature[29].

Following this confirmation, MCT β-CD is applied to bleached cotton for further optimisation studies.

3.2 Optimisation of MCT β-CD Complex Concentration on Cotton

Different concentrations of phenolphthalein solution (0.1% to 1%) are prepared, and their absorbance at 553 nm is determined to create a phenolphthalein absorbance standard curve. The obtained calibration curve gives a linear equation ($y = 0.07x - 0.0992$, $R^2 = 0.9868$). The absorbance of the phenolphthalein solution decreases with increasing MCT β-CD concentration due to the formation of an inclusion complex. The decrease in absorbance of the phenolphthalein solution is directly proportional to the increase in MCT β-CD concentration. Thus, the prepared calibration curve is used to quantify the bound MCT β-CD on the cotton fabric[5,25].

Weight add-on increases linearly from 2.00% to 9.24% as the MCT β-CD concentration increases from 10 to 90 g/L in a linear equation ($y = 0.7107x + 1.3434$; $R^2 = 0.9809$). However, concentrations above 70 g/L stiffen the fabric; therefore, 70 g/L is selected as the optimum concentration.

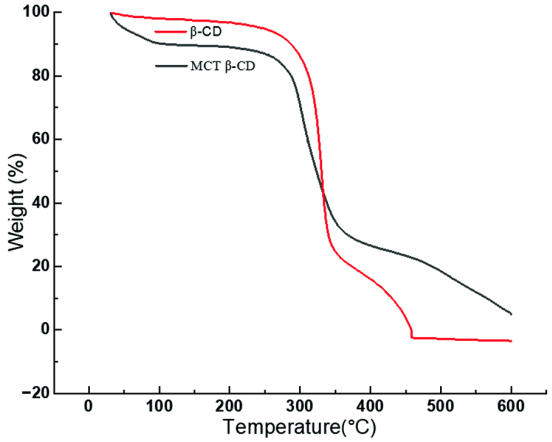

Fig. 3 — TGA spectra of β-CD and MCT β-CD

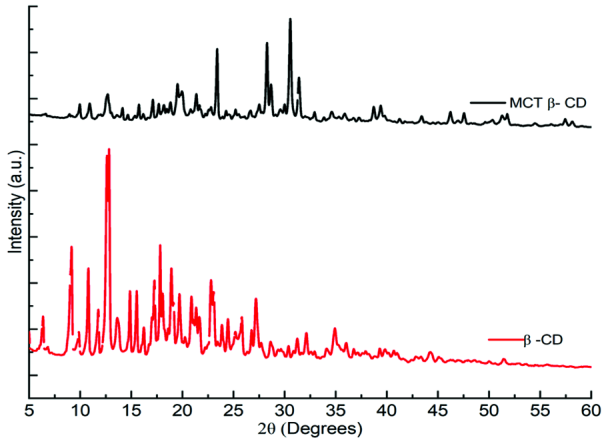

Fig. 4 — XRD patterns of β-CD and MCT β-CD

Weight loss in MCT β-CD finished cotton due to washing is observed up to six wash cycles, as shown in Table 1. Samples were taken in triplicate to determine the average weight loss over multiple wash cycles. It is observed that more weight loss occurs in the initial wash cycles, as physically adhered MCT β-CD is easier to wash off the fabric surface. In the later wash cycles, lesser weight loss is observed as physically adhered MCT β-CD is nominally available, whereas covalently bound MCT β-CD is difficult to wash away from the cotton surface. In addition, an increase in the concentration of MCT β-CD on cotton is accompanied by a corresponding increase in physical adsorption, potentially attributed to the elevated viscosity, which hinders the penetration of MCT β-CD into the cotton's interior. Due to the above reason, the 70 g/L concentration is optimised for application on cotton, achieving 5.97% add-on and 4.45% residual add-on on cotton even after 6 wash cycles. The aforementioned result indicates that molecules are strongly bound by a covalent bond, allowing them to efficiently hold clove oil through inclusion complexation for further studies.

The durability analysis of MCT β-CD finished cotton is also performed using a phenolphthalein solution, in which a slight increase in absorbance is observed, which is speculated to be the result of a small amount of MCT β-CD being gradually eliminated over the course of the washing cycles. The results obtained are in accordance with Table 1.

3.3 Application of Clove Oil on MCT β-CD Finished Cotton

Clove oil is applied to MCT β-CD using both a solvent method and an oil-in-water nanoemulsion method.

3.3.1 Optimisation of Clove Oil Concentration (Solvent Method)

The optimisation of clove oil concentration on MCT β-CD finished cotton is carried out by measuring the weight pick-up percentage of fabric samples after applying concentrations of clove oil, namely 1%, 2%, 4%, 6%, 8%, 10%, 12%, and 14%. Clove oil uptake increases with concentration up to 10 %, after which saturation occurs due to the limited number of empty MCT β-CD cavities for the inclusion complex. Based on this, 4%, 8%, and 10% clove oil are selected for subsequent experiments.

3.3.2 Formulation of Nanoemulsion and its Particle Size Analysis

Oil-in-water emulsions containing 1–10 % clove oil are prepared. It is observed that 1, 2, and 4 % clove oil formulations give stable emulsions, whereas 6, 8, and 10 % o/w formulations provide unstable emulsions, due to phase separation and sedimentation[35,36]. Thus, for future studies, 4 % clove oil in water emulsion is optimised for application on MCT β-CD finished cotton, with an average droplet size of 277.5 nm (Fig. 5).

3.3.3 Standard Absorbance Curve of Clove Essential Oil

The absorbance of clove oil with different concentrations in ethanol is measured at 280 nm using a UV/Visible spectrophotometer. The clove oil calibration curve ($y = 0.1408x - 0.1968$, $R^2 = 0.9765$) enables quantification of retained clove oil in treated fabrics.

3.3.4 Stability Against Atmospheric Exposure

As shown in Tables 2 and 3, clove oil, which forms an inclusion complex with MCT β-CD, is more stable than unfinished cotton when exposed to environmental conditions. Clove oil retention is

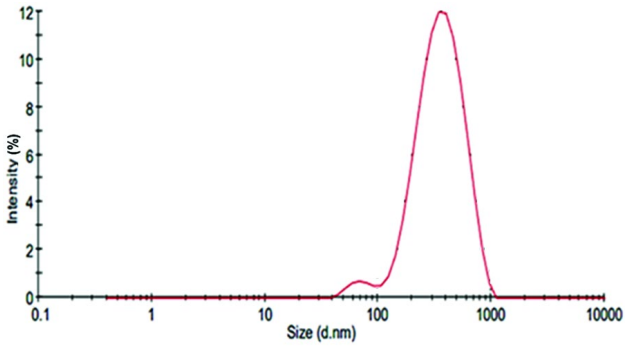

Fig. 5 — Particle size distribution of the 4 % clove oil nanoemulsion

Table 1 — Weight loss of MCT β-CD finished cotton after consecutive wash cycles

MCT β-CD conc., g/L	Initial add on, %	1st wash, %	2nd wash, %	3rd wash, %	4th wash, %	5th wash, %	6th wash, %
10	2.00	1.74	1.50	1.47	1.45	1.43	1.42
30	3.93	3.69	3.36	3.25	3.20	3.15	3.00
50	4.49	4.14	3.70	3.58	3.47	3.37	3.33
70	5.97	5.50	4.98	4.7	4.67	4.54	4.45
90	9.24	8.37	7.58	7.26	7.15	7.01	6.86

Table 2 — Clove oil retention in unfinished and MCT β-CD finished cotton using the solvent method

Days	4 % on unfinished cotton, % owf	4 % on MCT β-CD finished cotton, % owf	Inclusion complex in 4%	8 % on unfinished cotton, % owf	8 % on MCT β-CD finished cotton, % owf	Inclusion complex in 8%	10 % on unfinished cotton, % owf	10 % on MCT β-CD finished cotton, % owf	Inclusion complex in 10 %
0	4.80	5.76	0.96	6.14	8.02	1.88	6.71	8.73	2.02
1	3.27	4.22	0.95	5.08	6.22	1.14	5.61	7.3	1.69
5	2.5	3.5	0.95	3.61	4.57	0.96	4.18	5.16	0.98
7	2.13	3.06	0.93	3.41	4.35	0.94	3.96	5	0.94

Table 3 — Clove oil retention in unfinished and MCT β-CD finished cotton using the emulsion method

Days	4 % on unfinished cotton, % owf	4 % on MCT β-CD finished cotton, % owf	Inclusion complex in 4 %
0	4.49	5.48	0.99
1	3.51	4.47	0.96
5	2.71	3.66	0.95
7	2.67	3.61	0.94

Table 4 — Clove oil retention in unfinished and MCT β-CD finished cotton across wash cycles (solvent method)

No. of wash cycles	4 % on unfinished cotton, % owf	4 % on MCT β-CD finished cotton, % owf	Inclusion complex in 4 %	8 % on unfinished cotton, % owf	8 % on MCT β-CD finished cotton, % owf	Inclusion complex in 8 %	10 % on unfinished cotton, % owf	10 % on MCT β-CD finished cotton, % owf	Inclusion complex in 10 %
0	4.80	5.76	0.96	6.14	8.02	1.88	6.71	8.73	2.02
1	2.56	3.51	0.95	4	5.74	1.74	3.88	5.53	1.65
2	2.31	3.24	0.93	3.26	4.82	1.56	3.34	4.55	1.21
3	2.27	3.17	0.90	2.87	4.1	1.23	2.92	4.04	1.12
4	2.13	3.02	0.89	2.7	3.93	1.23	2.86	3.98	1.12

Table 5 — Clove oil retention in unfinished and MCT β-CD finished cotton across wash cycles (emulsion method)

No. of wash cycles	4 % on MCT β-CD unfinished cotton, % owf	4 % on MCT β-CD finished cotton, % owf	Inclusion complex in 4 %
0	4.50	5.48	0.99
1	2.32	3.27	0.95
2	1.98	2.91	0.93
3	1.92	2.84	0.92
4	1.84	2.75	0.91

higher in MCT β-CD finished cotton than in unfinished cotton. Rapid initial loss occurs due to evaporation of superficially absorbed oil, followed by slower loss from inclusion complexes. The maximum inclusion complex is 2.02% (w/w) for 10% clove oil in the solvent method. Comparison of solvent and emulsion methods at 4% shows similar inclusion complex values (0.96% vs 0.99% w/w). Whereas 0.93% (w/w) and 0.94% (w/w) clove oil remained as an inclusion complex even after 7 days of exposure in an atmosphere of MCT β-CD finished cotton samples for solvent and emulsion oil application methods, respectively. Thus, there is no significant difference found in retained clove oil by the fabric samples when the emulsion method was used as an alternative to the solvent method. Similar trends are observed even after fabric samples are exposed for several days.

3.3.5 Wash Durability of Clove Oil Treated MCT β-CD Finished Cotton

The MCT β-CD finished, and unfinished cotton samples are treated with 4, 8, and 10 % clove oil with solvent, as well as 4 % with the emulsion method and are washed up to five wash cycles. The concentration of clove oil retained by fabric samples in the solvent and emulsion methods is shown in Tables 4 and 5, respectively. With repeated washing, clove oil loss is rapid after the first wash and slower thereafter due to the stability of inclusion complexes. After four washes, 0.89 % (solvent) and 0.91 % (emulsion) of clove oil remain bound through inclusion. The performance of both methods is comparable; however, the emulsion method is environmentally advantageous as it eliminates the use of ethanol.

The current method of retaining clove oil analysis is based on the spectroscopy method, which utilises a

standard clove oil absorption curve. Although the lipophilic segment of surfactant may also get entrapped in cavities of MCT β-CD, as well as having significant absorption capability at 280 nm. The clove oil retention can be compromised due to the oily segments of the surfactant in the limited cavity of entrapping MCT β-CD. Thus, qualitative evaluation of retained clove oil by the fabric is also performed using a sniff rating test. In addition, the presence of surfactant, if any, in the cavities of MCT β-CD was analysed by FTIR.

3.3.6 Qualitative Evaluation of Fragrance Release from Cotton Samples

Fragrance assessment by a 14-member panel shows rapid fragrance loss in unfinished cotton due to a lack of inclusion sites (Table 6). MCT β-CD finished cotton retains fragrance for longer using both methods. The solvent method provides slightly higher fragrance intensity, likely because surfactants from the emulsion occupy some β-CD cavities. However, the emulsion method remains an attractive, eco-friendly alternative.

3.4 Characterisation of Clove Oil Treated MCT β-CD Finished and Unfinished Cotton

3.4.1 Sem Analysis

SEM images show that the surface of unfinished cotton is smooth, whereas the surface of MCT β-CD finished cotton becomes rough due to the deposition of MCT β-CD on cotton (Fig. 6). Clove oil treatment does not alter morphology significantly. Even after

Table 6 — Qualitative fragrance rating of clove-oil-treated MCT β-CD finished and unfinished cotton after atmospheric exposure and multiple wash cycles

Method used	Atmospheric exposure, days						Wash cycles					
	0	1	5	7	10	15	0	1	2	3	4	5
	Clove oil rating											
Clove oil treatment on unfinished cotton (solvent method)	5	3	2	2	1	1	5	3	3	2	1	1
Clove oil treatment on MCT β-CD finished cotton (solvent method)	5	4	3-4	3-4	3	2	5	4	3-4	3	3	2
Clove oil treatment on unfinished cotton (emulsion method)	5	3	2	1-2	1	1	5	3	2	1	1	1
Clove oil treatment on MCT β-CD finished cotton (emulsion method)	5	4-3	3	3-4	3	2	5	4-3	3	3-2	2	2

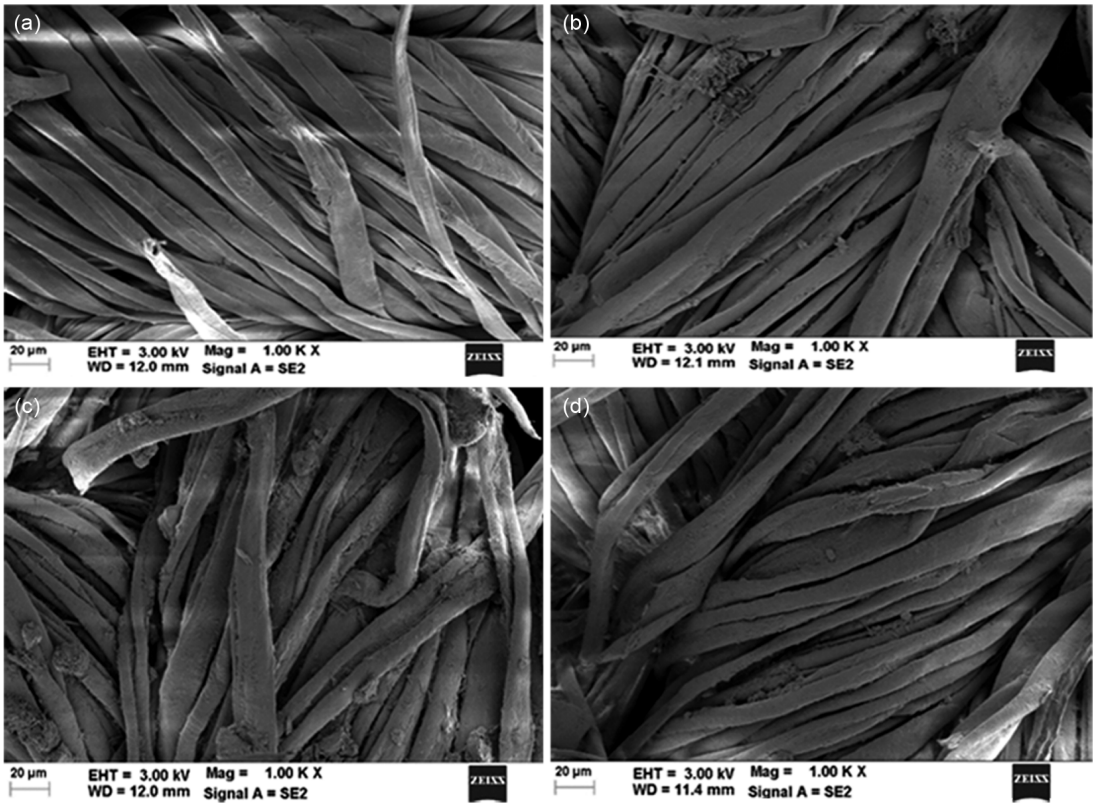

Fig. 6 — SEM image of (a) unfinished cotton, (b) MCT β-CD finished cotton, (c) MCT β-CD finished and clove oil-treated cotton, and (d) MCT β-CD finished clove oil-treated cotton after 6th wash

six washes, the fibre surface remains rough, indicating stable deposition of MCT β-CD.

3.4.2 FTIR Analysis of MCT β-CD Finished and MCT β-CD Finished Clove Oil Treated Cotton

FTIR spectra confirm successful fixation of MCT β-CD on cotton through characteristic ester and triazine peaks (Fig. 7). It is observed that O-H spectra in the range 3200-3400 cm^{-1} show the presence of a hydrophilic group in control cotton [Fig. 7(a)]. Furthermore, the carbon atoms in the cyclic ring are observed in a band at 1018 cm^{-1} in samples A, B, D, and G, indicating a cellulosic structure characteristic of cotton. The unique bands in the IR spectra of MCT β-CD treated Cotton (B) are recorded at 2920 due to C–H stretching and at 1640 cm^{-1} due to C=N stretching. The IR spectra of MCT β-CD finished cotton (B), at 1745 cm^{-1} and 1309 cm^{-1}, are observed due to the C-O stretching vibration of ester linkage in modified MCT β-CD finished cotton, whereas it is not particularly intense in control cotton (A). It is an indicator of an ester carbonyl group and verifies the presence of a cyclic ring on treated cotton, which has already proven the fixation of MCT β-CD on cotton. Also, a strong band at 756 cm^{-1} (C–Cl) is absent in the IR spectra of MCT β-CD finished cotton. FTIR spectra of MCT β-CD finished clove oil treated cotton by solvent method (D) are observed at 3310 cm^{-1} due to hydroxyl O-H stretch and at 1510 cm^{-1} due to aromatic C=C Stretching, which confirms the presence of clove oil, eugenol acetate and methyl 2-hydroxybenzoate[37]. The C-O stretching vibration of phenolic hydroxyl at 1265 cm^{-1}, while the C-O-C stretching vibration of aromatic ether at 1025 cm^{-1}[38] is observed in clove oils due to its key group including phenolic, hydroxyl, benzene ring, double bond, -O-, etc. Tartaric acid and other substances are also seen. As a result, carboxyl and ketone groups are present in clove oil[39]. Thus, the obtained FTIR spectra of clove oil, MCT β-CD finished cotton, and clove oil treated samples are in line with earlier reported literature[38,39].

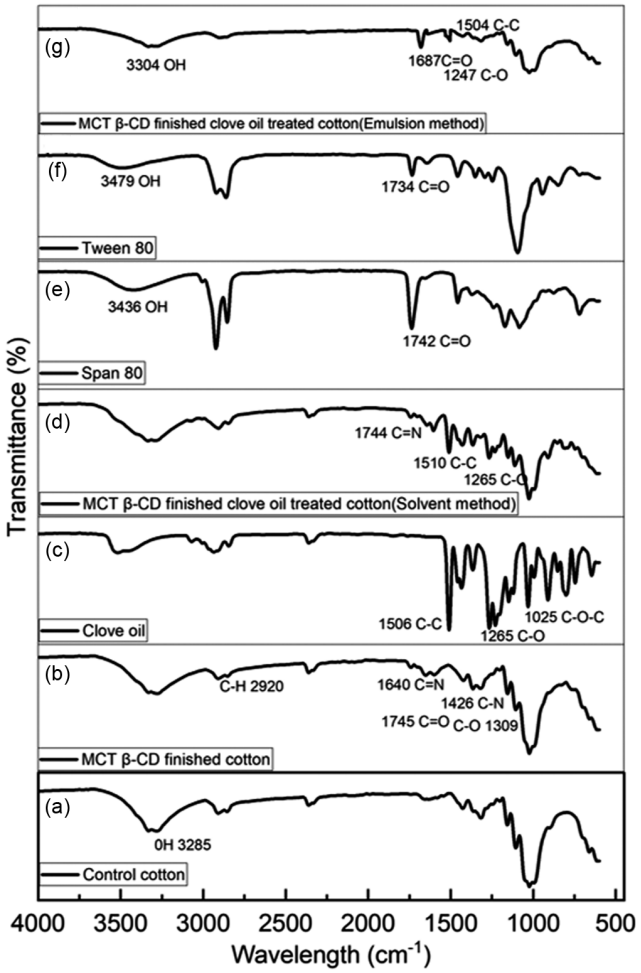

Fig. 7 — FTIR spectra of MCT β-CD finished clove oil-treated cotton by solvent and emulsion methods, showing (a) control cotton, (b) MCT β-CD finished cotton, (c) clove oil, (D) solvent-treated sample, (e) span 80, (f) tween 80, and (g) emulsion-treated sample

As shown in Fig. 7(e), peaks at 3436 cm^{-1} and 1742 cm^{-1} appear for the OH absorption band and C=O stretching vibration, respectively, of the span 80. Figure 7(f) shows peaks at 3479 cm^{-1} and 1735 cm^{-1} for the OH absorption band and C=O stretching for the ester group, respectively, of Tween 80. Similarly, Fig. 7(g) shows peaks at 3304 cm-1, 1687 cm-1, and 1504 cm-1 corresponding to the absorption bands of OH, C=O, and C-C stretch, respectively. The C=O stretching in the Figure indicates the presence of surfactant in the cavity of MCT β-CD[40], as it was used in conjunction with clove oil for emulsification. In total, the peak between 1600 $cm^{-1}$and 1700 cm^{-1} appeared for the emulsion-based treated fabric, which is absent in the solvent-based treated fabric. Therefore, it can be concluded that the C=O stretch is present in emulsion-based treated fabric, leading to confirmation of absorption of an emulsifier along with clove oil into the cavity of MCT β-CD of finished cotton fabric.

4 Conclusion

The study confirms that MCT β-CD synthesized from β-cyclodextrin and cyanuric chloride, with a yield of 68%, is pure and suitable for textile applications, as validated through solubility testing,

FTIR, EDS and TGA analyses. The grafted MCT β-CD shows strong stability on cotton and withstands multiple wash cycles, a property essential for the controlled and durable release of essential oils. Clove oil is applied to the MCT β-CD-finished cotton using both solvent and nanoemulsion methods. A stable oil-in-water nanoemulsion is achieved using a Span 80/Tween 80 blend at an HLB value of 12.5, with the 4% formulation demonstrating good storage stability and a mean droplet size below 277.5 nm. Spectroscopic and quantitative analyses reveal minimal differences between the two application methods in terms of initial inclusion complexation and retention after environmental exposure and successive washes. The clove oil uptake is comparable, at 0.99% owf for the nanoemulsion method and 0.96% owf for the solvent method. However, FTIR results indicate traces of surfactant on nanoemulsion-treated samples, suggesting partial occupancy of β-CD cavities by surfactants. This is consistent with the slightly reduced fragrance intensity observed in the sniff test. The findings establish MCT β-CD as an effective and durable host for controlled release of clove oil on cotton. The nanoemulsion method also demonstrates strong potential as a sustainable alternative to solvent-based application in developing functional, fragrance-retentive textiles.

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