

DURABLE MULTIFUNCTIONAL FINISHING OF FABRIC USING β -CYCLODEXTRIN-GRAFTED CHITOSAN AND LEMONGRASS (*CYMBOPOGON CITRATUS*) OIL

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Multifunctional finishing of textiles enhances the value of products by adding desired biological and functional properties. The purpose of this study was to extract essential oil from lemongrass and apply the extracted oil to traditional cotton fabric as finishing. Lemongrass oleoresin was obtained by extracting fresh blades of lemongrass for 16 h using a Soxhlet extractor, employing n-hexane as solvent, by the AATCC Method 30-25. The pad-dry technique was applied to impart fragrance to cotton fabric by using a finishing formulation containing lemongrass oil and β -cyclodextrin-grafted chitosan. The ester bond formation between β -cyclodextrin-grafted chitosan and cellulose was confirmed by FTIR spectroscopy (FTIR). After finishing, the fragrance release rate was evaluated by UV-visible spectroscopy. The fragrance release rate of the finished fabric was found to be durable up to 18 washing cycles and the fabric presented excellent antibacterial property and antioxidant activity. Standard test methods were used to evaluate the physical properties of the treated fabric.

Keywords: cotton fabric, lemongrass oil, fragrance, antibacterial property, β -cyclodextrin

INTRODUCTION

The surface modification of constituent fibres can modify the properties of fabrics and impart various desirable functionalities. Among all the available finishes, the application of fragrance or aroma is highly beneficial to enhance the aesthetic and hygienic value of textile materials. Various methods have been reported to impart such functional properties effectively and to control fragrance release during the use, achieving improved durability towards repeated washing.¹⁻³

Lemongrass (*Cymbopogon citratus*) is a tall perennial aromatic grass that contains essential oil with subtle lemon flavour. It is a genus of almost 55 species of grasses, grown in subtropical and tropical countries, being native to warm temperature regions.⁴ Citral is a biologically active agent of lemongrass, found in contents of 75% by weight in lemongrass essential oil.⁵ Lemongrass serves primarily for decorating houses, but is also used in indigenous medicine. Lemongrass tea helps to cure the central nervous system and is widely consumed in India.⁶ Also, the essential oil of lemongrass has been used to treat several diseases, and health conditions, such as oily skin, acne, flatulence, scabies, excess perspiration, as well as an antimicrobial, antiviral, antifungal and aroma agents.⁷ Additionally, people have utilized it to impart temporary perfume to their clothes.⁸ Netella fabric is an open structure of 100% cotton fabric used in the form of a scarf by Ethiopian men and women during auspicious occasions.^{9,10} Cotton as a cellulosic material is more susceptible to the attack of bacterial colonies, which may cause an unpleasant smell in the cotton fabric. Therefore, it would be interesting to investigate the possibility of eliminating the above-mentioned issue by finishing the cotton fabric with suitable functional agents.

β -Cyclodextrins (β -CDs) are cyclic oligosaccharides consisting of 7 glucose units, which are linked by a subunit of α -(1,4) glucopyranose, having a hydrophobic inner ring and a hydrophilic outer ring. Inclusion complexes with CDs can significantly increase the aqueous solubility of poorly soluble compound drugs, and thus improve the stability of fragile compounds, as well as aid in controlled release.¹¹ The cyclodextrins have various applications in the textile industry, starting from finishing to filtration, and other applications, such as UV protection, fragrance finishing, insecticide delivery, and antibacterial finishes.¹² Chitosan is a natural polysaccharide of N-acetyl-D-glucosamine and is prepared by N-deacetylation of chitin. It is biocompatible, non-toxic, mucoadhesive and antimicrobial, hence it has several applications in the pharmaceutical sector.¹³ According to Singh *et al.*, different techniques can be employed for fragrance finishing of textiles with the help of β -CDs. The β -CD-grafted chitosan finished cotton is a more desirable substitute for typical finishing.¹⁴ Several research works have reported the microencapsulation of lemongrass into β -cyclodextrins, with phenomenal results.¹⁵⁻¹⁸ Phunpee *et al.* studied the influence of spray drying on encapsulation of

lemongrass into β -cyclodextrins. They identified the controlled release activity of the capsules.¹⁹ Scacchetti *et al.* developed cotton fabrics with antimicrobial activity and thermoregulation by the encapsulation of mPCM and thyme oil in MCT- β -CD. The obtained cotton fabric offers protection against dermatophytosis and prevention to various infections.²⁰

In the present work, essential oil was extracted from lemongrass by utilizing a Soxhlet extractor. The extracted oil was loaded onto β -cyclodextrin-grafted chitosan to finish cotton fabric by the pad-dry-cure method. The effect of such finishing on the physical properties of cotton fabric was also studied. The novelty of this work consists in obtaining multifunctional cotton fabric. The durability of the finish was attained by the use of β -cyclodextrins. All the chemicals used in this research were eco-friendly, non-toxic and biocompatible.

EXPERIMENTAL

Materials and methods

100% cotton fabric was procured from a local market in Bahir Dar, Ethiopia. The specifications of the fabric are listed in Table 1. β -Cyclodextrin and chitosan were obtained from SDFCL Fine-Chem Limited Mumbai, India. All the laboratory-grade chemicals, such as acetic acid, citric acid, ethanol, methanol and n-hexane, were purchased from Addis Ababa, Ethiopia.

Essential oil extraction

Sample preparation

Lemongrass (*Cymbopogon citratus*) stems were collected from Lake Tana, which is the source of the Blue Nile and is the largest lake in Ethiopia. Before extraction, the lemongrass stems were cut to 2 mm and dried at 40 °C temperature for 12 h. After drying, the sample was placed in an air-tight bag.

Oil extraction

A Soxhlet extractor was used to extract the essential oil from dried lemongrass by utilizing n-hexane as solvent, for 16 h, by following the AATCC Method 30-25 (AATCC International, 2000).²¹

β -Cyclodextrin grafting to chitosan

The β -cyclodextrin-grafted chitosan was prepared according to the process explained by El-Tahlawy *et al.*²² β -CD citrate with a concentration of 0.54 g was added to a chitosan solution with a concentration of 0.6 g dissolved in formic acid (0.4 mL/1 g chitosan) using a M:L of 1:15. The reaction was performed at 100 °C for 3 h under magnetic stirring. Finally, 100 mL of NaOH solution (0.2 N) was added to the precipitated reaction product. The unreacted β -CD citrate was removed from the sample by washing with distilled water. The β -cyclodextrin-grafted chitosan was characterized using FTIR spectroscopy.

Calibration and optimization of lemongrass oil

A UV-visible spectrophotometer was utilized to calibrate the lemongrass oil for fragrance analysis by measuring the absorbance of various concentrations (1-10%) in 100% ethanol at $\lambda_{\max} = 272$ nm. A plotted calibration curve was used to detect the unknown fragrance concentration in the solution. The optimization of oil concentration was done by measuring the absorbance of removed lemongrass oil from the finished cotton sample at different time ranging from 2 h to 24 h.

Fabric treatment

The fabric sample was immersed in a bath solution with 9% (w/w) β -cyclodextrin-grafted chitosan, followed by padding to obtain a wet pickup of 80%, then drying for 2 min at 80 °C and curing at 150 °C for 3 min. The unreacted β -cyclodextrin-grafted chitosan was washed out from the cured cotton fabric, and the fabric was further dried at room temperature.²⁵

Table 1
Cotton fabric specifications

S. I.	Features	Details
1	Grams, m ²	41
2	Warp count	40s Ne
3	Weft count	30s Ne
4	Ends/inch	36
5	Picks/inch	30

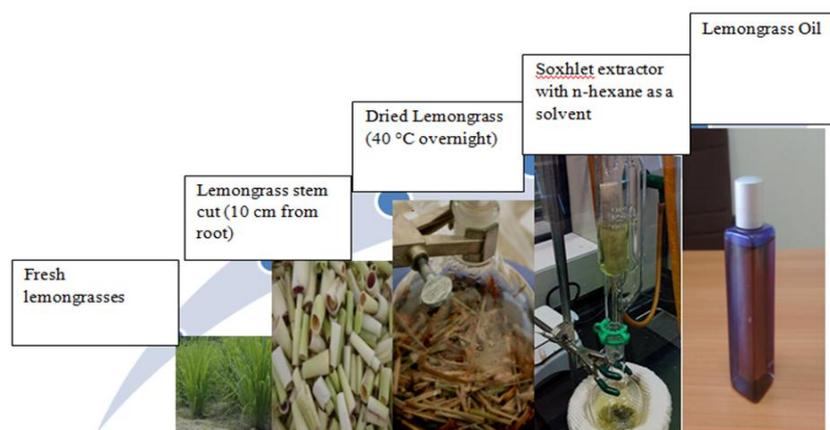


Figure 1: Lemongrass oil extraction process

The fabric sample finished with β -cyclodextrin-grafted chitosan was immersed into a 7% lemongrass concentrated solution in 80% ethanol and dried at 80 °C for 5 min. Then, the fragrance retention rate on the finished sample was examined by using a UV-visible spectrophotometer.

Testing methods

A Perkin-Elmer Lambda 25 UV-Visible Spectrophotometer (EiTEX Laboratory, Bahir Dar University, Ethiopia) was used to ascertain the absorbency index of lemongrass oil and the fragrance release rates quantitatively. A Spectrum Two FTIR Spectrometer by Perkin-Elmer (EiTEX Laboratory, Bahir Dar University, Ethiopia) was used to characterize the β -CD citrate and β -cyclodextrin-grafted chitosan. The agar plate method (AATCC 100-2004) was used for determining the antimicrobial activity of the finished cotton fabric.²⁴ The antioxidant activity of the finished fabric was evaluated using 2,2,1-diphenyl-1-picrylhydrazyl (DPPH) radical with methanol as solvent.²⁵

The durability to laundering was assessed according to ISO 105-C01:1989. Tensile strength testing was evaluated using a Mesdan Lab strength tester as per ISO 13934/1-EN, and drape was measured as per BS 5058:1973. Air permeability testing was carried out using an SDL Atlas M021A Air Permeability Tester following standard ASTM D 3574. Fabric padding was done using padder lab 3399 horizontal padders, with 80% expression and drying at 80 °C for 2 min.

RESULTS AND DISCUSSION

Extraction of lemongrass oil

A Soxhlet extractor was employed to extract oil from fresh lemongrass stems by the AATCC Method 30-25, as shown in Figure 1. The plant material was separated from the extract by encasing it in a paper 'thimble'. When full, the solvent in the thimble siphons off into the main vessel containing the extract, and the process continues. The amount of oil obtained using the Soxhlet extractor was 10 g per 500 g of dry lemongrass; this gives about a 2% yield of oil per 500 g of dry lemongrass.

Characterization of β -cyclodextrin-grafted chitosan

The β -cyclodextrin-grafted chitosan was characterized using FTIR spectroscopy, and the FTIR spectrum of the synthesized chemical is presented in Figure 2. The observed band at 1715 cm^{-1} was due to the stretching of the C=O bond of the citrate moieties and the band for N-H stretching was observed at 1657 cm^{-1} absorption, which confirmed the presence of the acetylated amino groups of chitosan, showing that the sample is not entirely deacetylated.²⁶

FTIR analysis is an appropriate technique to investigate the esterification between β -CD-grafted chitosan and cotton. The presence of β -CD-grafted chitosan on the finished cotton is illustrated in Figure 3, wherein an additional peak is observed at 1723 cm^{-1} and can be attributed to carbonyl stretching.

The FTIR spectrum of β -CD-grafted chitosan shows the amide bands at 1600-1700 cm^{-1} , which suggests the grafting of β -CD to chitosan by the amidation reaction. These results indicate the evolution of the ester and amide linkage between β -cyclodextrin-grafted chitosan and cotton fabric.

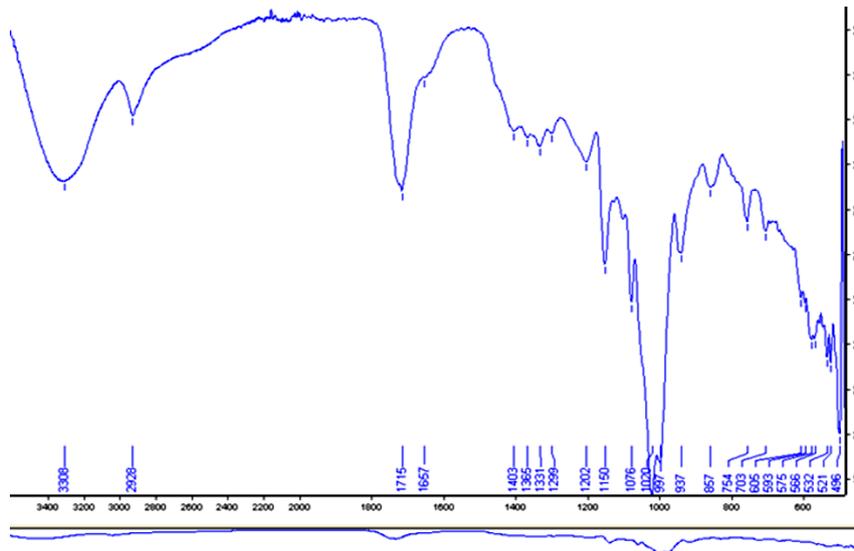


Figure 2: FTIR spectrum of synthesized β -CD-grafted chitosan compound

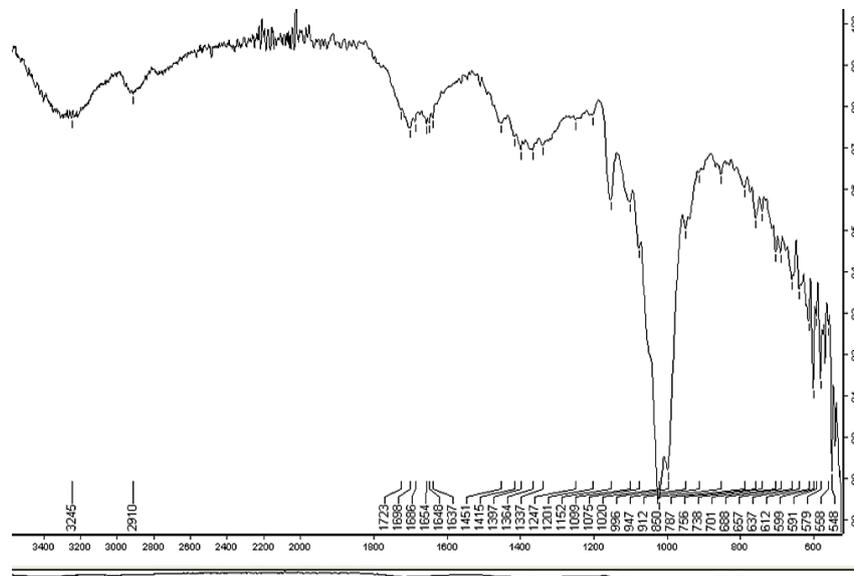


Figure 3: FTIR spectrum of cotton fabric finished with β -CD-grafted chitosan

Lemongrass oil calibration and optimization

The absorbance of different concentrations (1-10%) of lemongrass oil was evaluated against a blank sample at 272 nm. The concentration versus the absorbance curve showed a straight-line equation (1) as shown in Figure 4.

The slope of the line interpreted from Equation (1) was used to measure the unknown concentration of lemongrass oil in cotton fabric finished with β -CD-grafted chitosan:

$$y = mx + b \quad (1)$$

$$\text{Absorbance} = (\text{Slope} \times \text{Concentration}) + 0$$

$$= 0.088 \times \text{Concentration} \quad (2)$$

The optimization of the lemongrass oil concentration was carried out by finishing the cotton fabrics with different concentrations (1-10%) of the oil alone. Each finished fabric was cut to 2 mm and immersed in 10 mL of 80% ethanol solution to remove the oil from the finished fabrics. After that, the absorbance of the oil ethanol solution was measured using a UV-Visible Spectrophotometer at $\lambda_{\text{max}} = 272$ nm. The same procedure was followed for different times ranging from 0 h to 2 h. The result obtained confirmed the maximum absorbance, after 72 h, for the sample finished with 7% oil (Fig. 5).

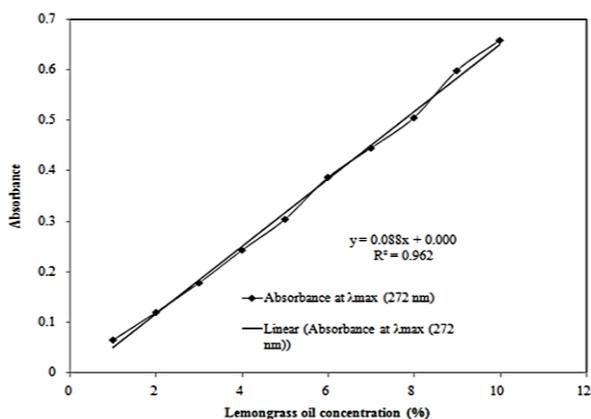


Figure 4: Calibration curve of lemongrass oil

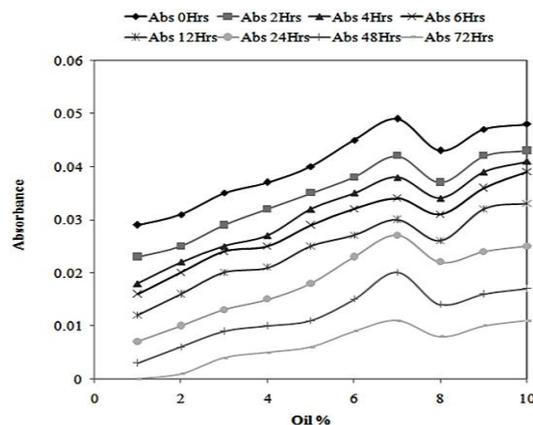


Figure 5: Lemongrass oil concentration optimization curves

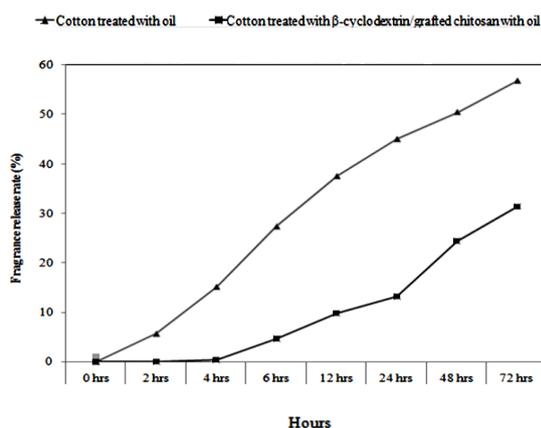


Figure 6: Fragrance release rate

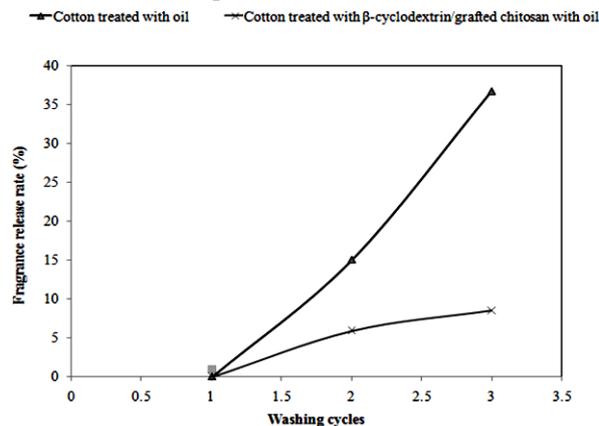


Figure 7: Durability to laundering

Table 2
Functional properties of the fabric finished with β -cyclodextrin-grafted chitosan

Samples	Antibacterial property		Antioxidant property (%)
	Bacterial colony reduction (%)		
	<i>E. coli</i>	<i>S. aureus</i>	
Finished sample	95	98	93

Functional properties of finished fabric

A UV-visible spectrophotometer was used to investigate the fragrance release rate. The cotton fabric finished with β -cyclodextrin-grafted chitosan showed a significant release rate even after 72 h, as compared to that of the fabric treated with oil alone. This long-lasting fragrance release performance may be due to the availability of β -CD cavities, which form an inclusion complex with the oil and are capable of holding oil fragrance for a more extended period. The ester linkages between the fabric and the β -CD might be another reason for the slow release rate, as shown in Figure 6.²⁷

The durability of the fragrance finishing was examined by subjecting the finished cotton to subsequent washing using 5 g/L of detergent solution for 30 min at 60 °C. After each washing cycle, the unknown concentration of oil from the fabric was determined by measuring the absorbance by using the UV-visible spectrophotometer. A significant amount of fragrance was still retained on the fabric, as shown in Figure 7.

The fabric finished with lemongrass oil was also investigated in terms of its antibacterial activity against *E. coli* and *S. aureus*, and the achieved results are tabulated in Table 2. The data in Table 2 indicate an excellent bacterial property of the finished fabric. It was found that *S. aureus* was more sensitive to lemongrass oil than *E. coli*. The presence of 75% of citral by weight in lemongrass essential oil leads to excellent antibacterial activity against a broad spectrum of bacteria.²⁸ The phenolic constituents of lemongrass interact with the bacterial cell membrane, degrading the membrane and affecting its permeability.²⁹ The presence of chitosan also inhibits the growth of bacteria. Being a cationic polymer, it can be attached to the negative charge of the bacterial cell membrane, which results in leakage of the membrane.³⁰ The finished fabric also showed excellent antioxidant properties. This might be due to the

presence of phenolic groups in lemongrass oil. The phenolic content present in lemongrass oil helps in free-radical scavenging.

Fabric performance

Tensile strength

The results of the tensile strength tests are illustrated in Figure 8, demonstrating that the fabric finished with β -cyclodextrin-grafted chitosan exhibits improved tensile strength.

It is interesting to note that the finishing treatments, in general, have detrimental effects on the tensile mechanical properties of cotton fabric. The improvement in strength is modest, but still, it is a significant advantage for the finished fabric. Singh *et al.* have reported similar results; the enhanced strength might be attributed to the plasticizing effect of β -CD citrate on fabric.¹⁴

Drape

The cotton fabric finished with β -cyclodextrin-grafted chitosan showed a higher drape coefficient, as compared to the unfinished fabric, as shown in Figure 9. This could be explained by the ester linkage formed between the fabric and the β -CD-grafted chitosan component, and probably due to the modified host as a binder for holding the fragrance on fabric.

Air permeability

The air permeability of 4 layers of fabric was examined before and after the finishing treatment. It was found that the air permeability of the fabric decreased slightly after the treatment with β -cyclodextrin-grafted chitosan (Fig. 10). The reason may be attributed to swelling of cotton, which modifies the fabric interstices, its thickness and porosity, leading to a reduction in air permeability of the cotton fabric.³¹

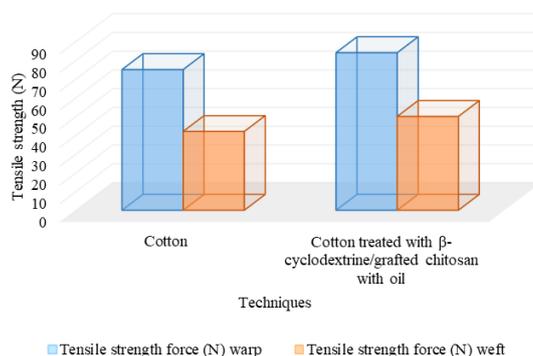


Figure 8: Effect of fragrance finishing treatment on tensile strength of fabric

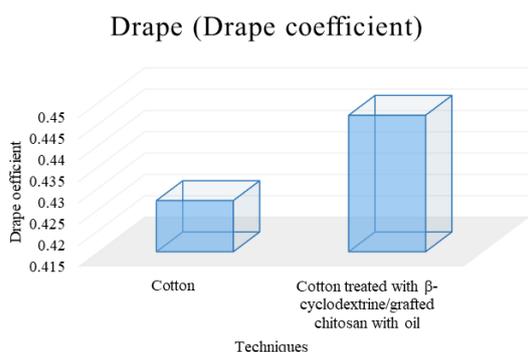


Figure 9: Drape coefficient of control and finished cotton fabric

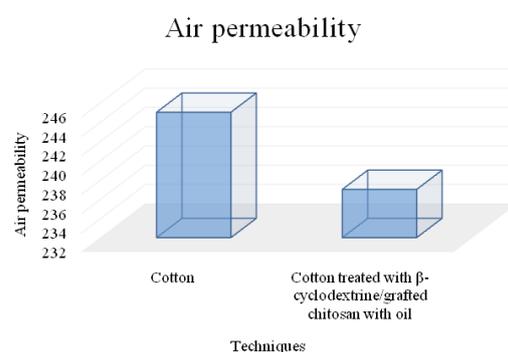


Figure 10: Air permeability of control and finished cotton fabric (cm³/cm²/s)

CONCLUSION

The novel application of β -CD-grafted chitosan on textile fabric for achieving slow release of volatile oil was successfully performed and investigated. The optimum yield of lemongrass oil obtained was $3.8 \pm 1\%$, by using a Soxhlet extractor, which is a quite significant aspect to explore in a further study. The optimized lemongrass oil concentration for achieving the maximum fragrance from the finished fabric was 7% in 80% ethanol. The results confirmed the significant role of β -CD cavities in the durability of the finish, and also

established the ability of β -CDs to store the volatile compound and release it in a controlled manner. Also, the finished fabric exhibited excellent antibacterial activity due to the presence of citral in lemongrass oil and the availability of cationic chitosan. The β -CD-grafted chitosan finished fabric presented improved tensile strength, higher drape coefficient and slightly reduced air permeability, which was not significantly hampering the physical properties of the fabric. It can be concluded that lemongrass oil could be used as part of a finishing treatment to impart fragrance to traditional clothing. Also, the application of β -CD-grafted chitosan in finishing home furnishing textiles and apparel opens up new horizons for unique textile products.

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