

Synthesis of Sulfated β -Cyclodextrin/Cotton/ZnO Nano Composite for Improve the Antibacterial Activity and Dyeability with *Azadirachta Indica*

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ABSTRACT: The sulfated β -cyclodextrin (sb-cd) was prepared from β -cyclodextrin and the sb-cd was crosslinked with cotton fabric using ethylenediaminetetraacetic acid (EDTA) as crosslinker. After crosslinking, the synthesized ZnO nanoparticles were padded on this fabric surface. Then, the treated fabrics were dyed with neem extract. The synthesized polymer, crosslinked and nanoparticle-treated cotton fabrics were characterized using fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), particle sized analyzer, and transmission electron microscopy (TEM) studies. The antibacterial test was done against *Staphylococcus aureus* and *Escherichia coli* bacterium. The composite coated with neem dyed cotton fabric has exhibited 71% of dye uptake with 2–3 fastness grade and it has 99% of antibacterial efficiency for *S. aureus* and 97% for *E. coli* bacterium. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: β -cyclodextrin; dyeing; neem; crosslinking; antibacterial activity; nanoparticles

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INTRODUCTION

Carbohydrate polymers like cotton, cyclodextrins, and chitosan are playing an important role in our society. Cotton is mostly used by textile sectors.¹ The consumption of world textile fiber, the cotton fabrics have increased due to population growth.² The application of cotton fabrics also increases day by day and also the consumers required more quality, functionality of cotton fabrics.³ The synthetic dyed fabrics may cause the skin problem to the wearer's skin and the synthetic dye effluent creates environmental pollution.⁴

In recent days, numbers of dyeing industries were closed due to environmental problem in and around Tirupur. The textile dyeing industries located at Tirupur in India has been facing a major problem for the usage of synthetic dyes. Tirupur is located at the bank of river Noyyal, a tributary to river Cauvery. The quality of Noyyal river water, soil, ground water, and climatic condition of Tirupur has been ideal for dyeing process since long time. At present, there are 712 dyeing industries has been shut down by High Court order due to synthetic dye effluents discharge without treatment in to Noyyal river.⁵ To avoid these problems, an eco-friendly modification, safe dyes, dyeing process or enzyme finishing methods are required. The structural modified cellulose fabric has some functional behaviors. The structural modification of cotton cellulose was successfully modified using β -cyclodex-

trin. The improved qualities and functionalities of cotton fabrics are necessary for our society.^{6,7} The improved antibacterial efficiency needed for kid's cloths, inner wears, medical bandage cloths, and so forth. These properties are improved by different modifications of cotton fabrics. Our recent report was sulfated β -cyclodextrin (sb-cd)-modified cotton fabric for antibacterial activity⁸ and we have already reported Polyvinylpyrrolidone (PVP) modification of cotton fabric and its improved antibacterial activity was tested with ZnO nanoparticles coating.⁹

Some of the natural dyes are extracted from leaves, sparks, flowers, and roots of medicinal plants. So, these natural dyes have some medicinal properties. The natural dyes are suitable for eco-friendly dyeing process.⁸ The fastness properties of natural dyed fabrics were improved by eco-friendly modifications and eco-friendly mordents. These natural dyes are biodegradable and generally has a better compatibility with the environment.^{10,11} Neem extract is used as a natural dye and this natural dyes exhibits good antibacterial activity on natural dyed cotton and wool fabric. The wash fastness of neem natural dyed fabric was improved by modification using dimethyloldihydroxyethelene.^{12,13}

The nanoparticle-coated fabrics have antibacterial activity, UV-protection, self cleaning, and so forth. Hence, the eco-friendly modified cotton with nanoparticle-coated fabrics showed very good functional behaviors. These types of textile

materials are required in the increasing demand of modern human society and our environment.^{14,15}

Xu and Cai have presented a simple method of fabricating superhydrophobic surface on cotton fabrics. The oriented hexagonal type of ZnO nanorods arrays were first grown on cotton fibers via a simple process at low temperature and then modified with *n*-dodecyltrimethoxysilane (DTMS). The fabrication processes can be easily applied using inexpensive laboratory equipment and chemicals which are desirable for use in multiple fields such as functional material devices, composites, and optoelectronic industries.¹⁶ Lee¹⁷ demonstrated that desired properties can be imparted by coelectro spinning of polymer materials with a functional material in a single step.

The superhydrophobicity was achieved by combining the rough surfaces created by SiO₂ nanoparticles and ZnO nanorods with DTMS modification.¹⁸ Mao et al. found that hot water treatment could transform the morphology of the ZnO nanoparticles on the surface of cotton fabric from sphere and rod to needle shape through a recrystallization process. Although hot water treatment could not significantly increase the amount of ZnO on the surface of cotton fabric, longer treatment time and higher treatment temperature can make the needle-shaped ZnO nanorods have smaller diameter and better crystalline perfection.¹⁹

Cyclodextrins are used in a variety of different textile applications and owing to the complex abilities of cyclodextrins.^{20,21} It performs new functional properties in textile materials. The possibility of permanent cyclodextrin fixation in polymeric materials has been studied.^{22–25} The cyclodextrin crosslinking may exhibit good dyeability due to its multihydroxyl groups and also the sulfur groups act as an antibacterial agent. Antimicrobial active substances are complexed by crosslinked cyclodextrins. The cyclodextrin-treated materials are convenient and safe for wearing.²⁶

The functionalized cotton and its composite materials have increased activities such as textiles, drug delivery systems, and personal care products.^{27–29} Aim of this work is to study the antibacterial behavior and dyeability with neem extract on sb-cd/ZnO nanoparticles/cotton composite fabric.

MATERIALS AND METHODS

Materials

Sulfuric acid, ethylenedinitrilo-tetraacetic acid, and calcium carbonate were purchased from Merck India products. β -Cyclodextrin purchased from Himedia Chemicals, India. The cotton was used as bleached knitted fabric from Tirupur textile industry. The natural dye source neem leaves were collected from local residential area in India at Karaikudi.

Preparation of Sulfated β -Cyclodextrin

The sb-cd was prepared from sulfonation of β -cyclodextrin, which was (10 g) mixed with 3 mL of 90% of sulfuric acid at 0–5°C temperature and was maintained for 2 h. The superfluous sulfuric acid was then counteracted with 1 *N* calcium carbonate solution. After filtering, 95 wt % of alcohol was added into the filtrate, the mixed solution was kept overnight at 0–5°C. The pH of the sedimentation was adjusted to 7 using acetic acid. The white sedimentation was obtained after adding a great amount of alcohol. The precipitate was washed with alcohol, acetone, and ether.³⁰ The powder was dried in a vacuum oven at 110°C for 15 min.

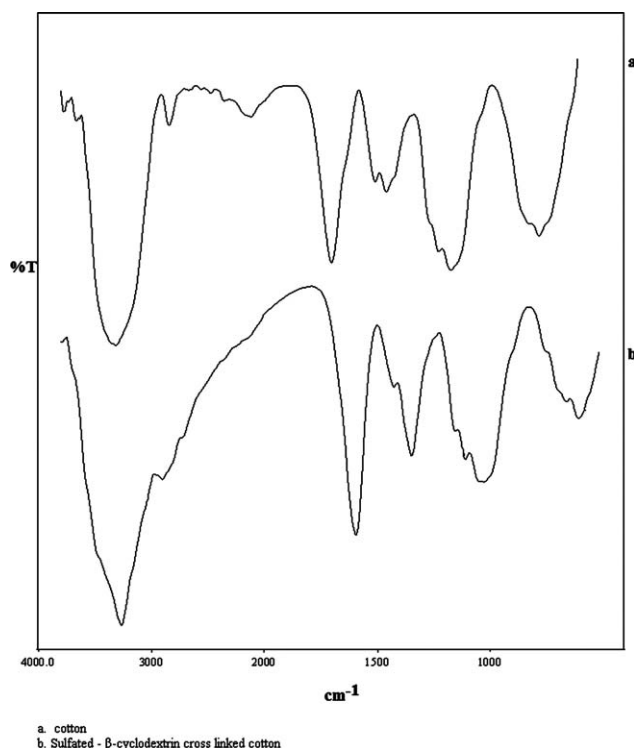


Figure 1. FTIR spectrum of β -cyclodextrin and sb-cd.

Modification of Cotton Fabric

sb-cd (5 wt %) was dissolved in water and 90% of wet pickup bleached 10 × 15 cm² of knitted cotton fabric was immersed in to this solution with 5 gpl EDTA for crosslinking.³¹ The treated cotton fabric was padded on two bowl padding mangle. Then, the padded samples were cured at 120°C for 2 min in an air oven.

Preparation of ZnO Nanoparticles

Thermolysis method was used for the preparing of ZnO nanoparticles and it is based on our previous report.³² About 7.43 g of zinc nitrate was dissolved by magnetic stirring (JSGW 13162) with 200 mL of 2% soluble starch solution. Sodium hydroxide (0.2 mol) was added drop by drop as precursor to this solution. The temperature was maintained from 60 to 70°C and the mixture was stirred for 2 h. After stirring, the precipitate was filtered. This precipitate was three times washed with distilled water. After washing, the nanoparticles were dried at 80°C for 12 h and then ZnO nanoparticles were obtained.

Coating of Cotton Fabrics with ZnO Nanoparticles

The prepared ZnO nanoparticles were coated by Pad-dry-curve method.³³ About 2% of ZnO nanoparticles were treated with unmodified and sb-cd modified cotton fabrics 5–20% of wet pickup. Then, these fabric samples were padded in a two bowl padding mangle. After completion of padding, these fabrics were cured at 120°C for 3 min. Then, the unfixed nanoparticles were removed by washing with 2 gpl of sodium lauryl sulfate. Finally, these fabrics were completely washed with water 10 times and dried.

Extraction of Natural Dyes

Alcohol (50 mL) with 15 g of *Azadirachta indica* leaves (neem) were added in the Soxhelt apparatus.³⁴ It was extracted at 50°C temperature. The final extract was used for treatment of cotton fabric.

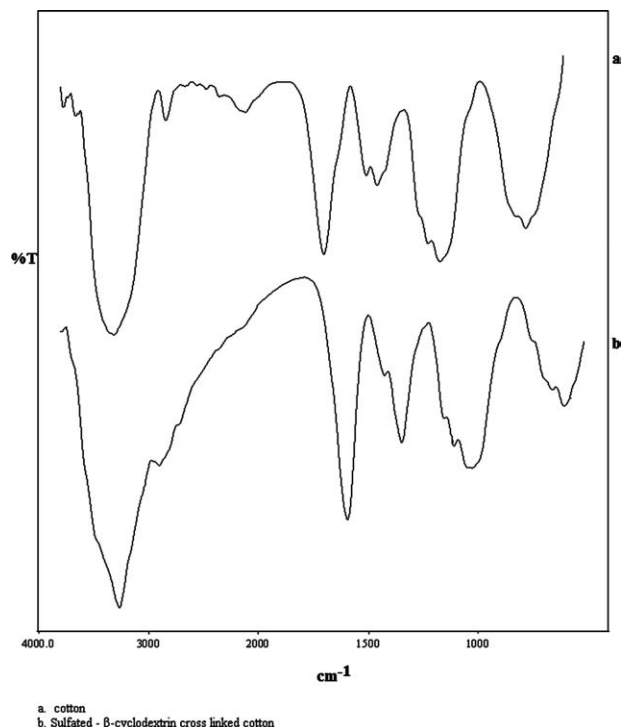


Figure 2. FTIR spectrum of untreated cotton and sb-cd cotton.

Natural Dyeing

Natural dye (2%) was dyed with unmodified, sb-cd modified, ZnO coated, and sb-cd nanoparticle-coated cotton fabrics with 1 :

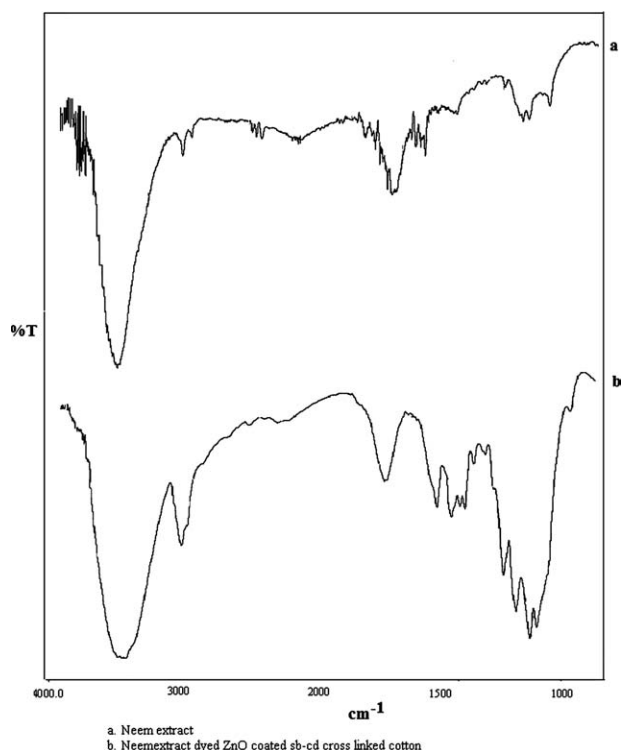


Figure 3. FTIR spectrum of neem extract and neem extract treated Sb-cd crosslinked cotton.

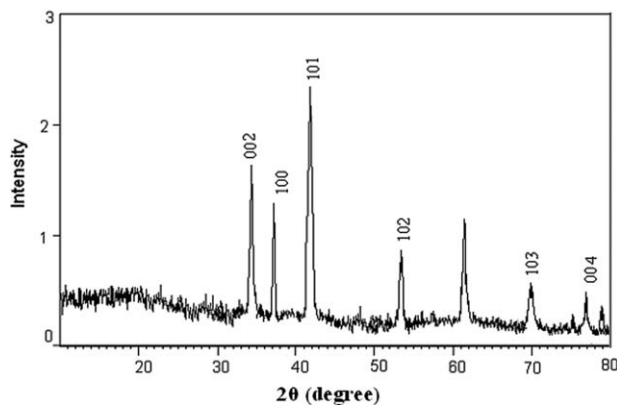


Figure 4. XRD pattern of ZnO nanoparticles.

15 MLR at 60°C for 1 h.³⁵ Then, the air dried dyed fabrics were tested for the fastness and dye uptake measurements.

Measurement of Dye Uptake

The exhaustion values of dyed samples were measured by taking the absorbency value of the dye liquor samples (before and after dyeing) using a Spectrophotometer (Systronics) at wavelength of maximum absorbency (λ max) of the dye concerned.³⁶ The exhaustion value was calculated using eq. (1):

$$\text{Exhaustion (\%)} = \frac{1 - A_1}{A_2} \times 100 \quad (1)$$

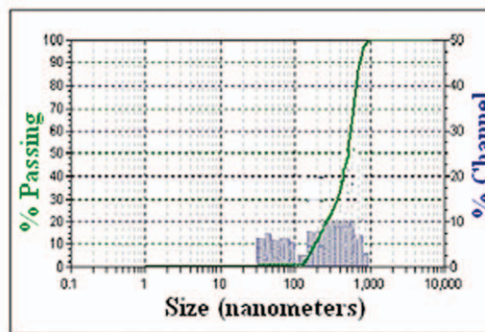
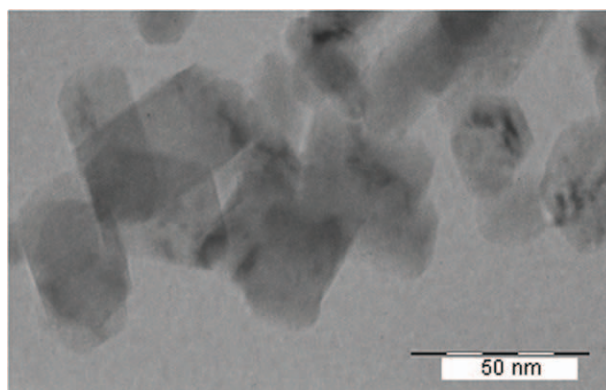


Figure 5. PSA and TEM images of ZnO nanoparticles images of unmodified cotton and sb-cd crosslinked cotton. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

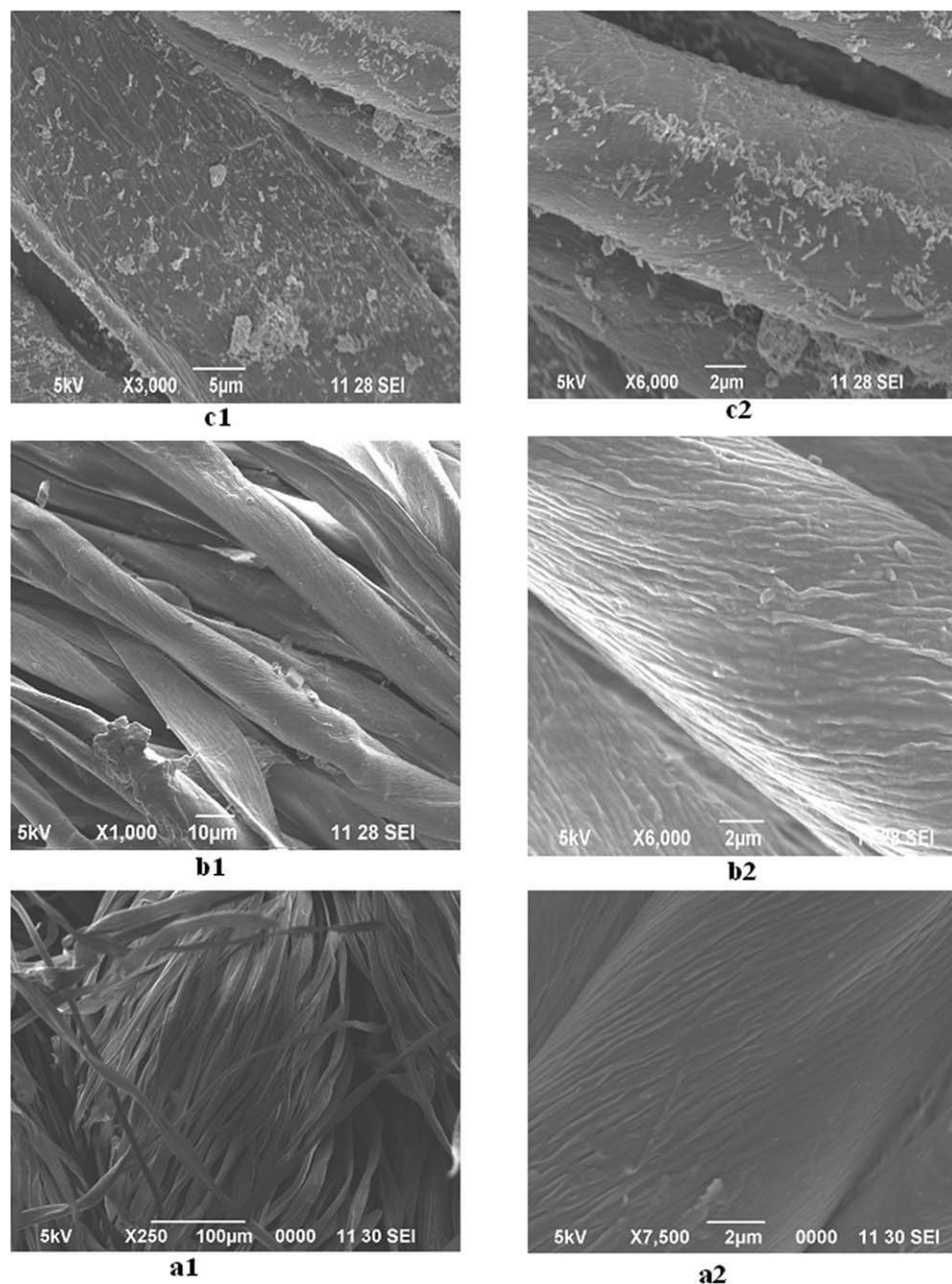


Figure 6. SEM images of untreated cotton, sb-cd and ZnO nanoparticle-treated cotton fabric.

where A_1 = absorbency of dye solution before dyeing and A_2 = absorbency of dye solution after dyeing.

Wash Fastness

Wash fastness of all dyed samples were measured by the (ISO 105-C03; 1989, Geneva) testing method.³⁷ Dyed fabric sample ($5 \times 5 \text{ cm}^2$) was taken, pinned with one of the shorter side of the adjacent bleached fabric and put into the Launderometer at 60°C for 30 min. Then, the specimen was washed with hot water, cold water, and dried.

Antibacterial Test

The antibacterial activities of untreated and treated fabrics were done by the reduction of colony forming units (CFUs) of *Staph-*

yllococcus aureus and *Escherichia coli* bacterium (AATC test method (100-1999)).^{38–40} The cell culture and analysis were done in Marine Bio-technology Lab, Alagappa University, Karaikudi, Thondi Campus. The initial concentration of *S. aureus* is $12 \times 10^5 \text{ CFU mL}^{-1}$ and *E. coli* concentration is $6 \times 10^5 \text{ CFU mL}^{-1}$. The percentage reduction of CFU was calculated by following eq. (2):

$$\text{Reduction in CFU (\%)} = \frac{C - A}{C} \times 100\% \quad (2)$$

where C and A are the bacterial colonies of the untreated cotton fabric and the treated cotton fabrics, respectively.

Table I. Antibacterial Activity Test of the Untreated and Treated Fabrics Against *S. aureus* and *E. coli*

Sample	<i>S. aureus</i>				<i>E. coli</i>			
	10 min. %R	15 min. %R	20 min. %R	30 min. %R	10 min. %R	15 min. %R	20 min. %R	30 min. %R
Control	0	0	0	0	0	0	0	0
Cotton	0	2	2	2	0	0	0	0
ZnO + cotton	33	61	80	86	21	44	60	87
Sb-cd + cotton	45	64	77	85	38	61	70	78
Extract + Cotton	38	66	78	81	37	68	72	80
ZnO + extract + cotton	79	86	98	98	69	76	81	88
Sb-cd + ZnO + extract + cotton	86	99 ^a	99	99	78	89	97	97

^aGood antibacterial activity.

RESULTS AND DISCUSSION

Perkin Elmer IR SPECTRUM ASCII PEDS 1.60 instrument was used to measure FTIR spectra of all samples measured by transmission mode using with KBr pellets. The β -cyclodextrin exhibited a broad peak represents due to the multihydroxyl groups. These hydroxyl groups exhibit from 3556 to 3246 cm^{-1} for —OH stretching [Figure 1(a)]. The peak values from 2932 to 2119 cm^{-1} could be attributed to the asymmetric stretching of —CH_2 groups. The peaks 1413–1079 cm^{-1} indicate C—O stretching vibration. Figure 1(b) represents the FTIR spectrum of sb-cd. The peak at 3201 cm^{-1} indicates the free hydroxyl groups and the peak values from 2924 to 2144 cm^{-1} indicates the —CH_2 stretching. From the above observation, the —CH_2 groups are not involved in the sulfonation reaction.^{41,42} The new S—O stretching peak showed at 699 cm^{-1} and 1152 cm^{-1} , 854 cm^{-1} that is asymmetric and symmetric stretching of SO_3 groups, respectively. It indicated that sulfonic acid group grafted on the β -cyclodextrin and its primary hydroxyl groups undergo sulfonation reaction.^{43,44}

Figure 2(a) exhibits the FTIR spectrum of unmodified cotton fabric. The —OH stretching corresponds from the broad peak at 3418 cm^{-1} and also the —CH_2 stretching corresponds at 2894 cm^{-1} region. The asymmetric stretching modes C—O—C have been separated at 1110 and 1049 cm^{-1} . From Figure 2(b), the peak 3269 cm^{-1} indicates the —OH stretching of alcoholic groups and the —CH_2 stretching corresponds at 2906 cm^{-1} .

Table II. Dye Uptake, Washing Fastness Properties and Color of Natural Dyed Cotton Fabrics

S. no	Sample types	Dye uptake (%)	Washing fastness grade	Color of dyed samples
1	Cotton	75	1	Yellow
2	Sb-cd modified cotton	84	1	Yellow
3	ZnO coated cotton	70	2–3	Yellow
4	Sb-cd modified ZnO coated cotton	71	2–3	Yellow

The peak at 1110 cm^{-1} represents S—O stretching. This value is the evidence for crosslinking of sb-cd with cotton. The peaks 1285 cm^{-1} and 1349 cm^{-1} refer the C—N stretching. This stretching is the C—N bond of EDTA. It confirms that the EDTA has crosslinked between sb-cd and cotton. The FTIR spectrum of neem extract reveals [Figure 3(a)] the —OH stretching corresponds from a peak at 3422 cm^{-1} and also the —CH_2 stretching corresponds at 2874 cm^{-1} region. This spectrum has exhibited some characteristic peaks of nimbin and nimbidine derivatives.⁴⁵ Figure 3(b) peak at 3309 cm^{-1} indicates the —OH stretching of nimbin derivatives groups and its —CH_2 stretching corresponds at 2900 cm^{-1} . The peak at 1100 cm^{-1} represents S—O stretching. These values are the evidence for crosslinking of sb-cd with neem extract treated cotton.

The crystalline and average particle size of synthesized ZnO nanoparticles was calculated from XRD pattern using XPERT PRO diffractometer. From Figure 4, the peaks at $2\theta = 36^\circ, 38^\circ, 43^\circ, 54^\circ, 70^\circ,$ and 77° of ZnO nanoparticles are corresponding to (002), (100), (101), (102), (103), and (104) in lattice (JCPDS NO. 87-0713). Hexagonal structure of ZnO was confirmed by the 102 crystalline peaks⁴⁶ and average crystal size was calculated using Debye-Scherrer ($D = 0.94\lambda/\beta \cos\theta$) formula. The average crystal size of synthesized ZnO nanoparticle is 37 nm.

The surface morphology was studied by transmission electron microscope. The average particle size was analyzed by Nanotract particle sized analyzer (PSA). The ZnO nanoparticles have particle size also appeared in nanometer scale from particle size analyzer (PSA) [Figure 5(a)]. The TEM analysis [Figure 5(b)] exhibited the hexagonal structure of ZnO nanoparticles and the size of the nanoparticles is almost 20 nm range. The prepared ZnO is visibly judged that the particle is in nanostructure and it has on track to produce but still maintained at a regular shape of hexagonal structure.

The unmodified cotton fabrics showed clean surfaces and no deposition on its surface [Figure 6(a1 and a2)] from scanning electron microscopy (SEM) images. However, sb-cd crosslinked fabric surfaces exhibit some deposition and swelling nature due to crosslinking [Figure 6(b1)]. At higher magnifications, the crosslinked cyclodextrin polymer clearly visible [Figure 6(b2)].

Figure 6(c1) exhibited the nanoparticles deposition also clearly showed on ZnO-coated crosslinked cotton fabric surface. The coated ZnO nanoparticles showed a rod formation on fabric surface at 12,000 magnifications [Figure 6(c2)]. The SEM studies proved that the coated nanoparticles deposited on the sb-cd crosslinked cotton.

Table I exhibits the antibacterial activity of Gram "+ve" bacteria (*S. aureus*) and Gram "-ve" bacteria (*E. coli*). The antibacterial activity was determined by CFUs with time intervals. Ninety-nine and ninety-seven percentage of antibacterial activity within short time period observed for sb-cd + ZnO + neem extracts treated cotton for *S. aureus* and *E. coli*, respectively. The nanoparticles with extract treated cotton fabric also exhibited reduction results 98% for *S. aureus* and 88% for *E. coli* at 30 min. The natural extract fabric resulted 81% and 80% of reduction for both bacterium at 30 min. The antibacterial activity of fabrics increased with modifications. This may due to the nimbin derivatives from extract and the sulfated or sulfonated polymers inhibit the *in vitro* growth of bacteria. Plants have defense systems against phytopathogenic bacteria and fungi. It is thought that phenolic metabolism in plants plays the role of antibiotics against environmental bacteria and fungi. These phenolic compounds could be used as antibiotics for human pathogenic bacteria and fungi.⁴⁷ Medicinal plants that have been used for a long time may be good sources of safe antibacterial agents. The biological activity of these products is mainly due to the presence of isoprenoids in neem extract.^{48,49} It was reported that isoprenoid group changes membrane fluidities in model membranes, suggesting that the hydrophobic nature reduces the fluidity of outer and inner layers of membranes.⁵⁰ The antibacterial effect of the isoprenoid-substitutions investigated here may also be due to a similar action. It is possible that the isolated hydroxyl group of these attackers plays the role of lance or talon against the lipid bilayer of target microorganisms. Conversely, hydrophobic groups may play the role of anchors and/or lances in the bilayer (hydrocarbon moieties of lipids or hydrophobic residues of proteins). *N*-sulfonated compounds acts as a microbial inhibition compound. The ZnO nanoparticles also inhibit the growth of bacterium. So, this type of fabric performed good antibacterial activity.^{51–53}

From Table II, the sb-cd modified fabrics exhibited maximum 84% of dye uptake for this natural dyeing and the sb-cd with nanoparticle-coated fabrics observed 71% of dye uptake. The untreated fabrics have 75% of dye uptake. The nanoparticle-coated fabric and the sb-cd modified with nanoparticle-coated fabric exhibited moderate fastness properties. This is may be due to the ZnO nanoparticles act as a mordant.^{54,55} All the treated and untreated fabrics produced yellow color. However, the sb-cd modified fabric exhibited slightly darker than other dyed samples. It may be due to the more number of free hydroxyl groups present in sb-cd polymer.^{56,57}

CONCLUSIONS

The β -cyclodextrin/cotton/ZnO nanocomposite has been successfully synthesized and the functional groups of the composite confirmed by FTIR studies. sb-cd modified fabric exhibited a

peak at 1110 cm^{-1} represents S—O stretching and also the two peaks 1285 cm^{-1} and 1349 cm^{-1} refer the C—N stretching. These results are confirmation of sb-cd crosslinking with EDTA. The hexagonal structure of prepared ZnO was confirmed and the average particles size is 37 nm from XRD pattern. The surface morphology studies of modified fabrics clearly exhibited the polymer and nanoparticles depositions. The synthesized nanocomposite with natural dyed fabrics performed good antibacterial activity for both gram positive and gram negative bacterium. In all the natural dyed fabrics produced yellow color but no change of color tone after modifications. The neem extract acts as a dye as well as antibacterial agent and it is an inexpensive material for textile products. This type of cotton fabric may recommend for surgical cloths, wound cloths, all inner wears and sport wears.

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REFERENCES

- Gao, Y.; Cranston, R. *Text. Res. J.* **2009**, *78*, 72.
- Isaeva, V. I.; Aizenshtein, M.; Soboleva, O. N. *Fibre Chem.* **2007**, *29*, 281.
- Teli, M. D.; Shrish Kumar, G. V. N. *J. Text. Assoc.* **2007**, *68*, 30.
- Joshi, M.; Wasez Ali, M.; Rajendran, S. *Ind. J. Text. Fiber Res.* **2009**, *295*, 304.
- Ranganathan, K.; Karunagaran, K.; Sharma, D. C. *Conservat. Recycl.* **2007**, *50*, 306, 318.
- Teli, M. D.; Shrish Kumar, G. V. N. *J. Text. Assoc.* **2007**, *68*, 30.
- Yadav, A.; Virendraprasad; Kathe, A.; Sheelaraj; Deepthyadav; Sundramoorthy, C.; Vigneshwaran, N. *Bull. Mater. Sci.* **2006**, *29*, 641, 645.
- Selvam, S.; Rajivgadhi, R.; Suresh, J.; Gowri, S.; Ravikumar, S.; Sundrarajan, M. *Int. J. Pharm.* <http://dx.doi.org/10.1016/j.jbbr.2011.03.031> (to appear).
- Selvam, S.; Sundrarajan, M. *Carbohydr. Polym.* **2012**, *87*, 1419.
- Kay, K.; de Manolo, A. *Econ. Bot.* **1988**, *43*, 191.
- [http://nopr.niscair.res.in/bitstream/123456789/8034/1/NPR%205\(6\)%20428-432.pdf](http://nopr.niscair.res.in/bitstream/123456789/8034/1/NPR%205(6)%20428-432.pdf). Accessed on 26 Dec, 2009.
- Mathur, J. P.; Anjula, M.; Romila, K.; Bhandari, C. S. *Ind. J. Fiber Text. Res. J.* **2003**, *28*, 99.
- Sarkar, R. K.; Purushottam, D. E.; Chauhan, P. D. *Ind. J. Text. Fiber Res.* **2003**, *28*, 331.
- Zhang, Y. H.; Yu, L.; Ke, S. M.; Shen, B.; Meng, X. H.; Huang, H. T.; Lv, F.; Xin, J. H.; Chan, H. L. W. *J. Sol-Gel Sci. Technol.* **2011**, *58*, 329.
- Wua, D.; Longa, M.; Zhoua, J.; Caia, W.; Zhua, X.; Chenb, C.; Wub, Y. *Surf. Coat. Technol.* **2009**, *203*, 3733.
- Xu, B.; Cai, Z. *Appl. Surf. Sci.* **2008**, *254*, 5904.

17. Lee, S. *Fibers Polym.* **2009**, *20*, 301.
18. Cai, Z.; Xu, B.; Wang, W.; Ge, F. *Surf. Coat. Technol.* **2010**, *204*, 1561.
19. Mao, Z.; Shi, Q.; Zhang, L.; Cao, H. *Thin Solid Films* **2009**, *517*, 2686.
20. Munroa, I. C.; Newberneb, P. M.; Young, V. R.; Bar, A. *Regul. Toxicol. Pharmacol. Cyclodextrins* **2004**, *39*, 13.
21. Merkus, F. W. H. M.; Verhoef, J. C.; Marttin, E.; Romeijn, S. G.; Van Der Kuy, P. H. M.; Hermens, W. A. J. J.; Schipper, N. G. M. *Adv. Drug Deliv. Rev.* **1999**, *36*, 57.
22. Voncina, B.; Majcen Le Marechal, A. *J. Appl. Polym. Sci.* **2005**, *96*, 1328.
23. Singh, M.; Sharma, R.; Banerjee, U. C. *Biotechnol. Adv.* **2002**, *20*, 359.
24. Szejtli, J. *Starch* **2003**, *55*, 196.
25. El Ghoul, Y.; Martel, B.; Morcellet, M.; Campagne, C.; El Achari, A.; Roudesli, S. *J. Incl. Phenom. Macro. Chem.* **2007**, *57*, 52.
26. Paudel, K. S.; Milewski, M.; Swadley, C. L.; Brogden, N. K.; Ghosh, P.; Stinchcomb, A. L. *Ther. Deliv.* **2010**, *1*, 131.
27. Roy, D.; Semsarilar, M.; Guthriea, J. T.; Perrier, S. *Chem. Soc. Rev.* **2009**, *38*, 2064.
28. Avila, A. G.; Hinestroza, J. P. *Nat. Nanotechnol.* **2008**, *3*, 458.
29. Fukuoka, A.; Dhepe, P. L. *Angew. Chem.* **2006**, *45*, 5163.
30. Yang, T. *Int. J. Hydrogen Energy* **2009**, *34*, 6924.
31. Ghoul, M.; Bacquet, M.; Crini, G.; Morcellet, M. *J. Appl. Polym. Sci.* **2003**, *90*, 799.
32. Salavati-Niasar, M.; Davar, F.; Fereshteh, Z. *Chem. Eng. J.* **2009**, *146*, 502.
33. Perelshtein, I.; Applerot, G.; Perkas, N.; Wehrschetz-Sigl, E.; Hasmann, A.; Guebitz, G. M.; Gedanken, ACS *Appl. Mater. Interfaces* **2009**, *1*, 361.
34. Datta, A.; Ghoshdastidar, A.; Singh, M. *Int. J. Pharm. Sci. Res.* **2011**, *2*, 104.
35. Ali, S.; Hussain, T.; Nawaz, R. *J. Clean. Prod.* **2009**, *17*, 61.
36. Shim, W. S.; Koh, J.; Lee, J. J.; Kim, I. S.; Kim, J. P. *Fibers Polym.* **2008**, *19*, 152.
37. Sundrarajan, M.; Vishnu, G.; Joseph, K. *Dyes Pigments* **2007**, *75*, 273.
38. AATCC Test Method 100-1999. Assessment of antibacterial finishes on textile materials. American Association of Textile Chemists and Colorists technical manual 2002. Research Triangle Park, NC: AATCC.
39. Li, Y.; Leung, P.; Yao, L.; Song, Q. W. *J. Hosp. Infect.* **2006**, *62*, 58.
40. Cao, Z.; Sun, Y. *Polymeric N-Halamine. Appl. Mater. Interfaces* **2009**, *1*, 494.
41. Jeon, J.-D.; Kwak, S.-Y. *J. Power Sources* **2008**, *185*, 49.
42. Abdelwahed, W.; Degobert, G.; Dubes, A.; Parrot-Lopez, H.; Fessi, H. *Int. J. Pharm.* **2008**, *351*, 289.
43. Khan, A. R.; Forgo, P.; Stine, K. J.; D'Souza, V. T. *Chem. Rev.* **1998**, *98*, 199.
44. Choi, J.-K.; Girek, T.; Shin, D.-H.; Lim, S.-T. *Carbohydr. Polym.* **2002**, *49*, 289.
45. www.agrineem.com/PDF-Files/FUNCTIONAL_BLOCKS_OF_NEEM_OIL.pdf. Accessed on 10 Jan, 2012.
46. Wu, D.; Huang, Z.; Yin, G.; Yao, Y.; Liao, X.; Han, D.; Huang, X.; Gu, J. *Cryst. Eng. Comm.* **2010**, *12*, 198.
47. Simoes, J. A.; Citron, D. M.; Aroutcheva, A.; Anderson, R. J., Jr.; Chany, C. J.; Waller, D. P.; Faro, S.; Zaneveld, L. J. D. *Antimicrob. Agents Chemother.* **2002**, *46*, 2695.
48. Fukai, T. *Med. Plants Res. (Nagasaki)* **2001**, *24*, 38.
49. Mitra, C. R.; Garg, H. S.; Pandey, G. N. *Phytochemistry* **1971**, *10*, 857.
50. Tsuchiya, H.; Iinuma, M. *Phytomedicine* **2000**, *7*, 161.
51. Biswas, K.; Chattopadhyay, I.; Banerjee, R. K.; Bandyopadhyay, U. *Curr. Sci.* **2002**, *82*, 1336.
52. Brickner, S. J.; Gaikema, J. J.; Greenfield, L. J.; Zurenko, G. E.; Manninen, P. R. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 2246.
53. Joshi, M.; Wazed Ali, S.; Rajendran, S. *J. Appl. Polym. Sci.* **2007**, *106*, 800.
54. Ibrahim, N. A.; El-Gamal, A. R.; Gouda, M.; Mahrous, M. *Carbohydr. Polym.* **2010**, *82*, 1205.
55. Kay, A.; Grá tzel, M. *Chem. Mater.* **2002**, *14*, 2930.
56. Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, P. A.; Seiler, B. D.; Shelton, M. C.; Tindall, D. *Prog. Polym. Sci.* **2001**, *26*, 1605.
57. Zhu, L.; Wang, C.; Qiu, Y. *Surf. Coat. Technol.* **2007**, *201*, 7453.