RJC

RASĀYAN *J. Chem.*
Vol. 15 | No. 1 |402-407| January - March | 2022
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

ANTIBACTERIAL PROPERTIES AND UV- PROTECTION OF COTTON FABRIC USING NANOHYBRID MULTILAYER ZnO-SiO_2/CHITOSAN AND DODECYLTRIETOXYSILANE (DTS)

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ABSTRACT

This study aims to conduct the synthesis and characterization of nanohybrid multilayer ZnO-SiO_2/Chitosan (NHM-ZnO-SiO_2/Chitosan) using SEM and TEM to show the rod-shape morphology. Furthermore, the compound is used as a textile fiber coating material for anti-bacterial and UV-protected applications. The process was followed by hydrophobization of *Dodecyltrietoxysilane* (DTS) using a 1,2,3,4-butane tetracarboxylic acid (BTCA) crosslinker. FT-IR showed that the coating of NHM-ZnO-SiO_2/Chitosan on textile fibers has covalent ester interactions with the appearance of the C=O stretching functional group at ~1700 cm^{-1} and each cotton fabric provided different intensity. Meanwhile, SEM showed that the layer has a rough surface, which is associated with the distribution of NHM-ZnO-SiO_2/Chitosan to create a hydrophobic surface, as evidenced by the water contact angle WCA = 100-119°. Furthermore, UV-DRS analysis was also conducted for UV protection testing and a decrease in the value of Eg = 2.87 eV on textiles coated with NHM-ZnO-SiO_2/Chitosan and DTS was obtained. Anti-bacterial activity of uncoated, BTCA - ZnO-SiO_2/Chitosan coating, BTCA - ZnO-SiO_2/Chitosan coating, and DTS textiles were evaluated against bacterial cells of *Staphylococcus epidermidis* (37.7 - 47.2) mm and *Pseudomonas aeruginosa* (42.0 - 49.2) mm.

Keywords: Anti-bacterial, Cotton Fabric, Hybrid Multilayer, ZnO-SiO_2/Chitosan, DTS.

RASĀYAN *J. Chem.*, Vol. 15, No.1, 2022

INTRODUCTION

Currently, nanotechnology development has spurred the innovation of improving product quality in the field of textile technology[1]. Textile coatings using materials designed with nanotechnology can improve the mechanical, physical, chemical, and biological properties of the fiber strength, fiber softness, and the desired aesthetic characteristics.[1] Furthermore, textile cotton fiber is naturally made from cellulose and is the most widely used in clothing manufacture. It is a material with superior properties such as flexibility, biodegradability, low cost, and high mechanical stability. However, due to the abundance of hydroxyl groups on the surface, the cotton fiber is hydrophilic or the surface absorbs water.[2] The function of hydrophilic cotton textile fibers has been modified into hydrophobic properties by using metal oxides nanomaterial compounds such as TiO_2, ZnO, Fe_2O_3, CeO_2, and their composites. They provide multifunctional properties on textile cotton fibers, including acting as anti-bacterial, anti-fungal[3], anti UV[4], self-cleaning[5], hydrophobic, and anti-fire (retardant).[1]

The hydrophobic nature of a surface is designed by observing the natural biological properties. Many characteristics of biological organisms examined are the surface wettability such as the self-cleaning properties of leaves.[2,3] Based on this, the production of a surface with a wettability level is usually made

http://dx.doi.org/10.31788/RJC.2022.1516702

by two methods: (1) introducing a roughness hierarchy to the substrate (2) coating a micro/nanostructured surface with low energy molecules.[4] Meanwhile, hydrophobization with the creation of surface roughness with low energy can reduce its moisture. The advantages of hydrophobic textiles can reduce the strength of fibers, protect them from microbial contamination, as well as prevent odor and stains.[5] The process can be conducted by using an inorganic material designed to be morphologically shaped like a rod (rod, cube), using silane hydrophobic materials such as Silane compounds to modify the surface properties of textiles. These compounds include hexamethyldisiloxane (HMDS), 1H,1H, 2H,2H perfluorodecyltrichlorosilane (PFDTS), dodecyltrimethoxysilane (DTMS)[6], (OTS).[7] Furthermore, synergized metal oxide coatings with hydrophobic silane materials have been reported, such as ZnO-SiO_2 on cotton fibers using octadecyltrimethoxysilane (OTS).[8,9] ZnO-SiO_2 coating on poly (ethylene terephthalate (PET) fibers uses a different binding agent, namely hexadecyltrimethoxysilane.[10]

A simple method of hydrophobic textile preparation was conducted using the dip-spin coating method and was reported with a one-step process. In addition, a thin layer of a composite compound containing NHM-ZnO-SiO_2/Chitosan with a hydrophobic compound of *Dodecyltrietoxysilane* (DTS) was reported. Hydrophobic textiles showed an excellent property of reducing moisture with a static water contact angle (WCA) on the surface of hydrophobic fibers indicated by WCA 90^o.

EXPERIMENTAL

Preparation of NHM- ZnO-SiO_2/Chitosan

The preparation method of NHM-ZnO-SiO_2/Chitosan was conducted based on the previous procedure, briefly described as follows: a 0.1 M Zn-nitrate precursor was hydrolyzed with 0.4 M NaOH hexamethylenetetramine buffer (HMT) at pH13. Furthermore, the crosslinkers Poly (diallyldimethylammonium chloride) (PDDA) 0.1 M and Poly (sodium 4-styrene sulfonate) (PSS) 0.1 M were used for the formation of composites with 0.1 M Tetraethylortosilicate (TEOS). CTAB and chitosan with a ratio of (5:1) were used as rods mold templates. Meanwhile, the mixture was placed in an autoclave at 180^{o}C, 24 hours, and continued calcining at 600^{o}C within 4 hours.[11]

Coating of NHM- ZnO-SiO_2/Chitosan dan DTS on Cotton Fabrics

The preparation of antibacterial and UV protect textiles was conducted based on the previous procedure, using NHM-ZnO-SiO_2/Chitosan coating material with 1,2,3,4-Butane-tetracarboxylic acid (BTCA) cross-linker and NaH_2PO_4 as a catalyst. The hydrophobization process was conducted by synergizing the coating composition of NHM-ZnO-SiO_2/Chitosan and DTS (5:1).[12]

Characterization of Cotton Fabric Finished

Morphology of NHM-ZnO-SiO_2/Chitosan and Cotton fabric was conducted with NHM-ZnO-SiO_2/Chitosan and DTS, characterized by Fourier transform infrared (FT-IR) spectra. The recording was conducted using a Perkin Elmer Spectrum Version 10.5.1, UV-DRS in a Hitachi U-3900 H spectrophotometer. The TEM (Transmission electron microscopy) used was JEOL JEM2100. Furthermore, SEM-EDX (Scanning electron microscopy- dispersive X-ray spectroscopy) was established by Mira 3-XMU-TESCAN FESEM (Czech).

Antibacterial Test of Cotton Fabric Finished

The antibacterial textile test was qualitatively conducted by the diffusion method according to the previous procedure, based on the inhibition zone measurement by a scale (cm^2/hour). Furthermore, the samples consisted of uncoated, BTCA cross-linker, BTCA-NHM-ZnO-SiO_2/Chitosan, BTCA-NHM-ZnO-SiO_2/Chitosan, and DTS textiles. Uncoated textiles were used as negative control while chloramphenicol antibiotic was used as a positive control.[13]

RESULTS AND DISCUSSION

Morphological Analysis of NHM-ZnO-SiO_2/Chitosan

Rilda et al., (2021) stated that the NHM-ZnO-SiO_2/Chitosan compound was synthesized using a PDDA and PSS cross-linker. The cross-linker form interaction between ZnO and SiO_2 as a composite compound

in the form of a core-shell, where the core is ZnO and the shell is SiO_2. Furthermore, NHM-ZnO-SiO_2/Chitosan has a rod-like morphology based on the SEM and TEM analysis as shown in Figure 1. The rod's shape has specifications of length (140-400) nm and diameter (20-150) nm. It can give the substrate surface roughness and hydrophobic properties when used as coating material.[11]

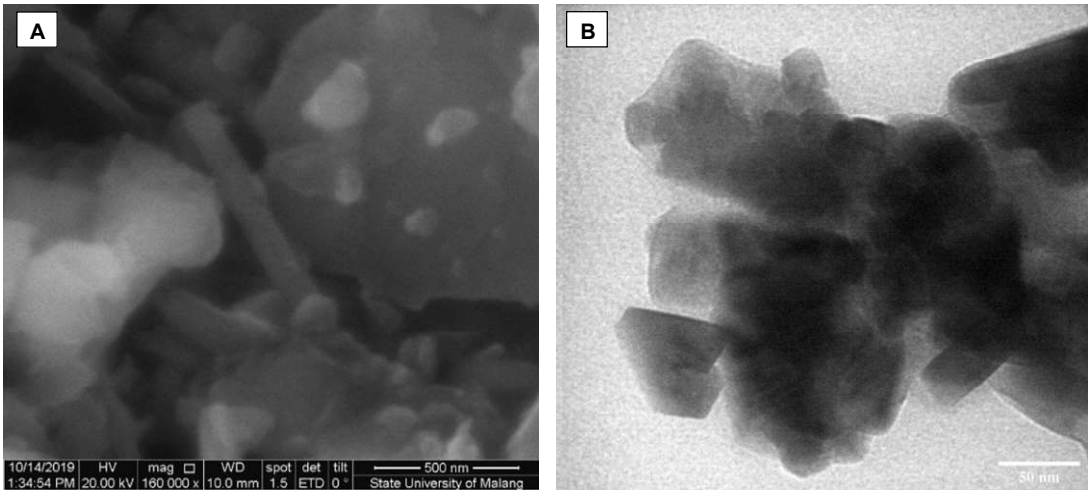

Fig.-1: (A) SEM and (B) TEM of NHM-ZnO-SiO_2/Chitosan

FT-IR Analysis of Cotton Fabric Finished

Coating of NHM-ZnO-SiO_2/Chitosan on textile fibers with cross-linker 1,2,3,4-Butane-tetracarboxylic acid (BTCA) provided four active sites of covalent ester interactions. The interactions were between hydroxyl groups of cellulose fibers for coating inorganic compounds NHM-ZnO- SiO_2/Chitosan, according to its four carboxylate groups. The stability of the coating was determined by the increasing number of active sites from the cross-linker and repeated washing of textiles[6]. Figure-2 (a, e) showed the FT-IR pattern of the textile coated with several coating treatments. The observations focused on the intensity of the C=O stretching group at wavenumbers 1633 cm-1 - 1717 cm^{-1} and the –OH group at 3260.25 cm^{-1} - 3320.26 cm^{-1}. Meanwhile, the difference in coating materials showed the difference in intensity in the two absorption regions as shown in Fig.-2. The intensity of the -OH group in Fig.-2f can be tested for water repellent properties with WCA > 90º after hydrophobic treatment with DTS compounds.

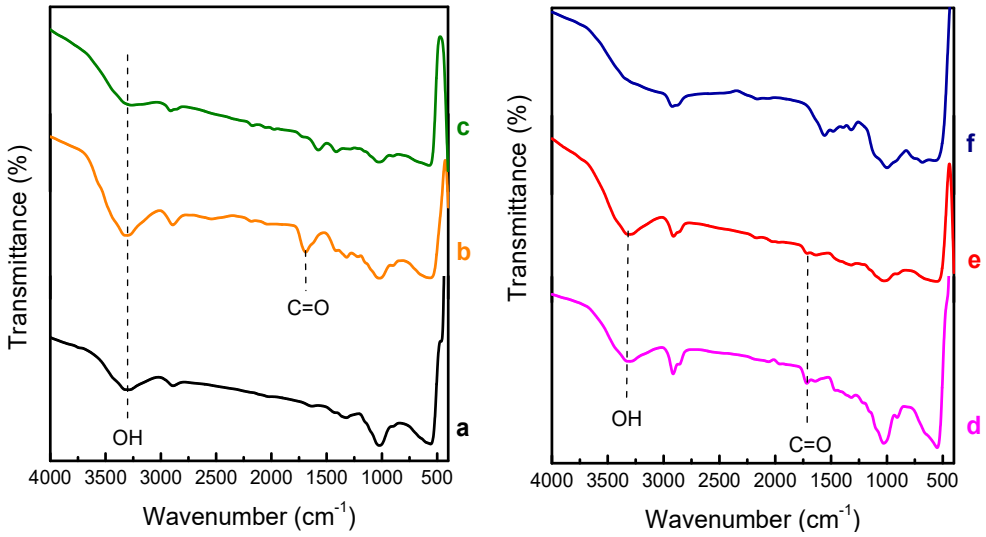

Fig.-2: Textile FT-IR pattern (a) without coating (b) BTCA (c) BTCA - ZnO/Chitosan (d) BTCA-NHM-ZnO-SiO_2/Chitosan (1:1) (e) BTCA-NHM-ZnO-SiO_2/ Chitosan (1:2) (f) BTCA-NHM-ZnO-SiO_2/Chitosan (1:1) and DTS

UV-DRS Analysis of Cotton Fabric Finished

UV-DRS analysis provided information about the ability of NHM-ZnO-SiO2/Chitosan compounds to absorb light as photons for photocatalytic reactions. The energy bandgap (Eg) was calculated through the Planck equation Eg = h.c/λ when Eg is small, then λ is large. Hydrophobic textiles can be UV protection, and the analysis showed a decrease (Eg) = 2.78 eV compared to NHM-ZnO-SiO_2/Chitosan without DTS (Eg) = 3.01 eV, as shown in Fig.-4. Furthermore, the hydrophobization process caused a shift in the absorption of textile fibers from UV to the visible light region or it can be assumed that the fiber is hydrophobic and UV impermeable.[14]

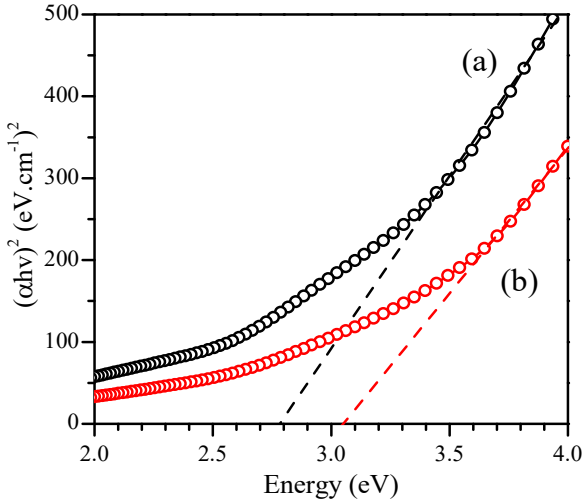

Fig-4: Textile UV-DRS pattern (a) BTCA - NHM-ZnO-SiO_2/Chitosan (b) BTCA – NHM ZnO-SiO_2/Chitosan and DTS

SEM Analysis of Cotton Fabric Finished

Figure-5 showed the SEM pattern of the textile surface (5a) without coating, (5b) with NHM-ZnO-SiO_2/Chitosan, (5c) NHM-ZnO-SiO_2/Chitosan, and DTS.

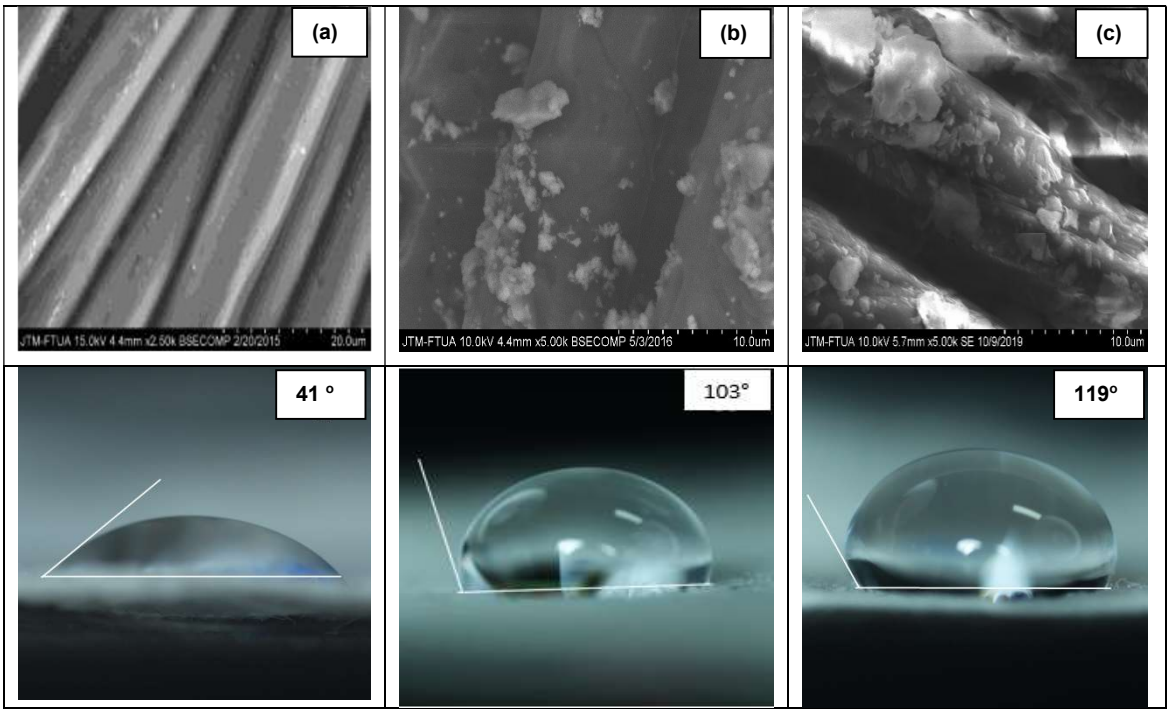

Fig.-5: Surface Morphology of Hydrophobic Textiles (a) Non-coated Textiles (b) NHM-ZnO SiO_2/Chitosan (b) NHM-ZnO-SiO_2/Chitosan and DTS

The SEM pattern was conducted by testing the hydrophobic properties based on WCA measurements when a liquid was dropped on the surface as shown in Fig.-5. Table-1 showed that the different compositions of textile coating materials provide different water repellent properties based on WCA measurements. Hydrophilic textile surface modification was conducted with a water-repellent coating material.[15] According to Barry (2006), the surface is hydrophobic at a contact angle of 90°, while hydrophilic has a WCA = 5 - 40° [16]. When the PSS ratio is greater than PDDA (1:2), then the hydrophobic properties are smaller due to the amount of Si adsorbed on the ZnO surface, when compared to NHM-ZnO-SiO_2/Chitosan (1:1).[17,20]

Table-1: Hydrophobic Properties of Cotton Fabric Finished

Sample of Textile	WCA
Textiles without coating	41°
ZnO/Chitosan Coating	95°
Coating of NHM-ZnO-SiO_2/Chitosan (1:1)	103°
Coating of NHM-ZnO-SiO_2/Chitosan (1:1) and DTS	119°
Coating of NHM-ZnO-SiO_2/Chitosan (1:2)	97°
Coating of NHM-ZnO-SiO_2/Chitosan (1:2) and DTS	100°

Antibacterial Textile Test of Cotton Fabric Finished

Evaluation of the textile antibacterial properties was tested on *Staphylococcus epidermidis* and *Pseudomonas aeroginosa* bacteria in vitro. The test bacteria were selected based on their pathogenic properties against the skin.[3,12,19] Generally, both bacterial species can be inhibited with NHM-ZnO-SiO_2/Chitosan with an inhibition zone of ≥ 20 mm categorized as very strong, as shown in Fig.-6. Table-2 showed that the composition of the coating material has different inhibition zones for the two species. The data can be related to the hydrophobic nature in Table-2, and the inhibition zone becomes very large with an increased hydrophobic surface.

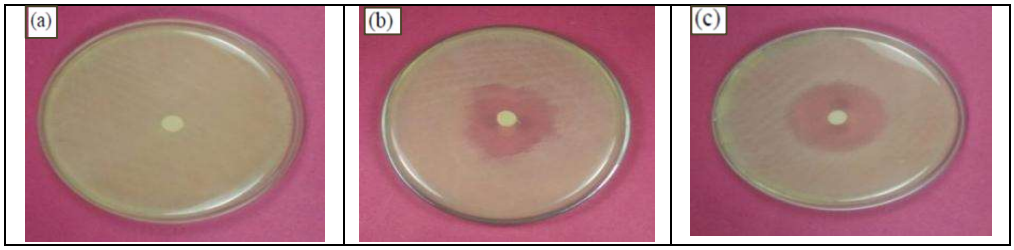

Fig.- 6: Inhibition of NHM-ZnO-SiO_2/Chitosan in Bacteria (a). Textiles without coating (b) *Staphylococcus epidermidis* and (c) *Pseudomonas aeroginosa.*

Table-2: Antibacterial Activity of *Staphylococcus epidermidis and Pseudomonas aeruginosa*

Textile Coating	Inhibition Zone (mm)	
	S.epidermidis	*P. aeruginosa*
Textiles without coating (Control -)	-	-
Chloramphenicol Coating (Control +)	40.3	42.5
Coating of NHM-ZnO-SiO2/Chitosan (1:1)	32.4	42.8
Coating of NHM-ZnO-SiO2/Chitosan (1:1) and DTS	47.2	49.2
Coating of NHM-ZnO-SiO2/Chitosan (1:2)	30.3	34.3
Coating of NHM-ZnO-SiO2/Chitosan (1:2) and DTS	37.7	42.0

CONCLUSION

Generally, nanohybrid multilayer ZnO-SiO_2/Chitosan (NHM-ZnO-SiO_2/Chitosan) particles showed broad-spectrum bactericidal activity for pathogenic bacterial species and had advantages over the antibiotic agent chloramphenicol. Furthermore, various coating formulations have been studied to show

an increase in antimicrobial activity. There was a significant increase when NHM-ZnO-SiO_2/Chitosan was synergized with DTS hydrophobic material. The results obtained WCA=100 - 119º and an increase in the inhibition zone on *Staphylococcus epidermidi*s and *Pseudomonas aeruginosa* by (37.7 - 47.2) mm and (42.0 - 49.2) mm respectively.

ACKNOWLEDGMENT

This study was supported by Andalas University under Research Contract No.T/2/UN.16.17/PP.IS-KRP1GB/LPPM/2021 the Fiscal Year 2021.

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