Employing Monocholorotriazine β-cyclodextrin to improve Wool-containing Fabrics' Reactive/Disperse Printability and Antibacterial Properties

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Abstract:

In this work, monochlorotriazinyl β-cyclodextrin (MCT-βCD) was grafted onto or within a structure made of wool-containing fabric to generate hydrophobic cavities. The above cavities had the capacity to form what so call host-guest inclusion complexes with Resocoton Red G (Mixtures Reactive/Disperse) dye particles in post-printing, and antimicrobial agents during in the subsequent final post-finishing stage with AgNPs/HBPAA (silver nanoparticles/ hyperbranched polyamide-amine) matrix. According to the aforementioned route, the resulting products' surface morphology, composition, coloration properties, and antimicrobial activities against (S. aureus) and (E. coli) harmful bacteria were examined. The obtained results highlight that grafting of MCT- βCD (20g/L), subsequently printing using reactive/disperse dye and subsequent after-treatment with AgNPs/HBPAA hybrid (10g/L) is an effective technique to create reactive/disperse prints with exceptional antimicrobial activities. SEM scans verified the active ingredient depositions on the fabric-treated surface.

Keywords:

Wool containing fabric, MCT-βCD, Pre-modification, Reactive/ Disperse printing, Ag-NP's, Post- antimicrobial finishing.

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1. Introduction:

Due to its improved qualities, such as eco-friendliness, hydrophilicity, comfortability, and biodegradability, textile fabrics made of wool have found wider applications in areas such as clothing, sportswear, leisure activities, fashion, home textiles, etc… (1).

Natural fibres, on the other hand, offer the right environment and surface for the harboring and growth of harmful microorganisms like bacteria, fungi, etc., which facilitates cross-infection, the development of objectionable odors, as well as the discoloration and deterioration of fabric (2,3). To reduce/avoid disease, prevent the growth of odors, and protect the textile material itself from microbial infection, the antibacterial operation of natural fiber textile material is attracting more attention as a method of protecting the textile material itself from microbial contamination. This is done by using appropriate antimicrobial agents with the capacity to either kill or block biologically static, the growth of harmful bacteria (4-7).

Furthermore, in the textile finishing field, complexation is the long-term fixing of β-Cyclodextrin derivatives to textile surfaces with a wide range of dyestuffs and/or botanical extracts within their hydrophobic cavities for the generation of improved quality colored and/or functionalized textile products (8-13).

In this study, a new simple method was created in which MCT-βCD (monochloro-triazinyl β-cyclodextrin) was pre-loaded onto fabrics containing wool to improve their post-reactive/ disperse printing and add new functionalities using the right active ingredients, specifically a composite made of hyperbranched poly (amid-amine, HBPAA) loaded with AgNPs.

2. Experimental

2.1. Materials

Fabrics with plain weaves of 100% mill-scoured and semi-bleached wool (220 g/m2), cotton/wool, viscose/wool (50/50, 180 g/m2), and wool/polyester (50/50, 230 g/m2) blended fabrics were also used.

Commercial-grade products included Ludigol® (an oxidising agent based on the sodium salt of m-nitrobenzene sulfonic acid, BASF, Germany), Cavasol® W7MCT (monochlorotriazinyl β-cyclodextrin, MCT- βCD, average molecular weight 1560, degree of substitution (0.3-0.6 per anhydroglucose unit- Wacker, Germany), Dialgin® LV-100 [Na-alginate of low viscosity, BF-Goodrich Diamalt, GmbH, Germany) and Leomin® W (nonionic wetting agent and detergent, BASF, Germany).

Resocoton Red G (Mixtures of Resolin® dyestuffs with Levafix® P or Levafix® P-A dyestuffs) (Bayer, Germany) were used for Reactive/Disperse printing of the nominated substrate.

As described before (14), a hyper-branched poly (amide-amine-HBPAA)/AgNPs composite was created. The resulting AgNPs were spherical in shape and ranged in size from 32 to 35 nm.

2.2. Methods

2.2.1. MCT-βCD Pre-loading

With continual stirring, an MCT-βCD aqueous solution (0–20 g/L) was created with sodium carbonate (10 g/L) and a nonionic wetting agent (2 g/L). To wet-pick up 80% owf, fabric samples were padded twice in the prepared solutions before being directly fixed at 125°C for 10 min. The partially hydrolyzed or unfixed MCT-βCD was then removed from the treated fabric samples by rinsing them for 10 minutes, and they were then dried at 100°C for 5 minutes.

2.2.2. Resocoton Red G (Mixtures Reactive/ Disperse) printing

The nominated reactive/disperse dyes were post-printed onto both the pre-modified and unmodified fabric samples using the flat screen technique under the following conditions:

Printing paste components	g/kg paste
Resocoton Red G dye	20
Na-alginate (10%)	500
Na-carbonate (Na2CO3)	10
Urea	100
Ludigol®	10
Water	X
Total	1000

Using an Ariolt® CSL-steamer, Italy, The samples of printed fabric were then dried at 100°C for 5 minutes and steam fixed for 15 minutes at 110°C. A part of reactive/disperse samples of printed fabric were fully washed, then soaped at 60°C for 15 min while being exposed to 2g/L Na2CO3 and 2g/L nonionic/detergent agent. After thoroughly rinsing again, the samples were dried at 100°C for 5 min.

2.2.3. AgNPs/ HIPAA hybrid Post-finished

A finishing formulation including AgNPs/HBPAA (10 g/L) and a nonionic wetting agent (2 g/L) was used to padding some of the prints twice at pH 5 using acetic acid, to give an 80% wet pick-up. Next, direct thermofixation at 150 °C for 3 min. was performed, followed by thorough rinsing, washing at 50 °C for 10 min. in the presence of a nonionic wetting agent.

2.3. Test

The nitrogen content %N was calculated using the micro-Kjeldahl method (15).

The depth of the produced Resocoton prints before and after post-finishing was measured with an automatic filter spectrophotometer at the wavelength of maximum absorbance and estimated using the Kubelka Munk equation (16).

According to AATCC Test Method (147-1988), the antibacterial activity of the treated and untreated fabric samples was evaluated qualitatively against Gram- positive (S. aureus, G+ve) and Gram-negative (E. coli, G-ve) pathogenic bacteria, and expressed as zone of growth inhibition (ZI, mm).

The fastness properties of the produced prints to washing, rubbing, perspiration, and light were examined using AATCC test methods: (61-1972), (8-1972), (15-1973) and (16A- 1972) respectively.

Using a JEOL, images from selected samples taken with a scanning electron microscope (SEM) were assessed.

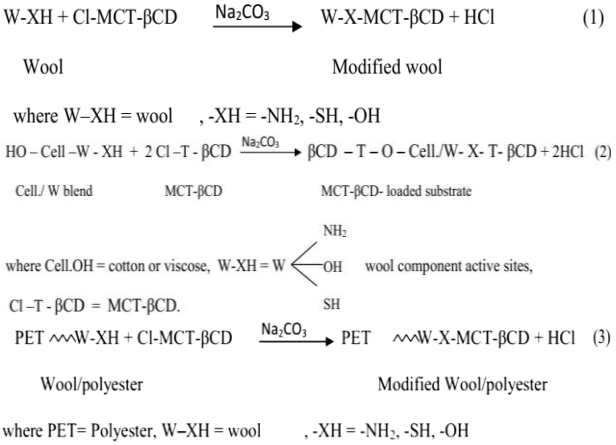
3. Results and Discussion

The following treatment sequence has been tried because the main objective of the study was to show the beneficial effects of loading MCT-βCD onto/into wool, cotton/wool (C/W), viscose/wool (V/W), and polyester/wool (PET/W) blended fabrics on improving its post-printing and improving the antimicrobial activities of the procured prints:

grafting of MCT-βCD→ post-printing with Resocoton dye (Mixtures Reactive/Disperse)dye→ after treatment with AgNPs/HBPAA hybrid antibacterial agents.

3.1. Effect of MCT-βCD concentration

The rise in the %N of the treated wool, viscose/wool, cotton/wool, and polyester/wool blended fabric samples is shown in Fig. 1a, demonstrating the attachment of MCT-βCD onto/into the wool-containing structure [Eq. 1, 2, 3].



When all other factors are held constant, the degree of pre-modification of the nominated substrates, expressed as %N, is as follows:W> V/W> PET/W> C/W, this is due to the differences between the four substrates, their weights, the availability of their reactive centers, and the degree to which the active components penetrated the structure of fabric. This in turn affected the degree to which MCT-βCD was loaded onto or into the fabric's structure (13, 14).

On other side, Fig. 1b depicts K/S representing the impact of pre-modifying the wool structure using MCT-βCD on the degree of post-printing, when Resocoton Red G (Mixtures Reactive/Disperse) dyestuffs are used. It is obvious that increasing the degree of MCT-βCD (20 g/L) fixation improves the K/S values of the resulting prints for a given set of premodification and post printing factors. The ability of the grafted MCT-immobilized CD's hydrophobic-inner cavities to establish inclusion complex with the designated Resocoton Red G (Mixtures Reactive/Disperse) dye could be explained in terms of both the hydrophilicity of the wool surface and the addition of many hydrophilic groups, i.e. - OH groups (17).

The rise in β-CD moieties is thought to be responsible for this improvement in the K/S values by increasing the extent of dye picking-up and fixing onto/within the wool, viscose/wool, cotton/wool, and polyester/wool structures (2).

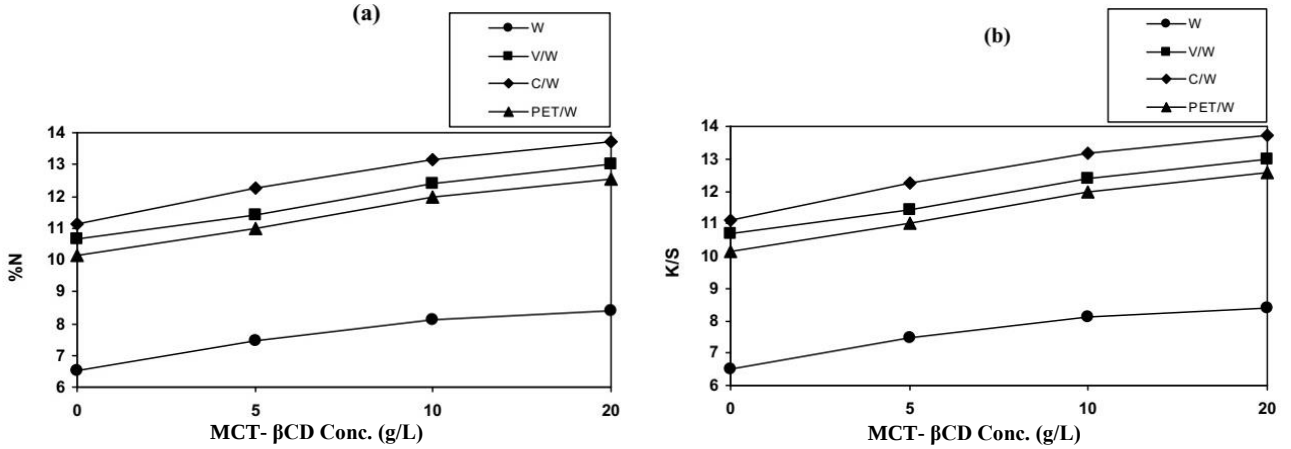
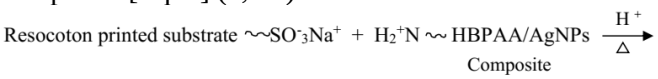


Fig 1. Effect of MCT- βCD concentration on the extent of modification of @: wool, V/W: viscose/Wool, C/W: cotton/wool and PET/W: polyester/wool blends (%N, a) and its impact on post- printing with the Resocoton Red G (Reactive/Disperse) dyestuff (K/S, b)

3.2. The effect of AgNPs/ HBPAA composite post-treatment on printed fabric samples

The effects of post-treating Resocoton Red G (Mixtures Reactive/Disperse) samples of printed fabric containing AgNPs/HBPAA on the %N and K/S values of the produced goods are shown in Fig. 2 (a, b). As can be shown, regardless of the substrate employed, increasing the composite quantity up to 20g/L improves both the K/S Values for depth of color and the %N values for nitrogen content. While maintaining other parameters constant, this advancement in the %N follows the descending order W>C/W>PET/W>V/W and in the K/S follows the descending order PET/W>C/W>V/W>W. This improvement is attributed to the used composite's capacity to interact with both the grafted MCT-CD and the Resocoton Red G dye solubilizing groups, thus increasing the extent of loading AgNPs/HBPAA composite [Eq .4] (3, 13).



AgNPs/ HBPAA- loaded substrate (4)

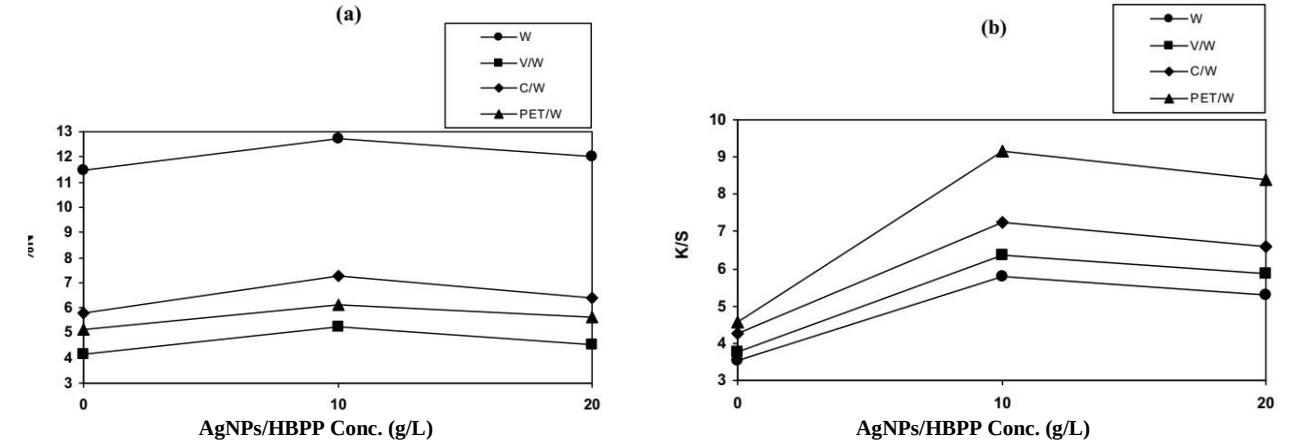
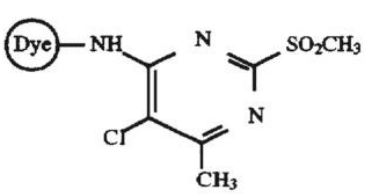
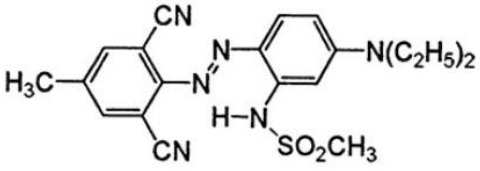


Fig 2. Effect of post-treatment of the W: wool, V/W: viscose/Wool, C/W: cotton/wool and PET/W: polyester/wool printed fabric samples with AgNPs/ HBPAA composite on (%N, a) and (K/S, b) val



Levafix® P (Reactive dye)



Resolin® Red (Disperse dye)

Fig. 3 Chemical Struture of Resocoton Red G Dye (Mixtures of Resolin) dyestuffs with Levafic P dyestuffs

The type of dye, location and extent of distribution as well as ability to bind/load the nominated hybrid onto the printed fabric surface, all affect how much the %N and K/S are improved. This improvement is due to interactions between the modified wool-containing fabric structure, which includes β-CD moieties, -NH2, -COOH, -OH groups, etc., the encapsulating Ag/NPs via hydrogen bonding, electrostatic interactions, and/or complex formation, the loaded Ag-NP's/HBPAA active sites, such as -NH2, -NH, ...etc., the fixed dye-functional and solubilizing groups, and so on (2,14,18).

3.3. Antibacterial functionalization, Fastness properties and Coloration:

Table 1. shows how the kind of substrate, the order of treatment, and the type of Resocoton Red G dye affect the antibacterial functionalization and coloration of the resulting wool, viscose/wool, cotton/wool, and PET/wool prints, as reflected in ZI values, K/S, and fastness properties, respectively. It is obvious that: the kind of dye, where and how much it is distributed, and how well it may bind or load the specified hyprid onto the surface of the printed fabric, determine the extent of improvement in the K/S, fastness properties, and antibacterial properties; These improvements are a result of interactions between the altered wool's structural components, including β-CD moieties, -NH2,-COOH, -OH groups, etc.., the improved antimicrobial effectiveness of the treated Resocoton Red G prints against Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria, the solubilizing groups and fixed dye-functional, the loaded Ag-NP's/HBPAA active sites, such as NH2, NH, and so on, and the trapped Ag/via NP's hydrogen bonding, electrostatic forces and/or complex formation, the amount of loaded hyperbranched polymer with its encapsulated AgNPs determines how much the antibacterial functionality is enhanced.

The antibacterial activity against the selected microorganisms (E. coli and S. aureus) is listed in decreasing order S. aureus > E. Coli, regardless of the dyestuff used.

The antimicrobial effect of the loaded AgNP's onto the prints of wool, viscose/wool, cotton/wool, and PET/wool samples, on the other hand, could be explained in terms of: i) possible DNA damage through the interaction of AgNPs with proteins containing sulphur or phosphorus and the detrimental effects on the respiration chain or cell division process, resulting in cell death, ii) Ag-ions released by Ag-NPs interact ionically with the bacteria's cytoplasm membrane in the manner described below (19): and or iii) the following reaction results in the creation of active oxygen (20, 21)

$$O_{2\,(aq)} + 4\,H_3O^+ + 4\,Ag_{(S)} \rightarrow 4\,Ag^+_{(aq)} + 6\,H_2O \qquad (5)$$

Table 1. Effect of pre-treatment with MCT- β -CD as well as post treatment with silver nanoparticles (AgNPs/HBPP) on Resocoton (Mictures Reactive/ Disperse) printed and Antimicrobial properties

Dyestuff	Substrate		%N	K\S	Incr. in K/S (%)	WF		RF		PF				LF	Antimicrobial Activity (zone mm)	
						Alt	C	Dry	Wet	Acidic		Alkaline			G +ve	G −ve
										Alt	C	Alt	C			
Resocoton Red G	W	UT	11.45	3.54	63.84	3-4	2	3-4	3	3-4	3-4	2-3	3	2-3	0	0
		T	12.70	5.80		4-5	3-4	4-5	3-4	4-5	4-5	4-5	4-5	4-5	17	15
	V/W	UT	4.15	3.78	68.78	4	3	4	3-4	4	3-4	3-4	4	3	0	0
		T	5.25	6.38		4-5	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	24	22
	C/W	UT	5.80	4.26	69.95	4	3	3	2-3	4-5	3-4	4-5	4	3-4	0	0
		T	7.22	7.24		4-5	4	4	4	5	4-5	5	4-5	4-5	22	20
	PET/W	UT	5.12	4.55	101.31	4	3-4	3	3	4	3	3-4	3-4	4	0	0
		T	6.12	9.16		4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	22	20

(i) Pretreatment conditions: MCT-β-CD (20 g/L). sodium carbonate (10 g/L), non-ionic wetting agent (2 g/L), Padding to a wet pick-up (70%) followed by direct fixation at 125 C for 100 min, rinsing in water, neutralization with acetic acid 30% (2 g/L) at 30 C for 5 min, rinsing in water and drying at 100 C for 3 min

(ii) Resocoton and G (Mixtures Reactive/ Disperse) printed conditions: Resocoton Dye (20 g/kg); stock-thickening agent- 10% (500 g/kg); Na-carbonate ($N_2 2CO_3$) (20 g/kg); Ludigol (10 g/kg); Urea (100 g/kg); drying at 100 C for 5 min and steaming at 110 C for 5 min; followed by after-washing at 60 C for 15 min; in presence of (2 g/L) nonionic wetting agent.

(iii) After treatment conditions: AgNPS/HBPP (10 g/L), acetic (2 m1/L), Padding to a wet pick-up (80%); followed by direct fixation at 150 C for 3 min rinsing in water and drying at 100 C for 5 min, N: nitrogen content; K/S: color depth: WF: wash fastness; RF: rubbing fastness; PF: perspiration fastness; LF: light fastenss; Alt: alteration; C: staining on cotton; Z1 zone of inhibition; w: wool; v/w: WOOL/VISCOSE, c/w: wool/cotton, pet/w: wool/ polyester blend; u1: untreated; T: pretreated

with MCT-β-CD, Resocoton printed and after treated with AgNPS/HBPP

Moreover, hyperbranched polymer matrix protonation of amino-groups (Fig. 4) makes it easier for them to interact with the negatively charged bacterial surface, which causes the cell membrane to rupture and become more permeable (3, 6, 22-26).

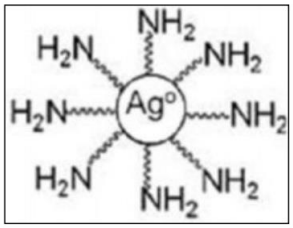
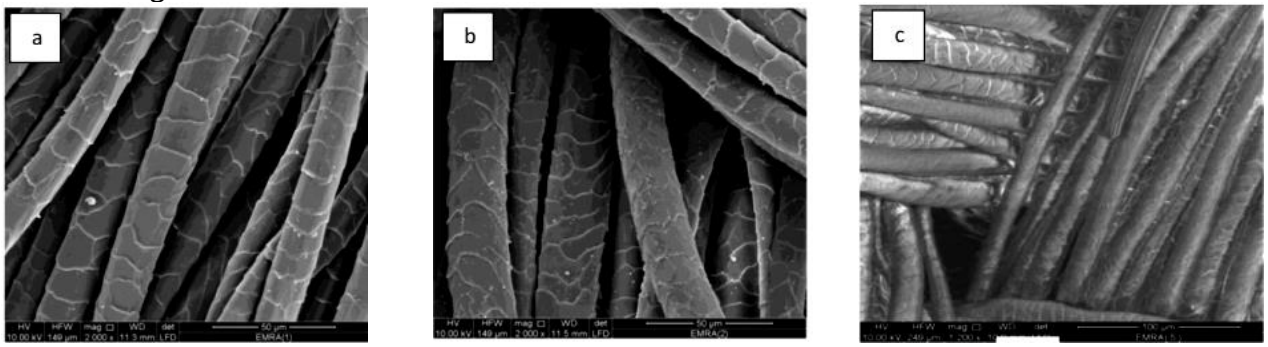


Fig. 4 AgNPs/HBPAA hyperbrid

3.4. SEM images:



(a) untreated wool

(b) Treated wool with MCT-β-Cyclodextrin

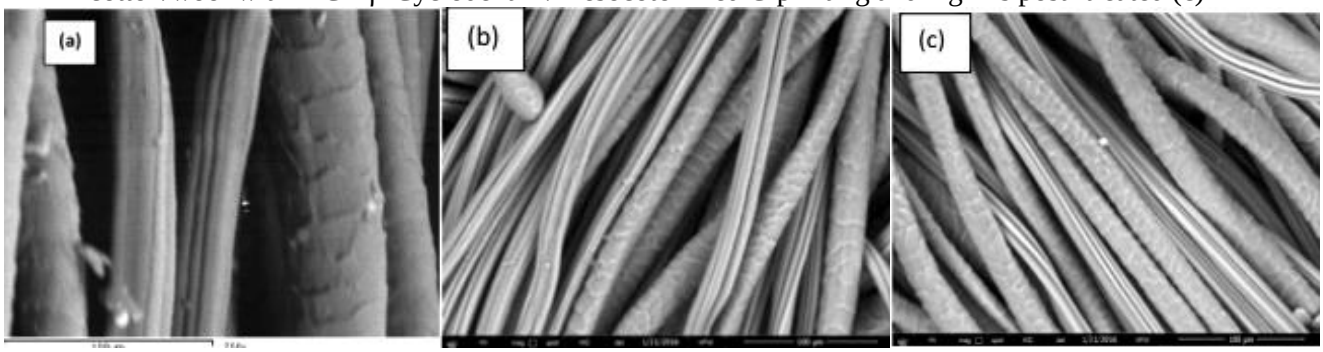
(c) Treated wool MCT-β-Cyclodextrin/ Resocoton Red and AgNPs-HBPP post-treated

Figures 5, 6, 7, and 8 respectively show SEM images of the surface of untreated, modified with MCT- β Cyclodextrin and MCT-Cyclodextrin Resocoton Red G (Mixtures reactive/disperse) printed W, C/W V/W, and PET/W blank samples in addition to fabric samples treated with AgNPs/HBPAA. The Resocoton Red G prints' SEM micrograph revealed a thin coating of printing paste spread across the fibre surface.

(b) Treated cotton/ wool with MCT-β-

(c) Treated cotton/ wool with MCT-β-Cyclodextrin/ Resocoton Red G and AgNPs-HBPP

Fig 6. SEM image of untreated cotton/ wool (a). treated cotton/wool with MCT-β-Cyclodextrin (b). treated cotton/wool with MCT-β-Cyclodextrin/ Resocoton Red G printing and AgNPs post- treated (c)

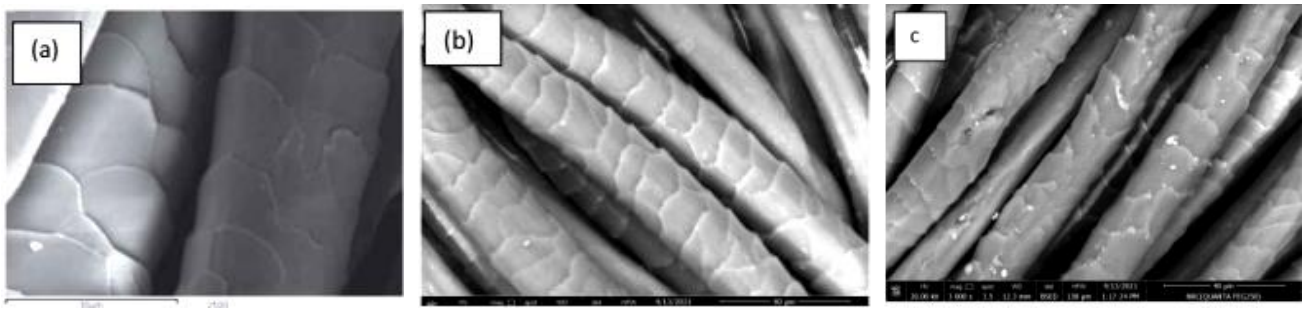


(a) Untreated Viscose/ wool

(b) Treated Viscose/ wool with MCT-β-

(c) Treated Viscose/ wool with MCT-β-Cyclodxtrin/ Resocoton Red G and AgNPS-HBPP

Fig 7. SEM image of untreated viscose/ wool (a). treated viscose/wool with MCT-β-Cyclodextrin (b). treated viscose/wool with MCT-β-Cyclodextrin/ Resocoton Red G printing and AgNPs post- treated (c)



(a) Untreated PET/ wool

(b) Treated PET/ wool with MCT-β-Cyclodextrin

(c) Treated PET/ wool with MCT-β-Cyclodextrin Resocoton Red G printing and AgNPs

Fig 8. SEM image of untreated PET/ wool (a). treated PET/wool with MCT-β-Cyclodextrin (b). treated PET/wool with MCT-β-Cyclodextrin/ Resocoton Red G printing and AgNPs post- treated (c)

4. Conclusions:

Through using Resocoton Red G (Mixtures reactive/disperse) dye to print the cellulose, polyester, and wool components in viscose/wool, cotton/wool, and PET/wool blended fabrics, this study introduces an efficient treatment method. Additionally, it demonstrates how to post-treat the printed substrates with AgNPs/HBPAA composite to give them a remarkable antibacterial property.

The results showed that the best method for producing Resocoton Red G prints with outstanding antibacterial capabilities against both S. aureus and E. coli pathogenic bacteria was the proposed substrates were pre-modified with MCT- βCD, followed by Resocoton Red G printing, and then post-finished with the proposed antibacterial agent. The type of substrate, degree of premodification, degree of fixation, type of post-finishing agent, load and interaction with the upgraded Resocoton Red G printed substrate, as well as kind of bacteria, all affect how much the coloration and functionalization properties in the obtained products are enhanced.

SEM imaging patterns for certain fabric samples supported the differences between treated and untreated fabrics in terms of Ag element loading and fabric surface morphology.

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