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Utilization of monochloro-triazine β-cyclodextrin for enhancing printability and functionality of wool

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ABSTRACT

Monochloro-triazine β-cyclodextrin (MCT-βCD) was successfully utilized to modify the wool fabric structure. The modified wool exhibited better post-printing, using different dyestuffs, and outstanding antibacterial activities most probably due to the remarkable capacity of grafted βCD moieties to form guest–host inclusion complexes in addition to the positive role of wool's active sites. The following treatment sequence: pre-modification, post-printing, followed by after-treatment with Ag-NP's colloid or triclosan derivatives was investigated. The extent of improvement in the aforementioned properties is governed by the degree of pre-modification, type of dyestuff and extent of fixation, type of antibacterial agent, its mode of interaction and extent of loading onto the modified printed wool. The imparted antibacterial functionalities were retained, more than 75%, even after 15 washing cycles.

1. Introduction

Wool is a heterogeneous mixture of proteins. The constituent protein in wool can show clear differences in changes by protonation and deprotanation of carboxylic and amino side-chain functionalities (Lewis, 2011). Pretreatment of wool fabrics prior to printing is absolutely essential to achieve full color yields, levelness and brightness. Wool may be colored with a variety of water soluble dyes but practically, it is invariably colored with sulphonated dyes (Bell, 1988; Lewis, 2011). On the other hand, the globalization of textile and clothing industries has, over the last decade, accompanied by a great changes in textile coloration as well as in textile functionalization which will continue to impact upon developments in the future (Holme, 2002).

Moreover, increasing global competition in textile and clothing field has created many challenges for textile researchers and industrialists, and generated many opportunities and options for the application of innovative technologies and finishes taking in consideration the consumer demand, as well as the economical and ecological concerns. Consumers are demanding textile products with enhanced functionalities, such as antibacterial, anti-UV, self-cleaning, antistatic, insect repellent and antiradiation (Bajaj, 2002; Gao & Cranston, 2008; Growri et al., 2010; Holme, 2005; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, & El-Batal, 2012; Ibrahim, Eid, & El-Zairy, 2011; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim & El-Zairy, 2009; Ibrahim, Refai, & Ahmed, 2010; Montazer & Pakdel, 2011; Montazer, Pakdel, & Behzardnia, 2011; Popescu, Mursean, & Grigoriu, 2011; Sayed & Jawale, 2006; Varesano & Tonin, 2008; Xu, Wu, Wel, & Chu, 2009). The enhancement in the imparted functional properties is governed by type of substrate, chemical structure and functionality of the reactive additive, mode and extent of fixation as well as application method (Holme, 2007; Ibrahim, Refai, et al., 2010).

Wool fiber is a high quality textile fiber due to its resilience and comfort attributes (Ibrahim, El-Shafei, et al., 2012; Liu, Lin, Peng, & Wang, 2012). Wool is also a hospitable host for the generation and propagation of microorganisms due to its large surface area and ability to offer oxygen, water and warmth thereby resulting in fiber damage, cross infection by pathogens, skin irritation and development of bad odor (Montazer et al., 2011; Tang et al., 2011). With increasing awareness of the importance of a hygienic health lifestyle, antimicrobial finishing of wool-based textiles has been received much attention in recent years (Dastjerdi & Montazer, 2010; Han & Yang, 2005; Ibrahim & El-Zairy, 2009; Liu et al., 2012; Montazer et al., 2011; Tang et al., 2011; Zhao & Sun, 2007).

This study investigates the chemical grafting of monochloro-triazinyl β-cyclodextrin (MCT-βCD) onto/into wool fabric, and the impact of wool modification on enhancing the extent of post-printing and subsequent antibacterial finishing.

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2. Experimental

2.1. Materials

Plain weave 100% mill-scoured and semi-bleached wool fabric (220 g/m^2) was used in this work.

Cavasol® W7MCT [monochlorotriazinyl β-cyclodextrin, MCT-βCD, average molecular weight ~1560, degree of substitution (0.3–0.6 per anhydroglucose unit) – Wacker, Germany], Ruco®-BAC MED [nonionic antibacterial finishing agent-based on diphenyl alkane derivative of triclosan – Rudolf Chemie], Invasan® [based on triclosan-Hunsman, USA], Dialgin® LV-100 [Na-alginate of low viscosity, BF-Goodrich Diamalt, GmbH, Germany], Ludigol® [oxidizing agent based on m-nitrobenzene sulfonic acid sodium salt-BASF-Germany], and Leomin® W [nonionic wetting agent and detergent-BASF-Germany] were of commercial grade.

Disperse Red 74, and Disperse Blue 183 (Sinochem Ningbo, China), Acid Red 266 and Acid Blue 40 (Thai Ambica, Thailand), Reactive Red 198 (hetero-bifunctional) and Reactive Blue 19 (vinyl sulfone (VS), OH young, Korea), as well as Reactive Blue 122 (homobifunctional, VS-VS, Dystar) were used as received.

Preparation of Ag nanoparticles (AgNP's) in hyper branched poly(amide–amine), HBPAA, and characterization of the obtained AgNP's/HBPAA hybrid were carried out as previously reported (Ibrahim, Abdel Rehim, & El-Batal, 2010; Ibrahim, Eid, et al., 2012).

All other chemicals used during this study such as citric acid, acetic acid, urea, sodium carbonate, sodium bicarbonate and silver nitrate were of laboratory reagent grade.

2.2. Methods

2.2.1. Grafting of wool with MCT-βCD

The fabric samples were padded twice in an aqueous solution containing MCT-βCD (0–20 g/L), Na-carbonate (0–10 g/L) along with a nonionic wetting agent (2 g/L) to wet pick-up 80%, followed by direct fixation at 120 °C for 10 min. The treated fabric samples were then washed under running water for 10 min to remove any unreacted and/or partially hydrolyzed MCT-βCD and finally dried at 100 °C for 5 min.

2.2.2. Post-printing

The modified wool fabric samples were post-printed using the flat screen technique and the following printed paste formulations:

Constituent	g/kg paste
(a) Disperse dye	20 g
Na-alginate (10%)	500 g
Acetic acid (30%)	15 g
Water	465 g
Total	1000 g
(b) Acid dye	20 g
Na-alginate (10%)	500 g
Citric acid	30 g
Urea	100 g
Water	350 g
Total	1000 g
(c) Reactive dye	20 g
Na-alginate (10%)	500 g
Na-bicarbonate	20 g
Urea	100 g
Ludigol®	10 g
Water	350 g
Total	1000 g

Printed fabric samples were then dried at 85 °C for 5 min and steam fixed at 110 °C for 15 min using Ariolt® CSL-steamer, Italy. A portion of post-printed fabric samples were rinsed thoroughly, soaped for 15 min at 60 °C in the presence of 2 g/L nonionic wetting agent, then thoroughly rinsed and finally dried at 85 °C for 5 min.

2.2.3. After treatments

2.2.3.1. Invasan®. A portion of printed fabric samples were padded twice to 80% wet pick-up with an aqueous formulation containing Invasan® (10 g/L) and a nonionic wetting agent at pH 5–6, with acetic acid, followed by thermofixation at 150 °C for 3 min in circulating air oven. The treated fabric samples were then rinsed thoroughly washed at 50 °C for 10 min in the presence of 1 g/L a nonionic wetting agent to remove excess and unfixed reagent, thoroughly rinsed, and finally dried at 85 °C for 5 min.

2.2.3.2. AgNP's/HBPAA hybrid. Another portion of printed fabric samples were padded twice in a finishing bath containing AgNP's/HBPAA (10 g/L), along with 2 g/L a nonionic wetting agent, at pH 5, using acetic acid, to give a wet pick-up of 80%, followed by direct thermofixation at 150 °C for 3 min, rinsed thoroughly, washed at 50 °C for 10 min in the presence of 1 g/L a nonionic wetting agent to remove excess and unfixed reactant, rinsed and finally dried at 85 °C/5 min.

2.2.3.3. Ruco®-BAC MED. The last portion of printed fabric samples were after-treated with Ruco® BAC aqueous solution (10 g/L) using a sample dyeing machine according to the following conditions: pH (5–6) using acetic acid, LR (1/20); agitation rate (40 rpm), at 50 °C for 30 min followed by squeezing to give a wet pick-up of 80%, thermofixed at 150 °C for 3 min, thoroughly rinsed to remove excess and unfixed active ingredients and finally dried at 85 °C/5 min (Ibrahim, Khalifa, El-Hossamy, & Tawfik, 2011).

2.3. Measurements

Nitrogen content (N%) was determined according to the Kjeldahl method.

The depth of the obtained prints, expressed as K/S, was measured at the wavelength of the maximum absorbance using an automatic filter spectrophotometer, and calculated by the Kubelka Munk equation (Judd & Wyszeck, 1975):

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

where K, S and R are the absorption coefficient, the scattering coefficient and the reflectance respectively.

Fastness properties to washing, rubbing, perspiration and light of the obtained prints were evaluated according to AATCC test methods: (61-1972), (8-1972), (15-1973) and (16A-1972) respectively.

Antibacterial activity assessment against G+ve bacteria (*S. aureus*) and G−ve bacteria (*E. coli*) was evaluated qualitatively according to AATCC test method (147-1988) and expressed as zone of growth inhibition (mm) and quantitatively, in case of using triclosan-based products, according to AATCC test method 100-1999, and the reduction percent in bacteria count was calculated using the following equation:

$$\text{Bacterial reduction } (\%) = \left(\frac{B-A}{A}\right) \times 100$$

where A and B are the number of colonies detected from the control and triclosan treated samples, respectively.

Durability to washing was assessed according to AATCC test method 124.

The morphology and particle size of the prepared AgNP's/HBPAA hybrid were determined by transmission electron microscope (TEM) using a JEOL JEM 2100F electron microscope at 200 kV.

The surface morphology of selected fabric samples (SEM) were observed with SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with

accelerating voltage 30 kV, (magnification14× up to 1,000,000 and resolution for Gun.1n) (FEI company, Netherlands).

3. Results and discussion

Since the main goal of the present study was to investigate the positive role of loading MCT-βCD onto/into wool fabric on enhancing its post-printing as well as upgrading the antibacterial activity of the obtained prints, the following treatment sequence has been tried: grafting of MCT-βCD → post-printing → after treatment with different antibacterial agents. Variables studied include: alkali and MCT-βCD concentration, type of dyestuff, as well as type of the antibacterial agent.

3.1. Catalyst concentration

The effect of Na_2CO_3, as a catalyst, concentration on the extent of loading of MCT-βCD, expressed as %N, onto/into the wool structure is represent in Fig. 1a within the range examined (0–20 g/L), increasing Na_2CO_3 concentration up to 10 g/L results in an increase in the %N of the treated wool fabric samples as a direct consequence of enhancing the extent of fixation of MCT-βCD onto/within the wool structure:

$$\underset{\text{Wool(I)}}{\text{W–XH}} + \text{Cl-MCT-}\beta\text{CD} \xrightarrow{Na_2CO_3} \underset{\text{Modified wool(II)}}{\text{W–X–MCT-}\beta\text{CD}} + \text{HCl} \quad (1)$$

where W–XH = wool, —XH = —NH_2, —SH, —OH.

Further increase in Na_2CO_3 concentration has practically no or a slight effect on the %N.

On the other hand, Fig. 1b shows the impact of premodification of wool structure with MCT-βCD on the extent of post-printing, expressed as *K*/*S* value, using different classes of dyestuffs namely disperse, acid and reactive dyestuffs. For a given set of premodification and post printing conditions, it is clear that increasing Na_2CO_3 concentration up to 10 g/L and the subsequent increase in the extent of MCT-βCD fixation bring about an improvement in the K/S values of the obtained prints, irrespective of the used dye. The enhancement in the depth of the obtained reactive and acid prints could be discussed in terms of introduction of additional hydrophilic groups, i.e., —OH groups, along hydrophilicity of wool surface, thereby improving the extent of dye uptaking as well as dye fixation via covalent and/or ionic bonding as follow:

$$\underset{\text{Reactive dye}}{\text{D}\cdot\text{SO}_2\cdot\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}} \xrightarrow[\text{Steam}]{\text{OH}^-} \underset{\text{Vinyl form}}{\text{D}\cdot\text{SO}_2\text{CH}=\text{CH}_2} + \text{NaHSO}_4 \quad (2)$$

$$\text{(I) or (II)} + \text{D}\cdot\text{SO}_2\cdot\text{CH}=\text{CH}_2 \xrightarrow[\text{Steam}]{\text{OH}^-} \text{wool or modified wool-reactive print} \quad (3)$$

$$\underset{\text{Reactive or acid dye}}{\text{(I) or (II)} + \text{D}(-\text{SO}_3^-\text{Na}^+)_n} \xrightarrow[\text{Steam}]{\text{H}^+} \text{wool or modified wool-reactive or acid print} \quad (4)$$

On the other hand, the improvement in the depth of the obtained disperse prints, by increasing Na_2CO_3 concentration up to 10 g/L in the pre-treatment bath, reflects the complexing power of the immobilized hydrophobic-inner cavities of the loaded MCT-βCD and their ability to form inclusion complex with the used disperse dye as follow (Ibrahim & El-Zairy, 2009):

$$\text{(II)} + \text{dispersedye} \rightleftharpoons \text{inclusioncomplex} \quad (5)$$

Further increase in Na_2CO_3 concentration has practically a slight negative impact on the extent of dye fixation, i.e., lower *K*/*S* value, most probably due to a shortage in and/or in accessability and in availability of dyeing active sites. On the other hand, partial hydrolysis of MCT-βCD at high Na_2CO_3 concentration, which in turn resulted in decreasing the extent of wool modification as well as subsequent printing with the nominated dyestuffs, cannot be ruled out (Ibrahim, Eid, et al., 2011)

$$\text{Cl-MCT-}\beta\text{CD} + \text{H}_2\text{O} \xrightarrow[\text{Steam}]{\text{OH}^-} \text{HO-MCT-}\beta\text{CD} + \text{HCl} \quad (6)$$

Therefore 10 g/L Na_2CO_3 was chosen as the optimal alkali concentration in the pre-modification step.

Additionally, variation in extent of improvement in the depth of the obtained prints reflects the differences among the nominated dyestuffs in molecular size, chemical structure, functionalities, degree of solubility, extent of release from the thickener film, affinity, mode of interaction, location and extent of fixation onto or within the modified wool structure (Aspland, 1997; Choudhury, 2006; Ibrahim, 2011; Ibrahim & El-Zairy, 2009).

3.2. MCT-βCD concentration

Fig. 2a shows that increasing MCT-βCD concentration up to 10 g/L is accompanied by an increase in the %N of the treated wool fabric samples confirming the fixation of MCT-βCD onto/into the wool structure [Eq. (1)]. Further increase, beyond 10 g/L, has practically a marginal effect on the %N, most probably due to the blocking of and/or a shortage in the wool active sites.

On the other hand, the impact of pre-modification of wool structure on its post-printing with the nominated dyestuffs is demonstrated in Fig. 2b. It is clear that increasing MCT-βCD up to 10 g/L in the pre-treatment bath is accompanied by a remarkable increase in the depth of the obtained prints as a direct consequence of enhancing the extent of dye picking-up and fixation onto/within the wool structure [Eqs. (3)–(5)]. Further increase in MCT-βCD concentration, i.e. beyond 10 g/L, has practically insignificant positive impact on the *K*/*S* values of the obtained wool prints.

Needless to say; the extent of post-printing, expressed as *K*/*S* values, is governed by the type and class of the used dyestuffs as discussed earlier.

3.3. After-treatments with antibacterial agents

3.3.1. After treatment with Invasan®

Effect of after-treatment of the pre-modified → printed fabric samples with Triclosan (10 g/L) on the printing and antibacterial properties are shown in Table 1. For a given pretreatment, post printing and subsequent Triclosan-finishing conditions, the data so obtained demonstrate that: (i) after-treatment of the printed-wool fabric samples with Triclosan results in an increase in *K*/*S* values as well as an improve in the fastness properties of the treated wool prints most probably due to the enhancement in the extent of dye fixation onto/into the wool structure, (ii) the extent of enhancement in the above mentioned properties is governed by the type of the used dyestuff as well as its ability to interact and/or entrap Triclosan molecules onto/within the modified wool structure, (iii) the remarkable improvement in the imparted antibacterial activity of the modified-printed wool reflects the ability of the immobilizaed hydrophobic cavities of the grafted βCD moieties to form host–guest inclusion complex with Triclosan, (iv) the imparted antibacterial activity against both the G+ ve and G− ve bacteria most probably is attributed to the inhibition effect of Triclosan on biosynthesis of fatty acid through the blocking of lipid bio synthesis (Ibrahim, Hashem, El-Sayed, El-Hussemy, & El-Enany, 2010; Orhan, Kut, & Gunesoglu, 2007), (v) the Triclosan-treated wool prints exhibited better antibacterial activity against G+ ve bacteria than G− ve bacteria, (vi) the extent of improvement in the antibacterial activity is governed by the extent and amount of loaded Triclosan, mode of interaction with the modified/printed wool structure, e.g. inclusion complex with βCD cavity, ionic bonding with W—NH_2, hydrogen bonding, etc., as well as its availability

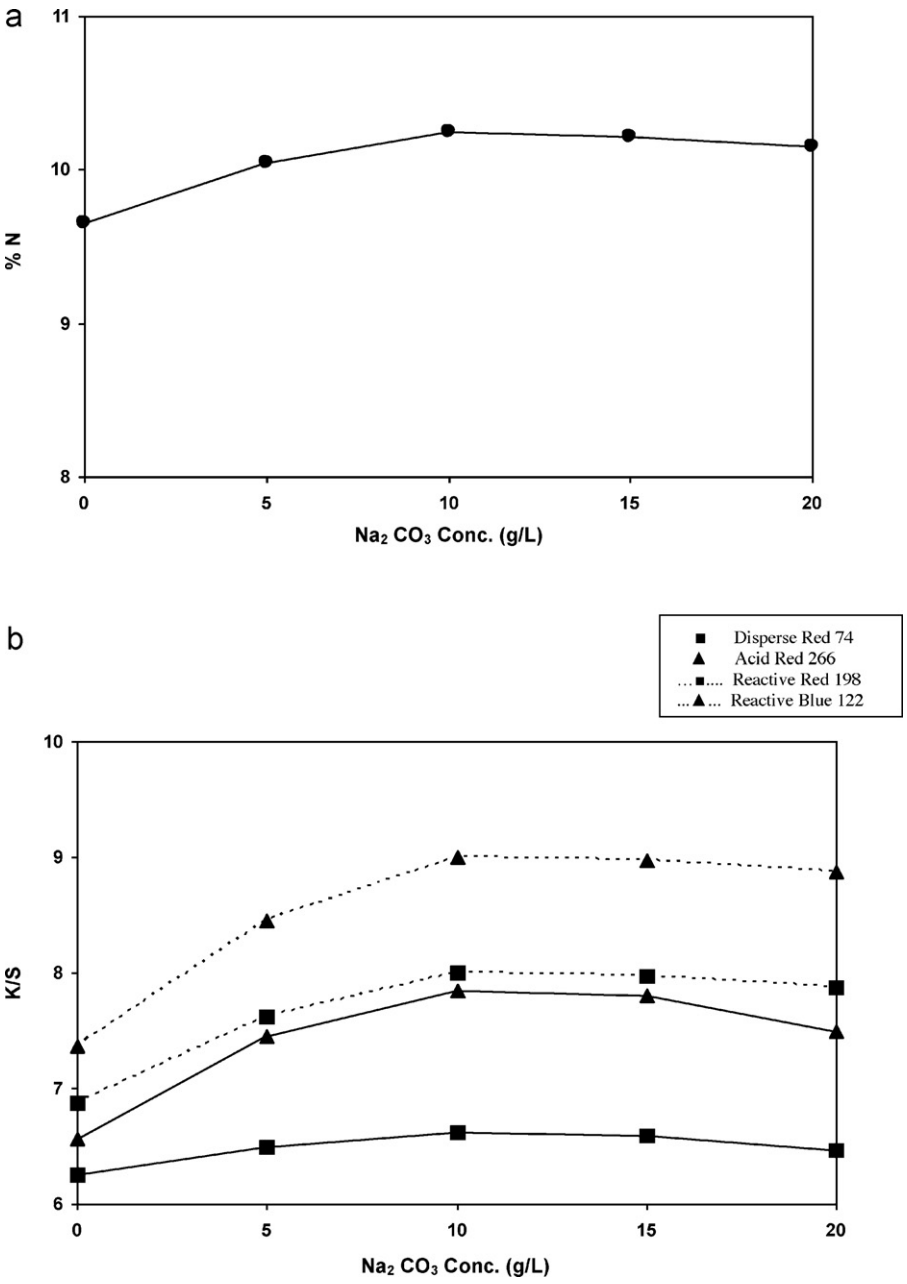

Fig. 1. Effect of Na_2CO_3 on extent of fixation of MCT-βCD onto the wool structure (%N, a) and its impact on post-printing with the nominated dyestuffs (K/S, b) MCT-βCD (10 g/L); nonionic wetting agent (2 g/L); wet pick up 80%; thermal fixation at 120 °C for 10 min.

and accessibility onto the fabric surface (Guan, Qian, & Xiao, 2007; Makarovsky et al., 2011), (vii) the difference in antibacterial activity against, the selected G+ ve and G− ve bacteria reflects their differences in membrane structure and amenability to destruction (Ibrahim, Refai, et al., 2010; Ibrahim, Aly, & Gouda, 2008), and (viii) the Triclosan-loaded wool prints retained their imparted antibacterial activities, more than 85%, even after-washing 15 cycles.

3.3.2. Ag-NP's/HBPAA hybrid

TEM micrograph (Fig. 3a) of the prepared Ag-NP's/HBPAA hybrid colloidal solution demonstrates a well dispersed AgNP's of 26–35 nm in size.

As far as the changes in the printing and functional properties of the modified → printed wool fabric samples after-treated with the hybrid solution (10 g/L), the data in Table 2 demonstrate that (i) post-treatment of the printed samples with the prepared hybrid brings about an improvement in the %N, *K*/*S* as well as the tested fastness properties, (ii) the extent of improvement in the aforementioned properties is determined by the type of dye, location and extent of distribution as well as ability to bind/load the nominated hybrid onto the printed fabric surface, (iii) the enhancement in the aforementioned properties reflects the positive impacts of interactions among the modified wool structure, e.g. -βCD moieties, —NH_2, —COOH, —OH groups, etc., the fixed dye-functional and solubilizing groups, the loaded Ag-NP's/HBPAA active sites, e.g. —NH_2, —NH, etc., and the encapsulated Ag/NP's via hydrogen bonding, electrostatic interactions and/or complex formation, (iv) post-treatment with the prepared hybrid is accompanied by a remarkable enhancement in the antibacterial activity of the treated samples, (v) the extent of enhancement in the imparted antibacterial functionality is governed by the amount of loaded hyperbranched polymer with its encapsulated AgNP's, (vi) the antibacterial activity against

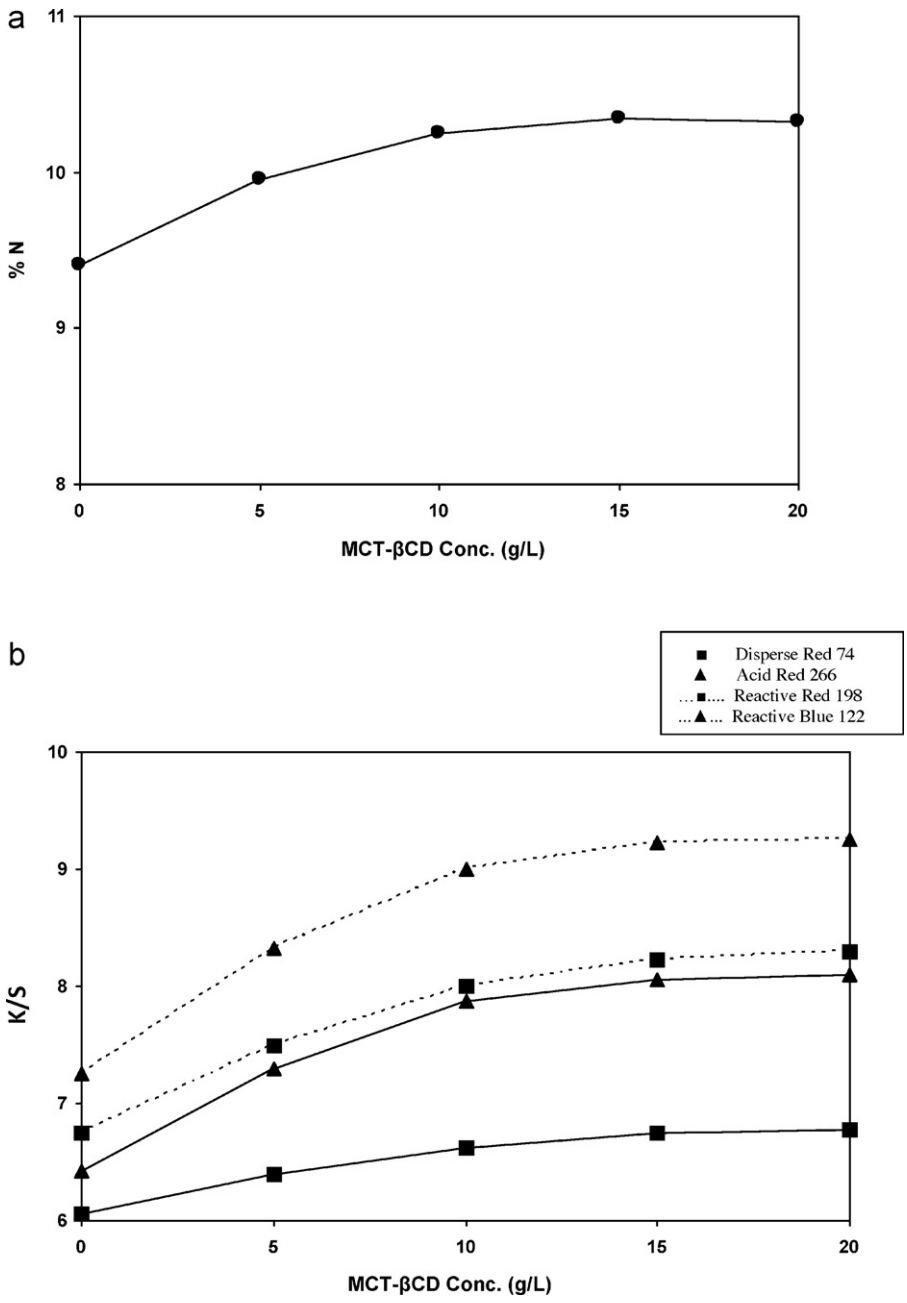

Fig. 2. Effect of MCT-βCD concentration on the extent of modification of wool (%N, a) and its impact on post-printing with the nominated dyestuffs (*K*/*S*, b) Na_2CO_3 (10 g/L); nonionic wetting agent (2 g/L); wet pick up 80%; thermal fixation at 120 °C for 10 min.

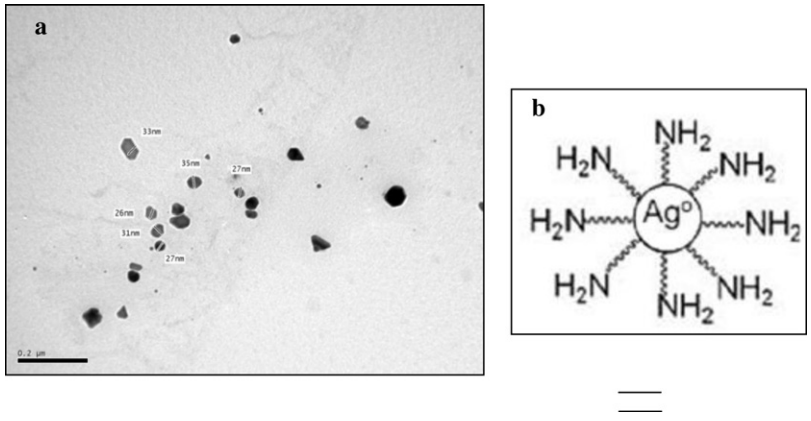

Fig. 3. TEM of prepared silver nano-particles (a), Ag-NPs/HBPAA hybrid (b).

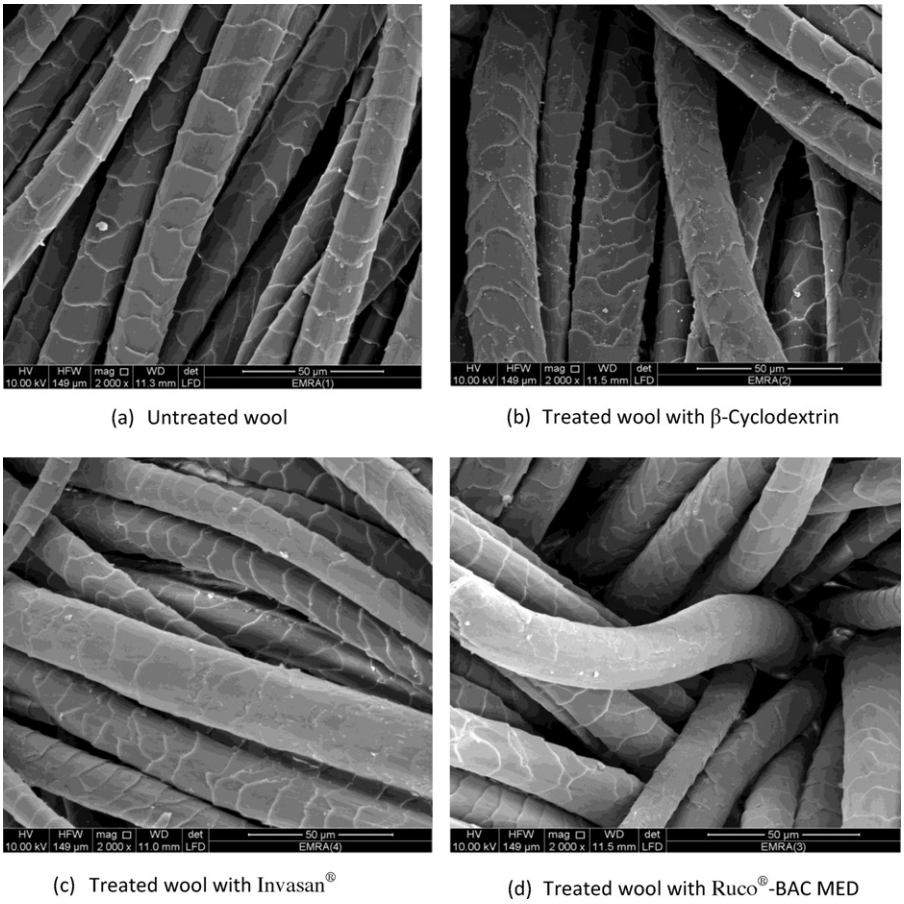

Fig. 4. SEM image of untreated (a), βCD-loaded (b), βCD-loaded → Acid Red 266 → Invasan® post-treated (c) and βCD-loaded → Acid Red 266 → Ruco®-BAC MED post-treated (d).

the selected bacteria, (*E. coli*) and (*S. aureus*), follows the decreasing order *S. aureus* > *E. coli*, irrespective of the used dyestuff, and (vii) the treated wool fabrics demonstrated powerful antibacterial functions even after 15 washing cycles.

On the other hand, the antibacterial effect of the loaded AgNP's onto the printed wool samples could be discussed in terms of: (i) possible damage of DNA via interaction of AgNP's with sulfur- or phosphorous-containing protein, and its negative impacts on the respiratory chain or cell division process thereby causing a cell death, (ii) ionic interaction between the cytoplasm membrane of the bacteria and the Ag-ions released from Ag-NP's as follows (Radetic, 2012):

$$O_{2(aq)} + 4H_3O^+ + 4Ag_{(S)} \rightarrow 4Ag^+{}_{(aq)} + 6H_2O \quad (7)$$

and or (iii) the formation of active oxygen according to the following reaction: (Dastjerdi & Montazer, 2010; Jones & Hoek, 2010):

$$H_2O + (1/2)O_2 \xrightarrow{Ag^+} H_2O_2 \rightarrow H_2O + [O] \quad (8)$$

Additionally, protonation of the amino-groups of the hyper-branched polymer matrix (Fig. 3b) enhances their ability to interact with the negatively charged bacterial surface thereby resulting in disruption of the cell membrane and an increase in its permeability (Simoncic & Tomsic, 2010).

3.3.3. Ruco®-BAC MED

Table 3 shows the effect of after-treatment of the printed wool fabric samples with the nominated nonionic antibacterial agent, based on diphenyl alkane-triclosan derivative, on their printing properties as well as their antibacterial functions. Results of Table 3 signify that: (i) post-treatment of the printed wool fabrics with the nominated antibacterial agent brings about an enhancement in dye fixation, confirmed by higher *K*/*S* values and better fastness properties, (ii) an outstanding improvement in the antibacterial activity of the after-treated wool prints, irrespective of the used dye, (iii) the substantial enhancement in the imparted antibacterial activity is attributed to the antibacterial activity of the loaded triclosan derivative via non specific action (multitarget) causing disruption of bacterial cells or via inhibition of a specific bacterial target, i.e. inhibition of bacterial fatty acid synthesis, especially at sub lethal concentration (Yazdankhah et al., 2006), (iv) the amount of loaded triclosan derivative is governed by its extent of fixation via: formation of host–guest inclusion complex with the -βCD moieties, formation of an electrostatic bonds via the hydroxyl group of its phenolic ring with the basic active sites available onto the modified-printed wool surface, and/or formation of hydrogen bonds by the phenolic hydroxyl group with other functional groups of modified printed wool structure, (v) the antibacterial activity against the tested G+ ve and G− ve bacteria follows the descending order G+ ve > G− ve, and (vi) the obtained wool fabric samples kept the antibacterial functionalities more than 75% even after washing 15 cycles.

3.4. SEM images and EDX spectrum

The obtained results were supported further by observation of surface morphology (SEM) as well as the corresponding composition analysis (EDX) of some wool samples Figs. 4 and 5 respectively.

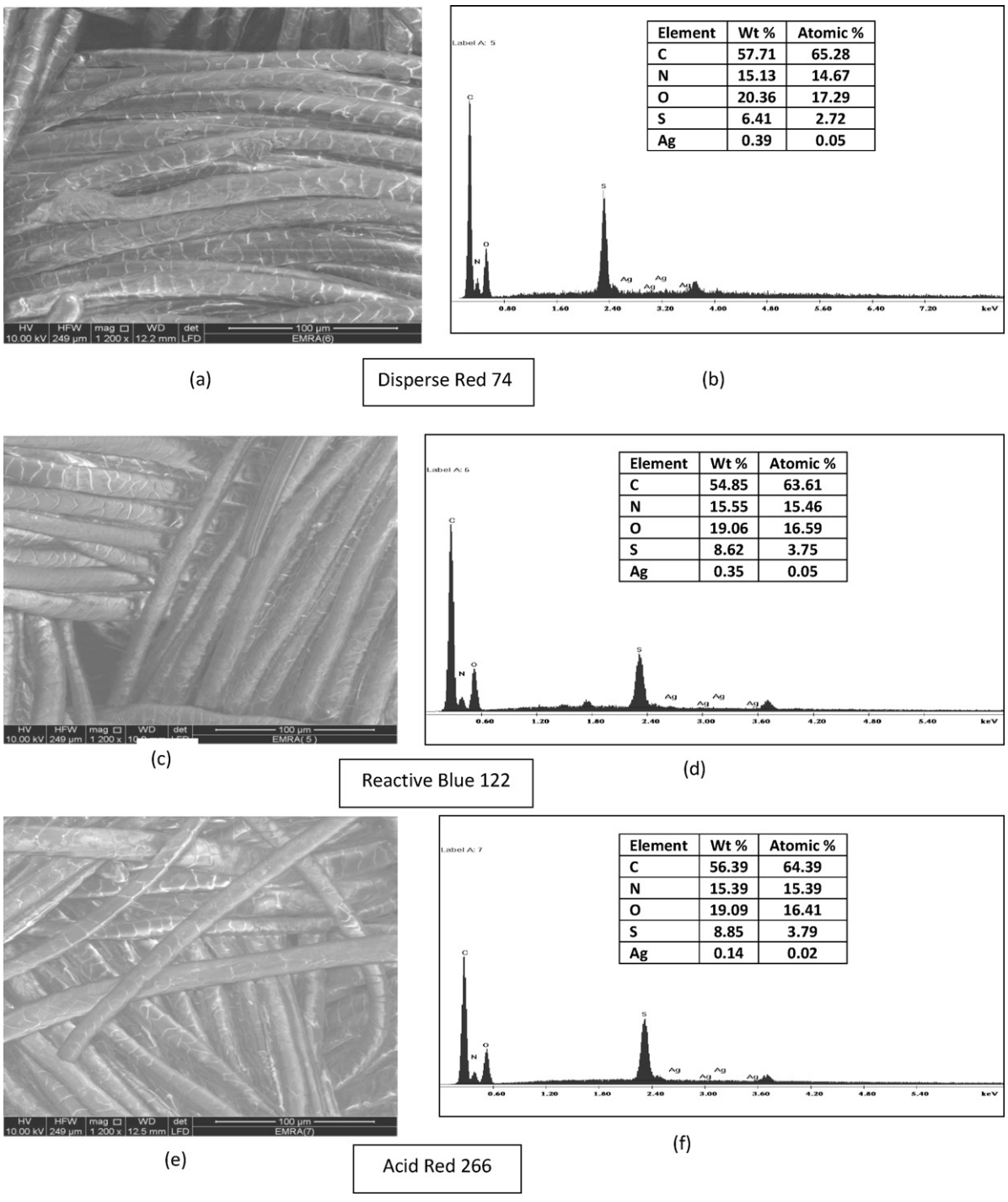

Fig. 5. SEM image and EDX spectrum of: disperse printed → AgNP's hybrid (a, b), reactive printed → AgNP's hybrid (c, d), acid printed → AgNP's hybrid (e, f).

SEM images of the untreated, βCD-treated, βCD-treated → Acid Red 266 printed → Invasan® post-finished, and βCD-treated → Acid Red 266 printed → Ruco® post-finished, wool samples were illustrated in Fig. 4(a)–(d) respectively. From the given images, it can be showed the deposition of βCD alone and admixture with the abovementioned antibacterial agents, i.e. Invasan® and Ruco® BAC, onto the modified → printed → post-treated wool samples. The amount, location and extent of distribution of these active deposits are governed by both the type of antibacterial agent as well as mode of application and fixation.

On the other hand, both the SEM images and the corresponding EDX spectra of some βCD-treated → printed → Ag-NP's/HBPAA hyrid-finished wool samples were demonstrated in Fig. 5(a)–(f). The presence of silver as well as some elements such as carbon, nitrogen, oxygen and sulfur on the modified → printed → post-finished wool samples were confirmed using EDX. The extent of fixation of silver as well as the variation in the amount of the

Table 1
Effect of after-treatment[a] using Invasan® on printing and antibacterial properties of obtained wool prints.

Dyestuff	Substrate	*K*/*S*	Incr. in *K*/*S* (%)	WF		RF		PF				LF	Bacterial reduction (%)	
				Alt	C	Dry	Wet	Acidic		Alkaline			G+ ve	G− ve
								Alt	C	Alt	C			
Disperse Red 74	UT	6.65	22.10	3	3	4	3–4	3–4	4	3	3–4	4	0	0
	T	8.12		4	4	4–5	4	4–5	4–5	4	4–5	4–5	90.8 (80.7)[b]	87.3 (77.6)
Disperse Blue 183	UT	20.26	20.19	3–4	4	3–4	3	4	4	4	4	3	0	0
	T	24.35		4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5	93.3 (82.0)	90.2 (79.3)
Acid Red 266	UT	7.85	14.52	3	3	4	3–4	3	3	4	4	4	0	0
	T	8.99		4	4	4–5	4–5	4	4	4–5	4–5	4–5	96.5 (85.2)	93.0 (82.8)
Acid Blue 40	UT	6.48	37.19	3	3	4	4	4	3–4	4	3	4	0	0
	T	8.89		4	4	5	4–5	4–5	4	4–5	3–4	4–5	91.0 (80.3)	88.0 (78.0)
Reactive Red 198	UT	9.00	14.11	3–4	4	4	4	4	4	4	4	4	0	0
	T	10.27		4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	88.5 (77.6)	86.1 (74.4)
Reactive Blue 122	UT	8.05	15.53	3–4	4	4	3–4	4	4	4	3–4	3–4	0	0
	T	9.30		4	4–5	4–5	4	4–5	4–5	4–5	4–5	4–5	87.0 (76.3)	85.4 (74.3)
Reactive Blue 19	UT	7.49	26.17	4	3–4	4	3–4	4	3–4	4	4	4	0	0
	T	9.45		4–5	4–5	4–5	4	4–5	4	4–5	4–5	4–5	96.0 (84.2)	92.5 (81.3)

[a] After-treatment: Invasan® (10 g/L); nonionic wetting agent (2 g/L); pH (5); wet pick-up (80%); thermofixation at 150 °C/3 min. *K*/*S*, color strength; WF, wash fastness; RF, rubbing fastness; PF, perspiration fastness; LF, light fastness; UT, untreated; T, aftertreated with Triclosan; Alt, alteration; C, staining on cotton.
[b] Values in parentheses indicate retained antibacterial activity after 15 washings.

Table 2
Effect of [a]after-treatment using Ag-NP's/HBPAA hybrid on printing and antibacterial properties of obtained wool prints.

Dyestuff	Substrate	%N	*K*/*S*	Incr. in *K*/*S* (%)	WF		RF		PF				LF	Antibacterial activity (ZI, mm)	
					Alt	C	Dry	Wet	Acidic		Alkaline			G+ ve	G− ve
									Alt	C	Alt	C			
Disperse Red 74	UT	10.65	6.65	24.81	3	3	4	3–4	3–4	4	3	3–4	4	0	0
	T	11.03	8.30		3–4	3–4	4–5	4	4–5	4–5	4–5	4–5	4–5	27 (24)[b]	25 (21.8)
Disperse Blue 183	UT	11.03	20.26	17.87	3–4	4	3–4	3	4	4	4	4	3	0	0
	T	11.32	23.88		4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5	21 (18)	18 (15.5)
Acid Red 266	UT	11.29	7.85	8.92	3	3	4	3–4	3	3	4	4	4	0	0
	T	11.50	8.55		3–4	3–4	5	4–5	4	4	4–5	4–5	4–5	22 (18.8)	20 (16.6)
Acid Blue 40	UT	11.15	6.48	34.26	3	3	4	4	4	3–4	4	3	4	0	0
	T	11.40	8.70		3–4	3–4	4–5	4–5	4–5	4	4–5	4	4–5	20 (17.5)	18 (15.3)
Reactive Red 198	UT	11.73	9.00	16.78	3–4	4	4	4	4	4	4	4	4	0	0
	T	11.91	10.51		4	4–5	5	5	4–5	4–5	4–5	4–5	4–5	18 (15.5)	16 (13.3)
Reactive Blue 122	UT	11.98	8.05	13.29	3–4	4	4	3–4	4	4	4	3–4	3–4	0	0
	T	12.25	9.12		4	4–5	4–5	4	5	4–5	4–5	4–5	4–5	25 (22)	22 (19.1)
Reactive Blue 19	UT	12.05	7.49	34.85	4	3–4	4	3–4	4	3–4	4	4	4	0	0
	T	12.32	10.10		4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	18 (15.2)	15 (12.6)

[a] After-treatment: Ag-NP's/HBAA hybrid (10 g/L); nonionic wetting agent (2 g/L); pH (5); wet pick-up (80%); thermofixation at 150 °C/3 min. N%, nitrogen content; *K*/*S*, color strength; WF, wash fastness; RF, rubbing fastness; PF, perspiration fastness; LF, light fastness; ZI, zone of inhibition; UT, untreated; T, aftertreated with hybrid; Alt, alteration; C, staining on cotton.
[b] Values in parentheses indicate retained antibacterial activity after 15 washings.

Table 3
Effect of[a] after-treatment using Ruco®-BAC MED on printing and antibacterial properties of obtained wool prints.

Dyestuff	Substrate	*K/S*	Incr. in *K/S* (%)	WF		RF		PF			LF	Bacterial reduction (%)	
								Acidic		Alkaline		G+ ve	G− ve
				Alt	C	Dry	Wet	Alt	C	Alt	C		
Disperse Red 74	UT	6.65		3	3	4	3–4	3–4	4	3	3–4	4	0
	T	8.54	28.42	4	4	5	4–5	4–5	4–5	4–5	4–5	4–5	92.4 (83.3)[b]	88.8 (78.9)
Disperse Blue 183	UT	20.26		3–4	4	3–4	3	4	4	4	4	3	0	0
	T	24.62	21.52	4	4–5	4–5	4	4–5	4–5	4–5	4–5	4	93.9 (84.4)	90.6 (81.0)
Acid Red 266	UT	7.85		3	3	4	3–4	3	3	4	4	4	0	0
	T	8.65	10.19	4	3–4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	97.0 (88.0)	93.4 (84.3)
Acid Blue 40	UT	6.48		3	3	4	4	4	3–4	4	3	4	0	0
	T	9.02	39.20	3–4	3–4	4–5	4–5	4–5	4	4–5	4	4–5	92.3 (83.1)	89.1 (80.0)
Reactive Red 198	UT	9.00		3–4	4	4	4	4	4	4	4	4	0	0
	T	10.12	12.44	4	4–5	4–5	4–5	4–5	4–5	4–5	4–5	4–5	90.2 (80.7)	87.5 (78.0)
Reactive Blue 122	UT	8.05		3–4	4	4	3–4	4	4	4	3–4	3–4	0	0
	T	9.30	15.53	4–5	4–5	4–5	4	5	4–5	4–5	4–5	4–5	98.6 (89.2)	95.8 (86.4)
Reactive Blue 19	UT	7.49		4	3–4	4	3–4	4	3–4	4	4	4	0	0
	T	10.69	42.72	4–5	4–5	5	4–5	4–5	4–5	4–5	4–5	4–5	96.7 (87.0)	93.2 (83.5)

[a] After-treatment: Ruco®-BAC MED (10 g/L); pH (5); LR (1/20); at 50 °C/30; thermofixation at 150 °C/3 min. *K/S*, color strength; WF, wash fastness; RF, rubbing fastness; PF, perspiration fastness; LF, light fastness; UT, untreated; T, aftertreated with; Alt, alteration; C, staining on cotton.
[b] Values in parentheses indicate retained antibacterial activity after 15 washings.

detected elements are determined by the type of the used dye as discussed earlier.

4. Conclusions

The results reported in this study demonstrate that premodification of wool fabric with MCT-βCD has positive impacts on printing properties using different dyestuffs as well as enhancing the extent of loading triclosan and Ag-NP's antibacterial agents using the following treatment sequence: premodification using MCT-βCD → printing → after-treatment with the selected antibacterial agents, thereby improving the performance properties of the obtained wool prints along with upgrading their antibacterial activities.

The performance and washing durability of the imparted antibacterial functions depend on the type of the used antibacterial agent as well as its extent of loading onto the modified-printed wool structure.

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