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Environmentally Sound Approach for Developing Antibacterial/Anticrease Cellulosic Fabrics

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Abstract

The presented study focused on the development of green antibacterial / anticrease cotton and viscose fabrics using an environmentally benign functional finishing formulations. The obtained results demonstrated that co-application of citric acid / Na-hypophosphite (CA / NaH_2PO_2) as formaldehyde-free-ester crosslinking system, Na-alginate and carboxy methyl cellulose (CMC), as safe binding / fixing agents, along with bioactive cationic agents namely Chitosan and Choline Chloride or nano active ingredients namely Ag NPs, ZnO NPs and Al_2O_3 NPs using the pad-dry-cure method resulted in an improve in antibacterial and anti-crease functionalities with marginal decrease in finished fabric hydrophilicity. The imparted antibacterial functionality against the tested pathogenic bacteria as well as the enhanced fabric resiliency were affected by kind of cellulosic substrate, nature of binding / fixing agent as well as type of the functional additive. Furthermore, SEM and EDX analysis of selected samples further confirmed the surface modification and immobilization of the used functional additives onto the fabric. Additionally, an integrated modification and functionalization mechanism was also proposed.

Keywords: Cellulosic fabric, Ester-crosslinking, Eco-friendly functional additives, Bi-functional finishing, Antibacterial / Anti-crease product

1. Introduction

Due to the ever-growing demands for comfortable, high value-added, multifunctional and sustainable textile products-based on cellulose, an urgent need and a great effort for adoption and implementation of emerging technologies, e.g., nano-, bio-, plasma, etc. in functional finishing area has arisen taking in consideration product and ecology quality in an economically beneficial application way [1-7].

Functional finishing of cellulosic fabrics focuses on: i) improving the textile product quality [8-10], ii) creating and imparting new and unique properties like antibacterial efficacy [11-17], UV-protection ability [18-21], self-cleaning [22-24], easy care [25-27], water/oil repellency [28-31], and flame retardancy individually and in combination [9, 11, 32-36], iii) satisfying the ever-increasing consumer demands alongside fast fashion, and iv) complying with the ever-growing environmental concerns, thereby increasing the added value of the developed textile products and widening their range of potential applications.

Therefore, the present study is focused on developing an environmentally sound single step approach for fabrication of functionalized cotton and viscose cellulosic fabrics through two options: i) co-application of chitosan or choline chloride, as bioactive cationic agent, and Na-alginate or CMC, as safe binding agent, and citric acid (CA)/ sodium hypophosphite (NaH_2PO_2) as formaldehyde-free ester- crosslinking system in one step using the pad-dry-cure technique to impart easy care and antibacterial functionalities , and ii) nano finishing of the cellulosic substrates through co-

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application of Ag NPs, ZnO NPs or Al_2O_3 NPs, as functional material, in the absence or presence of Na-alginate or CMC, as eco-friendly binding /fixing agent, along with the nominated ester crosslinking system using the pad-dry-cure method.

The imparted functional properties, easy-care/ antibacterial functions, were evaluated. SEM and EDX analysis for the selected samples were carried out. Moreover, the tentative interactions among the treated substrate, the binding agent and the used functional additives were suggested.

2. Experimental

2.1. Materials

Mill-scoured and bleached plain-weave cotton (160 g/m^2) and viscose (140 g/m^2) fabrics were used in this study.

Sodium alginate (Na-Alg, low viscosity, BF-Goodrich Diamalt, GmbH, Germany), Carboxy methyl cellulose (CMC, Mwt = 2.5 x 10^5, DS= 0.7, Sigma Aldrich, St. Louis, Missouri, USA) and Chitosan (degree of deacetylation > 82%, Sigma) were used.

Nano-Zinc Oxide (ZnO NPs, particle size 40-100 nm - *APS* powder, Alfa aesar Germany), Nano-Aluminum Oxide (Al_2O_3 -NPs, NanoAcr® AL-0450, 50% in H_2O colloidal dispersant, 45 nm *APS*, for dry powder, Alfa aesar, Germany) and Nano-sized silver (Ag NPs, 0.02 mg/L, *PAS* 40 nm, Sigma Aldrich) were used to impart appropriate functionalities to the treated cellulosic substrates.

All other chemicals used during this study like citric acid, Na-hypophosphite (NaH_2PO_2) and choline chloride were of laboratory reagent grade.

2.2. Methods

2.2.1. Functional finishing

The cellulosic fabric samples were treated by the pad-dry-cure technique. The samples were treated twice with an aqueous solution containing citric acid (25 g/L), as ester-crosslinking agent, NaH_2PO_2 (15 g/L), as a proper catalyst , along with CMC (5 g/L) or Na-alginate (5 g/L), as a biopolymer for enhancing the extent of fixation and immobilization of the used functional additives namely choline chloride (5 & 10 g/L), chitosan (2.5 &5 g/L), Ag NPs (20 g/L), ZnO NPs (20g/L) and Al_2O_3 NPs (20 g/L) individually to wet pick up of 80 %, and dried at 100˚C for 5 min, then cured at 160˚C for 3 min. The finished fabric samples were then thoroughly washed to remove unfixed and soluble-by products and finally dried.

2.3. Characterization

- Scanning electron microscope (SEM) images of the untreated and selected finished fabric samples were obtained with a JEOL, JXL 840A electron probe micro analyser, equipped with energy disperse X-ray (EDX) spectroscopy for the surface composition analysis.
- The percentage change in the weight (add-on %) was calculated as follows:

$$\text{Add - on (\%)} = \frac{Wa - Wb}{Wb} \times 100$$

where, Wb: weight before, and Wa: weight after treatment.

- The metal content (%) of the NPs-loaded substrates were determined by a Flame Atomic Spectrophotometer GBC- Avanta, Australia.
- Nitrogen content (%) of the cationized fabric samples, i.e., chitosan and choline chloride contained fabric samples, was determined according to the micro-Kjeldahl method.
- Antibacterial activity of the functionalized cellulosic fabrics against both *S. aureus* (G+ve) and *E.Coli* (G-ve) bacterial was evaluated qualitatively according to AATCC Test Method [37], and expressed as zone of growth inhibition (ZI, mm)
- The Crease recovery angle CRA (W+F)° of untreated and treated fabric samples were measured by using the *ASTM* of ISO 2313-1:2021.
- Wetting time of untreated and finished fabric samples was evaluated according to AATCC Test method 79-2018. The shorter the wetting time, the better the fabric hydrophility and water absorbency.

3. Results and Discussion

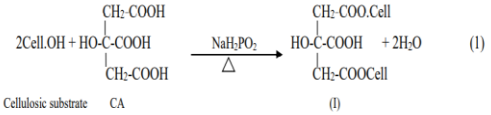
3.1. Incorporation of CMC or Na-Alg. in finishing formulation

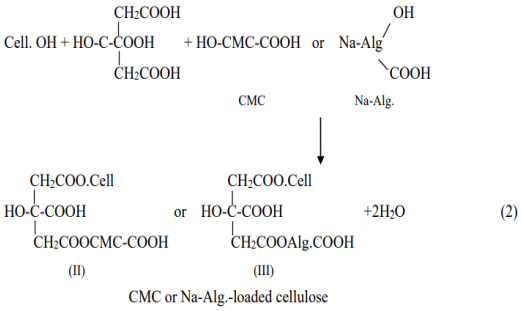
The data in Table 1 demonstrate that incorporation of CMC, as a modified biopolymer, and Na-Alg., as a biopolymer, individually into the finishing formulation using CA (25 g/L), as CH_2O-free ester-crosslinking agent, and NaH_2PO_2 (15 g/L), as appropriate ester catalyst for crosslinking of cellulose-OH, and the above mentioned biopolymers, results in an increase the add-on % as a direct consequence of loading of the nominated bio-polymer onto the ester-crosslinked cellulose structure during the thermo fixation step as follows [38-40].

Table 1. Effect of incorporation of carboxy additive in the finishing formulation

Additive (5 g/L)	Add-on (%)		Wett. time (sec)		ZI (mm) G+ve		ZI (mm) G-ve		CRA(W+F)°	
	C	V	C	V	C	V	C	V	C	V
None	1.702	3.831	1	<1	0.0	0.0	0.0	0.0	180	210
CMC	3.971	5.760	7	5	0.0	0.0	0.0	0.0	215	280
Na-Alg.	1.945	4.992	8	6	0.0	0.0	0.0	0.0	205	260

Finishing formulation, CA (25 g/L), NaH2PO2 (15 g/L); wet-pick up (80%), drying at 100°C for 5 min curing at 160°C for 3 min.
C: cotton; V: viscose; ZI: zone of inhibition; G+ve: S. aureus bacterium; G-ve: E. Coli bacterium, CRA: crease recovery angle, W: warp, F: weft
CRA(W+F)° of blank cotton: 100° , of blank viscose :130°





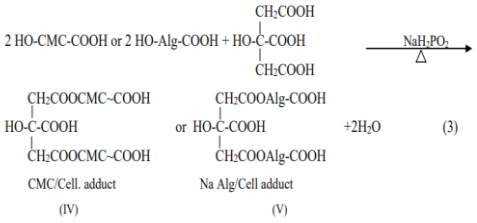
The extent of increase in the add-on % is governed by: i) type of cellulosic substrate, viscose > cotton, taking in consideration their differences in fabric structure. Amorphous/crystalline region ratio, availability and accessibility of active sites, i.e. -OH groups [40] and ii) kind of biopolymer CMC > Na-Alg. i.e. molecular weight, active centers i.e. -OH and -COOH groups, extent of interaction among the cellulosic fibre , the ester-crosslinking agent, and the added biopolymer in the presence of NaH_2PO_2 at 160˚C for 3 min [38, 41].

On the other hand, inclusion of any of the nominated biopolymer in the finishing bath results in a slight decrease in fabric hydrophilicity, expressed as wetting time, most probably due to surface coating of the fabric surface, a decrease in fabric porosity and a shortage in hydrophilic active sites at fabric surface thereby extending the wetting time [42-44], and the increase in wetting time of finished fabrics follows the orders: cotton > viscose keeping other parameters constant and CMC > Na-Alg.> None keeping the type of substrate fixed.

Moreover, incorporation of CMC or Na-Alg. along with ester- crosslinking constituents has practically no effect on the antibacterial activity against the tested G+ve (*S. aureus*) and G-ve (*E. Coli*) pathogenic bacteria, expressed as ZI value.

The data in Table 1 also show that using CMC or Na-Alg. as an eco-friendly additive is accompanied by an improve in easy care functionality of the ester-crosslinked cellulosic substrates in the presence than in absence of the used biopolymers, and the extent of improve in crease recovery angle is better in case of using viscose fabric substrate along with CMC as an additive compared with other counterparts ,i.e. CMC > Na-Alg. >None, keeping other parameters constant, which reflects the positive role of CMC in enhancing the extent of crosslinking of cellulose chains especially in the amorphous regions of cellulose structure [40].

Moreover, both CMC and Na-Alg. have abundance of -COOH and -OH groups which may facilitate. film and ester-crosslinked network structure-formation during the curing step as follows [40, 41, 45].



, which in turn, have positive or negative impacts on the finished fabric properties.

3.2. Effect of adding choline chloride and chitosan individually

The variation in some physico-chemical and functional properties of developed fabrics as a function of type and concentration of functional cationic additive, i.e., choline chloride or chitosan, and

CMC as bio-binder for more uptake, fixation and immobilization of choline chloride or chitosan onto the treated cellulosic substrates as well as a potential surface modifier are presented in Table 2. For a given set of treatment conditions, it is clear that increasing choline chloride concentration (up to 10 g/L) or chitosan concentration (up to 5 g/L) along with other ingredients, i.e., CMC, CA and NaH_2PO_2, results in an increase in the add-on %, an improve in fabric hydrophilicity, along with an increase in the % N properties, regardless of type and concentration of the cationic additive. The higher the cationic additive concentration, the better are the add-on %, hydrophilicity, and the %N values, keeping other parameters constant.

On the other hand, the variation in the add-on %, wetting time as well as in the imparted antibacterial and easy-care functional properties is governed by type of cationic additive, chemical structure, molecular weight, nitrogen content, number, and accessibility of cationic active sites, i.e. NH_2 in chitosan and $-N^+-$ in choline chloride, extent of penetration, interaction as well as fixation onto and / or within the modified / ester crosslinked cellulose structure in a single step application method as follows [38, 46]:

$$HOH_2C \sim Ch \sim NH_2 + H^+ \longrightarrow HOH_2C \sim Ch \sim N^+H_3 \quad (4)$$

$$HOH_2C\text{-}Ch \sim N^+H_3 + (I), (II), (III) \text{ and / or } (IV) \rightarrow \text{chitosan – loaded substrates} \quad (5)$$

$$(H_3C)_3\text{-}N^+Cl^- + (I), (II), (III) \text{ and / or } (IV) \rightarrow \text{Choline chloride-loaded substrates} \quad (6)$$

CH_2OH

Choline chloride

as a direct consequence of electrostatic interactions among the positively changed $>N^+$ groups (Eq's 5&6) and the negatively changed free-COO^- as suggested in Eq's 1,2,3,5 and 6. Additionally, the interactions among CMC and the positively charged cationic additives, i.e., choline chloride and chitosan, in the absence and presence of the used ester-crosslinking system, CA/ NaH_2PO_2, under the given finishing conditions can't be omitted.

The data in Table 2 also signify that incorporation of the nominated cationic additives individually into the finishing formulation results in a remarkable improvement in the imparted antibacterial activity, especially at higher concentration, i.e., choline chloride (10g/L) or chitosan (5g/L). Within the range examined, the imparted antibacterial functionality to the treated cellulosic substrates is governed by type of cationic agent, i.e., chemical structure, functional groups, extent of location and distribution onto / within the cellulose structure, degree of fixation and immobilization onto the fabric during the thermo fixation step as well as antibacterial action and follows the decreasing orders [9, 11, 47]: Chitosan > Choline chloride >> None, keeping other parameters constant. The imparted antibacterial activity reflects the differences between the nominated functional agents in antibacterial action and extent of electrostatic interaction of the positively charged amine groups ($-N^+H_3$) in chitosan structure or quaternary ammonium groups in choline chloride with the negatively charged sites at the cell membrane [38, 48]. Additionally, the imparted antibacterial functionality is determined by :i) kind of the pathogen as follows:

S. aureus (G+ve) > *E. Coli* (G-ve) reflects their differences in cell wall structure, amenability to damage the cell membrane/to disrupt the cell structure and response for inactivation by the used cationic functional agent [13], and the kind of cellulosic substrate, its fabric weight, amorphous/crystalline region, extent of modification and crosslinking during the thermofixation step and follows the decreasing order: Viscose > Cotton [13]. On the other hand, incorporation of the cationic additive, i.e. choline chloride or chitosan , along with ester-crosslinking chemicals (CA / NaH_2PO_2) , brings about a decrease in anti-crease functionality , expressed as WRA , as a direct consequence of decreasing the extent of catalization, which in turn negatively impacts the extent of ester-crosslinking of the nominated cellulosic substrates , and the decrease in easy care functionality follows the descending order : None > Choline chloride > Chitosan , keeping other parameters fixed. The variation in extent of ester-crosslinking as well as in fabric resiliency could be discussed in term of their difference in fabric weight , inherent fabric properties , amorphous / crystalline regions , location / extent of distribution of the finishing bath constituents as well as post-fixation and ester-crosslinking during the thermofixation step [11, 38].

For a given set of finishing formulations and conditions, the data in Table 3 demonstrate that incorporation of choline chloride or chitosan as a functional additive along with Na-alginate as eco-friendly binding / modifying agent and CA/NaH_2PO_2 as ester-crosslinking ingredients results in i) an increase in add-on % and improve in fabric wettability which follows the decreasing order : Choline chloride / Na-alg. > Chitosan / Na-alg. > Na-alg. , ii) an improve in % N and antibacterial efficacy which follows the descending order : Chitosan / Na – alg. >

Chlorine chloride / Na – alg. >> Na – alg. alone , iii) a decrease in crease – resistance property which could be ranked as follows : Na –alg. alone > Choline chloride / Na-alg. > Chitosan / Na-alg. , and iv) the variation in the physico–chemical and functional properties is governed by type of cationic additive , kind of cellulosic substrate as well as type of pathogenic bacteria especially in case of the assessed antibacterial activity as discussed earlier , keeping other parameters constant.

3.3. Nano finishing of the cellulosic substrates

The results in Table 4 clearly demonstrate that individual addition of Ag NPs , ZnO NPs and Al_2O_3 NPs to the finishing bath brings about an increase in both the add-on % , and metal content of finished fabrics , regardless of the used substrate . The increase in add on % and metal content follows the decreasing the order : Viscose > Cotton , irrespective of the added nano-material , reflecting their differences in fabric structure , amorphous / crystalline region , location and extent of penetration and fixation into /onto the cellulose structure [38, 40]. On the other hand, the increase in add-on and metal content is governed by extent of loading and immobilization of the used nanoparticles via the free – COOH groups in the crosslinked cellulose structure which can aid in coordination immobilization and fixation of the nominated nanoparticles as follows [9, 39, 49]:

$$\text{Ag NPs or ZnO NPs or } Al_2O_3 \text{ NPs} + (I) \xrightarrow{\Delta} \text{NPs-loaded substrate} \qquad (7)$$

,and the extent of immobilization and fixation is governed by type of inorganic nanomaterial and follows the decreasing order : ZnO NPs > Al_2O_3 NPs > Ag NPs > None, keeping type of cellulosic substrate constant.

It is quite clear that inclusion any of the nominated inorganic nanomaterial into the finishing formulation has practically a slight effect on the hydrophilicity of finished fabrics , expressed as wetting time.

The imparted antibacterial activity against both *S-aurous* (G+ve) and *E-coli* (G-ve) bacteria as a direct consequence of fixation and immobilization of the nominated nanomaterials is given in Table 4 . The data in Table 4 signify that incorporation of Ag NPs , ZnO NPs and Al_2O_3 NPs individually in functional finishing formulation is accompanied by a remarkable increase in the imparted antibacterial activity against the tested pathogenic bacteria and the enhancement in antibacterial functionality is governed by : (i) type of substrate: Viscose > Cotton, (ii) type of bacteria: G+ve > G-ve , and (iii) type of nanomaterial : ZnO NPs > Al_2O_3 NPs > Ag NPs >> None , keeping other parameters fixed , most probably due to their differences in : their shape, particle size , extent of loading onto and / or within the cellulose structure , capability to kill and /or inhibit the growth of pathogenic bacteria as well as mechanism of action [48, 50-52].

The imparted antibacterial efficacy against both G-ve and G+ve to viscose substrate is better than to cotton fabric , reflecting their difference in extent of loading and accommodation of nanomaterial as well as extent of releasing to the surrounding environment [53].

On the other hand , the imparted antibacterial activity against G+ve is higher than that against G-ve which could be attributed to their differences in cell constituents as well as their arrangement [8, 13, 48]

Table 2. Effect of inclusion of N-containg additive along with CMC in the finishing formulation

Additive	Conc. (g/L)	Add-on (%)		Wett. time (sec)		N (%)		ZI (mm)				CRA(W+F)°	
								G+ve		G-ve			
		C	V	C	V	C	V	C	V	C	V	C	V
None	0.0	3.971	5.760	7	5	0.00	0.00	0.0	0.0	0.0	0.0	215	280
Choline chloride	5.0	4.849	7.259	5	4	0.116	0.149	5	8	4	6	208	270
	10.0	6.923	9.292	4	3	0.151	0.190	14	16	12	14	190	255
Chitosan	2.5	4.701	6.390	6	5	0.148	0.166	9	12	7	10	185	240
	5.0	5.922	8.010	5	4	0.171	0.213	18	22	15	20	172	225

Finishing formulation: CA (25 g/L), NaH_2PO_2 (15 g/L); CMC(5g/L); choline chloride(5&10 g/L) or chitosan (2.5&5 g/L) ;wet-pick up (80%); drying at 100°C for 5 min curing at 160°C for 3 min.

Table 3. Effect of inclusion of N-containg additive along with Na-alginate in the finishing formulation

Additive	Conc. (g/L)	Add-on (%)		Wett. time (sec)		N (%)		ZI (mm)				CRA(W+F)°	
								G+ve		G-ve			
		C	V	C	V	C	V	C	V	C	V	C	V
None	0.0	1.945	4.992	8	6	0.00	0.00	0.0	0.0	0.0	0.0	205	260
Choline chloride	5.0	6.091	8.467	6	4	0.101	0.129	4	6	3	4	195	245
	10.0	8.204	9.615	4	3	0.138	0.155	10	13	7	11	180	222
Chitosan	2.5	2.480	3.195	7	5	0.120	0.140	7	10	5	7	174	228
	5.0	3.285	4.326	6	4	0.156	0.178	15	18	12	16	165	201

Finishing formulation: CA (25 g/L), NaH_2PO_2 (15 g/L); Na-alginate (5g/L); choline chloride (5&10 g/L) or chitosan (2.5&5 g/L) ;wet-pick up (80%); drying at 100 °C for 5 min. , curing at 160 °C for 3 min.

Table 4. Effect of inclusion of various nano materials into the finishing formulation

Nano-Additive (20 g/L)	Add-on (%)		Metal content (%)		Wett. time (sec)		ZI (mm)				CRA(W+F) °	
							G+ve		G-ve			
	C	V	C	V	C	V	C	V	C	V	C	V
None	2.702	3.831	0.0	0.0	1	<1	--	--	--	--	180	210
Ag NPs	5.201	7.666	0.078	0.096	3.0	2.5	18.0	21.0	16.0	18.5	200	237
ZnO NPs	8.541	9.680	5.093	5.177	3.0	2.5	23.0	25.0	20.5	22.0	282	302
Al_2O_3 NPs	7.102	8.062	2.121	2.357	3.5	3.0	20.0	23.0	18.0	21.5	232	261

Finishing formulation: CA (25 g/L), NaH_2PO_2 (15 g/L); Nano material (20g/L);wet-pick up (80%); drying at 100°C for 5 min. , curing at 160°C for 3 min.

Moreover , the antibacterial activity of loaded – Ag NPs is ascribed to : Ag^+-amino acid and /or DNA interaction, generation of *ROS* species and/or direct cell membrane damage [4, 54, 55]. On the other hand , the antibacterial activity of ZnO NPs – loaded substrates could be discussed in terms of : generation of *ROS* on the particles surface , the release of Zn^{2+} ions , membrane disfunction and ZnO NPs internalization thereby resulting in the inhibition of cell growth along with eventually leading to the cell death [19, 38, 49, 56]. But the imparted antibacterial activity of Al_2O_3 NPs– loaded substrates most probably is attributed to the surface charge interactions between Al_2O_3–NPs and the pathogenic bacterial cell wall thereby leading to its breakage , and causing cell damage and finally lysis [13].

Additionally , incorporation of the nominated nano inorganic materials , MNPs and MONPs , into the functional finishing bath has a positive impacts on fabric resiliency and easy care property , expressed as CRA , and the extent of improving in crease resistant functionality follows the decreasing order :
ZnO NPs > Al_2O_3 NPs > Ag NPs >> None , and V > C , keeping other parameters constant.

This enhancement in the imparted wrinkle recovery ability could be discussed in terms of the positive role of MONPs , e.g. ZnO NPs , in acting as a co-catalyst for ester- crosslinking cellulose a long with the ability of NPs to penetrate into the pores and amorphous regions of cellulose structure and adhere strongly into the fabric matrix thereby preventing the slipping of molecular chains , i.e high crease resistance [57, 58]].

3.4. Effect of inclusion of CMC or Na-Alg. into nano-finishing bath

For a givent set of finishing formlations and conditions the data in Table 5 demonstrate that inclusion of CMC or Na-Alg., as an effective binder, into the nano finishing formlations along with other constituents results in an increase in the metal content , a decrease in wetting time , a remarkable improve in the imparted antibacterial efficacy against the tested pathogens along with an enhancement in fabric resiliency , expressed as CRA, keeping other parameters constant. The extent of improvement in the aforementioned physico-chemical and functional properties, i.e antibacterial and anticrease functionalities, is governed by type of nano-inorganic material, i.e. ZnO NPs > Al_2O_3 NPs > Ag NPs>> None, kind of biopolymer (CMC > Na-Alg.), as well as nature of cellulosic substrate, i.e. V > C.

The change in the physico-chemical and the imparted functional properties reflects the difference among the finishing formulation constituents in extent of fixation and immobilization of the functional nano-materials onto and / or within the cellulose structure and fabric construction [38], via ester-crosslinking along with the positive role of CMC or Na-Alg. as an effective binder in promoting further interactions with both the cellulosic active centers and the inorganic NPs [26], i.e. high extent of fixation .

Moreover, the imparted antibacterial activity is determined by type of nano material , extent of fixation and distribution onto/within the treated fabric structure, type of pathogenic bacterial [18], as well as mode of action against *S. aureus* (G+ve) and *E. Coli* (G-ve) bacteria as discussed earlier. On the other hand, the improve in the finished fabric resiliency reflects the variation in the extent of ester-crosslinking and modification of the cellulose structure most probably due to the interactions among cell.OH, ester-crosslinking agent (CA), inorganic NPs (Ag NPs, ZnO NPs or Al_2O_3 NPs) and the added binding agent (CMC or Na-Alg.) during the curing step.

3.5. SEM and EDX analysis

A close view of (Fig.1 a, c, e and g) and (Fig.2 a, c, e and g), clearly shows the change in surface a morphology of select cotton and viscose fabric samples namely CMC/chitosan - , CMC/ZnO NPs - , and CMC/Al_2O_3 NPs – loaded fabric samples respectively compared with the untreated ones with a smooth surface (Fig.1a and Fig.2a). It is clear that the extent of variation in surface morphology and the extent of deposition of the finishing constituents is governed by type of cellulosic substrate, its surface morphology, fabric construction as well as availability and accessibility of its active sites, chemical composition of the used active ingredient , its molecular size, its mode of interaction, degree of fixation and immobilization as well as its location and extent of distribution onto and / or within the cellulose structure during the thermofixation step.

On the other hand, both Fig.1 (d, f, h) and Fig.2 (d, f, h) farther demonstrate and confirm surface deposition of chitosan, ZnO NPs and Al_2O_3 NPs, expressed as N, Zn and Al- elements respectively onto cotton and viscose substrates. Both type of functional additive, molecular size as well as extent of fixation and distribution onto and / or within the treated fabric structure determine the elemental composition of the treated cellulosic fabric surface.

4. Conclusion

An eco-friendly functional finishing approach for imparting antibacterial / anticrease functionalities to cotton and viscose fabrics in a single stage process using environmentally sound crosslinking, binding / fixing and functional agents was explored. The present research work successfully demonstrated a co-application of CA / NaH_2PO_2 (25/15 g/L), as ester-crosslinking system, CMC or Na-Alg. (5 g/L), as a

promising natural binding / fixing agent, and chitosan (5 g/L), Choline chloride (10 g/L) , Ag NPs (20 g/L), ZnO NPs (20 g/L) or Al_2O_3 NPs (20 g/L), as a functional additive, followed by padding and thermofixation at 160 °C for 3 min to develop eco-friendly antibacterial / anticrease cellulosic fabrics. The functionalized cellulosic substrates showed enhanced antibacterial activity against both *S. aureus* (G+ve) and *E. Coli* (G-ve) pathogenic bacteria and improved easy care property, without adversely affecting the fabric hydrophilicity. The chemical, SEM and EDX analysis confirmed the fixation and loading of the used functional additives. The extent of loading and subsequent variation in the imparted functional properties were governed by type of substrate, kind of fixing agent as well as nature of the used functional nanomaterial. Thus, it can be concluded that a facile and green fabrication finishing regime has been developed for upgrading both the antibacterial and anticrease functionalities of cellulosic substrates for a wide range of potential applications to meet various consumer demands.

Table 5. Effect of finishing formulation constituents on the imparted functional properties

Finishing bath constituents		Metal content (%)		Wett. time (sec)		ZI (mm)				CRA(W+F) °	
						G+ve		G-ve			
		C	V	C	V	C	V	C	V	C	V
CMC (5 g/ L)	Alone	--	--	7.0	5.0	--	--	--	--	215	276
	+ Ag NPs	0.089	0.112	4.5	3.0	20.5	23.0	19.0	21.0	226	290
	+ ZnO NPs	5.193	5.988	2.0	1.5	24.0	26.0	22.0	23.5	245	303
	+ Al_2O_3 NPs	3.510	3.710	2.5	2.0	22.0	24.0	20.0	22.5	235	289
Na-Alg. (5g/L)	Alone	--	--	8.0	6.0	--	--	--	--	205	260
	+ Ag NPs	0.081	0.105	5.0	4.0	17.5	19.0	16.0	18.0	220	270
	+ ZnO NPs	5.134	5.725	3.0	2.0	22.0	24.0	20.0	22.5	235	293
	+ Al_2O_3 NPs	2.340	2.830	4.0	3.0	20.0	22.5	18.5	21.0	229	280

Finishing formulation: CA (25 g/L), NaH_2PO_2 (15 g/L); Nano material (20g/L);wet-pick up (80%); drying at 100°C for 5 min. , curing at 160°C for 3 min.

C: cotton; V: viscose; ZI: zone of inhibition; G+ve: *S. aureus*; G-ve: *E. Coli*

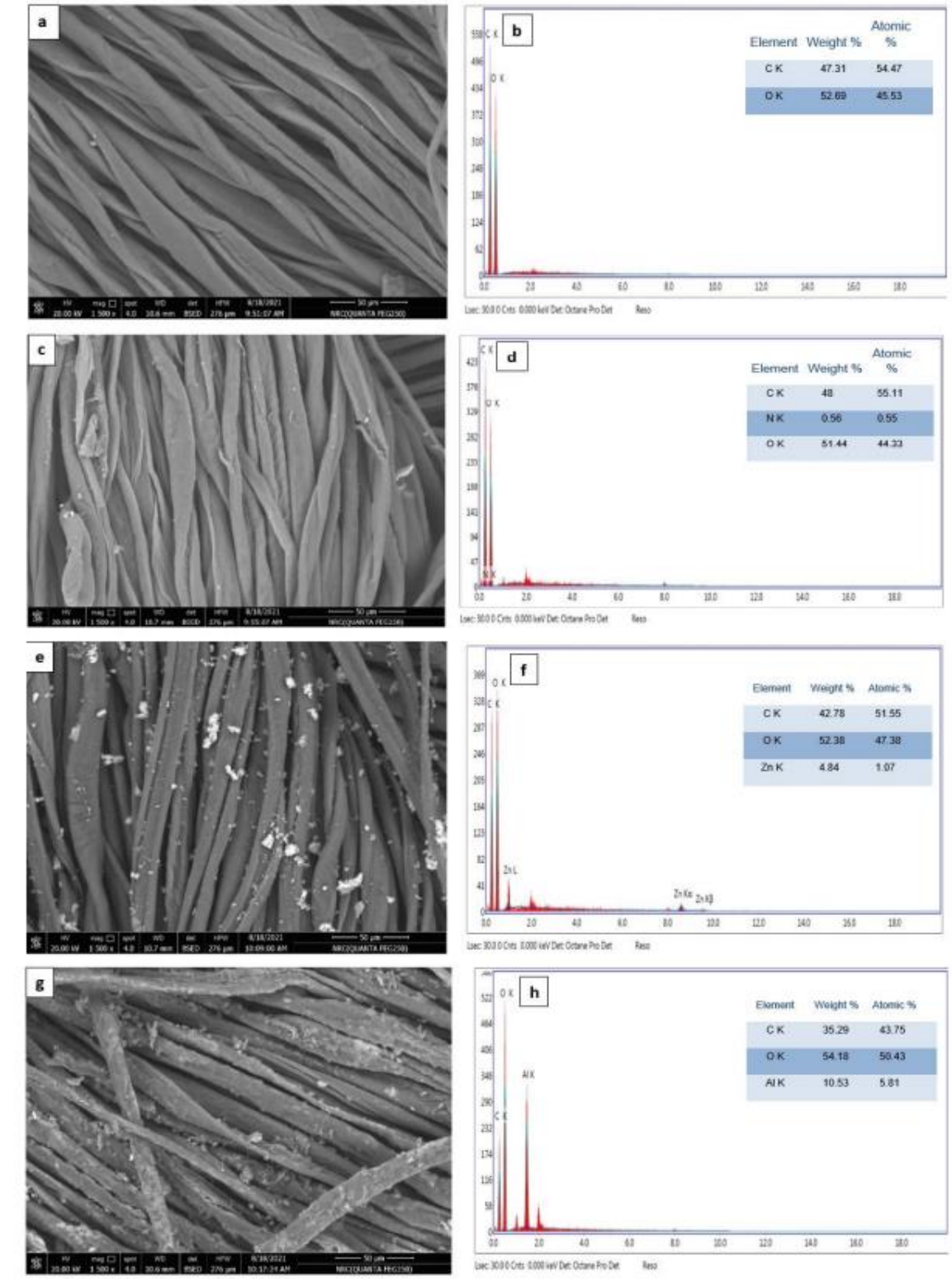


Fig.1. SEM and EDX spectra of untreated cotton samples (a , b), treated cotton samples with chitosan / CMC (5 / 5 g/L) (c , d), Nano Zinc oxide / CMC (20 / 5 g/L) (e , f) and Nano Aluminum oxide / CMC (20 / 5 g/L) (g , h).

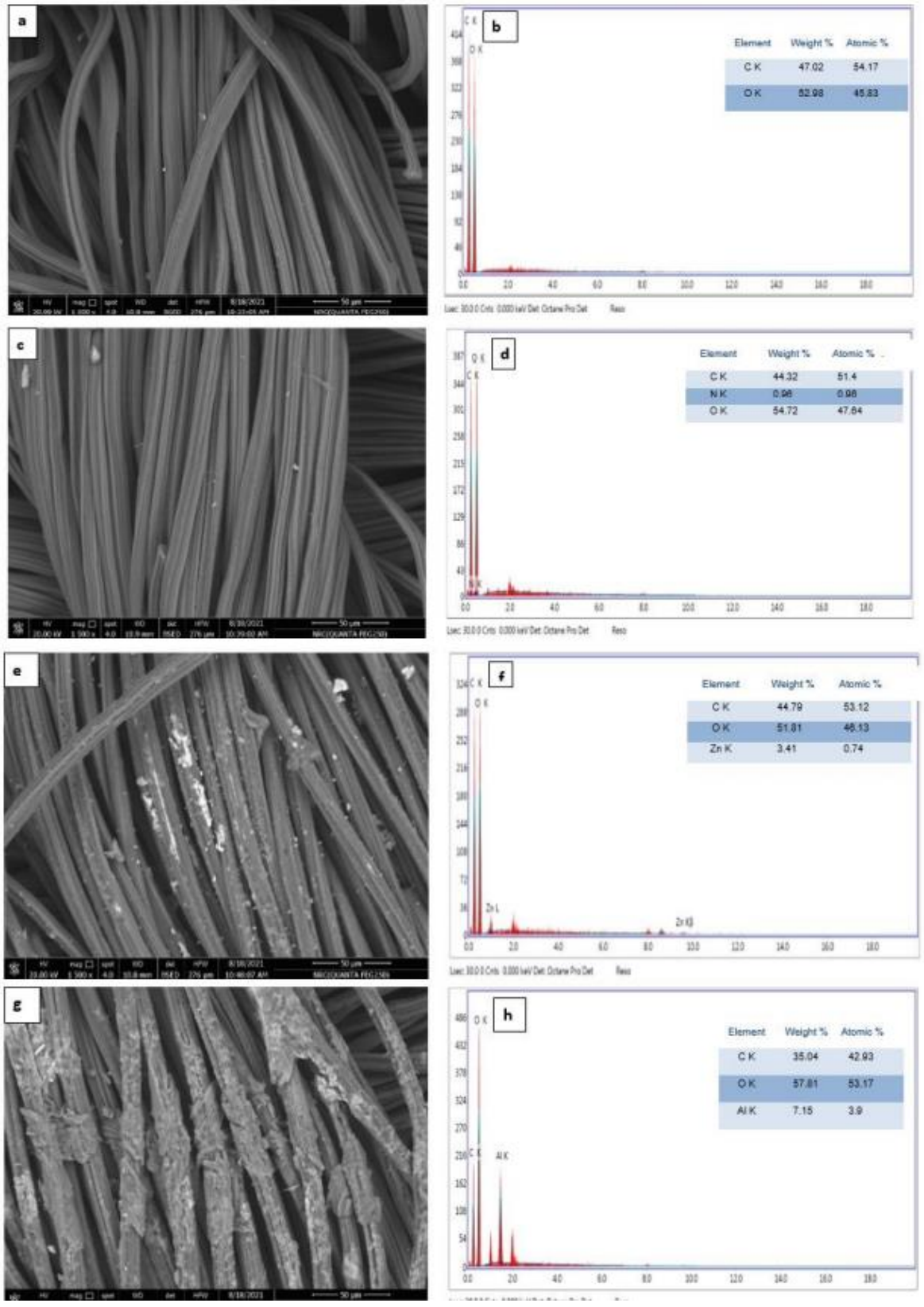


Fig.2. SEM and EDX spectra of untreated viscose samples (a , b), treated viscose samples with chitosan / CMC (5 / 5 g/L) (c , d), Nano Zinc oxide / CMC (20 / 5 g/L) (e , f) and Nano Aluminum oxide / CMC (20 / 5 g/L) (g , h).

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