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A smart approach to add antibacterial functionality to cellulosic pigment prints

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ABSTRACT

This study was devoted to enhancing the antibacterial functionality of pigment printed cotton, linen and viscose fabrics. Ag-NP's/PVP colloid, triclosan derivatives, chitosan or choline chloride was successfully incorporated into the pigment paste followed by printing and microwave curing to impart antibacterial activity to the cellulosic prints. Results obtained demonstrate that the modified pigment prints exhibit a remarkable antibacterial activity against the G+ve (*Staphylococcus aureus*) and G−ve (*Escherichia coli*) bacteria with a noticeable durability after 20 washing cycles without adversely affecting the printing and softness properties. The extent of printability and functionality of the nominated substrates are significantly governed by the type of: bio-active ingredient, binder, pigment and substrate. TEM, SEM and EDX analysis confirmed the formation of Ag-NP's/PVP colloid, of particle size range 7–14 nm, deposition of cross-linked-binder film onto the modified pigment prints, and the existence of elementary Ag and Si loaded onto fabrics surface, respectively.

1. Introduction

Cellulosic fabrics form the most commonly printed substrates. The vast majority of printed fabrics have been printed with pigment colorants, more than 50% of all prints, most probably due to simplicity, applicability to most of textile substrates, versatility, and quality of prints as well as the ability to avoid any after washing steps.

Successful pigment printing formulation comprises: pigment dispersion, thickening agent for giving the required rheology, as well as, the binding and cross-linking agents to fix the pigment colorant, which has no affinity for the textile fibers, onto the substrate by adhesion during the fixation step (Bahmani, East, & Holme, 2000; El-Molla & Schneider, 2006; Giesen & Eisenlohr, 1994; Gutjahr & Koch, 2003, Chap. 5; Ibrahim, El-Zairy, Zaky, & Borham, 2005; Iqbal, Mughal, Sohail, Moig, & Ahmed, 2012; Neral, Sostar-Turk, & Voncina, 2006; Schwindt and Fanlhaber, 1984; Waris, Iqbal, Aleem, & Ali, 2009; Yaman, Ozdogan, & Seventekin, 2012). In addition, a need remains for improving the performance properties of pigment prints as well as minimizing the environmental impacts of the pigment printing process.

On the other hand, cellulosic fabrics have been recognized as proper media to support the growth of microorganisms, e.g. bacteria, fungi, etc. The growth of microorganisms is accompanied by the generation of unpleasant odor, stains, discoloration, and partial deterioration along with increased likelihood of contamination (Gao & Cranston, 2008; Ibrahim, Eid, & El-Batel, 2012). So, it is highly desirable to stop or minimize the microbial growth on the cellulosic substrates without adversely affecting their quality and appearance taking in consideration both the consumer demands, i.e. the wearer, for hygienic clothing and active wear as well as the environmental concerns. Recently many approaches have been developed to confer antimicrobial textiles using various bioactive agents to effectively kill and/or control bacterial growth and to sustain durability such as: metal salts (Gao & Cranston, 2008; Ibrahim, Abo-Shosha, Gaffar, Elshafei, & Abdel-Fatah, 2006; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, Eid, Youssef, El-Sayed, & Salah, 2012; Ibrahim, El-Gamal, Gouda, & Mahrous, 2010; Ibrahim, Mahrous, El-Gamal, Gouda, & Husseiny, 2010), metal nanoparticles (Dastijerdi & Montazer, 2010; Gowri et al., 2010; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, & El-Batel, 2012; Ibrahim, Refaie, & Ahmed, 2010; Mahapatra & Karak, 2008); re-generable N-halamine compounds (Gouda & Ibrahim, 2008; Ibrahim, Aly, & Gouda, 2008; Lui & Sun, 2006; Qiam & Sun, 2004), quaternary ammonium compounds (Gao & Cranston, 2008; Son, Kaim, Ravikumar, & Lee, 2006), halogenated phenols, e.g. triclosan (Hashem, Ibrahim, El-Sayed, El-Husseiny, & Elanany, 2009; Ibrahim, Hashem, El-Sayed,

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El-Husseiny, & Elanany, 2010; Orhan, Kut, & Gunesoglu, 2009), chitosan (Lim & Hudson, 2003; Shin, Yoo, & Jang, 2001), Neem oil (Ibrahim, Eid, & El-Zariy, 2011; Joshi, Ali, & Rajendren, 2007) and immobilized enzymes (Ibrahim, Gouda, El-Shafei, & Abdel-Fattah, 2007).

Therefore, particular attention in this article has been paid on demonstrating the feasibility of the combined pigment printing and antibacterial finishing of cellulosic fabrics taking in consideration the environmental concerns.

2. Experimental

2.1. Materials

Plain weave 100% mill-scoured and bleached cotton (120 g/m^2), viscose (110 g/m^2) and linen (207 g/m^2) fabrics were used in this work.

Invansan® (Triclosan derivative, Huntsman, USA), Ruco®-BAC MED (nonionic antibacterial agent based on diphenyl alkane derivatives of triclosan, Rudolf chemie), chitosan (degree of deacetylation of >85%, Sigma), GBresin® CPN (based on hydroxymethylated 4,5dihydroxyethylene urea, GB Chem, BASF, Egypt), Durex® Silicone-1020 (based on modified polysiloxane microemulsion, Texchem, Egypt), Printofix® Binder MTB-01 liquid (acrylate based copolymer, anionic clariant), GBinder® FMD (based on polyacrylate, anionic, GB Chem, BASF, Egypt), Printofix® Thickener 160 EG liquid (synthetic thickening agent based on ammonium polyacrylate, Clariant), Printofix® Red H3BD pigment (Clariant), Imperon® Royal Blue SP pigment (DyStar), Unisperse® Yellow MR pigment (Ciba), were of commercial grade.

All other chemicals used during this study such as $AgNO_3$ (sigma), polyvinyl pyrolidone (PVP-40,000 Dalton, Merck) and ethylene glycol (Aldrich), ammonium persulphate $(NH_4)_2S_2O_8$ and choline chloride (Aldrich) were of laboratory reagent grade.

Fig. 1 shows the chemical structure of cellulose and active ingredients.

2.2. Methods

2.2.1. Synthesis of Ag-NP's/PVP colloid

The colloid of Ag-NP's/PVP was prepared in a manner analogous to the procedures proposed by Carotenuto, Pepe, and Nicolais (2000). PVP (1.728 g), as a protective agent, was dissolved in ethylene glycol (130 ml), as a solvent and reducing agent for $AgNO_3$ at room temperature, and to this solution, the required amount of $AgNO_3$ (86.9 mg) was added. The solution was stirred at room temperature until complete dissolution of the $AgNO_3$ and then kept at this temperature for 24 h without further stirring. The pH of the reaction solution was kept at pH 8.

2.2.2. Pigment printing

Guide formulation for aqueous pigment printing using flat screen technique follows:

Constituent	g/kg paste
Pigment	20
Thickener	20
Binder	100
Cross-linker	20
Softener	10
NH_4-persulfate	2
Bio-active material	20
Acetic acid	1
Water	807
Total	1000

Printed fabric samples were then simultaneously dried and fixed in a commercial microwave oven at output power of 386 W/5 min.

2.3. Measurements

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

Metal content of the treated samples was quantitatively determined by using Flame Atomic Absorption Spectrophotometer GBC-Avanta, Australia

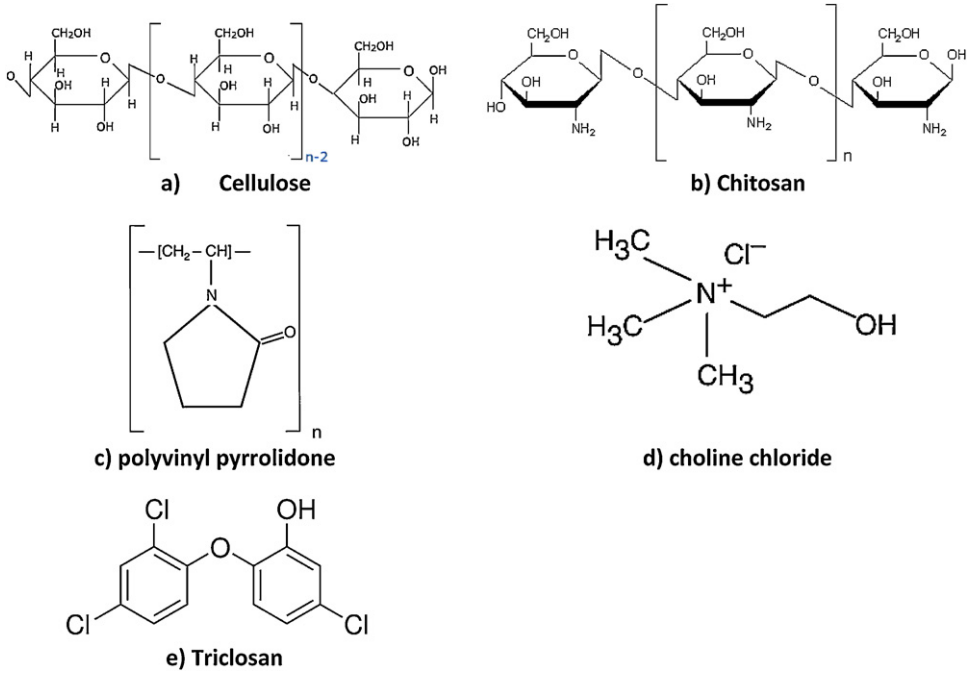

Fig. 1. Chamical structures of cellulose (a), chitosan (b), polyvinyl pyrrolidone (c), choline chloride (d), and triclosan (e).

The color strength (K/S) values were determined from the reflectance measurements using the Kubelka–Munk equation (Judd & Wyszeck, 1975) $K/S = (1-R)^2/2R$, where K/S is the ratio of absorption and scattering coefficient, R is the reflectance at the wave length of maximum absorbance of the used pigments.

Fastness properties to washing, rubbing and light of the obtained pigment prints were determined according to AATCC Test Methods (61-1972), (8-1972), and (16A-1972), respectively.

Antibacterial activity assessment against G+ve bacteria (*Staphylococcus aureus*) and G−ve bacteria (*Escherichia coli*) was evaluated qualitatively according to AATCC Test Method (147-1988), and expressed as zone of growth inhibition ZI (mm).

Durability to washing was evaluated according to ASTM Standard Test Method (D737-96).

The transmission electron microscopy (TEM) of the Ag-NP's/PVP colloid was performed with JEOL electron microscope model, JEM 2100 F electron microscope at 200 kV. Specimens for TEM measurements were prepared by dissolving a drop of colloid solution on a 400 mesh copper grid coated by an amorphous carbon film and evaporating the solvent in air at room temperature.

Scanning electron microscope (SEM) images of Ag-NP's/PVP colloid loaded-fabric samples were obtained with a JEOL, JXL 840A electron probe microanalyser, equipped with energy disperse X-ray spectroscopy (EDX) for the composition analysis.

3. Results and discussion

To study the technical feasibility of combined pigment printing and antibacterial finishing of cellulosic substrates, namely cotton, linen and viscose, taking in consideration the environmental, functional and quality concerns, the effect of application parameters such as type and concentration of the bio-active additive, type of binder and pigment colorant as well as kind of cellulosic substrate have been examined. Results obtained along with their appropriate discussion follow.

3.1. Type and concentration of antibacterial agent

For a given set of pigment printing conditions and within the range examined, the data in Table 1 demonstrate that increasing Invasan®, triclosan derivative, concentration up to 20 g/kg results in a slight increase in %N (from 0.298 up to 0.326), a reasonable improve in the K/S value (from 5.31 up to 6.83) along with a remarkable enhance in the antibacterial activity against G+ve (from ZI: zero up to 18) and G−ve bacteria (from ZI: zero up to 17).

The improvement in the aforementioned properties reflects the positive impact of increasing triclosan derivative concentration on enhancing the extent of formation and fixation of the binder film, in which both the pigment and triclosan derivative molecules become embedded/trapped/fixed, onto the printed fabric surface under the used microwave curing conditions, i.e. darker depth of shade as well as higher loading of triclosan derivative via interaction with the binder and/or cross-linker functional groups, i.e. —COOH and/or —NCH_2OH groups (Hashem et al., 2009; Ibrahim, Hashem, et al., 2010; Orhan et al., 2009).

The remarkable improvement in the antibacterial activity of triclosan-loaded pigment prints could be discussed in terms of non specific action; i.e. multi-target, causing damage of bacterial cells or via inhibition of a specific bacterial target, i.e. inhibition of bacterial fatty acid synthesis through the blocking of lipid bio-synthesis (Orhan et al., 2009; Yazdankhah et al., 2006)

On the other hand, the antimicrobial activity against the examined G+ve and G−ve bacteria follows the decreasing order: G+ve > G−ve, reflects the difference between them in membrane structure and amenability to disruption and destruction (Jones & Hock, 2010; Orhan et al., 2009).

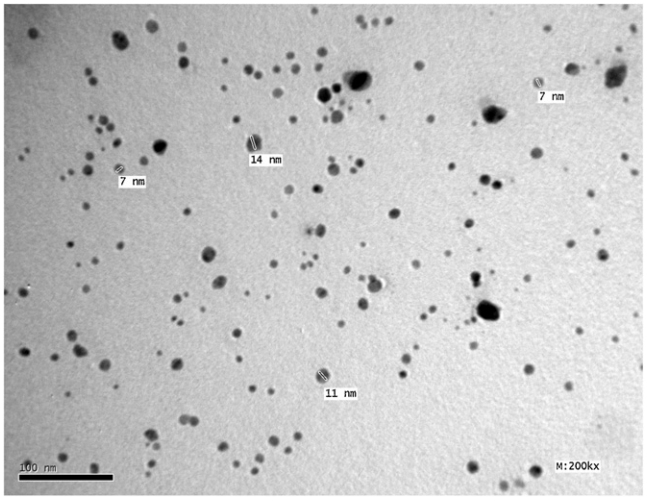

Fig. 2. TEM image of Ag-NP's/PVP colloid.

$$HOH_2CCH_2OH \xrightarrow{-H_2O} CH_3{-}CHO \quad (1)$$

$$2\,CH_3-CHO + 2Ag^+ \longrightarrow 2Ag^o + 2H^+ + CH_3CO.CO.CH_3 \quad (2)$$

$$Ag^+ \text{ or } H^+ + PVP \longrightarrow Ag\,(PVP)^+ \text{ or } H\,(PVP)^+ \quad (3)$$

$$CH_3-CHO + 2Ag\,(PVP)^+ + 2OH^- \longrightarrow CH_3COOH + 2AgNP's/PVP + H_2O \quad (4)$$

Scheme 1. The tentative mechanism.

Additionally, Ag-NP's/PVP colloid was successfully obtained by reduction of Ag-nitrate, as Ag–precursor, ethylene glycol, as solvent and reducing agent, along with PVP, as a protective agent at room temperature and pH 8 (Carotenuto et al., 2000). Fig. 2 shows the TEM image of the prepared Ag-NP's/PVP colloid, and demonstrates that the prepared nanoparticles are not aggregated, well dispersed with particle size in the range of 7–14 nm.

The formation of Ag-NP's/PVP colloid, i.e. Ag-NP's embedded and incorporated into the PVP matrix can be explained as follow (Scheme 1) (Carotenuto et al., 2000; Shaoo et al., 2009; Wang, Qjao, Chem, & Ding, 2005):

It is also evident (Table 1), that increasing the concentration of Ag-NP's/PVP colloid, as a bio-additive, in the printing formulation (0–20 g/kg) is accompanied by a remarkable increase in the Ag–content (from zero up to 1.42%), an improvement in the K/S value of the obtained prints (from 5.31 up to 7.89) as well as an outstanding increase in the antibacterial activity against G+ve and G−ve bacteria (from zero up to 15.5 and 14 mm, respectively). The enhancement in the aforementioned properties reflects the positive impact of the PVP in enhancing the extent of fixation of both the Ag-NP's and the pigment particles onto the printed substrate through supporting the formation of a three dimensional linked network, together with other ingredients, i.e. binder, cross-linker, and softener during the microwave curing step (Fahmy, Abo-Shosha, & Ibrahim, 2009; Ibrahim et al., 2005; Yaman et al., 2012). The higher the Ag-NP's/PVP colloid concentration, the better the improvement in the printability and functionality of the obtained pigment prints.

On the other hand, the remarkable antibacterial activity of Ag-NP's/PVP-loaded pigment prints most probably is attributed to: (i) the released of small amount of Ag^+ from Ag-NP's: according to equation (Radetic, 2012):

$$O_2\,(aq) + 4H_3O^+ + 4Ag^o \rightarrow 4Ag^+ + 6H_2O \quad (5)$$

Table 1
Effect of type and concentration of the incorporated bio-active agent into printing paste[a] on printability and antibacterial functionality of cotton fabric.

Bioactive additive	Invasan®				Ag-NP's/PVP colloid			
Concentration (g/kg)	%N[b]	K/S[c]	ZI (mm)[d]		Ag content (%)	K/S	ZI	
			G+ve	G−ve			G−ve	G+ve
0	0.298	5.31	0.0	0.0	0.00	5.31	0.0	0.0
5	0.306	5.66	4.5	3.0	0.06	6.16	2.5	1.5
10	0.312	6.50	11.0	9.5	0.104	7.03	8.5	6.5
20	0.326	6.83	18.0	17.0	0.142	7.89	15.5	14

[a] Printing paste components: Printofix® Binder MTB-01 (100 g/kg); Printofix® thickener 160 EG (20 g/kg); Printofix® Red H3BD (20 g/kg); GB Resin® CPN (20 g/kg); Silicone softener (10 g/kg); $(NH_4)_2 S_2O_8$ (2 g/kg); fixation at 386 watt for 5 min.
[b] N: nitrogen content.
[c] K/S: color strength.
[d] ZI: zone of inhibition; G +ve: (*S. aureus*); G−ve (*E. coli*).

with a subsequent ionic interaction with the cytoplasm membrane of the bacteria cell, (ii) interaction of Ag-NP's with sulfur rich protein in the bacterial cell membrane and interior of the cell, (iii) interaction of the Ag-NP's with phosphorous-containing compounds such as DNA and its negative impacts on the respiratory chain or cell division processes leading to a cell death, and/or (iv) the generation of active oxygen, in the presence of dissolved oxygen and Ag-NP's or Ag^+ as a catalyst as follow:

$$H_2O + 1/2\,O_2 \xrightarrow[\text{or } Ag^+]{\text{Ag-NP's}} H_2O_2 \rightarrow H_2O + [O] \quad (6)$$

with a subsequent oxidation of the molecular structure of bacteria (Jones & Hock, 2010)

The difference in antibacterial activity against the selected G+ve (*S. aureus*) and G−ve (*E. coli*) bacteria, G+ve > G−ve, could be attributed to their differences in cell wall structure, outer membrane, amenability to inhibition of enzymes function and/or inactivation of DNA replication (Jones & Hock, 2010; Orhan et al., 2009) as discussed earlier.

3.2. Binding agent type

Table 2 shows the effect of using different binders namely Printofix® Binder MTB and GBinder® FMD together with other ingredients on the printing and antibacterial properties of printed fabric samples. For a given printing condition, the data in Table 2 signify that: (i) the enhancement in the depth of the obtained prints, expressed as K/S values as well as the improvement in the imparted antibacterial activity, expressed as ZI, against the examined, G+ve and G−ve bacteria follow the descending order: Printofix® Binder MTB > GBinder® FMD, keeping other parameters constant, (ii) the slight improvement in both the %N and Ag-content follows the same order, (iii) both the wash and light fastness properties are the same, (iv) the rubbing fastness properties in case of adding Ag-NP's/PVP colloid are better than in case of using triclosan derivatives, keeping other parameters fixed, reflecting the positive impact of Ag-NP's/PVP colloid on enhancing the extent of pigment molecules accommodation, incorporation and fixation onto the binder/fabric matrix, and v) the antibacterial activity of the obtained pigment prints follows the descending order: triclosan > Ag-NP's/PVP regardless of the used binder, keeping other parameters constant, reflecting the differences between them in: concentration of active ingredients, antibacterial activity and durability, extent of loading and distribution, mode of action, compatibility with other ingredients as well as extent of functionalization under the given conditions (Gao & Cranston, 2008; Radetic, 2012; Yazdankhah et al., 2006).

The differences in the printability and antibacterial functionality of the obtained pigment prints using the abovementioned binders most probably attributed to the difference in: molecular weight, chemical composition, location and extent of distribution, film-forming properties, extent of polymerization and cross-linking, ability to form a three-dimensionally linked network with other ingredients and textile substrate as well as in Ag-NP's and pigment binding capacity under the given fixation conditions (Gutjahr & Koch, 2003, Chap. 5; Ibrahim et al., 2005).

3.3. Pigment colorant

For a given pigment formulations and subsequent microwave fixation conditions, the data in Table 3 signify that: (i) incorporation of pigment in the printing formulation results in a slight decrease in %N, % Ag as well as in the imparted antibacterial functionality, irrespective of the used pigment and the type of the bio-active ingredient, i.e. triclosan or Ag-NP's/PVP colloid, (ii) this slight decrease in the abovementioned properties most probably due to a slight decrease in the triclosan and Ag-NP's/PVP onto the resultant pigment prints, (iii) the variation in the printing properties, i.e. K/S and fastness properties, as well as in antibacterial functionality is governed by the type of pigment, e.g. form and

Table 2
Effect of using different binding agents in printing paste [a] on printability and antibacterial functionality of cotton fabric.

Bioactive additive	Invasan® (20 g/kg)								Ag-NP's/PVP colloid (20 g/kg)							
Binding agent (100 g/kg)	%N[b]	K/S[c]	ZI (mm)[d]		WF[e] alt	LF[f]	RF[g]		Ag content (%)	K/S	ZI		WF alt	LF	RF	
			G+ve	G−ve			Dry	Wet			G+ve	G−ve			Dry	Wet
Printofix® Binder MTB-01	0.326	6.83	18.0	17.0	4–5	5	4	3–4	0.142	7.89	15.5	14.0	4–5	5	4–5	4
GBinder® FMD	0.312	6.50	17.0	16.0	4–5	5	4	3–4	0.131	7.69	13	12	4–5	5	4–5	3–4

[a] Printing paste components: Printofix® thickener 160 EG (20 g/kg); Printofix® Red H3BD (20 g/kg); GB Resin® CPN (20 g/kg); bio-additive (20 g/kg); silicone softener (10 g/kg); $(NH_4)_2 S_2O_8$ (2 g/kg); fixation at 386 watt for 5 min.
[b] N: nitrogen content.
[c] K/S: color strength.
[d] ZI: zone of inhibition; G +ve: (*S. aureus*); G−ve (*E. coli*).
[e] WF: wash fastness, alt: alteration.
[f] LF: light fastness.
[g] RF: rubbing fastness.

Table 3
Effect of using different pigment colorants[a] in printing paste on printability and antibacterial functionality of cotton fabric.

Bioactive additive	Invasan® (20 g/kg)							Ag-NP's/PVP colloid (20 g/kg)							
Pigment (20 g/kg)	%N	K/S	ZI (mm)		WF alt	LF	RF	Ag content (%)	K/S	ZI		WF alt	LF	RF	
			G+ve	G−ve			Dry Wet			G+ve	G−ve			Dry	Wet
None	0.345	–	21.0	20.0	–	–	– –	0.153	–	17.0	15.5	–	–	–	–
Printofix® Red H3BD	0.386	6.83	18.0	17.0	4–5	5	4 3–4	0.142	7.89	15.5	14.0	4–5	5	4–5	4
Imperon® Royal Blue SP	0.320	10.06	19.5	18.0	4–5	5	3–4 3	0.130	11.51	16.5	15.0	4–5	5	3–4	3
Unisperse® Yellow MR	0.312	6.12	16.5	15.0	5	5	4–5 4	0.115	6.81	15.0	13.5	5	5	4–5	4

[a] Printing paste components: Printofix® Binder MTB-01 (100 g/kg); Printofix® thickener 160 EG (20 g/kg); pigment (20 g/kg); Bioactive additive (20 g/kg); GB Resin® CPN (20 g/kg); Silicone softener (10 g/kg); $(NH_4)_2 S_2O_8$ (2 g/kg); fixation at 386 watt for 5 min.
For explanation of abbreviation see footnote to Table 2.

size of pigment particles, chemical class and functionality of colorants, compatibility with other ingredients, extent of location and distribution and agglomeration as well as the extent of fixation entrapment onto/into the produced three-dimensionally linked network during the fixation step along with the bio–active ingredients (Giesen & Eisenlohr, 1994; Ibrahim et al., 2005; Uddin & Lomas, 2005) and (iv) the washing, light and rubbing fastness ranged from good to very good for all pigment prints.

3.4. Other active ingredients

The effect of inclusion other active ingredients namely chitosan, choline chloride and Ruco®-BAC, in comparison with Invansan® and Ag-NP's/PVP colloid, on the printability and antibacterial functionality of the pigment printed fabric samples as well as durability to wash was also investigated (Table 4). For a given set of printing formulations and conditions the data so obtained signify that inclusion of the abovementioned bio-active ingredients individually in the printing formulations results in: (i) a variation in the %N of the printed fabric samples and follows the descending order: choline chloride > chitosan > Ag-NP's/PVP > Ruco®-BAC > Invansan® > none, most probably due to the differences among the used additives in chemical structure, nitrogen content and subsequent fixation onto/within the binder/fabric matrix with other ingredients, ii) an improvement in the depth of the obtained pigment prints as follow: Ag-NP's/PVP > chitosan > choline chloride > Invansan® > Ruco®-BAC > none reflecting the differences among them in molecular size, extent of location and distribution, chemical composition, functionality as well as in subsequent ability to afford active sites for pigment particles accommodation and fixation during the microwave curing step, and iii) no practical changes in the fastness properties of the obtained pigment printing regardless of the used active ingredients.

On the other hand, Table 4 also shows that: (i) the imparted antibacterial activity is governed by type of the additive and follows the descending order: choline chloride > Invansan® > Ruco®-BAC > Ag-NP's/PVP > chitosan ≫ none, (ii) which reflects the differences among them in chemical structure, functionality, active ingredients, extent of fixation onto the substrate during microwave curing step as well as durability to wash in addition to its antibacterial activity and mode of action (Gao & Cranston, 2008; Ibrahim, Eid, et al., 2010; Maillard, 2002), (iii) antibacterial activity of chitosan-loaded pigment prints is attributed to its polycationic nature, especially in acidic medium, thereby interfering with bacterial metabolism by stacking the cell's surface and/or its binding ability with DNA to inhibit mRNA synthesis (Zemljic, Strand, Saupert, & Kleinschek, 2009; Zitao, Cheng, Jinmin, Yanlin, & Donghui, 2003), (iv) antibacterial functionality of choline chloride-loaded pigment prints most probably attributed to its ability to combine with membrane phospholipids hence causing disruption of the cytoplasmic membrane (Maillard, 2002), (v) repeated laundering (20 cycles) of the functionalized pigment prints is accompanied by a slight decrease in the imparted antibacterial activity most probably due to the higher extent of fixation of the used bio-active ingredients onto the binder/fabric matrix, and vi) the antibacterial efficacy against G+ve was better than G−ve bacteria, irrespective of the used active ingredients.

3.5. Type of cellulosic substrate

As far as the changes in printability and antibacterial functionality as a function of the type of substrate, Table 5 reveals that: (i) the %N of the printed fabric samples follow the descending order: cotton > linen > viscose, (ii) the depth of the obtained pigment prints follows the descending order: linen > cotton > viscose, (iii) the imparted antibacterial activity to the used substrates follows the descending order: cotton > linen > viscose, (iv) type of cellulosic substrate has practically no effect on the fastness properties of the obtained prints, (v) the variation in printability, expressed as K/S value, and functionality expressed as ZI value demonstrate the differences among the nominated substrates in surface area, fabric weight and thickness, cellulose content, non-cellulosic component,

Table 4
Effect of adding different bio-active agents in printing paste[a] on printability and antibacterial functionality of cotton fabric.

Bioactive additive	%N	K/S	ZI (mm)		WF alt	LF	RF	
			G+ve	G−ve			Dry	Wet
Invasan® (20 g/kg)	0.326	6.80	18.0 (15.5)[b]	17.0 (14.0)	4–5	5	4	3–4
Ag-NP's/PVP colloid (20 g/kg)	0.382	7.89	15.5 (13.0)	14.0 (11.5)	4–5	5	4–5	4
Chitosan (10 g/kg)	0.395	6.95	14.5 (12.0)	12.0 (10.0)	4–5	5	4–5	4
Choline Chloride (20 g/kg)	0.418	6.87	19.5 (16.5)	18.0 (15.5)	4–5	5	4–5	4
Ruco®-BAC (20 g/kg)	0.350	6.73	16.5 (14.0)	15.5 (12.5)	4–5	5	4	3–4
None	0.298	5.31	0.0	0.0	4–5	5	4–5	4

[a] Printing paste components: Printofix® Binder MTB-01 (100 g/kg); Printofix® thickener 160 EG (20 g/kg); Printofix® Red H3BD (20 g/kg); Silicone softener (10 g/kg); GB Resin® CPN (20 g/kg); $(NH_4)_2 S_2O_8$ (2 g/kg); fixation at 386 watt for 5 min.
[b] values in parentheses indicate retained function after 20 washing cycles.
For explanation of abbreviation see footnote to Table 2.

Table 5
Effect of printing[a] different cellulosic substrates on printability and antibacterial functionality.

Bioactive additive	Invasan® (20 g/kg)							Ag-NP's/PVP colloid (20 g/kg)						
Substrate	%N	K/S	ZI (mm)		WF alt	LF	RF	Ag content (%)	K/S	ZI		WF alt	LF	RF
			G+ve	G−ve			Dry Wet			G+ve	G−ve			Dry Wet
Cotton	0.326	6.80	18.0 (15.0) [b]	17.0 (14.0)	4–5	5	4 3–4	0.140	7.89	15.5 (13.0)	14 (11.5)	4–5	5	4 3–4
Linen	0.312	11.21	16.5 (14.5)	15.0 (12.0)	4–5	5	4 3–4	0.060	14.50	14.5 (12.5)	13.0 (11.0)	4–5	5	4 3–4
Viscose	0.300	6.46	15.0 (13.5)	13.0 (11.0)	4–5	5	4 3–4	0.120	7.50	12.5 (10.5)	11.5 (9.0)	4–5	5	4 3–4

[a] Printing paste components: Printofix® Binder MTB-01 (100 g/kg); Printofix® thickener 160 EG (20 g/kg); pigment (20 g/kg); Printofix® Red H3BD (20 g/kg); Silicone softener (10 g/kg); GB Resin® CPN (20 g/kg), $(NH_4)_2 S_2O_8$ (2 g/kg); fixation at 386 watt for 5 min.
[b] values in parentheses indicate retained function after 20 washing cycles.
For explanation of abbreviation see footnote to Table 2.

e.g. lignin in linen, amorphous/crystalline region, extent of diffusion and penetration, as well as extent of cross-linking and polymerization followed by subsequent formation of three-dimensional linked network during the microwave fixation step (Ibrahim et al., 2006; Ibrahim, Amr, et al., 2012; Ibrahim, Eid, et al., 2010), and (vi) the imparted antibacterial activity is still enough durable even after 20 washing cycles, irrespective of the used bioactive additives and substrates.

On the other hand, the SEM images and the corresponding EDX spectra of Ag-NP's/PVP colloid loaded cotton, linen and viscose prints were demonstrated in Fig. 3(a–c, respectively). The SEM images clearly exhibited the presence of cross-linked binder film on

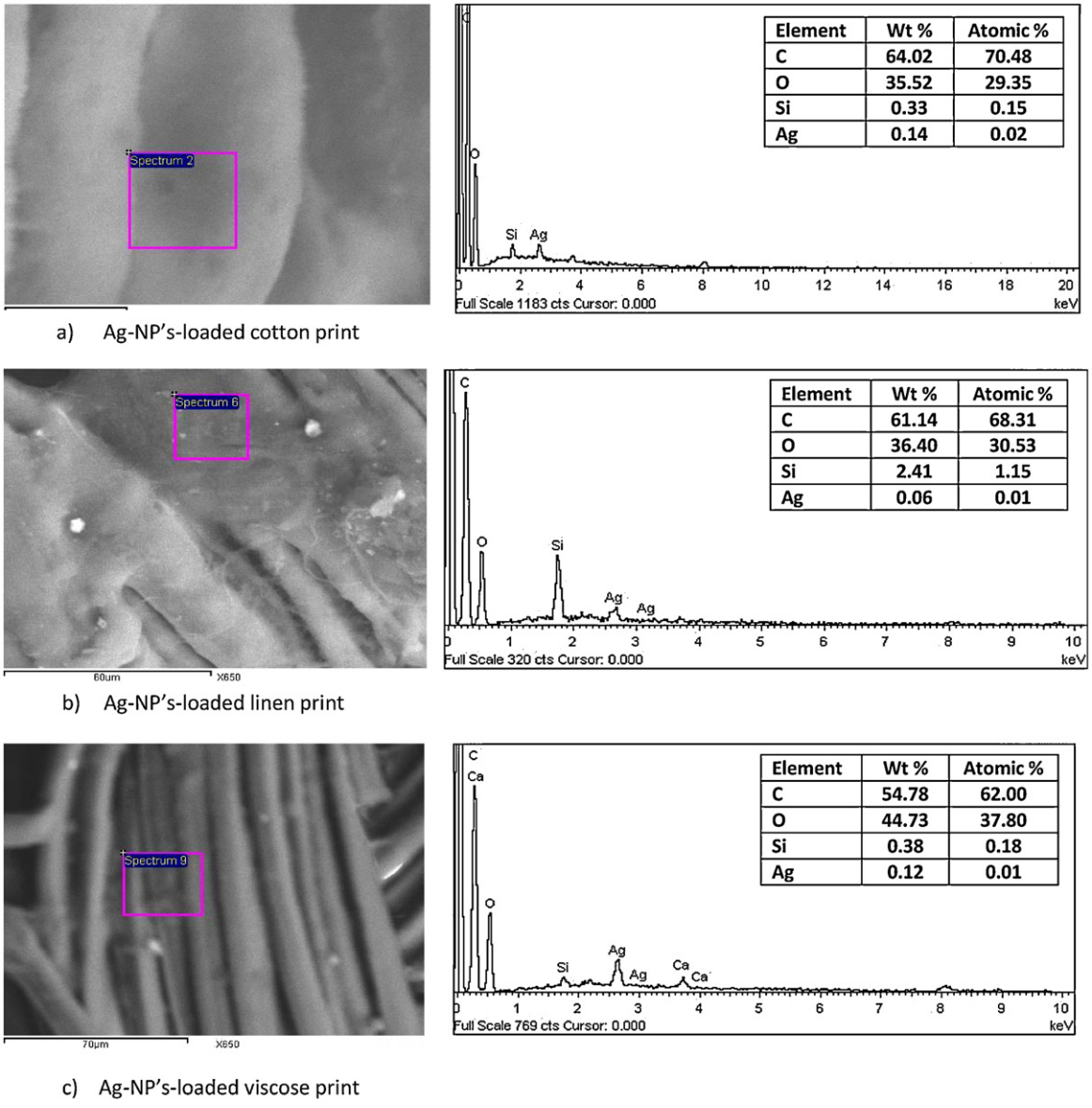

Fig. 3. SEM images and EDX spectrum of: Ag-NP's-loaded cotton print (a), Ag-NP's-loaded linen print (b), Ag-NP's-loaded viscose print (c).

the overall fibers. The location and extent of distribution of this film with its ingredients, e.g. pigment particles, Ag-NP's, silicone softener, etc., are governed by type of substrate, extent of modification as well as its surface morphology as discussed before. Additionally, the presence of silver as well as silicone elements on the obtained pigment prints was confirmed using EDX spectra.

4. Conclusion

In conclusion, we have demonstrated a simple, solvent–free, and eco-friendly approach for antibacterial finishing and pigment printing of cotton, linen and viscose fabrics.

The new approach is based on modification of solvent–free pigment formulation via incorporation of certain bio-active ingredients namely: triclosan based materials, Ag-NP's/PVP colloid, chitosan and choline chlorid along with other ingredients followed by printing and microwave curing.

The extent of printability and the improvement in the imparted antibacterial activity of the modified pigment prints are governed by type and concentration of the bio-active agent, type of binder, as well as pigment colorant, in addition to type of cellulosic substrate.

The modified pigment prints demonstrate a remarkable antibacterial activity against both the G+ve and G−ve bacteria.

The imparted antibacterial functionalities are highly retained even after 20 washing cycles.

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