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Functionalization of linen/cotton pigment prints using inorganic nano structure materials

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ABSTRACT

The present work opens up a novel strategy for the development of new multifunctional cellulosic pigment prints. The developed process aims at modifying the solvent-free pigment printing formulations via inclusion of certain inorganic nano materials namely silver (Ag-NPs), zinc oxide (ZnO-NPs), zirconium oxide (ZrO_2-NPs) or titanium dioxide (TiO_2-NPs) at 20 g/kg paste followed by screen printing and microwave fixation. The imparted functional properties together with the depth of the obtained prints are governed by the type of nano additives, type of binder and the pigment colorant. The imparted antibacterial and/or UV protection properties to the pigment prints were retained with an acceptable level (>70%) of durability even after 20 washing cycles. The presence of nano materials on the surface of the obtained pigment prints was confirmed using SEM images and EDX spectra.

1. Introduction

Cellulose is the most abundant natural polymer of glucose available today worldwide. The abundant hydroxyl groups on each anhydroglucose unit allow extensive inter/intra molecular hydrogen bonding thereby enhancing the strength of the cellulose structure as well as offer an active sites for chemical modification and coloration. Cotton fibers are the purest form of cellulose (≈90% α-cellulose). Cotton cellulose offers better overall quality. Cotton fibers combine durability with attractive qualities and comfort (Choudhury, 2006; Koh, 2011). Flax or linen is the best among the bast fibers. Flax fiber is very compact and its strength makes it superior to cotton for certain applications. It is smoother than cotton and provides excellent summer suiting due to its good heat conductivity. Its chemical properties are similar to those of cotton. On the other hand, blending of similar or dissimilar textile fibers is carried out to: overcome the drawbacks of the used fiber components, achieve economic advantages, upgrade the performance and quality properties as well as to develop innovative textile products to meet the consumer demands (Ibrahim, 2011).

Printing process is a localized application of dyes or pigments in thickened form to a substrate to create an attractive design with well defined boundaries. Textile printing process can give a quick response to changes in fashion, design, color trends and consumer demands thereby making just in-time processing feasible. In the textile industry, more than 50% of all printed substrates are cellulosic fabrics. Pigment printing dominates certain market and accounts for nearly 50% of printing production worldwide most probably due to its simplicity, low cost, minimum requirement for wet-processing as well as its applicability to a wide range of textile types. A typical pigment printing paste contains: pigment colorant, thickener, binder, cross-linker, handle modifier, surfactant and catalyst. Pigment printing stages are preparation of printing paste, printing of the fabric followed by drying and fixation. The development of textile printing has forced today's the researchers, designers, artists and industrialists to use latest technological innovations to move forward in the field of creation and production of innovative textile prints taking into consideration esthetic and production quality, functionality, environmental awareness, health and safety legislations, more design variety on shorter time and shorter production cycles (Dedhia & Shah, 2010; Giesen & Eisenlohr, 1994; Ibrahim, El-Zairy, Zaky, & Borham, 2005; Neral, Sostar-Turk, & Voncina, 2006; Park, 2010; Yaman, Ozdogan, & Seventekin, 2012).

On the other hand, functional finishes play a vital role for quality and value improvement of textiles and garments. Increasing consumer demands for innovative textile products and attitude toward hygiene and active lifestyle have created a rapidly increasing market for a wide range of antibacterial and UV-protection textiles, which in turn have stimulated intensive research and development efforts (Cakir, Budama, Topel, & Hoda, 2012; Cerkez, Kocer,

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Worley, Broughton, & Huang, 2012; Emam et al., 2013; Hashem, Ibrahim, El-Sayed, & El-Husseiny Sh Elanany, 2009; Hashemikia & Montazer, 2012; Hong & Sun, 2011; Ibrahim, Abdalla, El-Zairy, & Khalil, 2013; Ibrahim, Abo-Shosha, Gaffar, Elshafei, & Abdel-Fatah, 2006; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012; Ibrahim, Eid, & El-Batel, 2012; Ibrahim, Eid, & El-Zariy, 2011; Ibrahim, Eid, Hashem, Refai, & El-Hossamy, 2010; Ibrahim, Eid, Youssef, El-Sayed, & Salah, 2012; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013; Ibrahim, El-Zairy, El-Zairy, Eid, & Ghazal, 2011; Ibrahim, El-Zairy, El-Zairy, & Ghazal, 2013; Ibrahim, El-Zairy, & Eid, 2010; Ibrahim, Gouda, Husseiny, El-Gammal, & Mahrous, 2009; Ibrahim, Gouda, & Zairy, 2008; Ibrahim, Mahrous, El-Gamal, Gouda, & Husseiny, 2010; Ibrahim, Refaie, & Ahmed, 2010; Ibrahim, Refaie, Youssef, & Ahmed, 2005; Kathirvelu, D'souza, & Dhurai, 2008, 2009; Papaspyride, Pavlidou, & Vouyloukа, 2009; Sundaresan, Sivakumar, Vigneswaran, & Ramachandran, 2011). Additionally, the use of nanotechnology, as one of the key technologies of the 21st century, in the textile industry for medical, hygienic, and technical textiles has increased dramatically. The application of nano particles, especially nano-metals and metal oxides, to impart finished fabrics with a wide-range of functional performances has been the object of several studies (Dastjerdi & Montazer, 2010; Hebeish & Ibrahim, 2007; Simoncic & Tomsic, 2010; Wong, Yuen, Leung, Ku, & Lam, 2006).

With the above in mind, the main task of the present work is to find out the proper pigment printing formulations for attaining functionalized Linen/cotton pigment prints using certain inorganic nano-materials.

2. Experimental

2.1. Materials

Plain wave mill-scoured and bleached linen/cotton blend (65/35,180 g/m^2) was used throughout the study.

Printofix® Binder MTB-01 liquid (acrylate based copolymer, anionic, Clariant), GBinder® FMD (based on polyacrylate, anionic, BASF GB Chem., Egypt) Printofix® Binder 86 (acrylate based copolymer dispersion, Clariant), Alcoprint® PB-55 (aqueous dispersion of self-crosslinking butadiene copolymer, Ciba), Printofix® Thickener 160 EG liquid (synthetic thickening agent based on ammonium polyacrylate, Clariant), GBresin® CPN (based on hydroxymethylated 4,5 dihydroxyethylene urea, BASF/GB Chem., Egypt), and Durex® Silicone-1020 (based on modified polysiloxane microemulsion, Texchem, Egypt), Unisperse® Blue G pigment (Ciba), Unisperse® Red G pigment (Ciba), Imperon® Gold Gelb K-RN pigment (Dystar), Printofix® Blue R2H pigment (Clariant), Printofix® Yellow HRNC pigment (Clariant) and Imperon® Royal Blue SP pigment (Dystar), were of commercial grade.

Nano-sized ZnO (50 wt.% in water, particle size <35 nm avg.), ZrO_2 (10 wt.% in water, particle size <100 nm), and nano sized-Ag (0.02 mg/L, particle size 40 nm) were purchased from Sigma Aldrich.

All other chemicals used during this study such as Ti-tetraisopropoxide (analytical grade, Sigma), while ammonium persulphate [$(NH_4)_2S_2O_8$], nitric acid and 2-propanol were of laboratory reagent grade.

2.2. Methods

2.2.1. TiO_2 sol–gel preparation

TiO_2-nanoparticles were prepared as previously reported (Bozzi, Yuranova, & Kiwi, 2005) using titanium tetraisopropoxide precursor with 2-propanol and nitric acid particle size <10 nm (Ibrahim, Amr, et al., 2012).

2.2.2. All-in printing method

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

Printing paste components	g/kg paste
Pigment	20
Thickener	20
Binder	100
Crosslinker	20
Softener	10
$(NH_4)_2S_2O_8$	2
Nano-material	20
Water	808
Total	1000

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

2.3. Measurements

The color strength (K/S) values of the obtained pigment prints were determined from the reflectance measurements using the Kubelka Munk equation (Judd & Wyszeck, 1975):

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

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 pigment colorants.

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 (mm).

UV-protection factor (UPF) was assessed according to the Australian/New Zealand Standard Method 135-2000. According to the Australian classification scheme, fabrics can be rated as providing good protection, very good protection, and excellent protection if their UPF values range from is 15 to 24, 25 to 39, and above 40, respectively (Ibrahim, Refaie, et al., 2010).

Scanning electron microscope (SEM) images of the untreated and printed fabric samples were obtained with a JEOL, JXL 840A electron probe microanalyser, equipped with energy disperse X-ray (EDX) spectroscopy for the composition analysis.

The metal content of the obtained pigment prints was determined by a flame atomic absorption spectrophotometer GBC-Avanta, Australia.

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

3. Results and discussion

The main task of the current work is to introduce a facile novel one-step procedure for producing linen/cotton pigment prints with demanded functional performances via individual inclusion of Ag-, ZnO-, ZrO_2- and TiO_2-nanoparticles (NPs) into the pigment paste formulation. Results obtained along with appropriate discussion follow.

3.1. Effect of TiO_2-NPs concentration

Fig. 1a shows that, within the range examined, increasing the TiO_2-NPs from zero up to 20 g/kg paste followed by screen printing and microwave fixation at 386 W for 5 min results in a significant improvement in the depth of the obtained pigment prints,

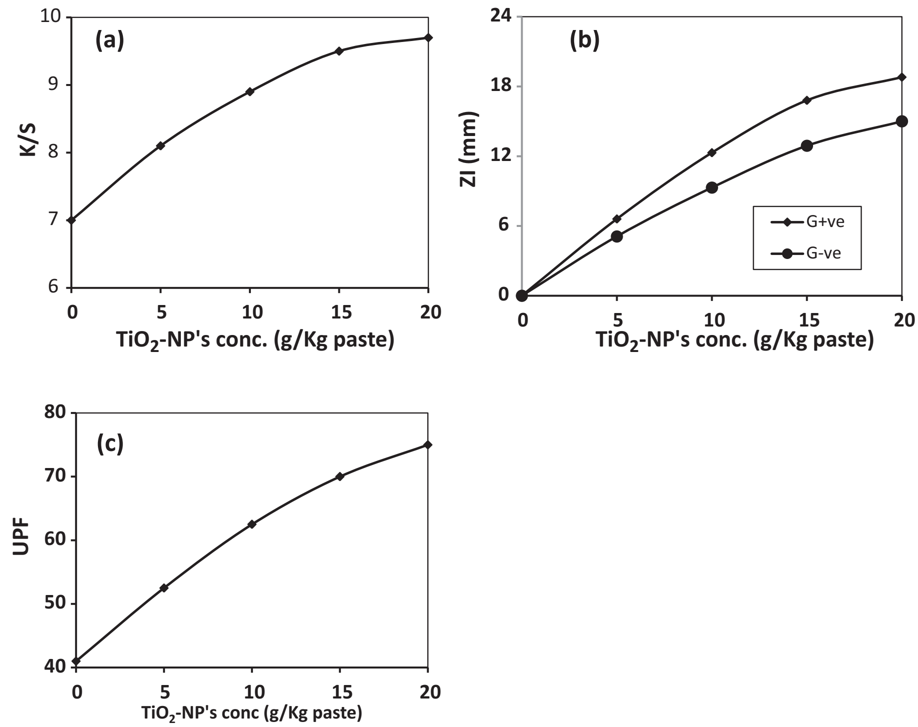


Fig. 1. Effect of incorporation of TiO_2-NPs into the pigment paste on K/S (a), ZI (b), and UPF (C) values of the obtained linen/cotton pigment prints. Printing paste components: Unisperse® Blue G (20 g/kg); Printofix® Binder MTB-01 (100 g/kg); Printofix® Thickener 160 EG (20 g/kg); resin (20 g/kg); silicone softener (10 g/kg); $(NH_4)_2S_2O_8$ (2 g/kg). Fixation: at 386 W/5 min.

expressed as K/S values. This can be attributed to the positive impact of TiO_2-NPs, as a co-catalyst, on enhancing the extent of cross-linking of the polyacrylate binder, facilitating the formation of a three-dimensional linked network and promoting its shielding effect onto the printed substrate during the curing step thereby increasing the extent of pigment particles encapsulation and fixation, i.e. darker depth of shade (Hanifi & Montazer, 2012; Hashemikia & Montazer, 2012; Ibrahim, Amr, et al., 2012).

For a given set of pigment printing/functional finishing conditions, Fig. 1b demonstrates that increasing TiO_2-NPs up to 20 g/kg paste brings about a significant improvement in the antibacterial activity of the obtained prints against G+ve and G−ve bacteria. The antibacterial activity of the TiO_2-NPs loaded pigment prints was a result of its-photo catalytic activity (Ibrahim, Amr, et al., 2012; Ibrahim, Refaie, et al., 2010; Rajagopal, Maruthamuthu, Mohanan, & Palaniswamy, 2006) via generation of extremely reactive species thereby attacking the bacteria cell membrane, losing of its essential functional followed by destroying it. On the other hand, the imparted antibacterial efficacy is determined by the type of bacteria and followed the descending order: G+ve > G−ve, most probably due to their differences in membrane structure and amenability to destruction (Ibrahim, Abdalla, et al., 2013; Ibrahim, Eid, & El-Batel, 2012; Ibrahim, El-Zairy, El-Zairy, et al., 2013; Shanmugasundaram, 2006).

UV-protection, expressed as UPF values, of TiO_2-NPs loaded pigment prints is presented in Fig. 1c. It is obvious from Fig. 1c that increasing the concentration of TiO_2-NPs in the pigment printing paste up to 20 g/kg results in a significant increase in the UPF value from ≈40 up to 75 as a direct consequence of upgrading the scattering/absorption ability of the TiO_2-NPs loaded pigment prints (Hashemikia & Montazer, 2012; Ibrahim, Amr, et al., 2012; Ibrahim, El-Zairy, Abdalla, et al., 2013). The so-obtained data signify the excellent shielding effect of loaded TiO_2-NPs as well as confirm the higher protection against the harmful UV-radiation. On the other hand pigment printing, in the absence of TiO_2-NPs, is accompanied by a noticeable increase in UPF values from 16 up

Table 1
Effect of using different binding agents in the printing paste formulation[a] on functionality and printability of the blended linen/cotton fabric.

Binder (100 g/kg)	ZI[b] (mm)		UPF[c]	K/S[d]	WF[e]		RF[f]		LF[g]
	G+ve	G−ve			St	Alt.	Dry	Wet	
Printofix® MTB-01	18.5 (8.0)[h]	15.0 (6.0)	75.0 (52.0)	9.70 (6.30)	4 (2–3)	4 (2)	4–5 (2–1)	4 (1)	5 (3)
Printofix® Binder 86	20.5	19.5	92.2	10.72	4	4	4	3–4	5
Alcoprint® PB-55	22.5	20.0	104.0	11.94	4	4	4	3–4	5
G® Binder FMD	19.0	17.5	83.5	9.98	4	4	4	3–4	5

[a] Printing paste components: Unisperse® Blue G (20 g/kg); Binder (100 g/kg); Printofix® Thickener 160 EG (20 g/kg); TiO_2-NPs (20 g/kg); resin (20 g/kg); silicone softener (10 g/kg); $(NH_4)_2S_2O_8$ (2 g/kg). Fixation: at 386 W/5 min.
[b] Zone of inhibition.
[c] UV-protection factor.
[d] Color strength.
[e] Wash fastness.
[f] Rubbing fastness.
[g] Light fastness.
[h] Values in the parentheses indicate printing and functional properties in the absence of the binding agent (control sample).

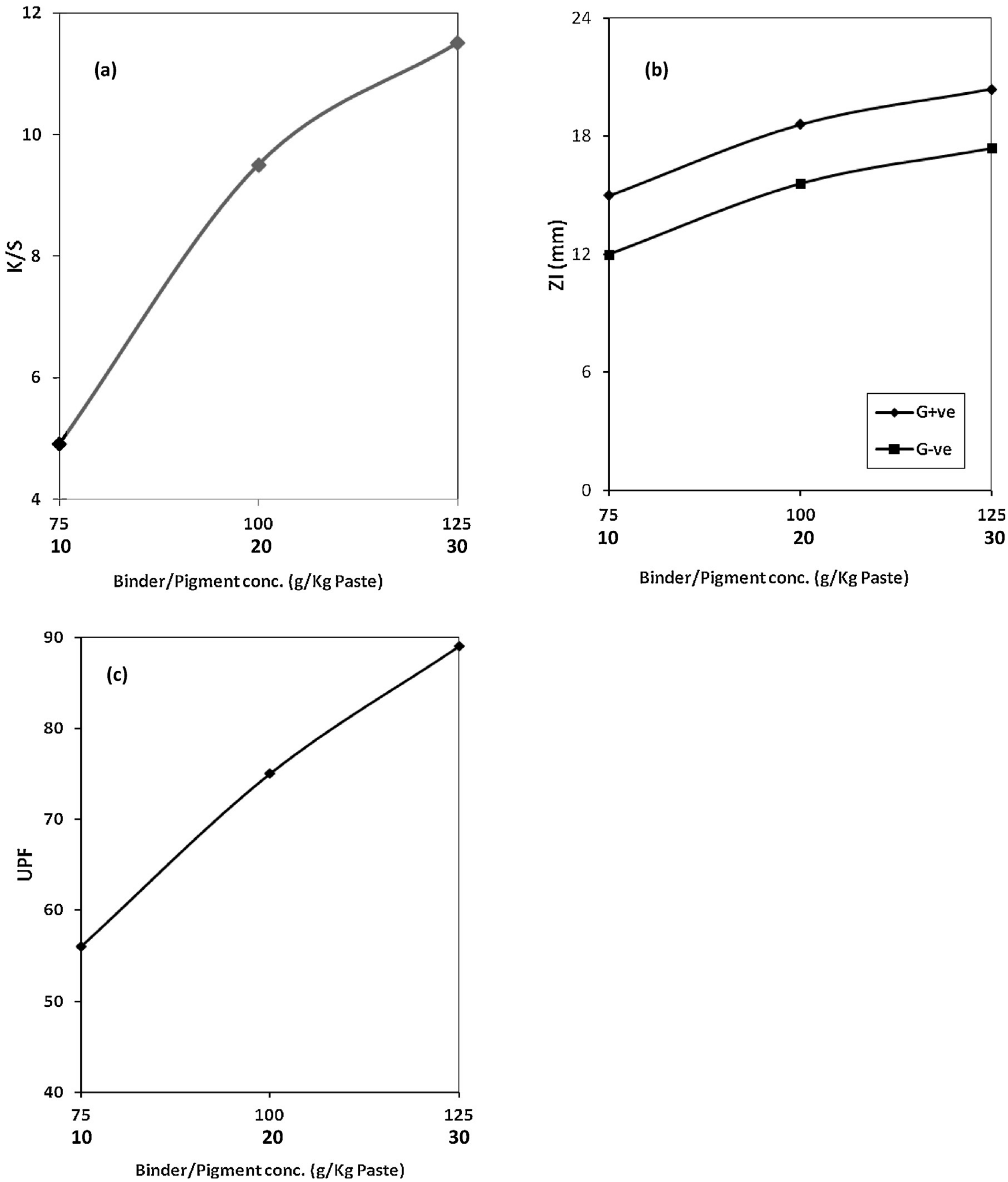


Fig. 2. Effect of binder/pigment concentration on K/S (a), ZI (b), and UPF (C) values of the obtained linen/cotton pigment prints. Printing paste components: Unisperse® Blue G (10–30 g/kg); Printofix® Binder MTB-01 (75–125 g/kg); Printofix® Thickener 160 EG (20 g/kg); resin (20 g/kg); TiO_2-NPs (20 g/kg) silicone softener (10 g/kg); $(NH_4)_2S_2O_8$ (2 g/kg). Fixation: at 386 W for5 min.

to ≈40 reflecting the positive impact of the used pigment colorant on increasing the absorption of the harmful UV-light (Ibrahim, El-Zairy, Abdalla, et al., 2013; Ibrahim, El-Zairy, El-Zairy, et al., 2013; Ibrahim, El-Zairy, El-Zairy, & Khalil, 2011).

3.2. Binder/pigment concentration

The effect of binder/pigment concentration on the depth of the obtained prints (K/S), the imparted antibacterial activity (ZI) as well as on the UV-protection capacity (UPF) of the obtained prints is shown in Fig. 2a–c, respectively. It is evident that increasing binder/pigment concentration from 75/10 up to 125/30 g/kg paste, in the presence of TiO_2-NPs 20 g/kg paste, results in a remarkable improvement in the depth of the obtained prints (from K/S = 4.95 up to 11.5), an enhancement in the antibacterial activity against G+ve bacteria (from ZI = 15 mm up to 20.5 mm) as well as G−ve bacteria (from ZI = 12 mm up to 17.5 mm), in addition to a significant increase in the UV-protection capacity of the obtained pigment prints from UPF = 55 up to 89.

The outstanding improvement in the aforementioned printing and functional properties reflects the positive role of using the binder at proper concentration to: achieve better film-forming properties, facilitate the formation of a three-dimensional linked network onto/with the substrate, to help accommodation and entrapment of the pigment particles in-between, as well as to ensure loading of proper amount of TiO_2-NPs onto the obtained

Table 2
Effect of using different pigment colorants in the printing paste formulation[a] on functionality and printability of the blended linen/cotton fabric.

Pigment colorant (20 g/kg)	ZI[b] (mm)		UPF[c]	K/S[d]	WF[e]		RF[f]		LF[g]
	G+ve	G−ve			St	Alt.	Dry	Wet	
Unisperse® Blue G	18.5	15.0	75	9.70	4–5	4–5	4–5	4	5
Unisperse® Red G	17.0	14.5	71	6.85	4–5	4–5	4–5	4	5
Imperon® Gold Gelb K-RN	13.5	10.5	36	10.45	4	4	4	3–4	5
Printofix® Blue R2H	16.5	14.0	40	6.52	4	4	4	3–4	5
Printofix® Yellow HRNC	19.0	16.5	54	7.33	4–5	4–5	4–5	4	5
Imperon® Royal Blue SP	11.5	9.5	30	5.07	4	4	3–4	3	5

[a] Printing paste components: pigment (20 g/kg); Printofix® Binder MTB-01(100 g/kg); Printofix® Thickener 160 EG (20 g/kg); TiO_2-NPs (20 g/kg); resin (20 g/kg); silicone softener (10 g/kg); $(NH_4)_2S_2O_8$ (2 g/kg). Fixation: at 386 W/5 min.
[b] Zone of inhibition.
[c] UV-protection factor.
[d] Color strength.
[e] Wash fastness.
[f] Rubbing fastness.
[g] Light fastness.

pigment prints (Ibrahim, El-Zairy, et al., 2005; Park, 2010). On the other hand, the antibacterial activity of the obtained bio-active pigment prints against the nominated bacteria follows the descending order: G+ve > G−ve, most probably due to the difference in their outer membrane surrounding the cell wall.

3.3. Type of binding agent

Several types of binder were tried to search for the proper one for attaining pigment prints with outstanding multifunctional properties, i.e. antibacterial and anti-UV, where other parameters were fixed (Table 1). For a given set of combined pigment printing and functional finishing in one step, the data so obtained signify that: (i) incorporation of any of the used binding agents in the printing paste results in a significant improvement in the imparted antibacterial, and UV-protection as well as in the printing properties, i.e. K/S and fastness ratings, and (ii) the enhancement in the aforementioned properties especially ZI, UPF and K/S values is governed by the type of binding agent and follows the descending order: Alcoprint® PB-55 > Printofix® Binder 86 > GBinder FMD > Printofix® MTB > none.

The variation in the extent of improvement in the imparted functional and printing properties by using the aforementioned binders is attributed to the differences among them in chemical composition, e.g. based on polyacrylate or butadiene copolymer, film forming properties, active ingredients, compatibility with other ingredients in the printing paste, binder capacity and efficiency, extent of encapsulation of the pigment particles and entrapment in between the binder and the surface of the substrate as well as in the holding capacity of TiO_2-NPs and extent of their loading onto the printed fabric surface (Ibrahim, El-Gamal, Hassan, & Abo-El-maged, 2007; Ibrahim, El-Zairy, et al., 2005; Park, 2010; Uddin & Lomas, 2005; Yaman et al., 2012).

It is also clear, Table 1, that G+ve bacteria are more susceptible to the imparted antibacterial functionality than G−ve bacteria, irrespective of the used binding agent. On the other hand, the fastness properties in case of using the binding agent are much better than in its absence as a direct consequence of enhancing the extent of pigment particles fixation during the microwave fixation step.

3.4. Type of pigment

Table 2 demonstrates the differences in the imparted functional and printing properties upon using different pigment colorants, keeping other parameters fixed. This reflects the differences among the used pigments in chemical nature, average particle size, pigment content, chromophore, hue, dispersion stability, extent of agglomeration, compatibility with other ingredients, location and extent of fixation and deposition, antibacterial activity, UV-absorption capacity, and its covering power (Giesen & Eisenlohr, 1994; Ibrahim, El-Zairy, et al., 2005).

Table 2 also shows that Unisperse® Blue G, Unisperse® Red G and Printofix® yellow HRNC pigment prints exhibited higher antibacterial activity, expressed as ZI, together with better UV-protection capacity, expressed as UPF, than the others which might be attributed to their own antibacterial effect and to their higher absorption capacity to the harmful UV-radiation along with the loaded TiO_2-NPs, i.e. due to synergistic effect of the nominated

Table 3
Effect of incorporation of different nano-materials into the printing paste formulation[a] on functionality and printability of the blended linen/cotton fabric.

Nano-materials (20 g/kg)	Metal content (%)	ZI[b] (mm)		UPF[c]	K/S[d]	WF[e]		RF[f]		LF[g]
		G+ve	G−ve			St.	Alt.	Dry	Wet	
None	0.00	0.0 (0.0)	0.0 (0.0)	40.5 (30.0)	7.03 (5.10)	4	3–4	3–4	3	4
Ag	0.220 (0.145)[h]	13.0 (10.0)	11.0 (8.0)	45.3 (34.0)	8.59 (6.52)	4	4	4	3–4	5
ZnO	0.503 (0.298)	15.0 (11.5)	12.5 (9.0)	88.4 (65.5)	10.11 (7.80)	4	4	4	3–4	5
ZrO_2	0.052 (0.031)	17.0 (13.0)	13.5 (10.0)	48.0 (34.5)	11.54 (8.92)	4	4	4–5	4	5
TiO_2	0.090 (0.062)	18.5 (14.0)	15.0 (11.5)	75.0 (59.5)	9.70 (7.04)	4	4	4–5	4	5

[a] Printing paste components: Unisperse® Blue G (20 g/kg); Printofix® Binder MTB-01(100 g/kg); Printofix® Thickener 160 EG (20 g/kg); nano-material (20 g/kg); resin (20 g/kg); silicone softener (10 g/kg); $(NH_4)_2S_2O_8$ (2 g/kg). Fixation: at 386 W/5 min.
[b] Zone of inhibition.
[c] UV-protection factor.
[d] Color strength.
[e] Wash fastness.
[f] Rubbing fastness.
[g] Light fastness.
[h] Values in parentheses indicate retained function and color strength after 20 washing cycles.

pigments and TiO_2-NPs on the fabric surface. Nevertheless, the printing properties, i.e. K/S value and fastness ratings, are governed by the type of pigments as discussed before. On the other hand, washing, rubbing and light fastness properties of the obtained pigment prints were good to very good. Moreover, the wet rubbing fastness were found to be slightly lower than the dry one, most probably due to presence of unfixed pigment particles entrapped in the printed substrate.

3.5. Type of inorganic nano material

Table 3 summarizes the functional and printing properties of simultaneously pigment printed and functionally finished linen/cotton blended fabric samples in the absence and presence of Ag-NPs, ZnO-NPs, ZrO_2-NPs or TiO_2-NPs (20 g/kg paste). For a given set of printing paste formulation and printing conditions, the results demonstrate that: (i) incorporation of any of the nominated nano-materials in the printing paste results in a remarkable improvement in their antibacterial activity, (ii) the extent of improvement in antibacterial efficacy of the obtained pigment prints follows the descending order: TiO_2-NPs > ZrO_2-NPs > ZnO-NPs > Ag-NPs ≫ none, and (iii) this variation in the antibacterial activity is attributed to their differences in chemical structure, size distribution of nanoparticles, concentration, extent of loading and fixation onto the binder/substrate matrix during the microwave fixation, availability and accessibility, mode of attack on microorganisms as well as compatibility with other ingredients in the printing paste (Dastjerdi & Montazer, 2010; Gao & Cranston, 2008; Sawhney, Condon, Singh, Pang, & Hui, 2008).

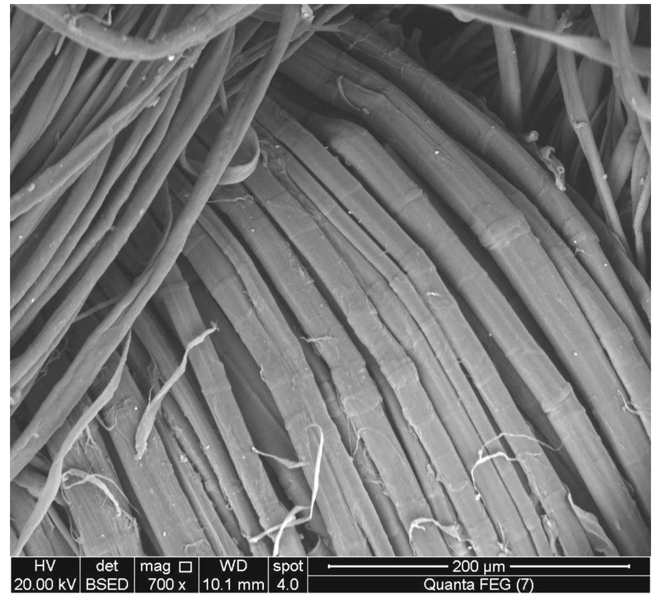
The enhancement in the antibacterial activity of Ag-NPs loaded pigment prints is a direct consequence of: damaging the cell wall structure, alteration of cell membrane permeability followed by an inhibition of cell membrane metabolisms causing the death of bacteria, and/or via catalyzation of the production of very active oxygen radicals:

$$H_2O + 1/2O_2 \xrightarrow{Ag^+} H_2O_2 \rightarrow H_2O + (O),$$

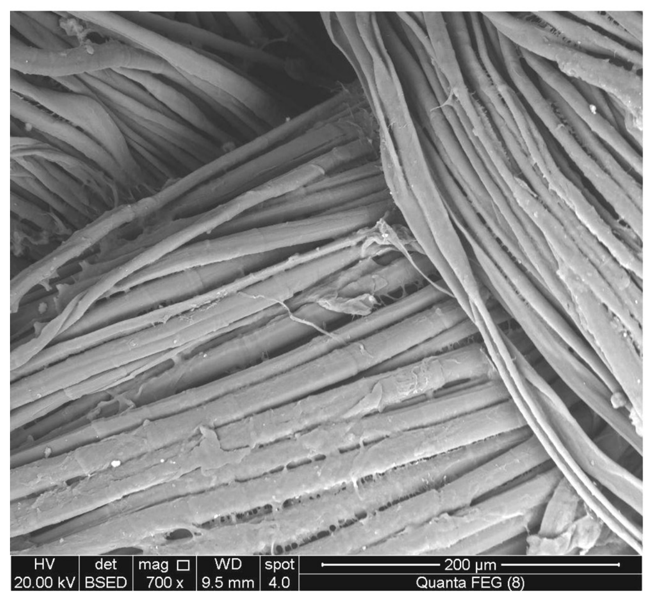
causing the destruction of the molecular structure of bacteria (Dastjerdi, Montazer, & Shahsavan, 2009; Ibrahim, Amr, et al., 2012; Ibrahim, Eid, & El-Batel, 2012; Montazer, Alimohammadi, Shamei, & Rahimi, 2012; Zhang, Peng, Huang, Zhou, & Yan, 2008). On the other hand, the antibacterial activity of the loaded nano-metal oxides, i.e. ZnO-NPs, ZrO_2-NPs and TiO_2-NPs, is a direct consequence of generation of extremely reactive oxygen species, e.g. super oxide anions, H_2O_2, single oxygen, hydroxyl radicals, causing destruction of bacteria cell due to the photocatalytic effect (Dastjerdi & Montazer, 2010; Erem, Ozean, & Skirfvars, 2011; Ibrahim, Refaie, et al., 2010). Moreover, the functionalized pigment prints showed a better antibacterial activity against G+ve bacteria in companion with G−ve one most probably due to the presence of the outer cell wall membrane in the G−ve bacteria thereby acting as a barrier to the antibacterial effect.

Additionally, the results in Table 3 also demonstrate that: (i) the imparted UV-protection functionality, expressed as UPF values, is governed by the type of substrate, i.e. printed > unprinted, as well as the type of loaded nano-inorganic material and follows the descending order: ZnO-NPs > TiO_2-NPs ≫ ZrO_2-NPs ≥ Ag-NPs ≥ none ≫ unprinted, (ii) the remarkable improvement in the UPF values especially in case of using ZnO or TiO_2-NPs reflects their scattering/absorbing ability to the harmful UV-B irradiation (Ibrahim, Amr, et al., 2012), (iii) incorporation of Ag-NPs or ZrO_2-NPs into the pigment printing formulation has insignificant effect on the imparted UV-protection function, and (iv) the used pigment colorant alone without the nominated nano-materials acts as an effective UV-absorber thereby upgrading the UPF of unprinted fabric sample values from 16 up to ≈40.

Moreover, the given data reveal that incorporation of the aforementioned nano materials into the pigment print formulations brings about an improvement in the depth of the obtained prints along with insignificant variation in the fastness ratings of the obtained pigment prints. The enhancement in the depth of the obtained prints most probably is attributed to: (i) an enhancement in the extent of pigment fixation during the microwave fixation step and the positive role of some nano-metal oxides, i.e. TiO_2-NP or ZnO-NPs, as a co-catalyst, and/or (ii) the positive role of the formed metal chelates, via picking up and retaining of the metal cations by the −COOH groups of the used binder, in darkening the depth of the obtained prints without adversely affecting the hue (Ibrahim, Mahrous, et al., 2010; Ibrahim, El-Zairy, El-Zairy, et al., 2013).



a- Unprinted linen/cotton fabric



b- Printed linen/cotton fabric

Fig. 3. SEM micrographs of (a) unprinted linen/cotton fabric and (b) printed one.

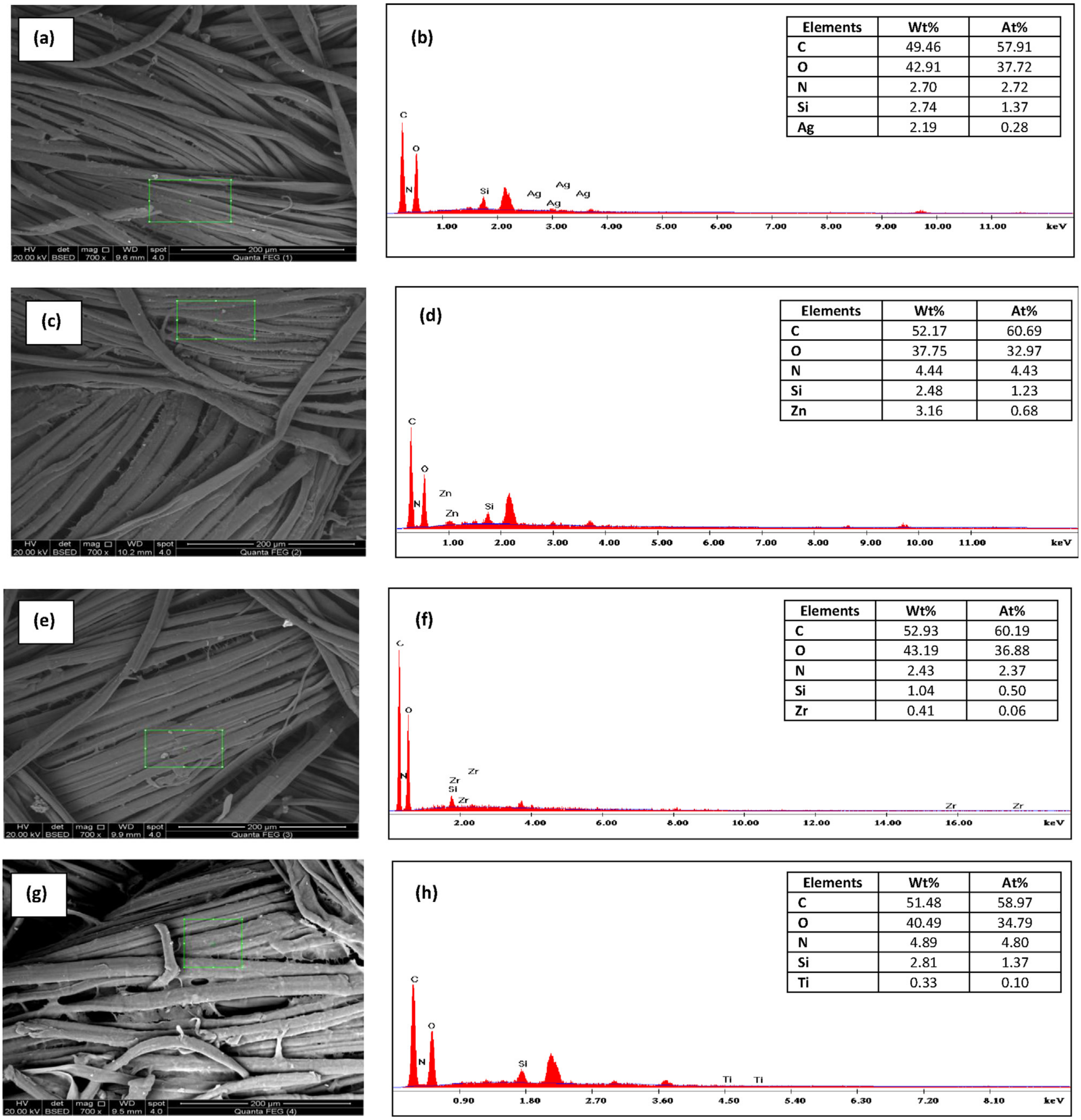


Fig. 4. SEM images and EDX spectrum of Ag-loaded pigment print (a and b); Zn-loaded pigment print (c and d); Zr-loaded pigment print (e and f); Ti-loaded pigment print (g and h).

On the other hand, the results of Table 3 revealed that retention of the imparted functional properties, i.e. antibacterial and UV-protection together with the depth of the obtained pigment prints were still high even after 20 cycles of consecutive laundries. This means that both the nano-metal or metal oxides together with the pigment particles were still tightly loaded and fixed onto the simultaneously printed and finished linen/cotton fabric surface.

3.6. SEM images and EDX spectra

Fig. 3a and b shows the SEM images of unprinted sample and the printed one, respectively. SEM micrograph in Fig. 3a shows that clean surface of unprinted fibers. Fig. 3b illustrates the SEM image of the printed sample. It was obvious that the fibers surface was coated with a polymeric film which provides a suitable carrier for bonding and fixing of the pigment particles onto the printed sample.

On the other hand, SEM-EDX micrographs of simultaneously pigment printed and functionalized samples (Fig. 4) confirmed the deposition of the print paste together with the loading of Ag (Fig. 4a and b), Zn (Fig. 4c and d), Zr (Fig. 4e and f) and Ti (Fig. 4g and h) onto the fiber surface of the printed samples along with silicone.

4. Conclusions

The present research work demonstrates, for the first time, the feasibility of enhancing both the functionality and pigment-printability of linen/cotton blended fabric in a one-step process. Obtained results revealed that:

- Incorporation of Ag-NPs, ZnO-NPs, ZrO_2-NPs or TiO_2-NPs (at 20 g/kg paste) into the solvent-free pigment print paste results in enhancing both the functionality and printability.
- The enhancement in anti-bacterial functionality is governed by the type of nano-material and follows the descending order: TiO_2-NPs > ZrO_2-NPs > ZnO-NPs > Ag-NPs ≫ none, keeping other parameters fixed.
- The UV-protection capacity of the modified-pigment prints follows the descending order: ZnO-NPs > TiO_2-NPs > ZrO_2-NPs ≥ Ag-NPs ≥ none ≫ unprinted.
- The printing properties, K/S and fastness rating values, are governed by type of binding agent, type of pigment colorant as well as kind of nano-additive.
- The imparted functional properties together with the depth of the obtained pigment prints were also stable and durable toward repeated laundering (20 cycles).
- The developed pigment printing method has industrial potential because very effective and durable antibacterial, anti-UV functionalized linen/cotton pigment prints could be produced via a fairly simple producer.

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