Carbohydrate Polymers 82 (2010) 1205–1211

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

A new approach for natural dyeing and functional finishing of cotton cellulose

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ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form 20 June 2010
Accepted 25 June 2010
Available online 27 July 2010

Keywords:
Cotton knits
Metal salts
Pre-mordanting
Natural dyes
UV-blocking
Antibacterial function

ABSTRACT

A new approach for upgrading the dyeing properties of cotton knits with natural dyes as well as to enhance both the UV-protection and antimicrobial functions of the obtained dyeings was investigated. Factors affecting the dyeing and multifunctional properties of the treated substrates such as fabric structure, type and concentration of mordant, kind and percent of natural dye extract as well as dyeing regime were studied. In situ deposition of the mordant as a metal oxide onto and/or within the fabric structure followed by dyeing results in a dramatic improvement in the color strength as well as the fastness properties, in addition to an outstanding enhancement in both the UV-protection, against the harmful UV-radiation and the antibacterial activity against the hazardous G+ve and G−ve bacteria. The extent of improvement in the aforementioned properties follows the descending order: pre-mordanting followed by dyeing > dyeing only > none, and is determined by type and content of metal, physical state/chemical structure as well as extent of dye interaction and fixation, along with the fabric construction. The UV-protection properties as well as the antibacterial activities of the obtained dyeings are maintained even after 20 washing cycles.

1. Introduction

Dyeing of textiles with synthetic dyestuffs is characterized by high negative impacts on the environment, dyers as well as the endusers. Therefore, interest in natural dyes has increased considerably on account of their high compatibility with environment, relatively low toxicity and allergic effects, as well as availability of various natural coloring sources such as from plants, insects, minerals and fungi (Patel, Agarwal, & Patel, 2003; Roshan, Malanker, & Sandeep, 1996). However, many attempts have been carried out to elucidate the fundamental aspects of natural dyes as well as to enhance their fastness properties, especially washing and light fastness, by using several metallic mordants taking in consideration the ecological aspects (Cristea & Vilarem, 2006; Patel et al., 2003; Roshan et al., 1996; Vankar, Shanker, & Verma, 2007). Little attention has been given to the other functions of mordants/natural dyes combination such as protection against solar UV-radiation and microorganisms (Gupta, 2007; Parmar, Giri, Singh, & Chabbra, 2006; Purwar & Joshi, 2004).

The UV-protection properties of textiles depend on their chemical composition, physical structure, e.g. porosity, weight, thickness, manufacturing regime, etc., as well as the presence of dyes, pigments and/or other auxiliaries, which have the ability to reduce or prevent transmission of harmful solar UV-radiation via blocking and/or absorbing such radiation most effectively in the region 290–400 nm and rapidly converting it to harmless heat (Feng, Zhang, Chen, & Zhang, 2007; Gupta, 2007; Parmar et al., 2006; Purwar & Joshi, 2004; Srinivasan & Gatewood, 2000).

On the other hand, textile materials based on natural fibers provide perfect conditions such as: large receptive surface area, suitable temperature, moisture, oxygen and nutrients, for the growth of microorganisms (Purwar & Joshi, 2004). The growth of microorganisms has negative effects related to hygiene and fabric biodeterioration. Therefore, there is an urgent need to a potentially effective means to control and/or inhibit microbiological growth to protect both the wearer and textiles (Gupta, Jain, & Panwar, 2005; Ibrahim, Gouda, El-Shafei, & Abdel-Fatah, 2007; Nakashima, Sakagami, Ito, & Matsno, 2001).

With the above in mind, the main task of the present work is to enhance the UV-protection and antibacterial functions of knitted cotton fabrics dyed with natural dyes.

2. Experimental

2.1. Materials

The specifications of the mill-scoured and half-bleached knitted cotton fabrics used throughout this work are given in Table 1.

Details of commercial grade natural dyes used in this study are shown in Table 2.

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doi:10.1016/j.carbpol.2010.06.054

Table 1
Specification of the experimental fabrics.

Substrate (half-bleached)	Count (Ne)	Wt./area (g/m^2)	Thickness (mm)	Air permeability (cm^3/cm^2/s)	Bursting strength (kg/cm^2)	Whiteness index	Absorbency time (s)
Pique	30/1	204.4	0.721	106.4	5.70	54.3	<1
Interlock	30/1	229.3	0.833	69.0	6.08	50.2	<1
Parasol	30/1	157.7	0.620	116.9	5.95	58.1	<1

Table 2
Details of the used natural dyes.

Botanical name	Common name	Chemical class	C.I. name	Part used
Rubia Tinctoria	Madder	Anthraquinones	Natural Red 16 and Natural Red 8	Roots
Curcuma Tinctoria	Curcuma	Diferuloye-methan	Natural yellow 3	Rhizomes
Alium Cepa	Onion	Flavonoid	Natural yellow10	Skin
Lawsone	Henna	Alpha-naphthoquinones	Natural orange 6	Leaves

The above-mentioned natural dyes were obtained from the local market.

The mordants selected for this work were: ferrous sulphate ($FeSO_4$), copper chloride ($CuCl_2 \cdot 2H_2O$), zinc chloride ($ZnCl_2$), zirconium oxy chloride ($ZrOCl_2 \cdot 8H_2O$), aluminum chloride ($AlCl_3 \cdot 6H_2O$), and alum [$Al_2K_2(SO_4)_4$] as well as other chemicals such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), di-sodium hydrogen phosphate (Na_2HPO_4), hydrogen peroxide (H_2O_2-35%, w/v), and acetic acid (CH_3COOH) were of laboratory reagent grade.

2.2. Methods

2.2.1. Extraction of natural dyes

Certain amounts of plant materials were dried, ground to powder, and extracted in required amount of water and boiled for 2 h. After the extractions were complete, the extracts were cooled to room temperature and filtrated to remove the insoluble residues. The resulting filtrate was then used as stock dye solutions (4–12% extracts) for the subsequent dyeing experiments.

2.2.2. Mordanting

The selected fabric samples were mordanted, using one of the aforementioned mordants, by the pre-mordanting method, i.e. prior to dyeing. The fabric samples were padded twice in aqueous solution of the metallic salt (0–150 mmol/L) to a wet pick up of 100%, followed by subsequent padding twice in the NaOH bath (pH 10.5), to a wet pick up 100%, and finally impregnated in H_2O_2 bath (5 mL/L-35%, w/v) for 5 min at room temperature without intermediate washing. The treated fabric samples were then rinsed thoroughly with hot water followed by cold water and dried at 100 °C/3 min.

2.2.3. Dyeing

The knitted fabric samples containing the in situ deposited metal oxides were immersed in a dye bath composed of the natural dye (0–12% owf); nonionic wetting agent (2 g/L), using the dye liquor ratio (1:30), at pH 4 using acetic acid. The dye bath temperature was gradually raised (about 1 °C/min) up to 100 °C, and was kept at this temperature for 60 min. The dye bath temperature was then allowed to cool to about 60 °C, then the dyed fabric samples were squeezed, rinsed thoroughly with hot and cold water and air dried.

2.3. Analytical procedures

2.3.1. Metal content

The metal content expressed as mmol/100 g fabric sample of the pre-mordanted samples, was quantitatively determined by using flame atomic absorption spectrophotometer, GBC-Avanta Australia, as follows: 0.5 g from dried fabric samples was dissolved in 10 mL of 72% H_2SO_4 at 3 °C, followed by taking 0.5 mL of this solution and diluting up to 25 mL using buffer solution (0.06 M Na_2HPO_4 + 0.02 M NaOH) before analysis.

2.3.2. Dyeing properties

Color strength of the dyed fabric samples, in terms of the *K*/*S* values, was obtained by using the Kubelka Munk equation (Garland, 1993):

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

where *K* is the light absorption coefficient, *S* is the scattering coefficient and *R* is the reflectance of the dyed samples at the wavelength of the maximum absorption using color – Eye® 3100 spectrophotometer.

Fastness properties to washing, crocking and light of dyed fabric samples were assessed according to AATCC Test methods (61-1972), (8-1972) and (16 A-1972), respectively.

2.3.3. UV-protection factor (UPF)

UPF values were assessed according to the Australian/New Zealand Standard (AS/NZS 4399-1996). According to the Australian classification scheme, fabrics can be rated as providing good, very good, and excellent protection if their UPF values range from 15 to 24, 25 to 39 and above 40, respectively. In no event was a fabric assigned a UPF rating greater than 50 (Gupta, 2007; Ibrahim, Allam, El-Hossamy, & El-Zairy, 2007).

2.3.4. Antibacterial activity

Antibacterial activity against Gram-positive bacteria (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*) was tested quantitatively by AATCC Test Method 100-1999.

2.3.5. Fabric thickness (FT)

FT was assessed according to ASTM D1777-96 using a dial thickness Gouge H (Teclcock®, Japan).

2.3.6. Air permeability (AP)

AP was measured according to ASTM D737, by Toyoseik®Tester, made in Japan.

2.3.7. Bursting strength (BS)

BS was measured according to ASTM D3786-87 by the Mullen®Tester, made in USA.

2.3.8. Whiteness index (WI)

WI was measured on each fabric using Datacolor Ultrascan PRO E 313, D65/10 made in USA.

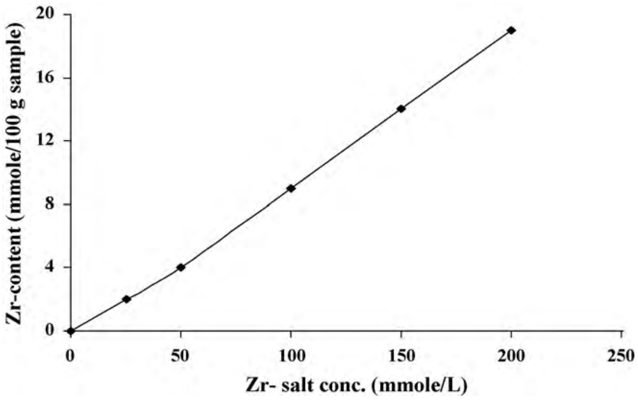

Fig. 1. Effect of Zr-salt concentration on the Zr-content of pretreated substrate.

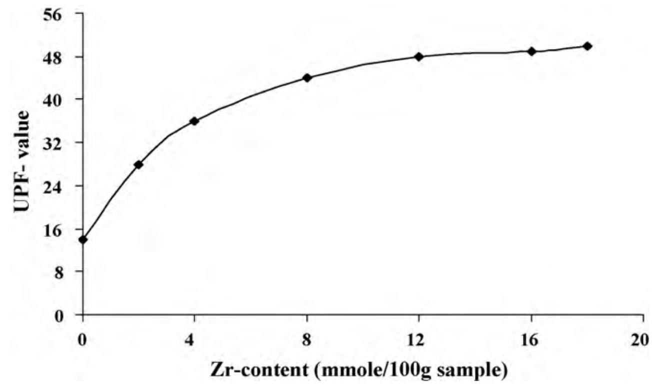

Fig. 3. Effect of Zr-content on the UPF values of dyed samples.

2.3.9. Absorbency time (AT)

AT of the treated fabric samples was determined according to AATCC Test Method 79-1992.

2.3.10. Durability to wash

The durability to wash was determined according to AATCC Method 124.

3. Results and discussion

With a view towards developing multifunctional protective textiles of high quality, high technical performance and high added value to cope with the growing awareness of health and hygiene, the present research work has focused on searching for the proper fabric structure, type and concentration of mordant, mordanting technique, kind and concentration of natural dye as well as the optimal application condition for attaining natural dyeings with outstanding protective properties against the harmful UV-radiation and against the growth of microorganisms. Results obtained along with their appropriate discussion are as follows.

3.1. Pre-mordanting with Zr-oxychloride

The obtained data, Fig. 1, showed that the Zr-content of pre-mordanted pique fabric samples has a linear relation with the concentration of Zr-salt in the pre-mordanting solution as a consequence of in situ deposition and fixation of Zr-oxide onto and/or within the pique structure after subsequent treatments with alkali (to give Zr-hydroxide), followed by H_2O_2 (to give Zr-oxide).

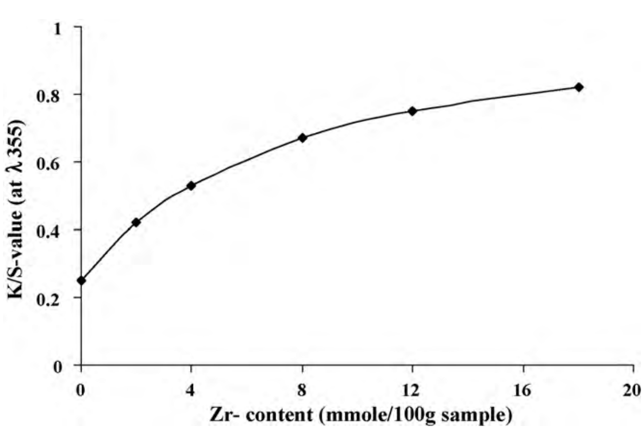

Fig. 2. Effect of Zr-content on post-dyeing with madder natural dye. Dye extract (10%); pH (4); LR (1/30); at100 °C for 60 min.

It is also evident, Fig. 2, that post-dyeing of half-bleached pre-mordanted pique fabric samples with madder extract results in a gradual increase in their *K*/*S* values (from 0.25 up to 0.82), reflecting the positive effects of the used mordant on enhancing both the dye adsorption as well as fixation onto and/or within the cellulose fibers at the molecular level (Feng et al., 2007).

Moreover, Fig. 3 illustrates the change in UPF values of pre-mordanted–post-dyed fabric samples. It is clear that increasing both the Zr-content as well as *K*/*S* value of the dyed samples results in a remarkable improvement in the UV-protection (ranging from <15, i.e. not good, up to >40, i.e. excellent) which mainly attributed to the synergistic effect of both mordanting cotton with the used Zr-salt as well as complex formation with the used natural dye thereby maximizing the extent of UV-absorption and minimizing the extent of UV-transmittance, i.e. remarkable UV-protection property of the dyed substrate.

3.2. Type of mordant

Taking in consideration both the *K*/*S* as well as the UPF values of the obtained dyeings, Figs. 2 and 3, 150 mmol/L of the Zr-salt mordant was selected as the most suitable dose for pre-mordanting.

Accordingly, as far as the variation in the metal content of pre-mordanted fabric samples, the changes in *K*/*S* and tints, as well as in the UPF values of the obtained dyeings as a function of the mordant type, keeping its concentration constant at 150 mmol/L, Table 3 shows that: (i) incorporation of any of the used Zr, Zn, or Al-salt mordant in pre-mordanting step results in a significant improvement in *K*/*S* of obtained dyeings and without adversely affecting the initial red color, (ii) the extent of increasing in both the metal content as well as the *K*/*S* follows the decreasing order: Zr-salt > Al-salt > Zn-salt > none, (iii) pre-mordanting with the used Cu-salt results in turning the shade from red to grey, (iv) pre-mordanting of the used substrate before natural dyeing is accompanied by a remarkable improvement in the extent of UV-protection property, irrespective of the used mordant, and can be ranked as follows: Zr-oxychloride ≈ Cu-chloride > Zn-chloride > Al-chloride > none, (v) the extent of variation in the above-mentioned properties is governed by the type of mordant, i.e. molecular weight, chemical composition, degree of deposition and oxidation, particle size, its location and extent of distribution, extent of modification of the pretreated substrate thereby enhancing its affinity to the used dye as well as dye–fiber interaction and fixation, in addition to ability to block and/or absorb the harmful UV-radiation alone and in combination with the used natural dye (Feng et al., 2007; Gupta, 2007; Parmar et al., 2006) and (vi) among the used mordants, pre-mordanting with the Zr-oxychloride salt gave both the best *K*/*S* and UPF values.

Table 3
Effect of mordant type on some properties of the half-bleached pique fabric samples dyed with madder.

Properties	Mordant type				
	None	Zr-oxychloride	Zn-chloride	Cu-chloride	Al-chloride
Metal content (mmol/100 g sample)	–	13.9	7.2	9.7	10.8
Visual color shade	Red	Red	Red	Grey	Red
K/*S*	0.25	0.78	0.38	0.55	0.49
UPF	13	48	33	47	21

Substrate: half-bleached pique fabric; mordant concentration: 150 mmol/L; dyeing conditions: madder extract (10%); pH (4); LR (1/30); at 100 °C for 60 min.

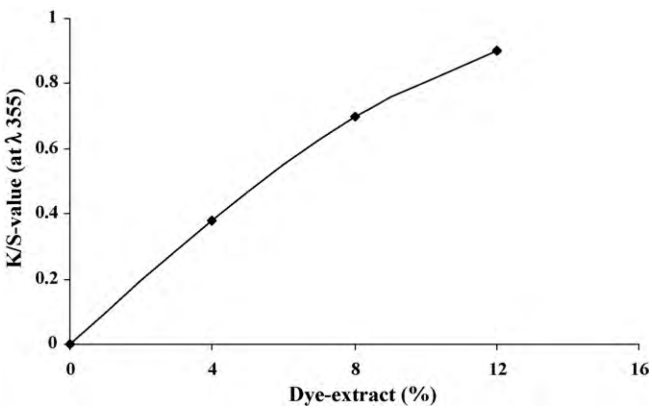

Fig. 4. Effect of madder extract concentration on the *K*/*S* values of the obtained dyeings . Zr-salt (150 mmol/L); dyeing at pH (4), LR (1/30), at 100 °C for 60 min.

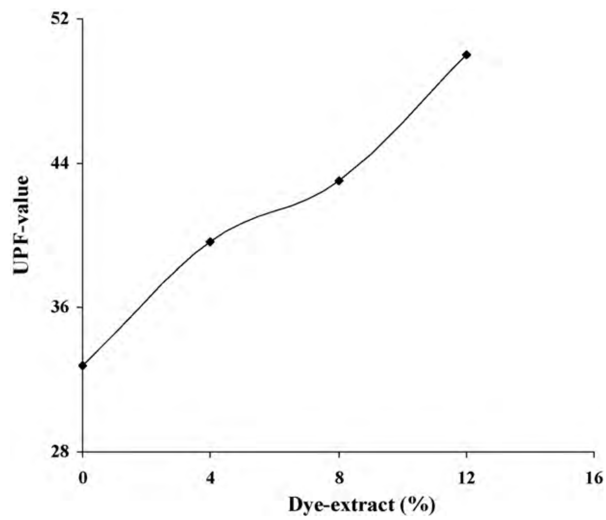

Fig. 5. Effect of madder extract concentration on the UPF values of the obtained dyeings. Zr-salt (150 mmol/L); dyeing at pH (4), LR (1/30), at 100 °C for 60 min.

3.3. Madder concentration

It is clear, Fig. 4, that for a given set of pre-mordanting conditions, Zr-salt (150 mmol/L), as well as post-dyeing conditions, increasing the madder natural dye percent (from zero up to 12%) is accompanied by a gradual increase in the *K*/*S* values of dyed samples (from 0 up to 0.9) which could be ascribed to the greater availability and accessibility of dye molecules onto and/or within the vicinity of the pre-mordanted substrate thereby enhancing the extent of dye absorption, and helping to bond the dye with the modified substrate, i.e. higher extent of dye interaction/fixation, and hence deeper color strength.

It is also evident (Fig. 5) that, increasing the dye concentration results in an enhancement in the UPF values (from 32: very good up to 48: excellent) thereby improving the extent of UV-protection property of the obtained dark shades, which could be discussed in terms of higher extent of blocking and/or absorbing the harmful UV-radiation. On the other hand, the higher UPF value of undyed substrate (32: very good) reflects the positive impact of the deposited Zr-oxide on blocking the porosity of the fabric structure as well as its absorbing capacity of solar UV (Ibrahim, Refai, Youssef, & Ahmed, 2005; Parmar et al., 2006; Saravanan, 2007; Yadav et al., 2006).

3.4. Type of natural dye

As far as the changes in the depth of the obtained dyeing, *K*/*S* values, as well as their UV-protection properties, expressed as UPF values and protection grade, as a function of the type of natural dye, using the Zr-oxychloride mordant (150 mmol/L) in the pre-mordanting step, Table 4 shows that: (i) pre-mordanting of the used fabric samples brings about a dramatic increase in the *K*/*S* values of the obtained dyeings, regardless of the used dye, (ii) the extent of improvement in the *K*/*S* is determined by the nature of used dye and follows the decreasing order: madder > onion > curcuma > henna, reflecting the differences among the aforementioned natural dyes in: physical state, structural features, chromophore, nature and numbers of constituents, stability pattern, affinity for the used substrate as well as extent of interaction and formation of strong complex with the mordanted substrate (Gupta, 1999; Nadiger, Sharma, & Jarag, 2004), (iii) the UPF values as well as protection grades of the pre-mordanted-dyed substrates are distinctly better than those of dyed samples without pre-mordanting, (iv) the extent

Table 4
Effect of using different natural dyes on both the *K*/*S* and UPF values.

Natural DYE	Visual color shade	*K*/*S*			UV-protection			
		No mordant	With mordant	Incr. (%)	No mordant		With mordant	
					UPF	Grade	UPF	Grade[a]
Madder	Red	0.25	0.78	312	13	Not good	48	Excell.
Curcuma	Yellow	0.27	0.56	207	14	Not good	42	Excell.
Henna	Orange	0.59	0.95	161	26	Very good	49	Excell.
Onion	Brown	1.64	3.99	243	38	Very good	50+	Excell.

Substrate: half-bleached pique fabric; mordant: Zr-oxychloride (150 mmol/L); dyeing conditions: dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. *K*/*S*: color strength; UPF: UV-protection factor.

[a] Protection grade[8]: UPF: <15 (not good); UPF: 5–24 (good); UPF: 25–39 (very good); UPF: >40 (excellent).

Table 5
Effect of fabric construction as well as its physical properties on the extent of dyeing and UV-protecting.

Substrate (half-bleached)	Physical properties					Madder		Curcuma		Henna		Onion	
	Wt. (g/m^2)	Thickness (mm)	Air perm. ($cm^3/cm^2/s$)	WI	UPF	K/S	UPF	K/S	UPF	K/S	UPF	K/S	UPF
Pique	204.4	0.721	106.4	54.3	9	0.78	48	0.56	42	0.95	49	3.99	50^+
Interlock	229.3	0.833	69.0	50.2	21	0.50	50^+	0.46	50^+	0.82	50^+	3.80	50^+
Parasol	157.7	0.620	116.9	58.1	6	0.99	29	0.78	25	1.04	35	5.12	50^+

Mordant: Zr-oxychloride (150 mmol/L); dyeing conditions: dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. Wt.: weight; Air perm.: air permeability; WI: whiteness index; *K*/*S*: color strength; UPF: UV-protection factor.

of upgrading the UV-protection properties by using the aforementioned natural dyes is governed by: the chemical structure of the dye, its absorption characteristics in the UV-region, extent of interaction and complexation with the pre-mordanted substrate as well as ability to block or absorb the hazardous UV-radiation, and (v) the improvement in the UV-protection level is determined by the dyeing regime, i.e. pre-mordanting followed by dyeing ≫ dyeing only, reflecting the synergistic effect of the mordant, the dye as well as complex formation between the dye and the mordanted substrate, thus giving an outstanding ability to block the UV-transmission and/or to absorb the harmful UV-radiation (Gupta, 2007; Srinivasan & Gatewood, 2000).

3.5. Fabric construction

As far as the changes in some physical properties of the used half-bleached substrates as a function of the fabric construction, Table 5 reveals that: (i) the weight and thickness follow the decreasing order: interlock > pique > parasol, (ii) the air permeability ranking follows the order: parasol > pique > interlock, and (iii) the degree of UV-protection follows the decreasing order: interlock > pique ≈ parasol.

On the other hand, current results, Table 5, reveal that: (i) the dyeability of the above-mentioned substrates with the natural dyes extracts under investigation is determined by the structural features of these dyes, i.e. onion > henna > madder > curcuma, irrespective of the used substrate, as well as the structure of the pre-mordanted cotton knit, i.e. parasol > pique > interlock, regardless of the used natural dye, (ii) dyeing of the pre-mordanted pique and interlock substrates with the nominated natural dyes gives an excellent UV-protection, (iii) the extent of increase in UPF values of dyed parasol fabric samples shows the following trend: onion > henna > madder ≈ curcuma > untreated, (iv) the changes in the aforementioned properties reflect the differences among the used substrate in thickness, weight, air permeability, degree of whiteness, extent of mordanting, extent of diffusion and penetration of the dye molecules within the fabric structure as well as extent of interaction and complexation to form stable bonds between the dye molecules and the pre-mordanted substrate which in turn affects extent of dye uptake and fixation as well as the UV-absorbance/transmittance ratio, and UV-protection (Gupta et al., 2005; Saravanan, 2007; Srinivasan & Gatewood, 2000).

3.6. Fastness properties

Table 6 shows the effect of pre-mordanting with Zr-oxychloride on the *K*/*S* as well as washing and rubbing fastness properties of the obtained natural dyeings. For a given set of pretreatment and dyeing conditions, it is clear that: (i) pre-mordanting with the nominated mordant brings about a significant enhancement in the *K*/*S* values of the obtained dyeings, regardless of the used natural dye, (ii) the extent of improvement is governed by the physical and chemical states of the dye and degree of fixation, (iii) pre-mordanting followed by dyeing gives dyeings with better fastness properties than those dyed without pre-mordanting and, (iv) the improvement in the dyeing properties, *K*/*S* and fastness, reflects higher extent of dye adsorption, interaction and bridging with the pre-mordanted substrate via different conjugated bonds (Feng et al., 2007).

3.7. Antibacterial function

Since the main task of the present study is to develop natural dyeings having multifunctional, it was considered worthwhile to search for the proper mordant, for pre-mordanting, as well as the proper natural dye, for subsequent dyeing, for attaining better protection capacity against the harmful UV-radiation as well as against microorganisms.

3.7.1. Mordant type

For a given set of pre-mordanting and dyeing conditions, Table 7 shows that: (i) the antibacterial activity, expressed as percent reduction in bacterial count, RBC %, of the obtained dyeings is governed by the dyeing sequence, and can be ranked descendingly as follows: pre-mordanting followed by dyeing > dyeing only ≫ untreated, (ii) dyeing only with the madder extract, without pre-mordanting, results in a remarkable improvement in antibacterial activity against both the G+ve (83.3%) and the G−ve (79.4%), (iii) this antimicrobial activity is mainly related to its content of active ingredients, i.e. anthraquinones group, of phenolic nature which are classified as active antimicrobial compounds (Gupta, Khare, & Laha, 2004; Shtayeh, Yaghmour, Faidi, Salem, & AL-Nuri, 1998), (iv) pre-mordanting with any of the selected mordant followed by dyeing with the madder extract brings about a further increase in the antibacterial activity, regardless of the used mordant, (v) the further enhancement in the antibacterial activity is determined by the nature of the mordant, i.e. chemical nature, extent of deposition, particle size, extent of agglomeration its location and content, ability to absorb and interact with the dye to

Table 6
Effect of pre-mordanting with Zr-oxychloride on some fastness properties of the obtained dyeings.

Natural dye	Mordant	K/S	Fastness properties			
			WF		RF	
			St.[a]	Alt.[b]	Dry	Wet
Madder	None	0.25	3–4	2–3	4–5	3
	Zr-salt	0.78	3–4	3	4–5	3–4
Curcuma	None	0.27	3	3	3	3
	Zr-salt	0.56	3–4	3–4	4–5	4–5
Henna	None	0.59	3	2–3	4	3–4
	Zr-salt	0.95	3–4	3–4	4–5	4–5
Onion	None	1.64	3	2–3	3–4	2–3
	Zr-salt	3.99	3	3	3–4	3

Substrate: half-bleached pique fabric; pre-mordanting with Zr-oxychloride (150 mmol/L); dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. *K*/*S*: color strength; WF: washing fastness.
[a] Staining on cotton.
[b] Alteration, RF: rubbing fastness.

Table 7
Effect of dyeing sequence and type of mordant on the antibacterial activity of the obtained dyeings.

Fabric sample (half-bleached pique)	K/S	G+ve (*S. aureus*)		G−ve (*E. coli*)	
		Count/mL	RBC (%)	Count/mL	RBC (%)
Untreated	–	15×10^7	0.0	17×10^7	0.0
Dyed without pre-mordanting (Blank)	0.25	25×10^6	83.3	35×10^6	79.4
[a]Pre-mordanted (Zr-oxychloride) dyed	0.78	5×10^6	96.6	8×10^6	95.2
Pre-mordanted (Al-chloride) dyed	0.49	2×10^7	86.6	3×10^7	82.3
Pre-mordanted (Cu-chloride) dyed	0.55	8×10^6	95.2	15×10^6	90.0
Pre-mordanted (Zn-chloride) dyed	0.38	4×10^6	97.3	7×10^6	95.8

[a]Pre-mordanted followed by dyeing; mordant (150 mmol/L); madder dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. K/S: color strength, G+ve: Gram-positive bacteria, *S. aureus*: *Staphylococcus aureus* strain; G−ve: Gram-negative bacteria; *E. coli*: *Escherichia coli* strain, RBC: reduction in bacteria count percent.

Table 8
Effect of type of natural dye on the antibacterial activity of the obtained dyeings.

Natural dye (dye extract 10%)	K/S	G+ve (*S. aureus*)		G−ve (*E. coli*)	
		Count/mL	RBC (%)	Count/mL	RBC (%)
None	–	15×10^7	0.0	17×10^7	0.0
Pre-mordanted without dyeing (blank)	–	4×10^7	76.4	6×10^7	66.3
Madder	0.78	5×10^6	96.6	8×10^6	95.2
Curcuma	0.56	15×10^5	99.0	5×10^6	96.6
Henna	0.95	5×10^6	96.6	6×10^6	96.4
Onion	3.99	5×10^6	96.6	9×10^6	94.7

Substrate: half-bleached pique substrate; mordant: Zr-oxychloride (150 mmol/L); dyeing conditions: dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. G+ve: Gram positive; *S. aureus*: *Staphylococcus aureus* strain; G−ve: Gram negative; *E. coli*: *Escherichia coli* strain; RBC: reduction in bacterial count.

form dye–fiber bond as well as ability to react with cellular protein by combining with the thiol group thereby leading to the inactivation of the protein (Purwar & Joshi, 2004), and can be ranked as follows: Zn-chloride > Zr-oxychloride > Cu-chloride > Al-chloride > none, (vi) the susceptibility of the tested microorganisms to killing as they contact the surface of dyed samples can be arranged descendingly as follows: G+ve > G−ve, most probably due to the fact that G+ve bacteria cell wall consists of a single layer, whereas, G−ve cell wall is multilayered structure bounded by an outer cell membrane (Shtayeh et al., 1998), and (vii) the extent of dyeing is governed by the extent of picking up, interacting as well as binding the dye molecules via the mordant bridge as discussed earlier.

3.7.2. Type of natural dye

As far as the change in the antibacterial activity, expressed as RBC %, of the obtained natural dyeings as a function of the type of the natural dye, Table 8 reveals that: (i) the enhancement in antibacterial activity follows the decreasing order pre-mordanted → dyed substrate > pre-mordanted substrate ≫ untreated, (ii) the variation in chemical structure of the nominated natural dyes has practically no significant effect on the RBC % and can be arranged as follows: curcuma > henna ≥ madder ≥ onion > blank ≫ none, (iii) the outstanding antibacterial activity against both the G+ve (*S. aureus*) and the G−ve (*E. coli*) bacteria reflects the biocidal effect of the Zr-oxide, natural dye and/or both of them synergitically thereby killing them via preventing cell production, blocking of enzyme, reaction of the cell membrane and/or the destruction of cell walls (Holme, 2007), and (iv) the variation in K/S values of the obtained dyeings reflects the differences among them in physical state, chemical structure, functionality, extent of absorption, interaction as well as complexation onto and/or within the pre-mordanted substrate as mentioned before.

3.7.3. Fabric structure

The dependence of the extent of dyeing, expressed as K/S values, as well as the antibacterial activity, expressed as RBC %, on the fabric structure is given in Table 9. The obtained data signify that: (i) the dye content and K/S depend on the extent of penetration and diffusion of the extracted dye molecules as well as their degree of fixation and complexation onto and/or within the knitted fabric structure and can be ranked as follows: parasol > pique > interlock, (ii) the antibacterial activity of the above-mentioned dyeings follows the same order, (iii) darker the color strength, i.e. higher the active ingredient of the extracted color, better will be the RBC % value.

3.7.4. Durability to wash

To examine the durability to wash, since the textile articles are washed many times during wear life, the obtained dyeings were subjected to, 1, 10, and 20 wash cycles in home laundering machine and subjected to K/S, UPF and antibacterial activity tests according the above-mentioned testing methods. As shown in Table 10, increasing the wash cycle from 1 to 20 results in a decrease in K/S value by 35.9%, a reduction in UPF value by 27%, as well as a decrease in RBC value by 3.1% for G+ve bacteria and by 5.2% for G−ve bacteria. The extent of decrease in the antibacterial activity of G−ve bacteria, e.g. *E. coli*, was more than that of the G+ve bacteria, e.g. *S. aureus*,

Table 9
Effect of fabric structure on both the K/S and RBC% values of the obtained dyeings.

Fabric structure	K/S	G+ve (*S. aureus*)		G−ve (*E. coli*)	
		Count/mL	RBC (%)	Count/mL	RBC (%)
Parasol	0.99	2×10^6	98.6	6×10^6	96.4
Pique	0.78	5×10^6	96.6	8×10^6	95.2
Interlock	0.50	1×10^7	93.3	15×10^6	91.0

Pre-mordanting with Zr-oxychloride (150 mmol/L); substrate: half-bleached. Dyeing with madder: dye extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. K/S: color strength; G+ve: Gram positive; *S. aureus*: *Staphylococcus aureus* strain; G−ve: Gram negative; *E. coli*: *Escherichia coli* strain.

Table 10
Durability to washing.

Washing cycles	*K/S*	UV-protection		Antibacterial activity			
		UPF	Grade	G+ve (*S. aureus*)		G−ve (*E. coli*)	
				Count/mL	RBC (%)	Count/mL	RBC (%)
1	0.78	48	Excell.	5×10^6	96.6	8×10^6	95.2
10	0.64	45	Excell.	7×10^6	95.8	11×10^6	93.5
20	0.50	35	Very good	11×10^6	93.5	15×10^6	90.0

Substrate: half-bleached pique; mordant: Zr-oxychloride (150 mmol/L); dyeing conditions: madder extract (10%); pH (4); LR (1/30); at 100 °C for 60 min. *K/S*: color strength; UPF: UV-protection factor; G+ve: Gram positive; *S. aureus*: *Staphylococcus aureus* strain; G−ve: Gram negative; *E. coli*: *Escherichia coli* strain; RBC: reduction in bacterial count percent.

most probably due to the multilayered structure of the G−ve cell wall, compared with a single layer of the G+ve cell wall, which needs more concentration of the extracted madder-active ingredients for killing. On the other hand, the retained color strength, very good UV-protection capacity (against the harmful UV-radiation), as well as the maintained excellent antibacterial ability (against the G−ve and G+ve bacteria) even after repeated 20 washing cycles indicating that the multifunctionality of the obtained dyeings using the new dyeing process, i.e. salt treatment → alkali-treatment → oxidation treatment to get in situ deposition of the mordant oxide followed by natural dyeing, is still durable.

4. Conclusions

Natural dyeings having multifunctionality, i.e. UV-protection and antibacterial activity, are easily achieved by in situ deposition of proper metal oxides onto and/or within the cotton knits, followed by post-dyeing of pre-mordanted substrates with the natural dyes extracts. The present study clearly indicates that the performance properties of the obtained dyeings are determined by the fabric structure, the type and concentration of mordant, the class and dye extract %, as well dyeing sequence, i.e. pre-mordanting followed by dyeing or dyeing only.

It can thus be concluded that:

- The UPF value of half-bleached substrates increased by increasing the weight, thickness as well as reducing the air permeability, interlock > pique ≥ parasol.
- Pre-mordanting of the cotton knits with the used metal salts brings about an improvement in both the *K/S* and UPF values, and follows the order: Zr-oxychloride ≥ Cu-chloride > Zn-chloride > Al-chloride > none, keeping the fabric structure (pique) and the natural dye (madder) constant.
- Post-natural dyeing of pre-mordanted substrates results in a remarkable improvement in both the *K/S* as well as the UPF values, and the extent of improvement in the gained properties is determined by the physical state/chemical structure/concentration of the natural dye extract, type of mordant as well as the knitted fabric structure.
- The antibacterial activity of the obtained dyeings depends on:
  - *Type of mordant*: Zn-chloride ≥ Zr-oxychloride > Cu-chloride > Al-chloride > dyed without pre-mordanting ≫ untreated.
  - *Nature of the extracted dye*: Has practically no significant effect.
  - *Kind of bacteria*: G+ve > G−ve.
- The UV-protection and antibacterial functions offered by these dyeings are maintained after repeated washing cycles (up to 20 cycles).
- Finally, it can be concluded that the novel pre-mordanting step is a very promising, simple and practical method for developing natural dyeings with outstanding protection properties against the harmful UV-radiation and hazardous microorganisms.

References

Cristea, D., & Vilarem, G. (2006). Improving light fastness of natural dyes on cotton yarn. *Dyes and Pigments*, *70*, 238–245.
Feng, X. X., Zhang, L. L., Chen, J. Y., & Zhang, J. C. (2007). New insights into solar UV-protective properties of natural dyes. *Journal of Cleaner Production*, *15*, 366–372.
Garland, C. E. (1993). In C. Gultekin (Ed.), *Colour technology in textile chemistry*. AATCC, pp. 107–112.
Gupta, D. (1999). Fastness properties of natural dyes, part II: Effect of chemical structure on light fastness. *Colourage*, 41–46. August.
Gupta, D. (2007). UPF characteristics of natural dyes and textiles dyed with them. *Colourage*, (April), 75–80.
Gupta, D., Jain, A., & Panwar, S. (2005). Anti UV and antimicrobial properties of some natural dyes on cotton. *Indian Journal of Fiber & Textile Research*, *30*, 190–195.
Gupta, D., Khare, S. K., & Laha, A. (2004). Antimicrobial properties of natural dyes against gram-negative bacteria. *Coloration Technology*, *120*, 167–171.
Holme, I. (2007). Innovative technologies for high performance textiles. *Coloration Technology*, *123*, 59–73.
Ibrahim, N. A., Allam, E. A., El-Hossamy, M. B., & El-Zairy, W. M. (2007). UV-protective finishing of cellulose/wool blended fabrics. *Polymer–Plastics Technology & Engineering*, *46*, 905–911.
Ibrahim, N. A., Gouda, M., El-Shafei, A. M., & Abdel-Fatah, O. M. (2007). Antimicrobial activity of cotton fabrics containing immobilized enzymes. *Journal of Applied Polymer Science*, *104*, 1754–1761.
Ibrahim, N. A., Refai, R., Youssef, M. A., & Ahmed, A. F. (2005). Proper finishing treatments for sun-protective cotton containing fabrics. *Journal of Applied Polymer Science*, *97*, 1024–1032.
Nadiger, G. S., Sharma, K. P., & Jarag, P. (2004). Screening of natural dyes. *Colourage Annual*, 130–137.
Nakashima, T., Sakagami, Y., Ito, H., & Matsno, M. (2001). Antibacterial activity of cellulose fabrics modified with metallic salts. *Textile Research Journal*, *71*, 688–694.
Parmar, M. S., Giri, C. C., Singh, M., & Chabbra, J. (2006). Development of UV and flame resistant fabric from natural coloured cotton. *Colourage*, (July), 57–60.
Patel, B. H., Agarwal, B. J., & Patel, H. M. (2003). Novel padding technique for dyeing Babool dye on cotton. *Colourage*, (January), 21–26.
Purwar, R., & Joshi, M. (2004). Recent developments in antimicrobial finishing of textiles—a review. *AATCC Review*, *4*(3), 22–25.
Roshan, P., Malanker, J., & Sandeep, R. (1996). Natural dyes: Classification, extraction and fastness properties. *Textile Dyer and Printer*, *29*, 16–24.
Saravanan, D. (2007). UV-protection textile materials. *AUTEX Research Journal*, *7*, 53–62.
Shtayeh, M. S. A., Yaghmour, R. M. R., Faidi, Y. R., Salem, K., & AL-Nuri, M. A. (1998). Antimicrobial activity of 20 plants used in folkoric medicine in the plaestinian area. *Journal of Ethnopharmacology*, *60*, 265–271.
Srinivasan, M., & Gatewood, B. M. (2000). Relationship of dye characteristics to UV-protection provided by cotton fabric. *Textile Chemist and Colorist & American Dyestuff Reporter*, *32*, 36–43.
Vankar, P. S., Shanker, R., & Verma, A. (2007). Enzymatic natural dyeing of cotton and silk fabrics without metal mordants. *Journal of Cleaner Production*, *15*, 1441–1450.
Yadav, A., Prasad, V., Kathe, A. A., Raj, S., Dadav, D., Sundaramoorthy, C., et al. (2006). Functional finishing in cotton fabrics using zinc oxide nanoparticles. *Bulletin of Materials Science*, *29*(6), 641–645.