Protection of humans from ultraviolet radiation (UVR) through the use of cotton clothes dyed with aqueous extracts of onion skin as the natural colorant

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Abstract: Prolonged human exposure to solar ultraviolet radiation (UVR) may result in acute and chronic health effects on the skin, eye and immune system and over the longer term exposure leads to premature skin aging, photodermatoses, actinic keratoses, cataracts and skin cancer. The present study was carried out to evaluate the UVR protection imparted by cotton fabric dyed with the aqueous extract of onion skin as the natural dyes. Onion skins (*Allium cepa* L.) dye was extracted, dried and analyzed for its coloring components using high performance liquid chromatography (HPLC). The major coloring components of the dye are including flavonols (86.86%), flavones (1.04%) and anthocyanidines (12.10%) which similar in part with the synthetic disperse dyes. Cotton fabric was dyed with the onion skin colorant and characterized with respect to fabric parameters including weight, thickness and thread count. Role of colorant concentration on the ultraviolet protection factor (UPF) was examined via color strength analysis. Spectral analysis of dyed cotton samples with onion skin colorant (OSC) has recorded the maximum absorption of at wavelengths of 200 nm (in the UVC region) and 330 nm (in the UVA region). OSC gives a yellow color which maximize in depth with the increasing of that dye concentration. UPF values for OSC applied at higher concentrations gave higher UPF values. Samples of dyed cotton fabrics with OSC were classified as having good to very good UV protection. When all dyed cotton fabrics were included in the statistical analysis, there was a positive significant ($p< 0.05$) relationship between UPF and K/S ($R^2= 0.913$). In conclusion, data from the present study will be useful for dermatologists advising patients regarding the UV-protective properties of clothing made from natural fibers dyed with natural colorants.

[Islam Hussein and Yousif Elhassaneen: **Protection of humans from ultraviolet radiation (UVR) through the use of cotton clothes dyed with aqueous extracts of onion skin as the natural colorant.** *J Am Sci* 2013;9(8):16-24]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 3

Key words: *Allium cepa*, onion skin dye composition, UPF, Fabric characterization, color strength.

1. Introduction

The ultraviolet radiation (UVR) region covers the wavelength range 100-400 nm and is divided into three bands: UVA (315-400 nm), UVB (280-315 nm) and UVC (100-280 nm). As sunlight passes through the atmosphere, all UVC and approximately 90% of UVB radiation is absorbed by ozone, water vapor, oxygen and carbon dioxide. UVA radiation is less affected by the atmosphere. Therefore, the UV radiation reaching the Earth's surface is largely composed of UVA with a small UVB component (http://www.spectroscopynow. com). Small amounts of UV (UVA-UVB) radiation are beneficial to health, and play an essential role in the production of vitamin D. However, excessive exposure to UV radiation is associated with different types of skin cancer, sunburn, accelerated skin ageing, cataract and other eye diseases. The National Toxicology Program, U.S. Department of Health and Human Services has classified UVR as a known human carcinogen (http://ehp.niehs.nih.gov /roc/toc10.html).There is also evidence that UV radiation reduces the effectiveness of the immune system (Capjack *et al.,* 1994).

WHO (2006) has published the report entitled "Global burden of disease from solar ultraviolet radiation" that provides detailed estimates of UV-associated disease burden worldwide. This report estimates that up to 60,000 deaths a year worldwide are caused by too much exposure to ultraviolet radiation (UVR). Of those 60,000 deaths, an estimated 48,000 are caused by malignant melanomas and 12,000 by skin carcinomas. In total, more than 1.5 million DALYS ("disability-adjusted life years")- a measure of the loss of full functioning due to disease and death are lost every year due to excessive UVR exposure. The most serious consequence of excess UVR is malignant melanoma, which has high cure rates only if detected early. Up to 90% of the global burden of disease from melanoma and other skin cancers are estimated to be due to UVR exposure.

The most frequently recommended form of UV protection include limit time in the midday sun, seek shade, wear protective clothing such as a broad brimmed hat to protect the eyes, face and neck, wear sunglasses and use sunscreen. Unfortunately, one cannot hold up a textile material to sunlight and determine how susceptible a textile is to UV rays. Even textiles which seem to be non-light transmitting may pass significant amounts of erythema-inducing UV irradiation (Rieker *et al.,* 2001). Therefore, knowledge of the factors that contribute to the protective abilities of textiles is vital. Important factors include fiber composition, fabric construction, fabric dyeing, finishing chemicals etc that may have been applied to the textile material.

Onion (*Allium cepa L.*) belongs to the *Lilliaceae* family and is grown all over the world. After tomatoes, they are the second most horticultural vegetable (Griffiths *et al*., 2002). Each processing step in onion preparation and processing is characterized by wastes and by-products, with possible impact on the environment. The amount of onion waste produced annually in the European Union is estimated at approximately 450,000 tons. The major by-products resulting from industrial peeling of onion bulbs are brown skin, the outer two fleshy leaves and the top and bottom bulbs. That onion skin is one of the most important sources of natural dye that gives yellowish to brown colorants. According to our knowledge, no study has investigated the ultraviolet properties of natural fabrics dyed with onion skin colorants. Such as reviewed by Capjack *et al.,* (1994) many studies have concluded that good UVR protection can be provided by synthetic fibers dyed with high concentrations of synthetic dyes. However, synthetic fibers such as polyester are hydrophobic and are generally not deemed to be comfortable for wear especially in warm weather. According to a report in Borland, (2000) natural fibers and natural dyes are back in demand due to worldwide public health concern and environmental consciousness. Therefore, the present study was carried out to prepare aqueous extracts of onion skin as the natural colorants. Cotton fabrics were dyed with that natural colorants and ultraviolet radiation protection properties will be evaluated.

2. Materials and Methods

2.1. Materials

Red onion (*Allium cepa* L.), variety Giza-20, skin was obtained from Tala City, Minoufiya Governorate, Egypt. Plain weave cotton fabric was purchased from El-Nasr Company for Spinning and Weaving, AlMahalla El-Kobra City, El-Gharbia Governorate, Egypt.

2.2. Chemicals

Phenolic compounds standards were purchased from Fluka Chemical Co., Switzerland, while vitamin C and amino acids standards from Sigma Chemical Co., St. Louis, Mo. All solvents and buffers, analytical grade, were obtained from Al-Ghomhoria Company for Chemicals, Drugs and Medical Instruments, Cairo, Egypt.

2.3. Extraction of red onion skins dye

Fresh red onion skins (*A. cepa* L.) were dried in sunlight (Temperature, 30±4 ^{0}C) for three days and crumbled using a blender, and then were used as the raw material for dye extraction, which was achieved by the reflux technique: 70 g of crumbled onion skin was mixed with one liter of distilled water and refluxed for 40 min. The aqueous extraction of the corresponding dye solution is double filtered in fine mesh nylon cloth and sintered glass crucible and the filtrate is evaporated using a vacuum oven at lower temperature (70°C) to a semi-dried solid mass and the same is then dried under reduced pressure using a rotary evaporator. The crude dye extract of the onion skins was then crumbled with a blender and used for the dying process.

2.4. Dyeing process:

Onion skin dyeing was done in stainless steel canisters (Al-Ahram Co., Egypt) using 1.5%, 3.0%, 4.5% and 6% dye on weight of fabric. The liquor-goods ratio was 40:1. Fabrics were introduced into the dyeing solutions at room temperature. Temperature was raised to the boil and dyeing continued at the boil for 40 minutes. After dyeing, fabrics were mordanted by treating with copper sulphate ($CuSO_4$) at boil for 30 minutes. The liquor ratio was 1:40 and $CuSO_4$ concentration was 10% on weight of the fabric. After mordanting, fabric was squeezed thoroughly, rinsed in water, washed using a non-ionic detergent and air-dried. Four replications were done for each dye concentration.

2.5. Method of analysis

2.5.1. Fabric characterization parameter

Fabric weight, thickness and thread counts were measured according to ASTM (2001) D3776-96, D1777-96 and D3775-98, respectively.

2.5.2. Color composition of the dye

For color composition of the dye analysis, a SP Thermo Separation Products Liquid Chromatography (Thermo Separation products, San Jose, CA, USA) was used with a pump Consta Metvic 4100, a Spectra Series AS100, Spectra System UV 1000 UV/Visible Spectrophotometer Detector, Spectra System FL 3000 and a PC 1000 system software. The columns used (Alltech, Baltimore, USA) was a reversed-phase water Spherosorb ODC-2 (3μM; 150 × 4.6mm I.d., Alltech, USA) for phenolics analysis and a guard column 7.5 x 3.2 mm containing 5 µm.

Flavonols and flavones were extracted and analyzed in HPLC according to the method of Hertog *et al.,* (1992). Sample peaks were quantified with the external standard method.

The anthocyanidines were extracted from onion skin by suspending 0.5 g of homogenized tissue in 5 mL of methanol (0.1% HCl) at room temperature for 10 min. The extract was filtered and used for HPLC analyses as described by Fossen *et al.,* (1996) with some modification described by Gennaro *et al*., (2002).

2.5.3. UV absorbance, UPF and Color strength measurement

UV absorbance through a fabric is the crucial factor determining the UV protection of textiles was measured according to Hoffman *et al.,* (2001). Ultraviolet protection factor (UPF) is the scientific term used to indicate the amount of Ultraviolet (UV) protection provided to skin by fabric. It was measured *in vitro* using ultraviolet absorbance analyzer (SPECTRO UV-VIS Spectrophotometer (D2 lamp power supply), LaboMed, Inc. USA) according to standard AS/NZ 4399 (AS/NZ, 1996). Fabrics were classified with a UPF value as follow:

UPF	UV protection Class
‹ 15	No Class
15 – 24	Good
25 – 39	Very good
40 or greater	Excellent

Measured UPF values were also correlated to the color strength of the dyed fabrics. Color strength was evaluated using K/S values such as mentioned in Sarkar, (2004). Higher the value of K/S greater is the color strength. All parameters were measured on triplicates and the values were presented as mean ±SD.

3. Results and Discussion

3.1. Natural organic dyes from onion skin

Onion (*Allium cepa* L.) has also been successfully grown in all parts of the world. The outer dry layers of onion bulbs, which are not edible and removed before processing, have been used all over the world as sources of natural dye that gives yellowish-brown colorants. The structures of the coloring components found in red onion peels are given in Table (1). The major coloring components of red onion skin extract are three flavonoids subgroup, flavonols, flavones, and anthocyanins, which is also an antioxidant. Such flavonoid compounds are responsible for the yellow, brown, red and purple color skins of many onion varieties (Griffiths *et al.,* 2002). It has been used as a food dye with high antioxidant properties (Prakash *et al.,* 2007a and Singh *et al.,* 2009). The major flavonoids found in dry peel of onion aquatic extract contain large amounts of flavonols (86.86%) and flavones (1.04%) and anthocyanidines (12.10%) as the minor components which similar in part with the synthetic disperse dyes. Amongst flavonoids, onion skin dye contain up to 78.20% of quercetin which represent the main color component in different onion varieties (Elhassaneen and Sanad, 2009). Like of these data are in accordance with that reported by Gülsen *et al.,* (2007) and Prakash *et al.,(*2007b), the major flavonoids found in dry peel of onion that has been considered usually as waste, contain large amounts of quercetin, quercetin glycoside and their oxidative product which are effective antioxidants against the lethal effect of oxidative stress. Flavonoids are considered very useful substances during the dyeing process because of their ability to fix dyes within fabrics. Cotton dyed with an aqueous extract of onion skin possessing a mordant compound displays a yellowish-brown color. Color fastness to water, washing, and perspiration and colour fastness to light were at good to very good levels (Data not listed). Like of these findings indicated that achieving a good dying, water solubility using natural dyes is not rather exceptional. No chemical group is capable of electrolytic dissociation or ionization in a molecule; an interesting and important exception is the anthocyanins (find in red onion skin dye), for example, pelargonidine, cyanidine, and betanidine are slightly cationic dyes and, therefore, also have relatively good solubility in water (Mongkholrattanasit and Krystufek, 2011). The chemical constitution of anthocyanin dyes has remarkable similarity with the modern synthetic disperse dyes: the solubility of more or less elongated molecules of chromogen is due to the presence of several polar groups (mainly –OH) on aromatic rings. No groups are capable of electrolytic ionization (with the exception of the anthocyanin find in red onion skin dye). From this follows that they only have low solubility in water. Empirically, it is known that it is impossible to strengthen dyeing of cotton with natural dyes, but it can be done by adding neutral electrolytes (sodium chloride in the present study) as substantive dyes (Mongkholrattanasit and Krystufek, 2011). So, from a technical point of view, red onion skin dye is providing only inexpressive wet fastness on cotton fiber, and the mordanting by salts of suitable metals (alum) as well as adding neutral electrolytes (sodium chloride) is also needed to improve wet fastness (deepen and intensify the color).

3.2. Undyed cotton fabric characterization parameters and UPF values

Undyed cotton fabric characterization parameters and UPF value are listed in Table (2). Such as mentioned in material and methods the undyed cotton fabrics with a weight of 124 g/m^2 and a thickness of 0.041 cm can not be rated as offering any degree of protection since their UPF values were less than 15. Like of that data are in accordance with that obtained by Sarkar (2004) who reported that fabric construction parameters of weight and thickness show a positive correlation with UPF values. Higher the weight and thicker the fabric, higher is the degree of UV protection afforded by the fabric. Also, Davis *et al.,* (1997) found that undyed bleached cotton, linen, acetate, and rayon fabrics afford poor protection against UV radiation which confirms that effect of fiber composition. The positive correlation between fabric weight and fabric thickness with UPF values could be attributed to the fabric porosity (Pailthorpe, 1993). Porosity is a measure of tightness of weave and is also called as cover factor i.e. the percentage area occupied by warp and filling yarns in a given fabric area. The more in the cover factor (increasing in opaque) of the fabric, the more is the UV absorption/protection (Reiker *et al.,* 2001). Such as mentioned by Pailthorpe (1993) and Crews *et al.,* (1999) the cover factor is affected by fabric weight and thickness. An increasing in fabric weight (smaller spaces between yarns) and thickness (density) leads to maximize the UV absorption. The data also recorded that thread count for the undyed cotton fabrics, 210 per inch had 4.3 UPF. In similar study carried out by Sarkar (2004) the cotton plain weave fabric with a thread count of 205 had a UPF of 3.2 whereas the sateen weave with a thread count of 106 and a UPF of 13.3 and the twill weave fabric with a thread count of 81 had a UPF of 19.2. All of these data indicated that the UV protection degree of the fabrics was affected by their thread count which has a negative correlation/relationship. Crews *et al.,* (1999) interpreted this correlation the fact that fabrics that are thinner tend to contain finer yarns and therefore have the highest thread counts.

Table 1. Color composition of red onion skin dye

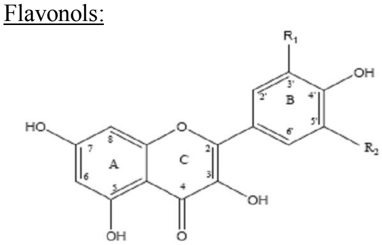
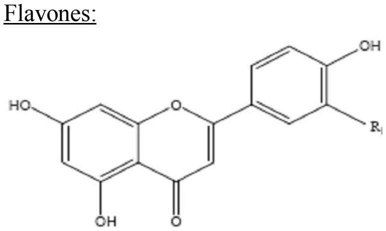
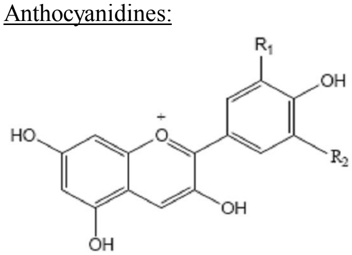
Phenolic compounds				Phenolic content (mg/100g) dry weight
Flavonols: 		R_1	R_2	
	Quercetin	OH	H	391.60
	Kaempferal	H	H	23.10
	Myricetin	OH	OH	20.27
Flavones: 		R_1		
	Apigenin	H		2.91
	Luteolin	OH		2.30
Anthocyanidines: 		R_1	R_2	
	Cyanidin	H	OH	25.95
	Delphinidin	OH	OH	20.93
	Pelargonidin	H	H	0.16
	Peonidin	OH	OME	13.54

Table 2. Fabric characterization parameters and UV absorbance of cotton fabric

Parameters	Value
Fabric structure	Plain weave 1/1
Weight (g/m^2)	124 ± 2.11
Thickness (cm)	0.041 ± 0.002
Thread count (per inch)	210 ± 0.00
Ultraviolet protection factor (UPF)	4.3 ± 0.17
UV protection class	No Class

3.2. Fabric characterization parameters and UV absorbance of cotton fabric

The value UV absorbance data in the presence and absence of onion skin dye for the cotton fabric is shown in Table (3) Figure (1). Undyed cotton fabric had no significant absorbance (significant transmittance) and consequently a very low UPF value of 4.3 as well as "no Class" for the UV protection class categories. Spectral analysis of dyed cotton samples with onion skin colorant has recorded the maximum absorption of at wavelengths of 200 nm (in the UVC region) and 330 nm (in the UVA region). It is noted that since the relative erythemal spectral effectiveness is extremely higher in the UVC region, higher in the UVB region compared to the UVA region, the UPF values depend primarily on absorbance in the UVC region and/or UVB region. The finding of this study, maximum absorption of prepared dyed cotton fabric occurs in the UVC region and UVA region, is an important requirement for those at the dangers of this kind of harmful rays.

UPF values and protection categories of the cotton fabric dyed with the different concentration of onion skin dye are listed in Table (4). It is clear that the onion skin dye gives a yellow color which maximize in depth with the increasing of that dye concentration. The results also show that UPF values for OSC applied at higher concentrations gave higher UPF values. For example, the UPF of the cotton fabric at a 1.5% onion skin dye on weight of fabric was 16.2 and that increased to UPF 34.2 at a concentration of 6%. Samples of dyed cotton fabrics with onion skin colorant could be classified as having good UV protection (UPF values between 15 and 24) to very good UV protection (UPF values between 25 and 39). The present data are in agreement with that reported by Reinert *et al.,* (1997) who showed that pale colored fabrics of cotton, silk, polyamide, and polyamide/elastan gave less protection against intense UV radiation. Also, Gies *et al.,* (1994) indicated that dyeing fabrics in deeper shades and darker colors improves sun protection properties.

Regarding the K/S values of the dyed fabrics which are a measure of color depth, it is reviewed that higher K/S increases UPF values (Sarker, 2004). As it is evident from the Table (4) data the cotton dyed samples with onion skin colorant when the K/S value increased from 0.42 to 1.02 the UPF values rose from 16.2 to 34.2. In the correlation analysis, important differences were found between ultraviolet protection factor (UPF) and color strength (K/S) of cotton fabrics dyed with onion skin (Figure 2). When all dyed cotton fabrics were included in the statistical analysis, there was a positive significant ($p < 0.05$) relationship between UPF and K/S (R2= 0.913). In line with this type of correlation, Sarkar and Seal (2003) reported that UPF values are dependent on a multitude of fabric construction factors such as pores in the fabric, thickness, and weight in addition to processing parameters such as dyeing and finishing.

3.3. Evaluation of the suggested/designed shirt and trouser

By application on twenty volunteers (youth, farmers and professions that require exposure to the sun for long periods of time), different designs of shirt and trouser have evaluated for many standards include: general shape, functional relevance, fitness climate, social suitability and color influence (Figure 3 and Table 5). The design number 4 has the highest total degree (42.2) while the lowest one was number 5 has total degree (32.7).

Table 3. Ultraviolet absorption (Abs) values of cotton fabric undyed and dyed with onion skin powder (OSP) at different concentrations

Treatment	Absorbance (Abs)																					
	190	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350	360	370	380	390	400
Undyed	1.151	1.220	1.216	1.231	1.191	1.051	1.006	1.030	0.969	0.941	1.014	0.989	0.979	0.900	1.150	1.040	1.070	1.008	0.935	0.928	0.924	0.931
1.5% OSP	1.232	1.543	1.421	1.401	1.342	1.145	1.153	1.117	1.072	1.073	1.136	1.147	1.131	1.055	1.316	1.218	1.202	1.120	1.054	1.031	1.022	1.041
3.0% OSP	1.254	1.601	1.456	1.423	1.400	1.179	1.175	1.144	1.096	1.073	1.161	1.162	1.147	1.063	1.458	1.258	1.250	1.136	1.069	1.053	1.064	1.069
4.5% OSP	1.379	1.686	1.599	1.564	1.501	1.264	1.244	1.198	1.172	1.210	1.215	1.237	1.215	1.120	1.632	1.417	1.265	1.191	1.116	1.091	1.090	1.111
6.0% OSP	1.411	1.817	1.732	1.652	1.600	1.301	1.343	1.301	1.256	1.259	1.323	1.327	1.313	1.198	1.712	1.421	1.353	1.259	1.158	1.150	1.149	1.154

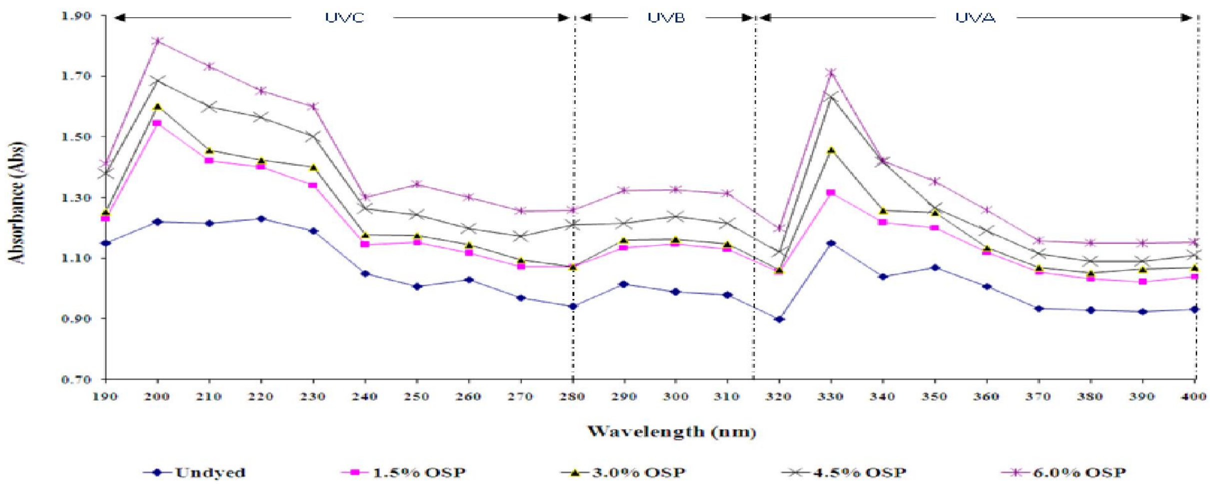
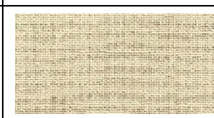


Figure 1. Ultraviolet absorption (Abs) curves of cotton fabric undyed and dyed with onion skin powder (OSP) at different concentrations

Table 4. Ultraviolet protection factor (UPF), ultraviolet protection class (UVPC) and color strength (K/S) of cotton fabric dyed with onion skin powder (OSP) at different concentrations

OSP conc. (%)	UPF	UVPC	K/S	Dyed sample
Undyed	4.3 ± 0.17	No Class	-------------	
1.5	16.2 ± 1.05	Good	0.42 ± 0.08	
3.0	18.8 ± 0.79	Good	0.51 ± 0.03	
4.0	30.8 ± 2.12	Very good	0.84 ± 0.09	
6.0	34.2 ± 1.82	Very good	1.02 ± 0.05	

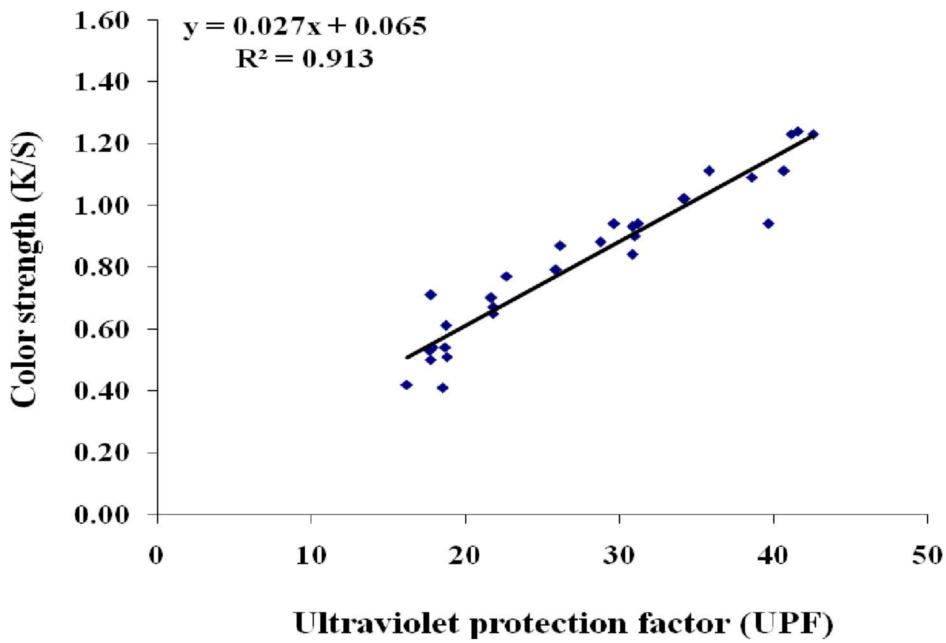
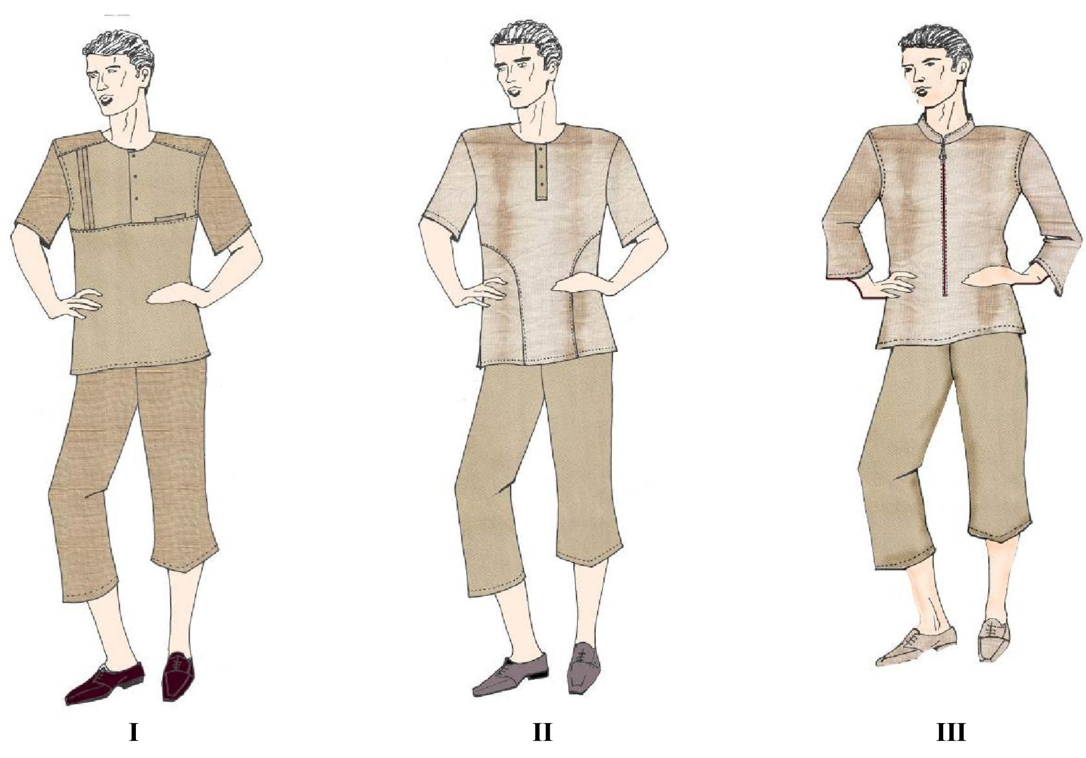


Figure 2. Correlation between ultraviolet protection factor (UPF) Vs. Color strength (K/S) of cotton fabrics dyed with onion skin



IV V VI

Figure 3. Suggested/designed shirt and trouser

Table 5. Panel tests values (Mean ±SD) of the suggested/designed shirt and trouser

Standards	Score	Design I	Design II	Design III	Design IV	Design V	Design VI
General shape	10	8.0 ± 0.4[a]	7.5 ± 0.6[b]	7.1 ± 0.5[b]	8.0 ± 0.5[a]	6.8 ± 0.4[c]	7.2 ± 0.2[b]
Functional relevance	10	6.9 ± 0.4[d]	8.0 ± 0.5[b]	6.8 ± 0.1	9.0 ± 0.2[a]	6.2 ± 0.6[e]	7.6 ± 0.4[c]
Fitness climate	10	7.8 ± 0.6[b]	8.2 ± 0.6[a]	6.9 ± 0.3[c]	8.5 ± 0.4[a]	6.6 ± 0.4[c]	8.4 ± 0.3[a]
Social suitability	10	7.0 ± 0.5[b]	7.8 ± 0.6[a]	7.2 ± 0.3[b]	8.0 ± 0.4[a]	7.0 ± 0.5[b]	7.0 ± 1.2[b]
Color influence	10	7.8 ± 0.5[b]	8.1 ± 0.6[b]	7.9 ± 1.1[b]	8.7± 0.4[a]	6.1 ± 0.3[c]	8.2 ± 0.5[b]
Total	50	37.5± 2.7[b]	39.6± 3.1[b]	35.9 ±2.1[c]	42.2 ±1.8[a]	32.7±3.5[d]	38.4±2.4[b]

* Different letters on the same raw means a significant difference at $p<0.05$.

4. Conclusion

Dyeing cotton fabric with aqueous extracts of onion skin as the natural colorant increases the ultraviolet protective abilities of the fabric and can be considered as an effective protection against ultraviolet rays. It is hoped that data of the present study could be useful for dermatologists advising patients regarding the UV-protective properties of clothing made from cotton fabric dyed with natural colorants.

Acknowledgments

The authors acknowledge the contributions and dedication of Dr. Abdallah Hussein, Dept. of Clothing and Textile, Faculty of Home Economics, Minoufiya University. Sincere thanks are also extended to Research Support Fund, Minoufiya University for financially support.

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6/12/2013