A promising perspective to upgrade cotton dyeing performances when dyed with a red fluorescent pigment

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HIND ALGAMDY

ABSTRACT – REZUMAT

A promising perspective to upgrade cotton dyeing performances when dyed with a red fluorescent pigment

This paper studied the dyeing with a fluorescent red pigment, and several dyeing performance problems were detected. This research aims to improve these performances, particularly those of dyeing fastness. Various surface treatments have been applied to bleached cotton fabrics to do this. Two commercial agents have been used, namely ST1 and ST2, which are essentially quaternary ammonium preparations with a cationic character. In addition, the dyeing process parameters have been studied, namely, the dyeing temperature, time and pH, to achieve the best conditions allowing acceptable dyeing performances with the fluorescent red pigment. Moreover, SEM images were taken for treated and untreated cotton fabrics, and no great morphological differences were detected. Finally, dyeing performances were evaluated based on the measurement of colourimetric coordinates, colour yield K/S and dyeing fastness properties. Very promising results have been found following a surface treatment with 8% of the agent ST1, a dyeing process of 30 inutes at 50°C for a pH of 8.

Keywords: *surface treatment, fluorescence, cotton, dyeing fastness, morphological aspect*

O perspectivă promițătoare pentru a îmbunătăți performanța vopsirii bumbacului cu pigment roșu fluorescent

În această lucrare a fost studiată vopsirea cu pigment roșu fluorescent şi au fost detectate mai multe probleme de performanță a vopsirii. Scopul acestei cercetări este de a îmbunătăți aceste performanțe, în special cele de rezistență la vopsire. Pentru a face acest lucru, au fost aplicate diferite tratamente de suprafață țesăturilor din bumbac albit. Au fost utilizați doi agenți comerciali și anume ST1 și ST2, care sunt în esență preparate de amoniu cuaternar cationic. În plus, au fost studiați parametrii procesului de vopsire, și anume temperatura de vopsire, timpul și pH-ul, pentru a obține cele mai bune condiții care să permită performanțe acceptabile de vopsire cu pigmentul roșu fluorescent. Mai mult, au fost realizate imagini SEM pentru țesături de bumbac tratate și netratate şi nu au fost detectate diferențe morfologice mari. În final, performanțele de vopsire au fost evaluate pe baza măsurării coordonatelor colorimetrice, randamentului tinctorial K/S și proprietăților de rezistență la vopsire. Rezultate foarte promițătoare au fost găsite în urma unui tratament de suprafață cu 8% din agentul ST1, un proces de vopsire cu o durată de 30 de minute la 50°C, cu un pH de 8.

Cuvinte-cheie*: tratament de suprafață, fluorescență, bumbac, rezistență la vopsire, aspect morfologic*

INTRODUCTION

The world of fluorescence is a world of colour and beauty. In the dark, the tints usually perceived by day disappear. Hence, only the intense colours of the fluorescent substances touched by ultraviolet rays emit a startling clarity. This natural fascinating phenomenon has become a research effect on several applications to different types of textile fabric especially for smart textiles. Fluorescent materials are widely used in a variety of fields because of their unique properties. They can absorb light of one wavelength and emit light of a different wavelength, which makes them useful for a wide range of applications [1]. Textiles that fluoresce could unlock a lot of novel promises for innovation: human safety in outdoor sports, special services in the armed forces, fashion, and trends [2]. It could also be successfully used for making clothing textiles since safety gear with light-sensitivity features is essential to protect competitors in outdoor sports played in low-visibility environments [3]. Indeed, the fluorescence phenomenon is founded on the notion that some materials can absorb light of a particular wavelength (ultraviolet) and subsequently emit light of another wavelength (visible). Moreover, a fluorescent dye appears brighter and more saturated in daylight or black light compared to the colours around it. Dyeing textiles with fluorescent pigments arouses more and more interest in the textile field [4]. However, they also present several challenges namely low dye yield as well as very poor dye fastness. However, this dye once made allows to achieve an impressive range of shades the fluorescent pigments make it possible to create unique and shattering visual effects. To produce a fabric with the needed functionality, several steps are required [5]. Sizing agents were utilized to increase absorbent capacity while oxidizing reagents were used to increase strength, hygroscopicity, dye absorption, and brightness, and dyes were used to generate specific colourations [6]. The most common

way to produce fluorescent textiles is to soak the textile materials in a solution containing fluorescent chemicals. However, covalent bonds between fluorophores and textile fibres should be formed to ameliorate the fluorescent features intensity and stability of the fluorescent characteristics. According to the literature, fluorescent pigments generally have no direct substance towards cotton since they contain an anionic dispersing agent whereas cotton is partially anionic. Thus, the substantivity between the cotton and the colouring pigment could be developed by creating cationic charges on the cotton using surface treatment agents with a cationic character [7–9]. Numerous experiments have been conducted to improve cotton dyeability with pigments using other chemical and physical modification approaches such as plasma treatment [10], ultrasound technique [11], microwave energy [12] and Gamma radiation [13]. Fluorescent dyes are one of those that are increasingly being used by manufacturers for dyeing textile materials to produce brighter colours. These pigments are brighter than traditional pigments, which enhances the colour of fabrics. Furthermore, cotton fabrics fade easily from light, washing, rubbing, and perspiration, so pigments are used more often to dye synthetic fabrics than cotton. To prevent coloured fabrics from fading or staining, cationization, antioxidants, and UV absorbers are often applied [14]. Several research used exhaust methods to dye cotton, polyester, and nylon 17 with fluorescent pigments and discovered that coloured had an unfortunate pigment accumulation and uniformity [15]. Therefore, fluorescent pigments are employed to dye the cotton-polyester blended textile under various conditions [16]. In addition, fluorescence dyes absorb ultraviolet (UV) or visible light and emit light at longer wavelengths. These dyes are defined as substances that absorb and emit strongly in the visible region, and which are concerned with their application potential due to their high fluorescence characteristics [17]. Normally, the fluorescent pigment's fastness qualities are poor. Thus, surface treatment with various levelling agents increased the levelness of the fluorescent pigment. This paper aimed to improve the dyeing performances of dyed cotton fabrics with a red fluorescent pigment. Hence, surface treatment was applied on cotton fabrics before the dyeing process as a preparation step for samples.

Table 1

GENERAL CHARACTERISTICS OF THE COTTON FABRICS USED

Characteristics	Values
Armor	Plain weave
Matter	100% cotton
Thickness (mm)	0.69
Weight ($g \cdot cm^{-2}$)	2.80
Warp density ($threads \cdot cm^{-1}$)	49
Weft density ($yarns \cdot cm^{-1}$)	23
Warp fineness (tex)	39.1
Weft fineness (tex)	64

MATERIALS AND METHODS

Fabric and dye

The cotton fabrics used in this study were purchased from one of the shops in (Taif, Saudi Arabia) in May 2021, it is a bleached fabric with the characteristics summarized in table 1.

These characteristics were measured in standard conditions of temperature and relative humidity (20 ± 2°C for temperature and 65 ± 5% for relative humidity). The Red fluorescent pigment dye studied in this paper belongs to the range of Cepolprint fluorescent dyes. These are water-based fluorescent pigment dispersions, activated by a fluorescent brightener and embedded in a triazine resin in powder form. These compounds are slightly anionic.

Surface treatment process description

Bleached Cotton fabrics were treated at first in a preparative bath before being dyed. The bath contained a specific amount of a surface treatment agent. As surface treatment agents, ST1 and ST2 were used in this study, they are two commercial products, and their characteristics are summarized in table 2.

The surface treatment was applied on cotton fabrics for 25 minutes at 40°C. Cotton fabrics were dried at the end of the process.

Table 2

GENERAL CHARACTERISTICS OF SURFACE TREATMENT AGENTS APPLIED

Surface treatment agent	Characteristics	Properties
ST1	Ionic character	cationic
	Solubility	Water soluble
	Composition	quaternary ammonium preparation
	pH	2–4
ST2	Ionic character	cationic
	Solubility	Water soluble
	Composition	quaternary ammonium preparation
	pH	3–5

Morphological characterization of surface-treated cotton fabrics

The untreated and surface-treated cotton fabrics by ST1 and ST2 agents were examined using an SEM Jeol JSM-6060 Scanning Electron Microscope EDX unit attached, with accelerating voltage18 kV. All the samples were coated with gold before SEM testing.

Dyeing process description

Cotton fabrics treated with a 4% surface treatment agent then undergo a dyeing step with 10% fluorescent red pigment. The dyeing lasted 30 minutes at a temperature of 40°C at a pH of 9. At the end, the dyed fabrics were rinsed and dried.

Colour yield and colorimetric parameters

A Spectra-flash spectrophotometer (DATACOLOR Spectraflash 600Plus, USA) was used. The colour yield K/S was estimated according to the Kubleka-Munck equation [18]:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0} \quad (1)$$

where K is the absorption coefficient, S – the scattering coefficient, R – the decimal fraction of the reflectance of dyed fabric and R_0 – the decimal fraction of the reflectance of undyed fabric.

Fastness properties assessment

The dyeing fastness properties were estimated according to the ISO standards: the ISO 105-B02: 2013 for dyeing fastness properties to light and ISO 105-C10:2006 for dyeing fastness properties to wash.

RESULTS AND DISCUSSION

Study of cotton surface treatment action on dyeing fabrics

Surface treatment on cotton fabrics consisted of applying several agents to select the best one offering the best dyeing fastness for the red fluorescent pigment.

ST1 and ST2 are the two surface treatment agents that were chosen to be used as a pre-dyeing preparatory step of cotton fibres.

Action on the dyeing properties

According to figure 1, it can be observed that the surface treatment of cotton improves its dyeability using red fluorescent pigment.

Results show that when increasing the amount of the two agents ST1 or ST2, the dyeing quality of cotton fabrics increases. Based on table 2, it can be observed that both surface treatment agents are quaternary ammonium compounds. These agents are recognized for their potential to improve the affinity of cotton fibres and dye fastness to several types of dyes. [19]. The surface treatment agents bind to the fibre by replacing a fraction of the hydroxyl groups, which affects the surface chemistry of the material. The substitution will not necessarily make the fibre charge positive, but it will at least make it less negative, which improves the interaction with the red fluorescent pigment and therefore the fixation of the dye on the fibre.

Moreover, based on figure 1, it could be deduced that the best dyeing quality was obtained for 8% of ST1, in fact, a colour yield *K/S* of 3 was reached at this amount.

Action on the dyeing fastness properties of cotton fabrics

The action of using several treatment agents to prepare the cotton fabrics before the dyeing with the red fluorescent pigment was studied in this part. The fastness properties were evaluated for (0-2-4-6-8-10%) of each surface treatment agent. Based on table 3, it could be observed that when the amount of ST1 or ST2 was increased, the dyeing fastness (to wash and to light) was increased too. Furthermore, when the surface treatment agent ST1 was used in amounts equal to or greater than 8%, higher fastness qualities were obtained. Indeed, the modification of cellulosic fibres with cationic agents leads to better fastness properties [20] which could be explained by the increase in the substantivity of dyes for cotton fibres through the introduction of cationic sites.

Analysis of morphological structure of surface-treated cotton fabrics

A scanning electron microscope (SEM) is an instrument that produces images of a sample by scanning the surface with a focused beam of electrons. In this paper, the goal of using this instrument is to detect morphological differences at the surface of untreated and treated cotton fabrics with ST1 and ST2 agents. Based on SEM images described in figure 2 taken at different magnifications, it could be deduced that there is no great morphological difference between the untreated and treated cotton fabrics.

Study of red fluorescent pigment dyeing parameters process

In this part, cotton fabrics were treated with 8% ST1 agent before being dyed at several conditions process.

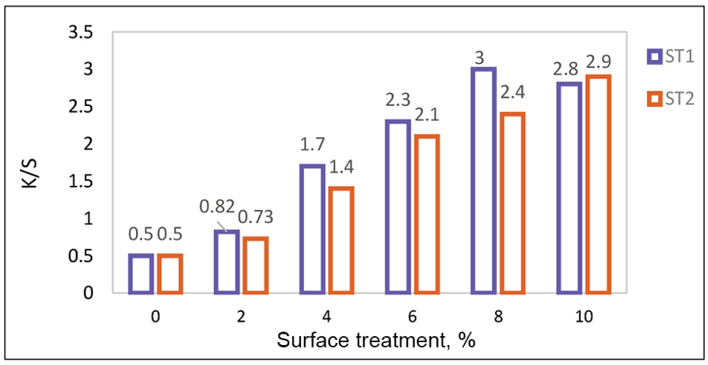

Fig. 1. Surface treatment action on colour yield (*K/S*) of dyed fabrics

Table 3

EFFECT OF SURFACE TREATMENT ON WASHING AND LIGHT FASTNESS PROPERTIES			
ST1 (%)	**Dyeing fastness to washing (ISO 105-C10:2006)**		**Dyeing fastness to light (ISO 105-B02:2013)**
	Colour change	**Colour staining (cotton)**	
0	1	1	1
2	1	1	2
4	1–2	1–2	2
6	2	1–2	3
8	3	2–3	4
10	3	2–3	4
ST2 (%)	**Dyeing fastness to washing (ISO 105-C10:2006)**		**Dyeing fastness to light (ISO 105-B02:2013)**
	Colour change	**Colour staining (cotton)**	
0	1	1	1
2	2	2	2
4	2–3	2	2
6	2	2–3	3
8	3	2–3	3
10	3	2–3	4

Study of dyeing temperature action

The effect of temperature on the dyeability of treated cotton fabrics with fluorescence pigment was conducted at various temperatures (from 40ºC to 80ºC). The colour yield was measured to appreciate the dyeing quality obtained.

Figure 3 illustrates the influence of dyeing temperature on the colour yield (*K/S*). According to the obtained data shown in this figure, the *K/S* values of dyed materials increased gradually with the increase of temperature from 40°C to 50°C. The highest values of *K/S* are observed for dyed cotton fabrics at 50ºC temperature. As the temperature increases, the fibre swelling effects improve, allowing the molecular structure to become more open, allowing dye uptake and thus obtaining a higher *K/S* value. This indicates that this temperature has a greater impact on the dye uptake values for fabrics [21]. Up to 50ºC, the dye uptake results start to decline which could be attributed to dye diffusion from the fibre's core. All centralised sites are occupied. Hence, the optimum value of temperature used may be 50°C, which helps in saving energy and all other dyeing parameters.

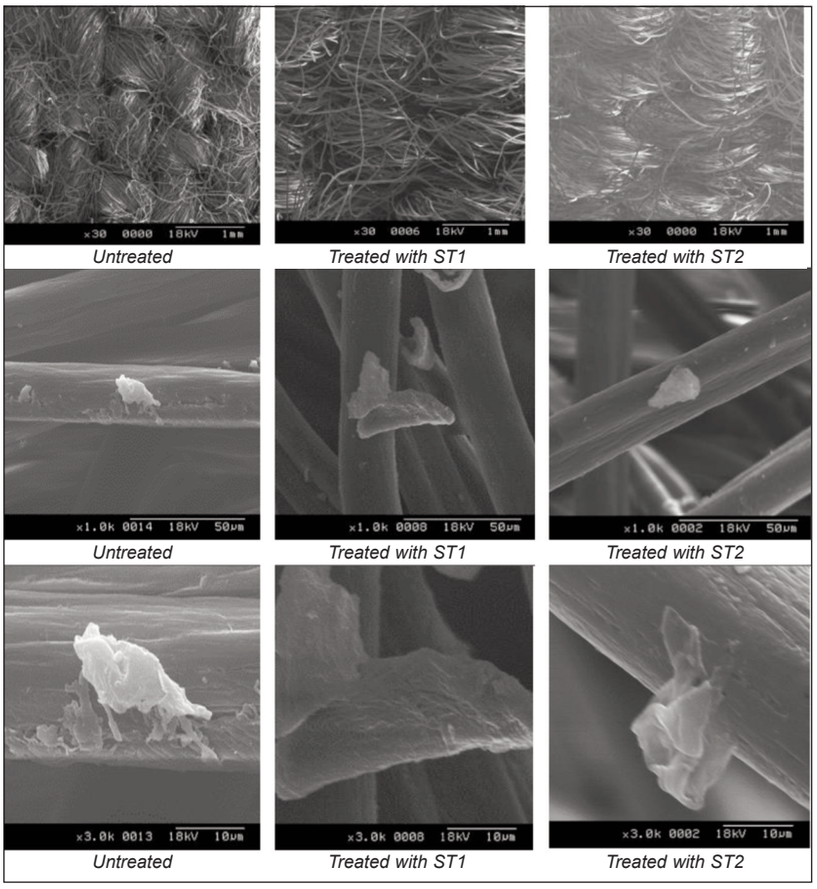

Fig. 2. SEM images at different magnifications of bleached cotton fabrics: untreated, treated with ST1 and treated with ST2 agents

Action on the dyeing fastness properties of dyed fabrics

Both light fastness and Washing fastness are performed to evaluate the colour change of samples dyed in different conditions of temperature. Grades of dyeing fastness are presented in table 4.

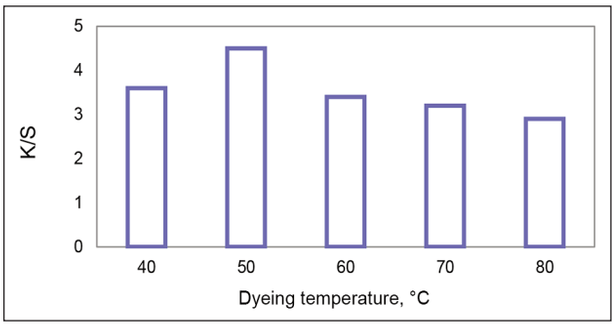

Fig. 3. Dyeing temperature action on colour yield (*K/S*) of dyed fabrics

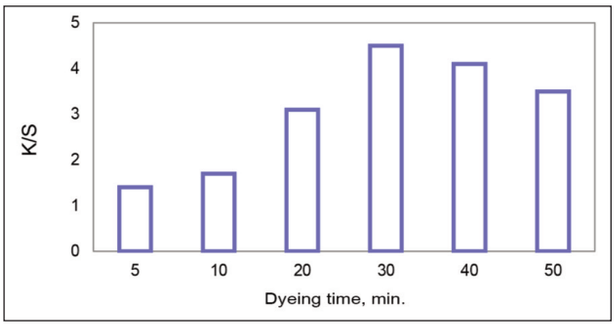

Fig. 4. Dyeing time action on colour yield (K/S) of dyed fabrics

Table 4

ACTION OF DYEING TEMPERATURE ON WASHING AND LIGHT FASTNESS PROPERTIES			
Dyeing temperature (°C)	**Dyeing fastness to washing (ISO 105-C10:2006)**		**Dyeing fastness to light (ISO 105-B02:2013)**
	Colour change	**Colour staining (cotton)**	
40	2–3	3	4
50	3	3–4	5
60	3	4	4
70	2–3	3	4
80	2–3	3	3

The overall dyeing fastness to light results of the samples is good to excellent. The light fastness value decreases with high temperature but remains good, which may be owing to good fixing of the pigment molecules to cotton-treated fibres.

Washing fastness properties are average (between 2 to 4). The minimum range for washing fastness is obtained for 40ºC and 80ºC. It is observed that the fabric sample dyed at 60ºC exhibits both good colour change and staining properties.

The depth of shade decreases as the temperature increases, according to the K/S values measured. As a result, when the dyed samples are exposed to the washing test, dye molecules come out from the fabric surface, lowering the value, and indicating that the washing fastness quality is not excellent at high temperatures.

Study of dyeing time action

Action on the dyeing properties of cotton fabrics

The dyeing results are influenced by the variable duration of the process. The dyeing time effect was studied in the range of 5 min to 50 min, while other parameters were constant. The effect of dyeing time on the colour yield is shown in figure 4.

Obtained values of K/S revealed that duration affected the dyes exhaustion significantly according to figure 4 which showed maximum colour yield at 30 min, whereas at 40 and 50 min decreases.

Action on the dyeing fastness properties of dyed fabrics

The results of the obtained fastness are summarized in table 5.

Obtained values show a better fastness property when decreasing the dyeing time for both washing and light fastness. Indeed, the duration of the dyeing

Table 5

ACTION OF DYEING TIME ON WASHING AND LIGHT FASTNESS PROPERTIES			
Dyeing time (min)	**Dyeing fastness to washing (ISO 105-C10:2006)**		**Dyeing fastness to light (ISO 105-B02:2013)**
	Colour change	**Colour staining (cotton)**	
5	2-3	2–3	2
10	3	2	3
20	3	2	3
30	3–4	3	4
40	4	3–4	4
50	4	4	5

Table 6

ACTION OF DYEING PH ON WASHING AND LIGHT FASTNESS PROPERTIES			
Dyeing pH	**Dyeing fastness to washing (ISO 105-C10:2006)**		**Dyeing fastness to light (ISO 105-B02:2013)**
	Colour change	**Colour staining (cotton)**	
3	3	3–4	3
5	3–4	4	3
6	3–4	4	4
7	4	4	4
8	4	4	5
9	4	4	5

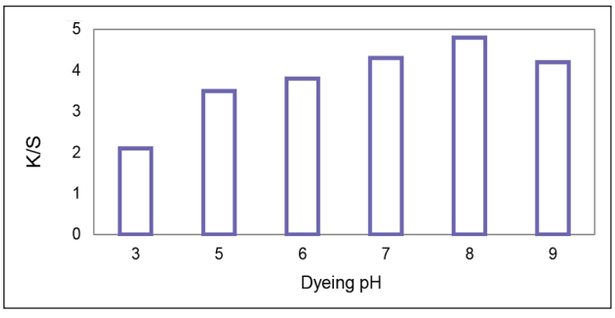

Fig. 5. Dyeing pH action on colour yield (*K/S*) of dyed fabrics

process can affect the uniformity and penetration of the dye into the fabric, which can, in turn, affect the dyeing fastness. The best results for washing and light fastness were obtained at 50 min.

Study of dyeing pH action

Action on the dyeing properties of cotton fabrics

The pH value of the dye bath can affect the dyeing fastness of the dyed textile. The influence of dye bath pH on the dyeability was investigated in the range of (3 to 9) and the obtained results are presented in figure 5.

Based on the results of this figure, it appears that the colour yield increases with increasing pH values, with the greatest result reached at pH 8. The effect of the dye bath pH can be explained by the correlation between the dye structure and surface-treated cotton fabrics. As the pH increased > 8, the *K/S* values of treated cotton decreased. Starting from this value, no additional dye is adsorbed since all of the protonated terminal amino groups attached to the surface of cotton fabric interact with the fluorescent dye [22].

Action on the dyeing fastness properties of dyed fabrics

The *K/S* values of cotton-dyed samples dyed at different pH are given in table 6.

From the tables, it can be seen that the *K/S* values of dyed fabrics are higher in alkaline conditions of pH than in acidic conditions. Wash fastness ratings for staining of adjacent fabrics are good (4) and also those for colour change. Dyeing fastness properties increase from 3 to 4 and 5 values when pH increases. As the pH increases, the dye uptake also increases which is reflected in the obtained results of *K/S*. This enhancement in *K/S* values is associated with the obtention of more solid fixation of fluorescent dye into the fibre structure which results in better fastness properties of washing and light. Also, this may be due to the degradation of the fluorescent dyes at acidic conditions.

CONCLUSIONS

Surface treatment is a very useful method to increase the dye uptake of cotton fabrics toward fluorescent dyes which have revealed a lot of not satisfying results of fastness properties.

Applying a surface treatment agent has two effects: the first improves the dye absorption of cotton fabrics; the other is that it greatly improves the dyeing fastness of the dyed fabrics.

The obtained fastness properties to wash and light of the treated dyed fabrics are good. Thus, the study of dyeing parameters on the colour yield and fastness properties has been developed for cotton fabrics treated with 8% of ST1 surface treatment agent which demonstrated better dyeing performances than ST2 surface treatment agent.

The best-obtained results of colour yield *K/S* and dyeing fastness are conditioned by the used dye parameters as temperature, duration and pH. According to the obtained results, temperature of 50, 30 min and pH of 8 are the best dyeing conditions.

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REFERENCES

[1] Yu, L.P., Zhang, X., Wei, D.X., Wu, Q., Jiang, X.R., Chen., G.Q., *Highly efficient fluorescent material based on rare-earth-modified polyhydroxyalkanoates*, In: Biomacromolecules, 2019, 20, 3233–3241

[2] Khattab, T.A., Rehan, M., Hamouda, T., *Smart textile framework: Photochromic and fluorescent cellulosic fabric printed by strontium aluminate pigment*, In: Carbohydr. Polym 2018, 195, 143–152

[3] Santos, G., Marques, R., Silva, S., Oliveira, J., Castro, P., Pereira, C., Pinheiro, M., *Innovative high-visibility protective clothing development*, In: Textiles, 2021, 1, 405–418

[4] Slama, N., Ben Ticha., M., Smiri, B., Dhaouadi, H., *Exploration of the Fluorescence Property of Acrylic Fibers Dyed with the Residues Extract of Juglans regia Barks*, In: Sustainability, 2022, 14, 19, 12275

[5] Patti, A., Cicala, G., Acierno, D., *Eco-sustainability of the textile production: Waste recovery and current recycling in the composites world,* In: Polymers, 2020, 13, 134

[6] Patti, A., Acierno, D., *Towards the sustainability of the plastic industry through biopolymers: Properties and potential applications to the textiles world*, In: Polymers, 2022, 14, 692

[7] Begum, A., Adnan, A.M., *Study on fluorescent and non-fluorescent pigments dyeing of different fabrics by both exhaust and padding methods*, In: Int. J. Sci. Eng. Res, 2017, 8, 12, 1629–1637

[8] Haddar, W., Baaka, N., Meksi, M., El ksibi, I., Mhenni, M.F., *Optimization of an ecofriendly dyeing process using the wastewater of the olive oil industry as natural dyes for acrylic fibres*, In: J. Clean. Prod, 2014, 66, 546–554

[9] Ben Ticha, M., Haddar, W., Meksi, M., Guesmi, A., Mhenni, MF., *Improving dyeability of modified cotton fabrics by the natural aqueous extract from red cabbage using ultrasonic energy*, In: Carbohydr. Polym, 2016, 154, 287–295

[10] Aminoddin, H., *Improved natural dyeing of cotton by plasma treatment and chitosan coating. Optimization by response surface methodology*, In: Cellulose Chemistry and Technology, 2017, 51, 975–982

[11] Hosseinnezhad, M., Gharanjig, K., Adeel, S., Rouhani, S., Imani, H., Razani, N., *The effect of ultrasound on environmentally extraction and dyeing of wool yarns*, In: Journal of Engineered Fibers and Fabrics, 2022, 17, https://doi.org/10.1177/15589250221104471

[12] Slama, N., Ben Ticha, M., Skhiri, W., Boudokhane, C., Dhaouadi, D., *Development and Optimization of a Sustainable Process Assisted by Microwave Energy to Dye Cellulosic Fabrics by Juglans regia Barks Residues Extract*, Sustainability, 2022, 14, 13, 7534

[13] Khan, A.A., Iqbal, N., Adeel, S., Azeem, M., Batool, F., Bhatti, I.A., *Extraction of natural dye from red calico leaves: Gamma ray assisted improvements in colour strength and fastness properties*, In: Dyes and Pigments, 2014, 103, 50–54

[14] Crews, P.C., Clark, D.J., *Evaluating UV absorbers and antioxidants for topical treatment of upholstery fabrics*, In: Text. Res. J., 1989, 60, 172–179

[15] Shree, Laleitha, G., Ashok, Kumar, A., Prithivraj, G., Vipin, V., Sathish, Kumar, M., *Fluorescent Dyeing in polyester and cotton blended fabrics*, In: Int. Res. J. Eng, Technol, 2020, 7, 5, 1769–1777

[16] Christie, RM., *Fluorescent dyes*, Woodhead Publishing Limited, 2011, 9

[17] Patra, A.K., Bhaumik, S., Kaur, H., *Studies on pigment dyeing of cotton by exhaust method,* In: Indian J. Fibre Text. Res, 2006, 31, 3, 450–459

[18] Kubelka, P., Munck, F., *Ein beitrag zur optik der farbanstriche*, In: Z. Techn. Phys, 1931, 12, 593

[19] Ruberto, G., Renda, A., Daquino, C., Amico, V., Spatafora, C., Tringali, C., De, Tommasi, N., *Polyphenol constituents and antioxidant activity of grape pomace extracts from five Silican red grape cultivars*, In: Food Chem, 2007, 100, 1, 203–210

[20] Baaka, N., Mahfoudhi, A., Haddar, W., Mhenni, M.F, Mighri, Z., *Green dyeing process of modified cotton fibres using natural dyes extracted from Tamarix aphylla (L.) Karst. Leaves*, In: J. Nat. Prod, 2016, 31, 22–31

[21] Debasree, P., Subrata, C.D., Tarikul, I., Md., Abu Bakar, S., Md, Abdullah, A.M., *Effect of Temperature on Dyeing Cotton Knitted Fabrics with Reactive Dyes*, In: J. Sci. Eng. Res, 2017, 4, 12, 388–393

[22] Baaka, N., Haddar, W., Ben Ticha, M., Mhenni, *Eco-friendly dyeing of modified cotton fabrics with grape pomace colorant: Optimization using full factorial design approach*, In: J. Nat. Fibers, 2019, 16, 652–661

Author:

HIND ALGAMDY

Taif University, Turabah University College, Fashion Design and Fabric Department,
P.O. Box 11099, Taif 21944, Saudi Arabia

Corresponding author:

HIND ALGAMDY
e-mail: h.saeed@tu.edu.sa