Egypt. J. Chem. **Vol. 64,** No. 12 pp. 7135 - 7145 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Eco-friendly Dyeing Using Hematoxylin Natural Dye for Pretreated Cotton Fabric to Enhance Its Functional Properties

Manal M.EL-Zawahry[1*], Gehan M. Shokry[2], Hala SH. EL-Khatib[2] and Hager Gamal Rashad[2]

[1] National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Dyeing, Printing, and Intermediate Auxiliaries Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt

[2] Textile Printing, Dyeing and Finishing Department; Faculty of Applied Arts, Helwan University, Giza, 12522, Egypt

Abstract

This study presents an environmentally benign bioactive dyeing and finishing of bio-mordanting cotton fabric via hematoxylin dye extracted from Haematoxylum Campechianum L. medicinal tree. A facile approach to fabricate bio-mordanting cotton fabrics based on gelatine and aloe vera for sustainable green dyeing with hematoxylin dye to achieve a wide range of functional properties and environmental benefits was explored. Optimization of dyeing conditions in terms of salt concentration and pH was conducted. Also, build-up properties and fastness characterization haswere studied in the presence and absence of bio-mordants. The natural functional groups of the dye extract were investigated by FTIR spectral analysis. The results reflect the success of bio-mordant chemical modification and mechanism for dyeing process in the course of increasing K/S values associated with improving colorfastness to washing and light as compared to unmordant fabric. All the dyed bio-mordanting fabrics in this work showed great potential value-adding applications in terms of excellent UV protection, antioxidant activity, and high antibacterial activity. The outcomes of this study deal to have implications to the eco-textile green dyeing for the achievement of healthy and sustainable environment applications.

Keywords: Hematoxylin dye, bio-mordants, cotton fabric, green dyeing, functional finishes

Introduction

Haematoxylum campechianum tree is a species of large flowering tree belong to the family of the Fabaceae and subfamily Caesalpinioideae. This tree is simply known as a bloodwood tree and or logwood tree grown in Mexico and Central America. The heartwood of the tree is an important source for hematoxylin dye which was most widely used as a staining agent in histology and anatomic pathology laboratories. **[1]** Chemically Hematoxylin is a flavonoid compound, which acts as a widely distributed group of plant chemicals and may involve natural coloration. Hematoxylin dye ($C_{16}H_{14}O_6$) C.I. 75290 is colorless but it oxidized rapidly by atmospheric oxygen into the reddish-brown hematein to purple dye ($C_{16}H_{12}O_6$) to form the quinone structure as shown in **Figure 1**. Hematoxylin dye is an active staining ingredient that imparts a strong colored dye lake by complexing with certain metal ions such as iron, aluminum, and chromium salts. It is extensively used in medicine for the treatment of diarrhea, dysentery, kidney disorders, toothache, heart problems, and depression. Also, hematoxylin dye extract is mainly used as a sweetener, in inks, wood, and textile dyeing products. **[1-4]** Previous studies reported and identified the chemical compounds of hematoxylin dye which contain small amounts of brazilein, hematein, flavonoids derivatives, and large amounts of tannins. **[2, 3]** Likewise, the dye extract show or has potential antimicrobial, antioxidant, anti-inflammatory, antifungal, and anticancer activities. **[1, 2, 5]**

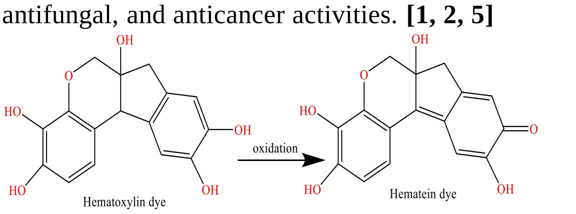


Figure 1: Chemical mechanism of oxidation process from hematoxylin to hematein

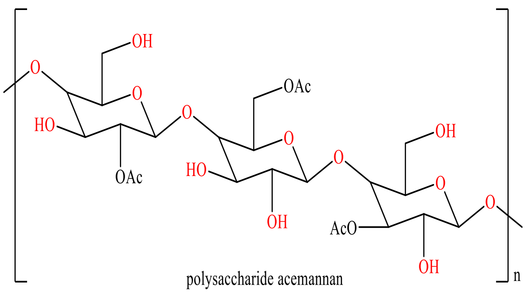
Nowadays, due to the rapid development of people's

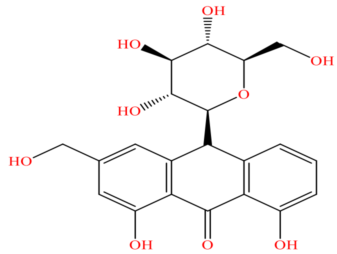
*Corresponding author e-mail: manalzawahry@yahoo.co.uk.; (Manal M.EL-Zawahry).
Receive Date: 23 June 2021, Accept Date: 04 July 2021
DOI: 10.21608/EJCHEM.2021.82158.4049

awareness for natural products of environment-friendly colored textile fabrics with natural dyes was a necessary obligation to integrate the functional properties (antimicrobial activity, UV protection, antioxidant, anti-inflammatory, and wound healing properties) to the dyed fabric. This simultaneous dyeing and finishing process was needed for the production of sustainable value-added technical textiles to maintain ecological balance and a healthy environment. **[6-8]**

Meanwhile, natural cotton fabrics have a low affinity for many of the natural dyes, to avoid this problem cationization of cotton fabric with cationic agents including quaternary ammonium salt, polyethyleneimine, chitosan, polydopamine, and bovine serum albumin which has been reported previously was used to increase the dyeability and functional properties of the fabric. **[9-19]** Additionally, the rapid development of bio-mordants shows a wide unfold interest in the dyeing and printing of textile fabrics with natural colorants and thickeners considering their higher biodegradability and better compatibility associated with low toxicity comparing t use synthetic ones. **[20, 21]** Also, the utilization of bio-mordant or their combination with metallic mordant were studied to build up the color properties and characterization. Bio-mordants including wood ash, tannin, lemon, aloe vera, chlorophyll, … etc. **[22-24]**

Aloe Vera bio-mordant gel consists of 99% water and the remaining 1% solid compounds contain vitamins, minerals, polysaccharides, enzymes, phenolic compounds, and organic acids. Among the bioactive ingredients, polysaccharide acemannan and barbaloin is the main functional phenolic component. Aloe Vera simultaneous mordanting shows an enhancement in both washing fastness and color strength values and they possess a high potential of being used as bio-mordants if it was used or applied under the respective mordanting technique. **[22]** It is noteworthy that some research showed that aloe vera bio-mordant exhibits antimicrobial, antifungal, and antiviral properties. **[22, 25-27]** The structure of barbaloin and acemannan was shown in **Figure 2**.





Barbaloin: 1,8-Dihydroxy-10(beta-D-glucopyranosyl)-3-(hydroxymethyl)-9 (10H)-Anthracenone

Figure 2: Main chemical structure of aloe vera extract bio-mordant

Gelatin is a high molecular weight polypeptide chain composed of primary, secondary and tertiary helicoid structures and has good biocompatibility and biodegradability. **[28]** Gelatin has been recently shown great potential as an excellent carrier or matrix to host bioactive compounds such as carvacrol, **[29]** tea polyphenols, **[30]** pomegranate seed juice -product, and also enhanced antioxidant and antimicrobial functionalities. **[31]** In general, when the bio-mordants or natural dye was applied on fabric, the surface, color, and fastness properties changes and the bio-mordanting dyed fabric with natural dyes have gained considerable attention in the field of medical and health care textiles. **[11, 32]**

The present study highlights a facile green method for the fabrication of the bio-mordanting cotton fabric with aloe vera and gelatin, which will serve as effective and environmentally friendly bio-mordanting finishing agents. In this study, we deal with dyeing bio-mordanting cotton fabrics with the aqueous extract of hematoxylin dye to gain a huge potential application in various fields of medicine and the science economy. FTIR analysis of the dye aqueous extract solution was analyzed. The unmordant and bio-mordanting dyed fabric were characterized in terms of color strength (K/S) value, color properties as well as to build up the fastness properties. The UV protection ability, antimicrobial, antifungal, and antioxidant activities of the dyed fabrics were also evaluated.

Experimental

Materials

Misr Spinning and Weaving Co., Mehala El–Kobra, Egypt supplied us with mill-scoured and bleached cotton fabric (200g/m^2). Gelatine, citric acid, sodium hypophosphite (SHP), sodium chloride, and others were all laboratory-grade chemicals. The cotton fabric was treated with a solution containing 3 g/L nonionic detergent (Hostapal CV, Clariant) and 5 g/L sodium carbonate at liquor ratio (L.R.) 1:50 for 4 hr at 100°C. Finally, thoroughly rinsed with tap water and dried at room temperature.

Natural dye source: Chips of the heartwood tree Haematoxylum campechianum L. tree was purchased from Wild Colors Company, UK. Natural mordants: Aloe vera leaves from Orman garden.

Methods

1.1.1. Crushing of Haematoxylum campechianum L. chips

The chips of the heartwood tree were electrically crushed with a grinder into a fine powder and used as a natural dye for the coloration of cotton fabric.

1.1.2. The extraction method used for Hematoxylin dye

10 g of dye powder was boiled in 100 ml distilled water associated with vigorous stirring for 1 hr. After boiling, the mixture was filtered through a nylon mesh fabric.

1.1.3. Extraction of aloe vera gel

Fresh leaves of aloe vera were collected then, washed thoroughly with rinsed water. The outer green surface of the leave was peeled off and the gel was taken out by spoon and blended using a blender to the semi-liquid solution followed by boiling for 30 min and finally filtered to obtain the red solution. **[33]**

1.1.4. Bio-mordanting of cotton fabric

Mordanting treatment of cotton fabric with the four designed bio-mordant of aloe vera and gelatine in one or two-bath treatment process was conducted after the fabric was pre-treated with citric acid as a crosslinking agent in presence of SHP at 2:1g/L associated with good shaking for 15 min at room temperature. Then squeezed and the fabric was dried in thermofixation at 100ºC for 3 min. **[34]** Finally, the crosslinked pre-treated cotton fabrics were immersed in the bio-mordanting solutions via the following procedures:

1.1.4.1. Bio-mordanting cotton fabric with aloe vera (BMA)

The crosslinked pre-treated cotton fabric was immersed in aloe vera red solution for a period with good shaking followed by pad-dry-cure methods according to the previous study but with little change. After padding, the fabric was dried at 150ºC for 2 min and cured at 200ºC for 2 min. **[33]**

1.1.4.2. Bio-mordanting cotton fabric with gelatine (BMG)

The crosslinked pre-treated cotton fabric was treated with 2% w/v gelatine by the pad-curing method. [11]

1.1.4.3. Bio-mordanting cotton fabric with aloe vera and gelatine (BMA+G)

The pre-treated cotton fabric BMA was immersed in 2% gelatine followed by the pad-curing method at 120ºC for 5 min to form BMA+G fabric.

1.1.4.4. Bio-mordanting cotton fabric with blended aloe vera and gelatin (BMAG)

Gelatine solution stirred vigorously under hot plate magnetic stirrer at room temperature followed by the gradual addition of aloe vera extract solution for 30 min in 1:1 ratio. The required amounts of gelatine and aloe vera extract solution were applied to the pre-treated crosslinked fabric by the pad-dry-cure method. After padding, the fabric was cured at 120ºC for 5 min. **[32, 33]**

1.1.5. Dyeing process

Dyeing unmordant and bio-mordanting cotton fabrics were carried out with L.R. 1:30 of the aqueous dye extract, at different pH values (3-11) after the addition of salt (0-40 g/L) at 100ºC for 1 h. After completion of the dyeing process, soaping was done with 3 g/L non-ionic detergents at 60ºC for 30 min. Finally, thoroughly rinsed with water and air-dried.

Measurements

1.1.6. Color strength and color value

K/S values of all the dyed fabrics were measured at 455 nm using Ultra Scan Pro, Hunter Lab spectrophotometer, USA as well as color value (L*, a*, and b*) also recorded in the same spectrophotometer.

1.1.7. Colorfastness testing

Colorfastness to washing, rubbing, and light of unmordant and bio-mordanting cotton fabrics dyed with hematoxylin aqueous extract was assessed according to standard methods. **[35-40]**

1.1.8. The UV protection factor (UPF)

Australian/New Zealand Standard method AS/NZ S4399:1996 by using JASCO U-750 spectrophotometer as described in AATCC Test method 183:2010 was used for UPF measurements of the unmordant and bio-mordanting dyed cotton fabrics using hematoxylin dye extract in the range of 290-400nm. The final results are the average values of three measurements for each fabric sample. **[41-43]**

1.1.9. Evaluation of antibacterial and antifungal properties

The evaluation of antibacterial and antifungal activity for all the undyed and dyed fabric samples was quantitatively measured by the percentage reduction method. **[44]** Four selected microorganisms using diffusion assay against *S. aureus*, *B. subtilis* as a gram +ve bacteria and *E. Coli*, *P. Aeruginosa* as a gram –ve bacteria as well as *C. Albicans* as a fungal activity. The results are the average values of three measurements for each fabric sample.

1.1.10. *Evaluation of antioxidant properties*

The antioxidant activity for both the undyed and bio-mordanting dyed cotton fabrics was assessed via radical scavenging ability DPPH assay. **[45]**

1.1.11. *ATR- FTIR spectrum*

The functional groups present in hematoxylin aqueous extracted dye solution were analyzed using ATR-FTIR spectra measured on a high-resolution JASCO FTIR-4700 spectrophotometer (JASCO Analytical Instrument, Easton, USA). The spectra were collected with a wavenumber range of 4000–500 cm^{-1}using transmission mode (T %).

Results and Discussion

Our interest work is focused on bio-mordanting cotton fabric with four fabricated or designed bio-mordant based on aloe vera and gelatine. These bio-mordant approaches occur independently in combination with each other with different methods successfully in one and two steps. The crosslinked pre-treated cotton fabric with citric acid in presence of a catalyst (SHP) was treated with aloe vera extract to functionalize the fabric surface with more hydroxyl groups and increase the concentration of gelatine as a masked layer on the fabric surface. Moreover, gelatine in both methods would render the fabric surface more cationic in the acid medium. Therefore, it ameliorated the green dyeing system of cotton fabric with natural hematoxylin dye extracted from the Haematoxylum Campechianum L. plant tree. Additionally, the bio-mordanting dyed fabric enhanced or importing multifunctional finishing properties to the fabric based on the type of bio-mordanting fabric used.

The mechanism of fabrication of the four bio-mordanting cotton fabrics BMA, BMG, BMA+G and BMAG using green chemistry was as follow:

The cotton fabric was pre-treated first with citric acid in presence of a catalyst as a crosslinked agent in which the two carboxylic groups of citric acid linked or interact by covalent bonds with the cellulose hydroxyl groups of cotton fabric (see **Figure 3**).

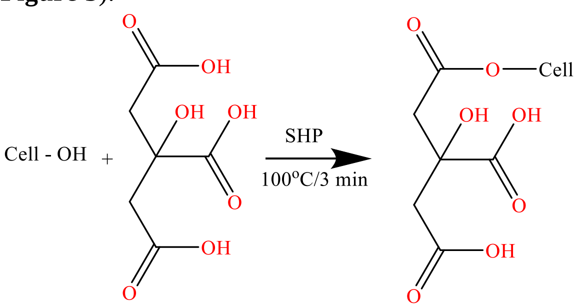


Figure 3: pre-treated mechanism of cotton citric acid in presence of the catalyst

In the case of treating the pre-treated crosslinked cotton fabric with aloe vera extract (BMA) fabric, hence its active ingredients barbaloin and polysaccharides containing aplenty of -OH in their chemical structure as strong hydrogen bonds were formed between the -OH groups of the crosslinked cellulose backbone chain, carboxylic groups of citric acid and polyphenolic -OH groups of aloe vera extract. Further, the reaction was fixed by the curing process (see **Figure 4**). **[46]**

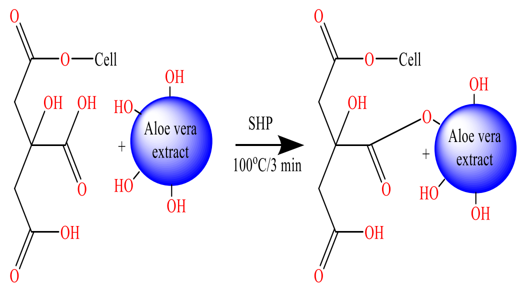


Figure 4: treatment mechanism of pre-treated crosslinked cotton fabric with aloe vera extract (BMA)

Based on gelatine possess polyamines on their surfaces which form an amide bond with carboxylic and-OH groups molecules, due to that it contributes or participates in the design of the other three bio-mordanting cotton fabrics isolated and conjugated with aloe vera extract and act as a natural cationic agent. On the other hand, when the cotton fabric was pre-treated with citric acid in presence of the catalyst, the carboxylic groups of citric acid linked or interact by a covalent bond with the hydroxyl groups crosslinked with gelatine to fabricate BMG (see **Figure 5**). **[28, 47]**

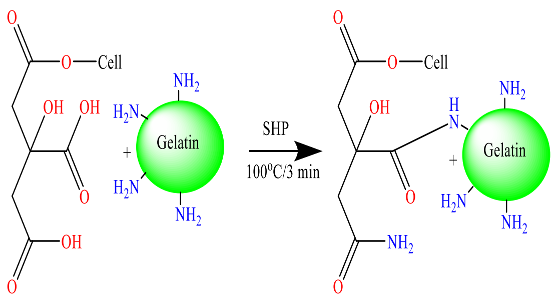


Figure 5: treatment mechanism of pre-treated crosslinked cotton fabric with gelatine extract (BMG)

Otherwise, the bio-mordant pre-treated crosslinked cotton fabric with aloe vera extract was treated with gelatine to form BMA+G fabric (see **Figure 6**).

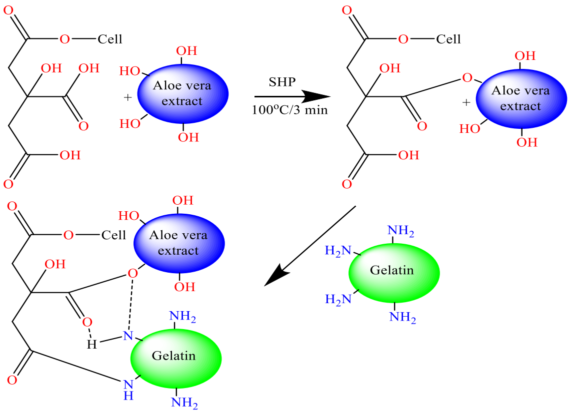


Figure 6: treatment mechanism of pre-treated crosslinked cotton fabric with aloe vera extract then with gelatine (BMA+G)

In the case of pre-treated crosslinked cotton fabric with a combination or a blend of 1:1 aloe vera extract and gelatine, the bio-mordant BMAG cotton fabric was obtained via nucleophilic substitution reaction. **[28]**

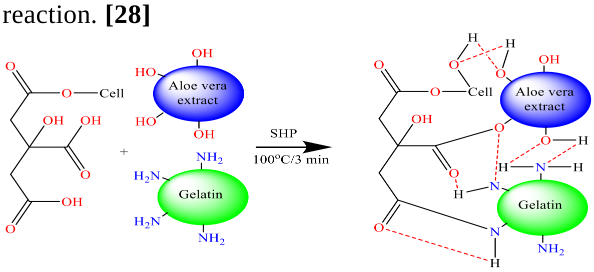


Figure 7: treatment mechanism of pre-treated crosslinked cotton fabric with aloe vera extract and gelatine min one step (BMAG)

The blank and the four bio-mordanting cotton fabric BMA, BMG, BMA+G, BMAG were dyed with the hematoxylin dye to achieve optimal color reproducibility as well as maximum color yield as K/S values of hematoxylin dyed cotton fabric and impart performance multifunctional properties, the addition of electrolyte and the effect of dyeing bath pH have been studied.

Effect of Electrolyte addition

Figure 8 represents the effect of electrolyte addition on the color strength of the blank and the four bio-mordanted fabric. It was observed from the figure that color strength efficiency (K/S) values increased as the electrolyte concentration increased from 0-40 g/L for all dyed fabric. Considering, this result may be attributed to gradually adding electrolytes reduce the solubility of the hydroxyl anionic group of the hematein dye molecule, prevailing the energy barrier against the negative charge of the cellulosic fabric based on cellulose dyeing theory. [48] In the case of dyeing blank cotton fabric with hematein dye, rapid adsorption occurs and the dye molecules remain agglomerated on the fiber surface and stain it associated with a slight increase in K/S values. Therefore, the ionic bond cannot be formed and the dyeability, as well as colorfastness, will certainly be poor. However, dyeing bio-mordanting fabrics with hematein dye K/S values significantly increased as the concentration of salt increased and the staining disappeared completely. In general, dyeing cotton fabric with hematin dye confirm the need for a high concentration of electrolyte for the dyeing process in a homogeneity hue. [49]

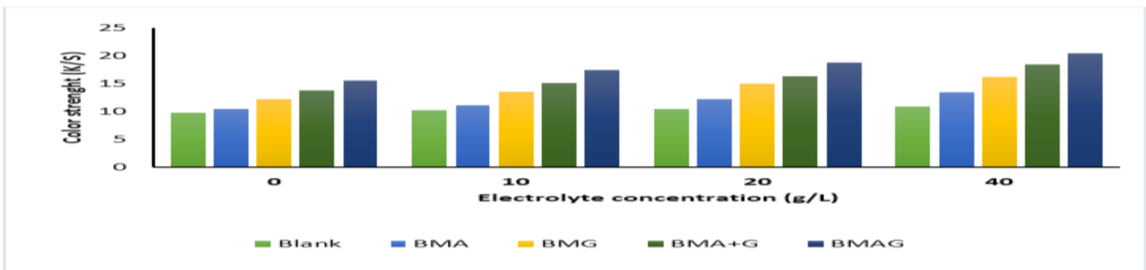


Figure 8: Effect of electrolyte addition on the color strength of hematoxylin dyed fabric Dyeing condition: L.R 1:30, pH 4.56, at 100 ºC for 60 min

Effect of dye bath pH

The effect of dyeing bath pH on the color strength values of hematoxylin dye on the blank and the four bio-mordanting cotton fabrics were shown in Figure 9. The results indicate that the highest color strength (K/S) value of the dyed fabric was observed at pH 4.56. However, the strongly acidic and alkaline pH shows the lowest color efficiency K/S value due to the instability of hematein dye is strongly acidic or basic medium. **[50]** On the other hand, the higher K/S values were observed by using bio-mordanting cotton fabric BMA+G and BMAG at pH 4.56 due to increasing the ionic interactions i.e. attraction forces between the negatively charged hydroxyl polyphenolic groups of the dye molecules and the protonated bio-mordanted cotton fabric. **[11]**

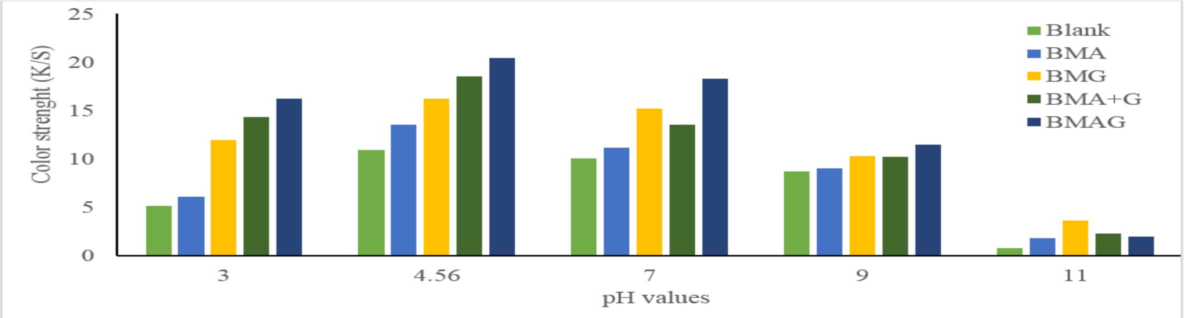


Figure 9: Effect of dye bath pH on the color strength of hematoxylin dyed fabrics Dyeing conditions: L.R 1:30, 40g/L NaCl at 100 ºC for 60 min

FTIR analysis of hematoxylin dye

Hematoxylin extracted dye was screened for the functional group identification using FTIR spectral analysis. **Figure 10** shows the FTIR spectrum of hematoxylin extracted dye in an aqueous solution. The spectrum showed characteristic absorption bands at 3335.59 cm^{-1} assigned to phenolic -OH stretching vibration of aromatic rings of hematein, tannin, and flavonoid components. The peak appears at 1637.61 cm^{-1} belongs to –C=O stretching vibration of a ketonic group of hematein, flavonoid, and their derivatives, while peaks appeared at 1598.57 and 1503.81 cm^{-1} was revered to -C-C- aromatic stretching vibration. In addition, a peak at 1367.84 cm^{-1} was assigned to -C-O stretching vibration of phenolic groups. The bands between 1249.76 and 1026.79 cm^{-1} erewere attributed to -C-O-C stretching vibration of phenol or ester groups. The peak at 1173.74 cm^{-1} assigned to a bond between aromatic ring and oxygen. The small peaks appear around 832.62-634.99 cm^{-1} belong to the stretching vibration of C-H groups of benzene ring present in the aromatic system. Furthermore, the presence of sharp peaks in the range of 1503.81 – 605.50 cm^{-1} correspond to hematein and other colorants components such as a derivative of brazilein, tannins, flavonoids, and its derivatives present in hematoxylin dye extract. **[51]**

Effect of bio-mordanting on color coordinates

The color values measured in terms of L*, a*, b*, and K/S values of blank and bio-mordanting pretreated cotton fabric dyed with hematoxylin natural dye extracted from logwood chips are shown in **Table 1**. As it can be seen from the table that the blank and four bio-mordanting dyed fabrics show a positive value of a* and b* which indicates that the color was a shift towards the red-yellow coordinate zone. However, the higher K/S value was achieved in the case of bio-mordanting cotton fabric BMAG as a result of providing efficient active sides in the form of – NH_2 of gelatine and OH groups of aloe vera extract bio-mordanting fabric- dye interaction. The result depends on the ionic interaction between the phenoxide ions of hematein, flavonoids, and phenols present in the dye molecules and $NH^{+\ 3}$ protonated amino groups of gelatine as well as van der Waals forces between hydrophobic parts of dye anion and hydrophobic parts of BMAG cotton fabric and hydrogen bonding. Therefore, these interactions increase the amount of dye onto the BMAG cotton fabric as depicted by higher K/S values and lower L* value compared to the other bio-mordants and blank fabrics.

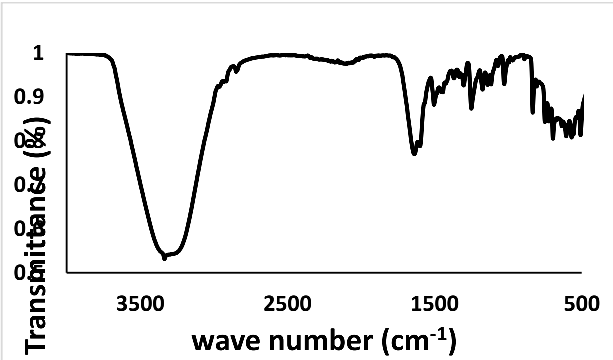


Figure 10: FTIR spectrum of hematoxylin dye extract

Table 1: Color coordinates of cotton fabric dyed with Hematoxylin dye.

Bio-mordant Samples	L*	a*	b*	K/S
Blank	29.3	5.92	5.74	10.89
BMA	30.74	6.87	11.68	13.50
BMG	29.05	9.09	14.98	16.25
BMA+G	27.69	7.69	12.68	18.50
BMAG	21.88	5.32	5.58	20.46

Color fastness properties

The fastness properties rating of bio-mordanting cotton fabrics dyed with hematoxylin dye is reported in **Table 2**. The washing fastness revealed that staining on cotton range from good to very good and staining on wool also range from good to very good. However, the dyed bio-mordanting cotton fabrics show an improvement in washing fastness than the unmordant fabric (Blank). In addition, it was observed that dry rubbing fastness was better than wet rubbing fastness ratings of all the dyed samples. Otherwise, the light fastness properties show an excellent rating of all the dyed samples as a result of increasing chemicals interactions and Van der Waal forces between the hematoxylin coloring component and the bio- mordanting fabrics.

Table 2: Colorfastness to washing, rubbing, and light of bio-mordanting cotton fabric dyed with hematoxylin dye

Bio – mordanting samples	Washing fastness			Rubbing fastness		Lightfastness
	CC	SC	SW	Dry	Wet	
Blank	3-4	3-4	2	3-4	2-3	6
BMA	4	4	3-4	4	2-3	6
BMG	4	4-5	4	4	3-4	6
BMA+G	4	4-5	4	4	3-4	6
BMAG	4	4-5	4	4	3-4	6

CC: change in color, SC: staining on cotton, and SW: staining on wool

Washing and rubbing evaluation on the gray scale: 1, poor; 2, fair ;3, good; 4, very good, and 5, excellent. Light fastness evaluation on blue scale : 1,very poor ;2,poor ; 3, fair ; 4, moderate ; 5, good ; 6, very good and 7, excellent.

Ultraviolet protection

UPF rating for both undyed and dyed bio-mordanting fabric samples was presented in **Table 3**. From **Table 3,** it was observed that the undyed blank and bio-mordanting fabrics show lower UPF values as well as UV protection ability. However, the bio-mordanting dyed fabrics exhibited a higher UV protection performance than the undyed counterparts associated with a significantly increased UPF value. This result regardless of the type of bio-mordanting method used and K/S values. In general, the higher the fabric color shade depth (K/S) the higher UPF values. Meanwhile, this result may be attributed to the absorption of more UV radiations in the case of dark shades as seen in BMA+G and BMAG as the K/S values increased from 18.50 to 20.46. Therefore, due to the presence of polyphenols in hematoxylin aqueous extracted dyes that may help to block the UV rays and flavonoids can absorb UV rays and protect the skin from damage and cancer. Moreover, it was reported that the free radical scavenging capabilities of polyphenol and flavonoids present in the hematoxylin dye extract may be responsible for imparting UV blocking property of the dyed bio-mordant fabric and show excellent UV protection category. This result mean that the combination between bio-mordant aloe vera and gelatine treated fabric shows the dark brown shade after dyeing and helps to absorb more UV rays and protect the human skin. **[6, 52]**

Table 3: Ultraviolet protection of undyed and dyed cotton fabrics with hematoxylin dye.

Bio-mordant samples	UVA (315-400nm)	UVB (290-315nm)	UPF (290-400nm)	Protection category
undyed fabric				
Blank	59.1	61.4	1.5	No protection
BMA	20.8	19.50	5	No protection
BMG	28.9	26.9	3.50	No protection
BMA+G	18.8	17.4	5.6	No protection
BMAG	23.6	22.1	4.4	No protection
Dyed fabric				
Blank	4.9	5	19.7	poor
BMA	2.3	2.3	43.2	Very good
BMG	2.8	2.8	35.0	Very good
BMA+G	2.1	2.1	55.2	Excellent
BMAG	2.5	2.4	46.1	Excellent

Antibacterial and antifungal activity

Table 4 shows the bacterial percent reduction assay of some pathogenic microorganisms selected on undyed and dyed blank cotton fabrics as well as bio-mordanting cotton fabrics. The results indicated that the undyed blank and BMG cotton fabric showed no activity against all the tested microorganisms and fungi. Also, the bacteria reduction present of undyed cotton fabrics bio-mordanting with BMAG was higher than BMA+G cotton fabric. The reason for these results may be attributed to that when cotton fabric was treated first with aloe vera antimicrobial agent, then treated with gelatin which forms a coating layer on the fabric surface less antimicrobial functional groups were created. In contrast, in the case of BMAG fabric, the gelatin blended with aloe vera extract in a onestep is more effective and more antimicrobial agents. This result may be due to the presence of more functional antimicrobial agent groups on the fabric surface associated with synergistic effect and illustrate more biocidal activity than BMA+G fabrics. **[53]** Conversely, the antifungal activity of BMA+G was higher than BMAG against *C. Albicans* reached 56.01% and 47.52% receptivity. Among all the bio-mordanting fabrics used in this study, BMA+G dyed fabric with hematoxylin dye was greatest against *S. aureus* 94.12% followed by B. *subtilis* then *P. aeruginosa*. Thus, BMAG is effective against gram-positive bacteria and gram-negative bacteria. Meanwhile, BMA+G and BMAG are more effective to gram-positive bacteria than gram-negative bacteria and show maximum resistance against both of them. This result may be due to the higher K/S values that indicate the higher dye uptake of hematoxylin dye who is leading to the presence of hematein, tannin, and isoflavonoid on the fabric surface. As a result, a greater number of antimicrobial functional groups present in the dyed cotton fabric attack the cell walls of bacteria and inhibit their growth. **[31, 32, 49]**

Table 4: Antimicrobial and antifungal activity of undyed and dyed cotton fabrics with hematoxylin dye

Bio-mordant samples	Reduction %				
	S. aureus	B. subtilis	E. coli	P. aeruginosa	C.albicans
undyed fabric					
Blank	0	0	0	0	0
BMA	29.25	34.00	20.81	15.92	43.48
BMG	0	0	0	0	0
BMA+G	37.21	54.31	31.43	33.47	56.01
BMAG	70.21	81.52	75.31	91.32	47.52
Dyed fabric					
Blank	39.00	53.19	46.81	54.04	31.67
BMA	41.50	57.45	55.31	92.8	61.65
BMG	59.24	68.12	56.71	31.50	62.26
BMA+G	94.12	79.76	62.19	71.90	71.96
BMAG	88.59	78.89	61.56	64.15	48.71

Antioxidant activity

The antioxidant properties of undyed and dyed bio-mordanting cotton fabrics with hematoxylin dye were displayed in **Figure 11**. The undyed bio-mordanting cotton fabrics showed very low antioxidant activity, while the dyed fabrics showed a significant increase in their antioxidant activity. The results of the high antioxidant potential of dyed bio-mordanting cotton fabrics may be attributed to the presence of various bioactive compounds such as brazilein, hematein, flavonoids derivatives, and a large number of tannins present in the hematoxylin dye. **[2, 3]** Also, the increased radical scavenging activity of the dyed BMG fabric (85.22%) as a result of increasing the active cationic side on the fabric surface which increase the yield of hematoxylin dye uptake ingredient. **[11, 54]** Additionally, the decrease in the antioxidant properties of BMAG dyed fabric maybe because aloe vera extracting bioactive compounds occupied some of the amino acids of gelatin functional groups as well as crosslinked cellulose carboxylic groups. Meanwhile, the number of gelatin functional groups decreased followed by loss of free –OH phenolic groups of dye molecules leading to the reduction in its scavenging ability **/**15**/**. In general, the result suggests that hematoxylin dye bioactive constituents present in the aqueous extract play an important role as a strong antioxidant property that can be used to develop bioactive textile fabric for use in the biomedical textile sector. **[55].**

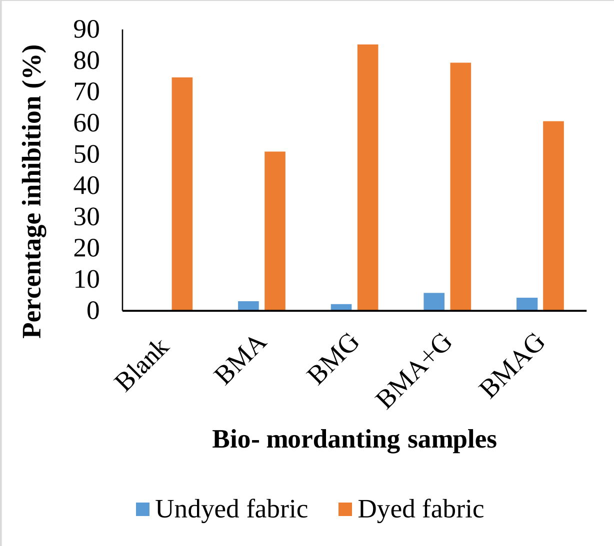


Figure 11: Antioxidant activity of undyed and dyed bio-mordanting cotton fabrics with hematoxylin dye Dyeing conditions: L.R 1:30, 40g/L NaCl, pH 4.56 at 100 ºC for 60 min.

Conclusion

This research highlight a facile green method for dyeing bio-mordanted cotton fabric based on aloe vera and gelatin with hematoxylin dye aqueous extract to furnish and gain value-added properties dyed fabric. All the bio-mordants dyed fabric produces reddish-brown shade without staining than the unmordant dyed fabric. Moreover, the dyebath effluent will be saved for disposal. The presence of bioactive compounds of the dye extract was confirmed by the FTIR spectrum. The fastness properties of the dyed bio-mordanting fabrics to washing and light show an enhancement as compared to the unmordant dyed fabric. Additionally, bio-mordanting cotton fabrics BMA, BMG, BMA+G and BMAG dyed with hematoxylin dye produce appreciably improvement in ultraviolet protection factor (UPF), as well as BMA+G fabric, possess maximum resistance against gram-positive bacteria (94.12 %) *S. aureus* and *C. Albicans* antifungal (71.96 %). In addition, BMAG dyed fabric shows a maximum reduction percent (88.59 %) against gram-positive bacteria *S. aureus*. All the dyed fabrics exhibited higher antioxidant behaviors ranging from good, very good to excellent inhibition percent.

The outcomes of this work provide a potential use of hematoxylin dye aqueous extract as value-added sustainable color for the eco-textile dyeing industry where there is a great challenge by natural dye through the production for medical textile and greener textile coloration.

Abbreviation
Sodium hypophosphite (SHP)
Liquor ratio (L.R)
Bio-mordanting cotton fabric with aloe vera (BMA)
Bio-mordanting cotton fabric with gelatin (BMG)
Bio-mordanting cotton fabric with aloe vera and gelatin (BMA+G)
Bio-mordanting cotton fabric with blended aloe vera and gelatin (BMAG)
UV protection factor (UPF)

References

[1] C. Ortiz-Hidalgo, S. Pina-Oviedo, Hematoxylin: Mesoamerica's Gift to Histopathology. Palo de Campeche (Logwood Tree), Pirates' Most Desired Treasure, and Irreplaceable Tissue Stain, 27(1) (2019) 4-14.

[2] A. Escobar-Ramos, C.E. Lobato-García, A. Zamilpa, A. Gómez-Rivera, J. Tortoriello, M. González-Cortazar, Homoisoflavonoids and Chalcones Isolated from Haematoxylum campechianum L., with Spasmolytic Activity, Molecules 22(9) (2017).

[3] M. Bronzato, A. Zoleo, B. Biondi, S.A. Centeno, An insight into the metal coordination and spectroscopic properties of artistic Fe and Fe/Cu logwood inks, Spectrochim. Acta Part A: Molec. Biomolec. Spectro. 153 (2016) 522-529.

[4] C. Canevari, M. Delorenzi, C. Invernizzi, M. Licchelli, M. Malagodi, T. Rovetta, M. Weththimuni, Chemical characterization of wood samples colored with iron inks: insights into the ancient techniques of wood coloring, Wood Sci. Technol. 50 (2016).

[5] E.G. Jung, K.I. Han, H.J. Kwon, B.B. Patnaik, W.J. Kim, G.M. Hur, K.W. Nam, M.D. Han, Anti-inflammatory activity of sappanchalcone isolated from Caesalpinia sappan L. in a collagen-induced arthritis mouse model, Arch. Pharm. Res. 38(6) (2015) 973-83.

[6] S. Jose, P. Pandit, R. Pandey, Chickpea husk – A potential agro waste for coloration and functional finishing of textiles, Industrial Crops and Products 142 (2019) 111833.

[7] L.J. Rather, c.Q.L. Mohd Shabbir, F. Mohammadc, Coloration, UV Protective, and Antioxidant Finishing of Wool Fabric Via Natural Dye Extracts: Cleaner Production of Bioactive Textiles, (2019).

[8] A. Sharma, S. Kadam, P. Mathur, S. Islam, J. Sheikh, Re-using henna natural dyeing wastewater for coloration and multifunctional finishing of linen fabric, Sustainable Chemistry and Pharmacy 11 (2019) 17-22.

[9] M.M. Kamel, M.M. El Zawahry, N.S.E. Ahmed, F. Abdelghaffar, Ultrasonic dyeing of cationized cotton fabric with natural dye. Part 2: Cationization of cotton using Quat 188, Industrial Crops and Products 34(3) (2011) 1410-1417.

[10] S. Kesornsit, P. Jitjankarn, W. Sajomsang, P. Gonil, J.B. Bremner, M. Chairat, Polydopamine-coated silk yarn for improving the light fastness of natural dyes, 135(2) (2019) 143-151.

[11] R. M El-Shishtawy, N. Ahmed, S. Nassar, Novel green coloration of cotton fabric. Part I: Bio-mordanting and dyeing characteristics of cotton fabrics with madder, alkanet, rhubarb and curcumin natural dyes, Egy. J. Chem. 63(5) (2020) 6-8.

[12] S. Rattanaphani, M. Chairat, J.B. Bremner, V. Rattanaphani, An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan, Dyes Pigments 72(1) (2007) 88-96.

[13] S. Janhom, R. Watanesk, S. Watanesk, P. Griffiths, o.-a. Arquero, W. Naksata, Comparative study of lac dye adsorption on cotton fibre surface modified by synthetic and natural polymers, Dyes Pigments 71 (2006) 188–193.

[14] S.A. Ebrahim, A.G. Hassabo, H. Othman, Natural Thickener in Textile Printing (A Mini Review), Journal of Textiles, Coloration and Polymer Science 18(1) (2021) 55-64.

[15] M.L. Yousef, A.G. Hassabo, Environmentally Friendly Inorganic Materials for Anti-flammable Cotton Fabrics, Journal of Textiles, Coloration and Polymer Science 18(2) (2021) 97-110.

[16] M.Y. Kamel, A.G. Hassabo, Anti-microbial finishing for natural textile fabrics, Journal of Textiles, Coloration and Polymer Science 18(2) (2021) 83-95.

[17] A.L. Mohamed, A.G. Hassabo, Cellulosic fabric treated with hyperbranched polyethyleneimine derivatives for improving antibacterial, dyeing, pH and thermo-responsive performance, Int. J. Biol. Macromol. 170 (2021) 479-489.

[18] M. Diaa, A.G. Hassabo, Self-Cleaning Properties of Cellulosic Fabrics (A Review), Biointerface Research in Applied Chemistry 12(2) (2022) 1847 - 1855.

[19] D.M. Hamdy, A.G. Hassabo, pH and Temperature Thermosensitive for Modification of Cotton Fabric (A Review) Biointerface Research in Applied Chemistry 12(2) (2022) 2216 -2228.

[20] D.M. Hamdy, A.G. Hassabo, H. Othman, Recent use of natural thickeners in the printing process, Journal of Textiles, Coloration and Polymer Science 18(2) (2021) 75-81.

[21] M.M. Ragab, A.G. Hassabo, H. Othman, Synthetic Thickeners in Textile Printing, Journal of Textiles, Coloration and Polymer Science 18(1) (2021) 65-74.

[22] A. Zubairu, Y. Madu Mshelia, Effects of Selected Mordants on the Application of Natural Dye from Onion Skin (Allium cepa), (2015) 26-32.

[23] A. Jahangiri, S.M. Ghoreishian, A. Akbari, M. Norouzi, M. Ghasemi, M. Ghoreishian, E. Shafiabadi, Natural Dyeing of Wool by Madder (Rubia tinctorum L.) Root Extract Using Tannin-based Biomordants: Colorimetric, Fastness and Tensile Assay, Fibers Polym. 19(10) (2018) 2139-2148.

[24] Q. Zhou, L.J. Rather, A. Ali, W. Wang, Y. Zhang, Q.M. Rizwanul Haque, Q. Li, Environmental friendly bioactive finishing of wool textiles using the tannin-rich extracts of Chinese tallow (Sapium sebiferum L.) waste/fallen leaves, Dyes Pigments 176 (2020) 108230.

[25] M. Saljooghianpour, T.A. Javaran, Identification of phytochemical components of aloe plantlets by gas chromatography-mass spectrometry, Afr. J. Biotechnol. 12(49) (2013) 6876-6880.

[26] B. Raksha, Bioactive Compounds and Medicinal Properties of Aloe Vera L.: An Update, Journal of Plant Sciences (Science Publishing Group) 2(3) (2014) 102.

[27] D.-P. Das, D.-A. Srivastav, Phytochemical Extraction And Characterization of the Leaves of Aloe vera barbadensis For Its Anti-Bacterial And Anti-Oxidant Activity, International Journal of Science and Research (IJSR) 4 (2015) 658-661.

[28] H.M. Ibrahim, A.A. Aly, G.M. Taha, H.I. Ibrahim, Production of Antibacterial Cotton Fabrics via Green Treatment with Nontoxic Natural Biopolymer Gelatin %J Egyptian Journal of Chemistry, 62(Special Issue (Part 2) Innovation in Chemistry) (2019) 655-669.

[29] G. Kavoosi, S.M.M. Dadfar, A. Mohammadi Purfard, R. Mehrabi, Antioxidant and Antibacterial Properties of Gelatin Films Incorporated with Carvacrol, 33(4) (2013) 423-432.

[30] L. Dou, B. Li, K. Zhang, X. Chu, H. Hou, Physical properties and antioxidant activity of gelatin-sodium alginate edible films with tea polyphenols, Int. J. Biol. Macromol. 118(Pt B) (2018) 1377-1383.

[31] A. Valdés, E. Garcia-Serna, A. Martínez-Abad, F. Vilaplana, A. Jimenez, M.C. Garrigós, Gelatin-Based Antimicrobial Films Incorporating Pomegranate (Punica granatum L.) Seed Juice by-Product, Molecules 25(1) (2019).

[32] M.I.H. Mondal, J. Saha, Antimicrobial, UV resistant and thermal comfort properties of chitosan-and Aloe vera-modified cotton woven fabric, J. Polym. Environ. 27(2) (2019) 405-420.

[33] D. Ashish, Z. Ismat, H. Md Mahmudul, NiloySarker, A. Kayum, M. Faysal, Natural Dyeing of Cotton Fabric by Extruded Pelargonidin of Red Onion Skin and Finished it Naturally with Aloe Vera, International Journal of Environmental Sciences & Natural Resources 14(3) (2018) 47-51.

[34] A.G. Hassabo, S. Shaarawy, A.L. Mohamed, A. Hebiesh, Multifarious cellulosic through innovation of highly sustainable composites based on Moringa and other natural precursors, Int. J. Biol. Macromol. 165 (2020) 141-155.

[35] AATCC Test Method (61-2013), Color Fastness to Laundering: Accelerated, Technical Manual Method American Association of Textile Chemists and Colorists, 2017, p. 108.

[36] AATCC Test Method (8-2016), Colorfastness to Crocking. Crockmeter Method, Technical Manual Method American Association of Textile Chemists and Colorists, 2018, pp. 17-19.

[37] AATCC Test Method (16.1-2014), Colour Fastness to Light: Outdoor, Technical Manual Method American Association of Textile Chemists and Colorists, 2015, pp. 33-48.

[38] M.H. Abo-Shosha, F.A. Nassar, K. Haggag, Z. El-Sayed, A.G. Hassabo, Utilization of Some Fatty Acid/PEG Condensates as Emulsifiers in Kerosene Paste Pigment Printing, RJTA 13(1) (2009) 65-77.

[39] M.M. El-Zawahry, F. Abdelghaffar, R.A. Abdelghaffar, A.G. Hassabo, Equilibrium and kinetic models on the adsorption of Reactive Black 5 from aqueous solution using Eichhornia crassipes/chitosan composite, Carbohydr. Polym. 136 (2016) 507-515.

[40] A.L. Mohamed, A.G. Hassabo, S. Shaarawy, A. Hebeish, Benign development of cotton with antibacterial activity and metal sorpability through introduction amino triazole moieties and AgNPs in cotton structure pre-treated with periodate, Carbohydr. Polym. 178 (2017) 251-259.

[41] M.S. Kamal, E. Mahmoud, A.G. Hassabo, M.M. Eid, Effect of Some Construction Factors of Bi-layer Knitted Fabrics Produced for Sports Wear on Resisting Ultraviolet Radiation, Egy. J. Chem. 63(11) (2020) 4369 - 4378.

[42] M. Zayed, H. Othman, H. Ghazal, A.G. Hassabo, Psidium Guajava Leave Extract as Reducing Agent for Synthesis of Zinc Oxide Nanoparticles and its Application to Impart Multifunctional Properties for Cellulosic Fabrics, Biointerface Research in Applied Chemistry 11(5) (2021) 13535 - 13556.

[43] M. Zayed, H. Ghazal, H. Othman, A.G. Hassabo, Psidium Guajava Leave Extract for Improving Ultraviolet Protection and Antibacterial Properties of Cellulosic Fabrics, Biointerface Research in Applied Chemistry 12 (2022).

[44] N. Ibrahim, F. El-Sakhawy, M. Mohammed, M. Farid, N. Abdel-Wahed, D. Deabes, Chemical composition, antimicrobial and antifungal activities of essential oils of the leaves of Aegle marmelos (L.) Correa growing in Egypt, JAPS (2015) 001-005.

[45] R.M.S. Al-Muniri, M.A. Hossain, Evaluation of antioxidant and cytotoxic activities of different

extracts of folk medicinal plant Hapllophyllum tuberculatum, Egyptian Journal of Basic and Applied Sciences 4(2) (2017) 101-106.

[46] S.W. Ali, R. Purwar, M. Joshi, S. Rajendran, Antibacterial properties of Aloe vera gel-finished cotton fabric, Cellulose 21(3) (2014) 2063-2072.

[47] A. Ketema, A. Worku, Antibacterial Finishing of Cotton Fabric Using Stinging Nettle (<i>Urtica dioica</i> L.) Plant Leaf Extract, J. Chem. 2020 (2020) 4049273.

[48] A. Sutlović, I. Brlek, V. Ljubić, M.I. Glogar, Optimization of Dyeing Process of Cotton Fabric with Cochineal Dye, Fibers Polym. 21(3) (2020) 555-563.

[49] M.M. Kamel, H.M. Helmy, H.M. Meshaly, A. Abou-Okeil, Antibacterial Activity of Cationised Cotton Dyed with Some Natural Dyes, Journal of Textile Science & Engineering 5(5) (2015) 1000180.

[50] C. Bettinger, H.W. Zimmermann, New investigations on hematoxylin, hematein, and hematein-aluminium complexes. I. Spectroscopic and physico-chemical properties of hematoxylin and hematein, Histochemistry 95(3) (1991) 279-88.

[51] S.A. Centeno, M. Bronzato, P. Ropret, A. Zoleo, A. Venzo, S. Bogialli, D. Badocco, Composition and spectroscopic properties of historic Cr logwood inks, 47(12) (2016) 1422-1428.

[52] S. Roy Maulik, L. Chakraborty, P. Pandit, Evaluation of Cellulosic and Protein Fibers for Coloring and Functional Finishing Properties Using Simultaneous Method with Eucalyptus Bark Extract as a Natural Dye, Fibers Polym. 22(3) (2021) 711-719.

[53] N. Krifa, W. Miled, N. Behary, C. Campagne, M. Cheikhrouhou, R. Zouari, Dyeing performance and antibacterial properties of air-atmospheric plasma treated polyester fabric using bio-based Haematoxylum campechianum L. dye, without mordants, Sustainable Chemistry and Pharmacy 19 (2021) 100372.

[54] M. Shabbir, L. Jameel, F. Mohammad, Economically viable UV-protective and antioxidant finishing of wool fabric dyed with Tagetes erecta flower extract: Valorization of Marigold, Industrial Crops and Products 119 (2018).

[55] E. Koh, K.H. Hong, Gallnut extract-treated wool and cotton for developing green functional textiles, Dyes Pigments 103 (2014) 222-227.