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Efficient, green and sustainable chemical treatments of cotton fabrics to improve dyeability, fastness, and antibacterial activity

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Abstract

Dyeability, fastness, and antibacterial activity of Egyptian cotton fabric samples were improved via three efficient, green, and sustainable chemical treatment formulas. The formulas included ethylmalonate, ethylactoacetate esters, and Dimethyloldihydroxyethyleneurea. Both pretreated and untreated cotton fabric samples were dyed with two dyes; the red direct dye (Chrisophene G) and the blue vat dye (thioindigo). Dyeability, fastness, and antibacterial activity were evaluated and resulted in encouraging standards. The green and sustainable concepts of the processes were outlined via preventing or minimizing non green components of the traditional procedures and optimizing the green context of the current study.

Keywords: Cotton fabric, Dyeability, Chemical modifications, Antibacterial, Green practices, Sustainability.

1. Introduction

Cotton species (Gossypium hirsutum) reside in Mexico and Central America and have been localized for extensive use in Egypt, accounting for more than 80% of Egyptian production with the most famous groups known as long staple (LS) cotton and extra-long staple (ELS) [1]. The Egyptian cotton, titled white gold, retires its importance not only as a mere crop, but also, as rebirth of modern Egyptian economy [2, 3]. Egyptian cotton fibers are composed mostly of α-cellulose (88-96.5% w/w) and non-cellulosic fibers that are located on the outer layers and inside the fiber lumen including proteins (1-1.9% w/w), waxes (0.4-1.2% w/w), pectin (0.4-1.2% w/w), inorganic (0.7-1.6% w/w), and other substances (0.5 to 8% w/w). The specific chemical composition of cotton fibers varies according to variety and growth conditions [4].

Chemical treatment formulas have been established as cellulose crosslinking agents, hence, as a competitive pathway to develop cotton fabrics employed for the production of wound dressings imparting ease of care characteristics and durable press properties to cotton apparel, cost effectiveness, and efficiency [5-8].

With this upsurge in human health awareness, researchers have focused their attention on designing antimicrobial finished textiles to safeguard the wearer from bacterial invasion more than simply protecting the garment from fiber degradation [9, 10].

Whenever practicable, green chemistry and sustainability concepts should be highlighted in all our chemical processes and practices to make up the atrocious face of traditional chemistry practices [11].

Herein, we report three chemical treatments formulas for Egyptian cotton fabrics dyed with two dyestuff, nominated red direct dye and blue vat dye, to improve its dyeability, fastness, and antibacterial efficiency and our research practices goes hand-in-hand with the escalation of the concept of green chemistry and sustainability.

Experimental

Generally, all chemicals were purchased from local dealers, liquids were of analytical grade and used without further purification. The present investigation was carried out using scoured loom state (100%) cotton (333 meq./ 100 gm fabric) that was prepared according to reported method [12].

Preparation of fabric

Cotton fabrics were mercerized in the slack conditions [13] and divided into strips.

The 1st strip samples were padded in a solution content (Ethylmalonate ester (EME) 2%, $MgCl_2$ 0.8%, and Mercerol wetting agent 0.1). The 2nd strip samples were padded in a solution content (ethylacetoacetate ester (EAAE) 2%, $MgCl_2$ 0.8%, and Mercerol wetting agent 0.1%). The 3rd strip samples were padded in a solution content (Dimethyloldihydroxyethyleneurea (DMDHEU) 2%, $MgCl_2$ 0.8%, and Mercerol wetting agent 0.1%). The 4th one was kept untreated as blank sample for comparison.

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Dyeing processes

Both the pretreated cotton fabric samples, 1; 2; 3, and the untreated samples, 4, were dyed with both red direct dye chrisophenine G and blue vat dye thioindigo.

Dyeing with red direct dye chrisophenine G

In a given dyebath, the dyestuff, 1.8%, shade was pasted with water. Warm water, 40 ^{0}C, was added, portion-wisely, with continuous stirring till liquor ratio 50:1 was attained. Sodium carbonate solution, 0.7%/ weight of fabric, (wof), and a wetting agent Ismawere ICB, 3g/L, were added. The samples of cotton fabric were soaked into the dyebath and its temperature was, gradually, raised to 70 ^{0}C, 4^{0}C/ minute. The dyeing process was maintained for 30 minutes and, finally, the cotton fabric samples were worked up via water wash, and air dryness.

Dyeing with blue vat dye thioindigo

The given fabric samples were immersed in the given dyebath containing the dyestuff at 40 ^{0}C and the dyebath is allowed to cool down. Glober's salt, 5 g/L water, was gradually added. The materials was worked up till 10 minutes, and developed in a developing bath containing 1g/L sodium nitrite and 20 cc/L sulfuric acid at 70 ^{0}C. After 30 minutes, the bath was neutralized, soaped, using 2g soap and 1g soda ash, and finally washed in water.

Dye exhaustion

The dye uptake of a given dye by the cotton fabric samples was evaluated by testing the dyebath specimen before and after dyeing on a Shimadzu UV-2401 PC UV/Visible spectrophotometer at the given absorption maxima, (λ_{max}), value using a calibration curve previously obtained using known dye concentrations (g/L) employing the equation, ***{E% = [1-(C_2/C_1)] x 100}.***

E%: The percentage of dyebath exhaustion, C_1 and C_2: dye concentrations before and after dyeing of the given dyebath specimen.

Color measures

The color parameters of the undyed and dyed cotton fabric samples were determined by means of an Ultra Scan spectroscopy (Hunter Lab) with a D_{65} illuminant and 10° standard observer [14, 15]. K/S values were calculated from the reflectance data at the given λ_{max} of the dye.

Fastness Testing

Dyed cotton fabric samples, both pretreated and/or untreated, after washing using 2 g/L nonionic detergent at 70°C for 10 min, were studied by standard ISO methods:

Wash fastness (ISO 105-C02 (1989); Crock fastness (ISO 105-X12 (1987); Fastness to perspiration (ISO 105-E04 (1989)

These three were evaluated using the visual ISO Gray Scale for both color change, (AATCC Evaluation Procedure (EP) 1-similar to ISO 105-A02), and color staining (AATCC EP 2-same as ISO 105-A03). Light fastness, (carbon arc), was evaluated using ISO 105-B02.

Antibacterial activity

The antibacterial activity were evaluated, for the dyed cotton fabric samples with the three treatment formulas and compared with blank untreated one, via disc diffusion method [16], against four bacterial strains including Staphylococcus aureus (Stap.), Escherichia coli (Esch.), Pseudomonas (Pseu.), and Serratia (Serr). Fresh inoculants for antibacterial assessment were prepared on nutrient broth at 37 ˚C for 24 hours. Untreated, undyed and impregnated cotton fabric samples with the reference Ampicillin were tested via the same methods and at the same conditions. Standard inoculums were dispersed evenly, through glass spreader, on the surface of sterilized plates (9 cm diameter) containing bacterial media (nutrient agar broth), and permitted to dry. Sterile discs of 5 mm of the cotton fabric given samples were kept under aseptic technique into the surface of the poisoned agar plate. The plate was incubated for 24 h at 37ºC. The diameter of the produced inhibition zone (IZ) was reported in millimeter scale. Each experiment was triplicated in absence of photo irradiation and ampicillin was taken as a reference, Table 5.

Green and sustainable Action

The procedures of all processes constituted the experimental part were redesigned to maintain the principles of green chemistry and the commands of sustainability whenever practicable to elevate the environmental impact and high atom economy of the current study. The non-green components of the classical procedures were prevented or minimized and green practices were substituted.

Results and Discussion

General

Polymer molecular models, of cotton fabric, constitute folded chains and fringed micelles that possess areas of variable crystallinity and the rigidity of the fibers is attributed to strong inter-polymer bonding. Hence, highly oriented fibers are those whose polymer chains have strong interactions due to their regularity within the fiber. Dye diffusions of the dyestuff take place into the less crystalline areas of the cotton fiber and dye fixation occurs via three linkage forms, hydrogen bonding, dipole interactions, and Van Der Waals forces. Chemical treatments increase de-crystallinity, hence, the less crystalline areas would be increased and the availability of bonding would be more, leading to more dye fixation into the cotton fabric.

Color is associated with energy absorptions, maxima, due to electron transitions, inside the dye molecule bonding, from highest occupied molecular orbitals HOMO to the lowest unoccupied molecular orbitals LUMO and . Whenever these electronic transitions, energy absorptions, occur in the visible range of the radiation, the material said to be colored and could be seen by the human eyes.

Color and dyeing fastness

A color space could be defined as expression of the color of an entity via some symbolization, such as numbers. Commission International de l'Eclairage (CIE), an authority on the science of light and color, has demonstrated color spaces, including CIE XYZ, CIE L*a*b*, and CIE L*C*h, for collaborating and expressing object color. These methods evaluate color attributes, recognize inconsistencies, and precisely instruct their findings in numerical terms, [17].

In this study, two dyes were employed to dye three pretreated cotton fabric samples with three different treatment formulas and one sample untreated named blank.

The 1st strip was padded in solution content (EME 2% L, $MgCl_2$ 0.8% L, and Mercerol wetting agent 0.1% L. The 2nd was padded in solution content (EAAE 2% L, $MgCl_2$ 0.8% L, and Mercerol wetting agent 0.1% L. The 3rd was padded in solution content (DMDHEU 2% L, $MgCl_2$ 0.8% L, and Mercerol wetting agent 0.1% L. The 4th one was kept untreated as a blank sample.

The fabric was then dyed with red direct dye (chrisophenine G) and blue vat dye (thioindigo). The different samples with different chemical treatments were all dyed in the same dye bath at the same conditions to assure consistent practices.

The first dye was the red direct (chrisophenine G). Structurally, the color originating groups, chromophores, are two azo groups and the extended conjugated double bonds and both two ethoxyls and sulfonates are acting as auxochromes resulting in the bright red color of the dye, Figure 1.

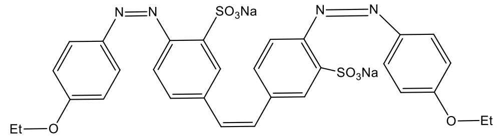

Figure 1: Red direct dye Chrisophenine G**,** sodium (Z)-5,5'-((Z)-ethene-1,2-diyl) bis(2-((Z)-(4-ethoxyphenyl)diazenyl) benzenesulfonate).

Table 1: Colorimetry values of the dyed cotton fabric samples via direct dye red (Chrisophenine G).

λmax	Sample	ΔE	K/S	L*	a*	b*
	1	65.32	0.78	64.85	6.20	-4.79
520 nm	2	65.32	0.85	63.73	7.43	-4.53
	3	56.40	1.69	54.80	10.28	-8.52
	4	69.86	0.52	69.62	5.64	-1.48

Colorimetric values, revealed that sample 2- with treatment formula including EAAE was the highest color strength and the lowest strength was sample 4-, untreated or so called, blank. Furthermore, both samples 1- and 3- with treatment formulas including EME and DMDHEU, respectively, gave excellent color strengths if compared with the untreated dyed sample 4-. This, strongly, indicate the importance of the treatment formula comprising, EME, EAAE, and DMDHEU, in dye diffusion, fabric de-crystallinity, and dye fixation through delivering effective linkage and extra hydrogen bonding, Figure 2.

The second dye was the blue vat (thioindigo). Herein, the indigoid structure with its canonical shapes, that allow electronic transitions hence energy absorption, acts as color originating groups, so called chromophores, resulting in the deep blue color of the dye. Figure 1.

Noticeably, the dyed 3- sample, treatment formula incorporating DMDHEU, of cotton fabric samples dyed with blue vat dye (thioindigo), showed the highest color strength of others, 1-, 2-, and 4- untreated sample, so called the blank, showed the lowest, Table 2,3. In addition, both 1- and 2- samples treated formula with EME and EAAE revealed excellent color strength comparing with the 4- untreated sample. Markedly, these outlined the conjoint structure correlation of the treatment formulas 1-,2-, and 3- constituting EME, EAAE, and DMDHEU and the cotton fabric dye ability with the blue vat dye, Figure 2.

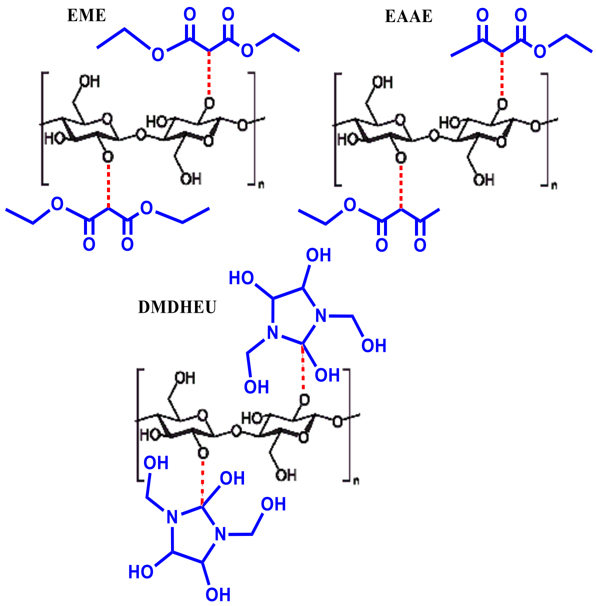

Figure 2: Expected intermolecular bonding between EME, EAAE, DMDHEU, and cotton fabric cellulose

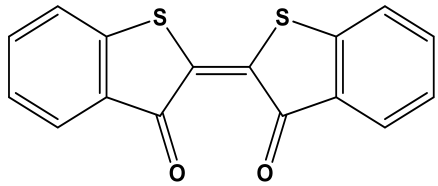

Figure 3: Blue vat dye (Thioindigo), (Z)-3H,3'H-[2,2'-bibenzo[b]thiophenylidene]-3,3'-dione

Table 2: Colorimetry values of the dyed cotton fabric samples via blue vat dye (thioindigo).

λmax	Sample	ΔE	K/S	L*	a*	b*
565 nm	1	61.52	4.20	54.69	-13.85	-4.79
	2	62.56	4.01	55.44	-13.84	-4.53
	3	58.19	6.73	48.73	-11.24	-8.52
	4	53.49	5.37	48.20	-12.26	-1.48

Table 3: Colorimetry values of the un-dyed fabric samples of whiteness (W) and yellowness (Y).

Sample	ΔE	K/S	W	Y
1	86.86	0.22	52.94	6.74
2	87.62	0.30	47.89	9.26
3	88.74	0.24	55.60	7.00
4	83.41	0.53	17.66	18.48

Table 4: Fastness properties of dyed cotton fabrics samples using red direct dye and blue vat dye, 2% weight of fabric (wof), at 70°C.

Sample	Dye	Fastness to rubbing		Wash Fastness			Fastness to perspiration						Light
							Alkaline			Acidic			
		Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
1	Red	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
	Blue	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
2	Red	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
	Blue	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
3	Red	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
	Blue	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
4	Red	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
	Blue	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5

Alt, color change of dyed sample; SC, staining on cotton; SW staining on wool.

Antibacterial activity

The potency of the cotton fabric pretreated, untreated, dyed samples were tested against Staphylococcus aureus (Stap.), Escherichia coli (Esch.), Pseudomonas (Pseu.), and Serratia (Serr.), and compared with the potency of ampicillin as a reference to insure the study impacts, Table 5.

Frequently, all pretreated cotton fabric dyed samples imparting high to medium antibacterial potency due to the action of two effective factors, treatment formula and dyestuff, that directly responsible for the inhibition of the bacterial growth. In addition, sample 3- including DMDHEU+ treatment formula showed higher potency more than 1- and 2- samples including EME+ and EAAE+ treatment formula. This could be attributed to the strong inhibition activity of the treatment formula of the sample 3- whatever the dyestuff would be. Furthermore, it could be outlined that the samples dyed with the blue vat thioindigo dye emitted higher potency more than those dyed with red direct dye Chrisophenine G, whatever the samples were pretreated or untreated. This markedly, confirmed the inhibition efficiency of the dyestuff thioindigo. Overly, the antibacterial evaluation of all the tested cotton fabric dyed samples pretreated or untreated samples was highly marked, promising, and encouraging further pharmaceutical studies, especially when the results were compared with the patent reference Ampicillin, Table 5.

Table 5: Antibacterial activity of the pretreated and untreated dyed cotton fabric.

Sample	Red direct dye dyed cotton fabric				Blue vat dye dyed cotton fabric			
	Stap.	Esch.	Pesu.	Serr.	Stap.	Esch.	Pesu.	Serr.
1	17	14	20.5	24	21	20	21	24
2	19.5	18	20.5	23	20	21	23.5	27
3	21.5	22	22	22.5	23	20.5	23	27
4	10	9	12	12	14	13.5	13	15
Ampicillin	20	20	24	24	20	20	24	24

IZ ≥ 20, High; IZ < 20, > 10 Medium; IZ ≤ 10 Low

Green and sustainable Action

Green and sustainable practices were established via redesigning the traditionally reported procedure to become greener and more sustainable. Moreover, the classical reported procedures, highlighting the hazardous component, for a particular processes were replaced with a greener one incorporating invention, design, development and application of chemical processes that prevented, reduced or eliminated the usage and generation of substances hazardous to human health and environment. Evidently, waste was prevented as possible and the practical yield of chemical treatments and dyeing was optimized emphasizing much high atom economy. Both chemical treatments and dyeing procedures were redesigned to generate substances that possess little or no toxicity to human health and the environment. Energy requirements were recognized for their environmental and economic impacts and were minimized and both chemical treatments and dyeing

methods were conducted at ambient conditions of temperature and pressure. The whole study was redesigned to prevent or minimize the potential of chemical accidents, including releases, explosions, and fires...
Markedly, fair comparison between the classical reported procedures that were formerly reported, with its non-green components, and the current greener practices, of chemical treatment and dyeing of the cotton fabric, would prove the superiority of the current study with its optimized green and sustainable context over the traditional practices.

Conclusion

The dyeing proficiency, fastness to rubbing, perspiration fastness, light fastness, and color strength were markedly enhanced for pretreated cotton fabric with the three nominated treatment formulas. The antibacterial activity was also highly recognized and encouraging further pharmaceutical investigation for the pretreated cotton fabric and this would recommend applicability in medicinal clothes design. Moreover, the dependence of color strength, fastness, and antibacterial activity, of the tested cotton fabric samples, on both dye structure and chemical treatment formula of the fabric were highly pronounced. Therefore, such pretreated dyed cotton fabric of the study would be excellent precursors for fabrics and clothes industry. The green and sustainable perceptions of the study were highly pronounced via elevating benign concepts such as safety, atom economy, energy proficiency, environmental impacts, waste minimization, low risk, and hazard prevention.

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Conflict of interest

The authors declare no conflict of interest.

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