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Dyeing of Cotton Fabric with Natural Dyes without Mordant Usage Part I: Determining the Most Suitable Dye Plants for Dyeing and UV Protective Functionalization

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Abstract: Natural dyes are gaining importance in textile dyeing applications in recent years due to the fact many synthetic dyes are carcinogenic, mutagenic, and allergic. In this study, cotton knitted fabrics were dyed with extract solutions of 40 different dye plants without the mordant usage. Afterwards color efficiency and fastness values of dyed samples were evaluated. Dye plants that are able to give good color efficiency with sufficient fastness values were determined. According to the experimental results it can be said that for yellow color pomegranate peel and turmeric; for red color madder and quince; for blue color indigo; for green color myrobalan; for brown color white onion peel and catechu give the optimum results. Furthermore, it was tested whether ultraviolet protection effect could be obtained via dyeing with white onion peel or turmeric and it was found that both of these plants gave very good UV protection functionalization to cotton fabrics.

Keywords: Cotton, Natural dye, Fastness, Ultraviolet protection

Introduction

Natural dyes are gaining importance in textile dyeing applications in recent years due to the fact many synthetic dyes are carcinogenic, mutagenic, and allergic. Natural dyes can be categorized into two main classes as substantive dyes (which can be applied without mordanting) and mordant dyes (which can only be applied to mordanted materials) in terms of chemical structure [1]. Most of the natural dyes are mordant dyes, and a few are the substantive dyes. There are direct, vat, acid, and basic dyes among the substantive dyes and there are no sulfur, reactive, and disperse based natural dyes [2]. The chemistry of bonding of natural dyes to fibers is complex. They bind to fibers through H-bondings and hydrophobic interactions [3]. As the H-bondings and hydrophobic interactions are weak interactions, it is necessary to use heavy metal salts named as mordant in order to obtain good color fastness values [4]. In case of mordant usage, dyes are bound to the fibers through chemical bridges with the aid of mordants. Dye molecules having suitable functional groups (e.g. two hydroxy groups or a hydroxy group with carbonyl, nitroso, or azo group in adjacent positions) make coordination complexes with the metal ion coming from the mordant [3]. Environmental pressures have caused water authorities to tighten their requirements for effluent quality. For this reason in many countries limits have been set, or new limits imposed, for chromium and/or heavy metals in effluent [5]. The indicative maximum permissible quantities of different metals in the ultimate product are as follows: As: 1 ppm, Pb: 1 ppm, Cd: 2 ppm, Cr: 2 ppm, Co: 4 ppm, Cu: 50 ppm, Ni: 4 ppm, and Zn: 20 ppm. The upper limits of the presence of metals vary from product to product as well as different Eco-Mark [4]. Nowadays chromium is in the red-list according to the eco-regulations and for this reason, it is important not to use chromium salts in order to achieve eco-friendly production in terms of both the dyed textile material and the discharged effluent. Although copper is also listed in the restricted category, permissible levels for copper ion are higher and therefore the permissible limit on dyed material will not be exceeded if it is used in small quantities [6]. On the other hand, there is no upper limit for aluminum, iron, and tin [4]. Tin is not limited by many eco-labels, but its presence in waste water is not desired from an environmental viewpoint [6]. Hence, it can be said that the use of aluminum and iron salts as a mordant is safe. However, their quantities should be optimized so as to minimize the pollution load [4]. But it is important to note that for a natural dyeing to be meaningful in terms of ecology, it should be avoided from the mordant usage. One of the disadvantages of mordant usage is that it is not possible to see the final color to be obtained until the addition of the mordant as mordants change the color via complex formation with natural dyes and color cannot be reversed due to the beginning of coordination bond formation after mordant is added. This situation reduces the reproducibility and is not welcomed in terms of dyeing [7]. One of the other disadvantages of mordants is that the chroming step causes significant fiber damage [5] and dyeing period is long due to the mordanting step, which increases the energy consumption of dyeing.

When the literature is examined, it is seen that there are many studies on the dyeing of cotton fabrics with natural dyes [8-17]. The majority of these are based on the evaluation of color and fastness values in dyeing with various plants in the presence and absence of different mordants. On the other hand, there are increasing number of studies on ultraviolet (UV) protective effects of natural dyes.

Sun protective fabrics are designed to absorb or reflect the

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sun's UV radiation (UVR) as a means of protecting skin from damage [18]. The UV-protection efficiency of a fabric is defined by its ultraviolet protection factor (UPF). The higher the UPF value is, the greater the fabric's protection level is [19]. UPF value can be thought of as a time factor for the protection of Caucasian skin compared to exposure without protection. For example, if a person would show visible sunburn after 5 min of exposure, fabric with a UPF of 50 extends that time to 5 min × the protection factor, i.e. 250 min or roughly 4 h. Sunburn, skin cancers, premature skin ageing, and suppression of the immune system are all about skin exposure to UV light [18]. UVR transmission properties of textile materials depend on many parameters such as structure and physiochemical properties of fiber; dyestuffs and finishing chemicals present on the fabric; thickness, porosity, and moisture content of the fabric. Fabric color is also very important in terms of UV protection [20]. In general, it can be said that dyed fabrics have higher UV protection levels compared to undyed ones, because pale shades reflect solar radiation more efficiently than dark ones and thanks to multiple scattering part of the solar radiation have chance to penetrate the fabric more easily [19]. Thus, higher dyeing depth means higher UV protection levels.

In the study carried out by Sarkar, bleached and mercerized cotton woven fabrics were dyed with madder and indigo in 3 different depths (2-4-6 %) after mordanting with potassium aluminum sulfate, then the UV protection values of these fabrics were measured. It was found that while undyed fabric and fabric dyed with 2 % madder did not have UV protection effect, fabrics dyed with 4 % and 6 % madder showed good UV protection. However, UV protection values obtained with indigo dyed fabrics were excellent at all concentrations [21]. Gupta *et al.* examined the UV protection effects of bleached cotton woven fabrics dyed with 10 different plants including myrobalan, pomegranate peel, and catechu. It was found that all plants had high absorbance in the UVB region. Although undyed fabric did not show UV protection properties; in the measurements made on the dyed fabrics, it was observed that at the concentrations of 6, 9, 12, and 15 %, the fabrics dyed with catechu gave good UV protection effect [22].

When the chemical structures of natural dyes are examined in detail, it can be understood that there would be some natural dyes potentially having the ability of dyeing cotton fibers without the need of mordant usage. Based on this hypothesis, in this study it has been tried to determine the color gamut which can be obtained with natural dyes on cotton fabrics without mordant usage by working with a large number of dye plants. For this aim, cotton knitted fabrics were dyed in the absence of mordant. Then both color efficiency and fastness values of dyed samples were evaluated. Furthermore UV protection effects of some plants were tested and it was investigated whether it is possible to obtain various colors and at the same time UV protection effect on cotton fabrics without the mordant usage. As in the literature there is not any comprehensive study in which various dye plants were investigated for obtaining saturated colors with good fastness values on cotton fabrics without mordant usage, the present study is thought to be original.

Table 1. Common and botanical names of plants used in experiments

Common name	Botanical name	Part of plants used
Bilberry	*Vaccinium myrtillus L.*	Fruit
Blackberry	*Rubus canescenc DC.*	Leaf
Brom	*Spartium junceum L.*	Leaf
Buckthorn	*Rhamnus cathartica*	Leaf
Bugloss/*Alkanet*	*Alkanna tinctoria* (*L.*) *tausch*	Root and peduncle
Catechu	*Acacia catechu*	Heartwood
Cherry	*Cerasus avium (L.) moench*	Peduncle
Chestnut	*Castanea sativa*	Peel
Daisy	*Leucanthemum vulgare*	Flower and peduncle
Elderberry	*Sambucus nigra L.*	Leaf
Eucalyptus	*Eucalyptus camadulensis dehn.*	Leaf
French lavender	*Lavandula stoechas L.*	Leaf
Grape Leaf	*Vitis vinifera L.*	Leaf
Hawthorn	*Crataegus monogyna*	Leaf
Henna	*Lawsonia inermis L.*	Leaf
Hibiscus	*Hibiscus sabdariffa*	Flower
Indigo	*Indigofera tinctoria L.*	Leaf
Lemon Balm	*Mellissa officinalis L.*	Leaf
Lime Tree	*Tilia tometosa*	Leaf
Madder	*Rubia tinctorum L.*	Root
Mallow	*Malva sylvestris*	Leaf
Mulleins	*Verbascum* sp.	Leaf
Myrobalan	*Terminalia citrina*	Fruit
Myrtle	*Myrtus communis L.*	Leaf
Nettles	*Uritica dioica L.*	Stem
Pennyroyal	*Mentha pulegium*	Peduncle and leaf
Pomegranate	*Punica granatum L.*	Fruit peel
Quince	*Cydonia oblonga miller*	Leaf
Rose hip	*Rosa canina*	Leaf
Rose of Sharon	*Hibiscus syriacus*	Leaf
Safflower	*Carthamus tinctorius L.*	Leaf
Silver Birch	*Betula pendula roth.*	Leaf
Spearmint	*Mentha spicata L.*	Leaf
St John's Wort	*Hypericum perforatum L.*	Stem
Sweet Flag	*Acorus calamus*	Root
Sumac	*Rhus coriaria L.*	Fruit
Turmeric	*Curcuma longa L.*	Root
White Onion	*Allium cepa L.*	Peel
Yarrow	*Achillea* sp.	Flower and peduncle
Yellow Bedstraw	*Galium verum L.*	Stem

Experimental

In the experiments 100 % cotton plain knitted fabric (190 g/m^2) was used. All experiments were carried out using pure water in a Thermal HT dyeing machine. The common and botanical names of the plants used in the experiments and the part of the plants used are given in Table 1 and photographs of plants are shown in Figure 1.

Dyeing Procedure for Plants (except Indigo)

50 g plant was boiled in 1 *l* of pure water for half an hour, then the extract was filtered with a gauze fabric. Afterwards the volume of the extracts was adjusted to 1 *l* with distilled water. This filtered dye solution was used as a dyeing liquor in experiments. 10 g of cotton fabrics were dyed with these extracts at their own pH values in the absence of mordant at a liquor ratio of 1:15. The dyeing graph is given in Figure 2. After dyeing, the samples were subjected to cold rinsing - warm rinsing - warm soaping - cold rinsing - cold rinsing, and drying consecutively. The color yield (*K/S*) and CIEL*a*b* values of the dyed samples were then measured with spectrophotometer. The colors of the dyed samples were also visually evaluated and photographed under daylight. Furthermore, washing, rubbing, light, and perspiration fastness values of the dyed samples were also tested.

Dyeing Procedure for Indigo

Dyeing started at 60 ^{o}C with a liquor including all of the caustic soda (2.88 g/*l*) and half portion of the hydrosulphite (2 g/*l*), after 5 min 3 % indigo dye was added. Fabric was treated with this liquor for further 15 min and then the second portion of hydrosulfite (2 g/*l*) was added [23]. 5 min later, salt (30 g/*l*) was added and vatting was continued for 5 min. Then cotton fabric was put into the liquor and dyeing process was proceeded for 30 min. The dyeing with indigo was carried out by using the graph given in Figure 3 at a liquor ratio of 1:30. After dyeing, cold rinsing - oxidation (with 2 g/*l* H_2O_2) - cold rinsing - warm soaping - cold rinsing procedures were applied consecutively.

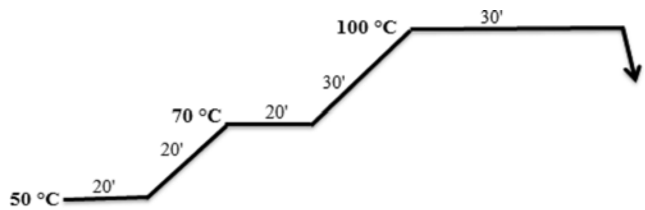


Figure 2. Dyeing graph used for dyeing with natural dyes except indigo.

Color Measurements

CIEL*a*b* color values and reflectance values of dyed samples were measured with Gretag Macbeth E700 (D 65/ 10^o) and color yields (*K/S*) were calculated by Kubelka Munk equation:

Figure 1. Photographs of dye plants used in experiments.

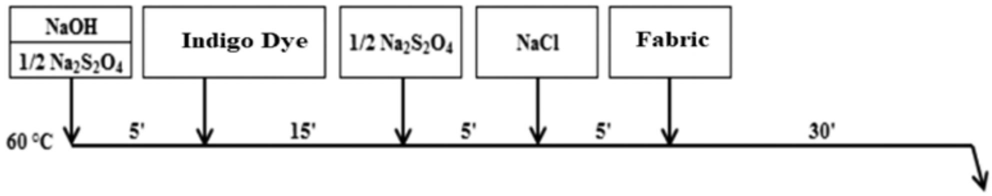


Figure 3. Dyeing graph used for dyeing with indigo.

$$K/S = (1-R)^2/2R$$

where R is reflectance value at maximum absorption wavelength (nm), K is absorption coefficient, and S is scattering coefficient.

Fastness Tests

Washing (at 60 °C), rubbing (dry and wet), perspiration (acidic and alkaline), and light fastness values of dyed samples were assessed according to ISO 105 C06 [24], ISO 105-X12 [25], ISO 105-E04 [26], and ISO 105 BO2 [27] standards, respectively.

UV Transmission Analysis

UV transmission analysis of fabric samples were performed according to the AS/NZS 4399: 1996 standard using a Labsphere UV Transmittance Analyzer, Model-UV 2000S. 5×5 cm samples were cut and transmission measurements were made between 290-400 nm. The average (%) of UVA (315-400 nm) and UVB (290-315 nm) transmission values obtained as a result of the calculation of three measurements for each. According to this standard, samples with UV protection values between 10 and 19 are considered medium, samples between 20 and 29 are considered high, samples between 30 and 49 are considered very high, and samples with 50 and above are considered maximum [28].

Results and Discussion

Results Related to Determining the Most Suitable Dye Plants for Dyeing Cotton Fabrics without Mordant Usage

Color yield (*K/S*) and CIEL*a*b* values and photos of cotton fabrics dyed with 40 different plant extracts in the absence of mordant are given in Table 2. As can be seen from the photographs given in Table 2, the colors that can be obtained on the cotton fabrics without using any mordant are generally yellow and brown tones. Only the dye plant providing blue color on cotton is indigo. On the other hand, madder and quince gives reddish nuances on cotton.

From the color yield values (*K/S*) and photos of samples dyed in the absence of mordant, it can be said that plants can be divided into four groups according to their dyeing ability of cotton fabrics. While some plants do not dye or just slightly stain the cotton (those with color yield values under 0.35), the others give low color yield (values between 0.35 and 0.84), medium color yield (values between 0.85 and 1.79), or high color yield (values of 1.80 and greater). For determining the dyeing ability of plants, visual evaluations were taken into consideration. It was observed that plants with the color yield of less than 0.35 did not give a color on the cotton, whereas plants with the color yield greater than 1.80 gave a quite saturated color on the cotton. The limit values (lower and upper values) determined for each class in this research are not absolute values and different values can be taken as limit values. The aim of this classification was just to put the plants into 4 different groups (from the lowest to the highest ability of dyeing cotton fabric) considering the color yield values. The classification of plants according to the mentioned grouping criteria is given in Table 3.

According to the experimental results, it can be said that 4 of the 40 plants are not able to dye cotton or slightly stain it, 25 of 40 plants can dye cotton in low color yield values. While 5 of 40 plants gave medium color yield values, saturated colors were obtained with only 6 plants. As stated before, most of the natural dyes are "mordant dyes" which means they don't have enough affinity for fiber and a mordant usage is obligatory in order to obtain high color yield values. But in this study the heavy metal salt (mordant) usage was avoided and hence high color yield values were obtained only with a few dye plants in the absence of mordant.The plants that are able to dye cotton fabric in high color yield values can be listed as follows according to the colors to be obtained:

- *Yellow:* turmeric, pomegranate peel
- *Blue:* indigo
- *Green:* myrobalan
- *Brown:* catechu (reddish brown), white onion peel (yellowish brown)

As can be seen from the list, none of the plants gave a red color with high color yield on cotton fabric. But, with madder and quince fairly pale reddish colors were obtained, which means they can be used when red color is desired.

One of the most important issues for natural dyes used in textile dyeing is the color yield that can be obtained from the unit amount. It would not be appropriate to use a plant which does not provide a high color yield even at the high extract concentrations like 50 g/*l*. If it is taken into account that plants generally contain up to 5 % dye over their total weight [6]; dyeing with 50 g/*l* extract solution is equivalent to a dye

Table 2. Color yield (*K/S*) and CIEL*a*b* values and photos of cotton fabrics dyed with 40 different plant extracts in the absence of mordant

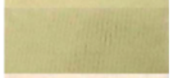
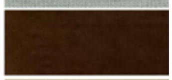
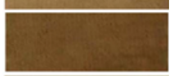
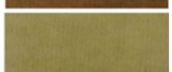
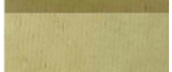
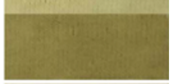
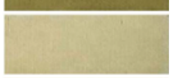
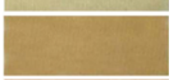
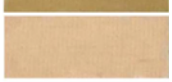
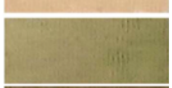
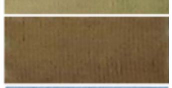
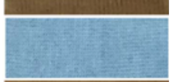
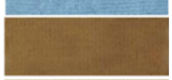
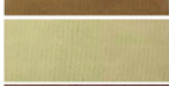
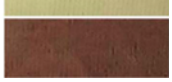
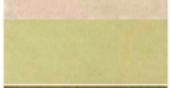
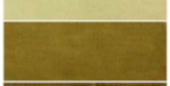
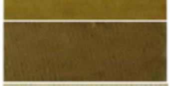
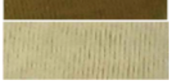
No	Plant	Color	L^*	a^*	b^*	C^*	$h°$	λ (nm)	%*R*	*K/S*
1	Bilberry		80.52	3.60	9.19	9.87	68.59	400	41.82	0.40
2	Blackberry		85.36	0.07	16.47	16.47	89.76	400	35.62	0.58
3	Brom		81.86	1.87	11.98	12.12	81.14	400	41.06	0.42
4	Buckthorn		89.22	0.01	7.95	7.95	89.93	400	55.78	0.18
5	Bugloss/*Alkanet*		74.14	-0.08	0.21	0.24	109.32	400	43.50	0.37
6	Catechu		59.27	8.62	13.16	15.74	56.77	400	15.40	2.32
7	Cherry		77.63	6.60	10.56	12.45	58.01	400	38.60	0.49
8	Chestnut		69.84	5.91	11.76	13.16	63.32	400	26.91	0.99
9	Daisy		82.03	1.89	14.39	14.52	82.52	400	37.58	0.52
10	Elderberry		82.78	1.50	13.78	13.87	83.78	400	38.27	0.50
11	Eucalyptus		78.80	2.00	12.63	12.79	81.01	400	33.29	0.67
12	French lavender		78.35	2.00	10.35	10.54	79.06	400	36.46	0.55
13	Grape Leaf		76.82	4.19	16.11	16.65	75.44	400	27.20	0.97
14	Hawthorn		78.65	6.35	9.44	11.38	56.08	400	41.74	0.41
15	Henna		74.62	1.54	7.72	7.87	78.72	400	35.51	0.59
16	Hibiscus		69.16	3.25	6.85	7.58	64.63	400	29.73	0.83
17	Indigo		57.77	-4.90	-17.48	18.15	254.34	660	15.10	2.39
18	Lime Tree		74.64	6.87	10.86	12.85	57.70	400	26.31	1.03
19	Lemon Balm		81.19	1.65	11.64	11.76	81.92	400	37.47	0.52
20	Madder		69.55	6.96	5.83	9.08	39.96	400	33.51	0.66
21	Mallow		81.42	2.74	8.16	8.60	71.43	400	44.96	0.34
22	Mulleins		85.69	0.96	15.91	15.94	86.56	400	42.53	0.39
23	Myrobalan		71.92	0.73	22.92	22.94	88.17	400	12.14	3.18
24	Myrtle		74.94	2.83	13.62	13.91	78.24	400	27.11	0.98
25	Nettles		75.79	1.48	8.37	8.50	79.98	400	36.35	0.56

Table 2. Continued

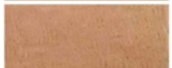
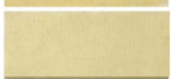
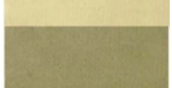
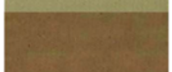
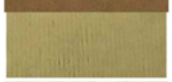
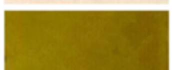
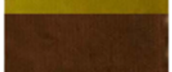
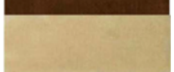
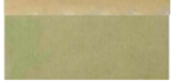
No	Plant	Color	L^*	a^*	b^*	C^*	$h°$	λ (nm)	%*R*	*K/S*
26	Pennyroyal		79.04	0.50	11.64	11.66	87.54	400	33.50	0.66
27	Pomegranate		73.76	2.67	24.32	24.47	83.73	400	18.30	1.82
28	Quince		71.80	9.96	11.18	14.98	48.29	400	32.07	0.72
29	Rose hip		83.10	3.64	10.85	11.44	71.48	400	42.88	0.38
30	Rose of Sharon		88.12	0.44	9.13	9.14	87.21	400	50.91	0.24
31	Safflower		80.14	2.08	17.68	17.80	83.29	400	31.56	0.74
32	Silver Birch		82.07	1.35	12.40	12.47	83.77	400	39.63	0.46
33	Spearmint		79.44	1.11	9.62	9.68	83.43	400	38.92	0.48
34	St John's Wort		76.79	3.39	11.84	12.31	74.00	400	33.86	0.65
35	Sumac		78.86	2.64	9.66	10.01	74.70	400	35.64	0.58
36	Sweet Flag		87.94	1.43	6.81	6.96	78.13	400	57.24	0.16
37	Turmeric		82.73	3.36	54.62	54.73	86.48	440	16.33	2.14
38	White Onion		65.93	7.32	17.57	19.03	67.40	400	17.41	1.96
39	Yarrow		80.68	2.33	15.44	15.61	81.42	400	34.06	0.64
40	Yellow Bedstraw		85.77	0.11	14.22	14.22	89.55	400	40.53	0.44

Table 3. Classification of dye plants according to their dyeing ability of cotton fabric

Non-dyeing	Low color yield		Medium color yield	High color yield
Buckthorn	Bilberry	Mulleins	Chestnut	Catechu
Mallow	Blackberry	Nettles Pennyroyal	Grape Leaf	Indigo
Rose of Sharon	Bugloss/*Alkanet*	Quince	Hibiscus	Myrobalan
Sweet Flag	Brom	Rose hip	Lime Tree	Pomegranate
	Cherry	Safflower	Myrtle	Turmeric
	Daisy	Silver Birch		White Onion
	Elderberry	Spearmint		
	Eucalyptus	St John's Wort		
	French lavender	Sumac		
	Hawthorn	Yarrow		
	Henna	Yellow Bedstraw		
	Lemon Balm			
	Madder			

Table 4. Chemical classes and the Color Index numbers (C.I. No) of the dyes present in the structure of the plants providing high color yield on cotton fabric without mordant usage

Source	Chemical class	Main colorant	C.I. No	Literature
Catechu	Tannin	Catechin	C.I. Natural Brown 3	[29]
Indigo	Indigoid	Indigotin	C.I. Natural Blue 1	[6]
Myrobalan	Tannin	Chebulic acit	C.I. Natural Brown 6	[30,31]
Pomegranate peel	Tannin	Ellagic acid	C.I. Natural Yellow 7	[29,32]
Turmeric	Diferuloye-methane	Curcumine	C.I. Natural Yellow 3	[33]
White onion peel	Flavonoid	Quercetin	C.I. Natural Yellow 10, 13	[32]

concentration of 3.75 % in a dyeing carried out at 1:15 liquor ratio. Therefore, it can be said that the plants which are able to dye cotton in high color yield values are suitable to be used directly (without mordant usage) in cotton dyeing. In order to understand why these plants are able to dye cotton fibers efficiently, it is necessary to clarify the coloring groups of these plants. When the literature is examined, it is seen that techniques such as high performance liquid chromatography (HPLC), thin layer chromatography (TLC), high performance thin layer chromatography (HPTLC), mass spectroscopy are used in various studies for this purpose. With a comprehensive literature search, it was determined that dye plants giving saturated colors on cotton fabrics without the mordant usage contained the main colorants given in Table 4. Table 4 also lists the chemical classes and the Color Index numbers (C.I. No) of the dyes present in the structure of these plants.

The chemical formulas of the main colorants present in plants providing high color yield are given in Figure 4. From this figure, it is seen that the dyes giving high color yield values on cotton fabrics contain phenolic hydroxyl (-OH) or imino (-NH-) groups in their chemical structures. Therefore, in addition to the van der Waals attraction forces and dipole-dipole interactions between these dyes and cotton fibers, hydrogen bridges will be formed between the hydrogen atoms of the hydroxyl (-OH) or imino (-NH-) groups of the dyes and oxygen atoms of the hydroxyl groups present in the structure of the cotton fibers.

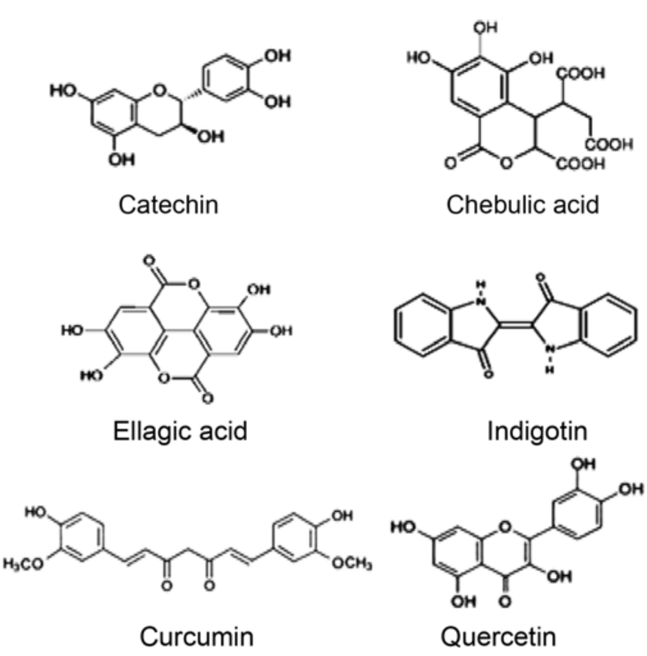


Figure 4. Chemical formulas of the main colorants present in plants providing high color yield values [6,29-34].

In terms of dyeing, besides the color, the fastness is also a very important factor. Washing (color staining), rubbing, and light fastness values of the samples dyed with catechu, indigo, myrobalan, pomegranate peel, turmeric, and white onion peel, which provide high color yield values in dyeing of cotton fabrics in the absence of mordant, are given in Table 5.

When Table 5 is examined, it can be seen that washing, rubbing, and light fastness values of the fabrics dyed with these plants (except turmeric) vary between moderate and very good. On the other hand, for turmeric, washing, rubbing, and light fastness values are moderate, very good, and very low, respectively.

Perspiration fastness (color staining) values of dyed fabrics are given in Table 6. When Table 6 is examined, it can be said that both acidic and alkali perspiration fastness values of natural dyes, except catechu, are between medium to very good levels.

Another parameter that gains importance for a natural dye to be used in industrial production is affordability. If evaluation is done in this respect, it can be said that accessibility of turmeric is easier than the others. Pomegranate peel and white onion peel are waste, and they can only be supplied from the wastes of food factories where pomegranate and onion are processed. However, the fact that a waste will be recycled in this case makes natural dyeing, which is already environmentally freindly, even more attractive from the view of ecology. On the other hand, catechu, indigo, and myrobalan are plants cultivated in limited quantities and they grow in specific regions of the world. In addition to accessibility, cost is an important criterion. While the price of catechu, indigo, and myrobalan is high, the price of

Table 5. Washing (color staining), rubbing and light fastness values of the cotton fabrics dyed with dye plants giving high color yield values

Plant	Washing fastness						Rubbing fastness		Light fastness
	WO	PAC	PES	PA	CO	CA	Dry	Wet	
Catechu	5	5	5	3	4	4-5	4	3-4	3
Indigo	5	5	4	3	5	3	5	4	4-5
Myrobalan	5	5	5	5	5	5	5	2-3	5-6
Pomegranate peel	5	5	5	5	5	4-5	5	4	4-5
Turmeric	5	5	5	2-3	3	4-5	5	4-5	1-2
White onion peel	5	5	5	4	4-5	4-5	4-5	4	3

Table 6. Acidic and alkali perspiration fastness (color staining) values of the cotton fabrics dyed with dye plants giving high color yield values

Plant	Acidic perspiration fastness						Alkali perspiration fastness					
	WO	PAC	PES	PA	CO	CA	WO	PAC	PES	PA	CO	CA
Catechu	2	4	4	3	3	4	1-2	3-4	3-4	3	2-3	4
Indigo	5	5	5	5	5	5	5	5	5	5	5	5
Myrobalan	4	4-5	4-5	4	3-4	4-5	3-4	4	4-5	4	2-3	4-5
Pomegranate peel	3	3-4	3-4	3-4	3	4	2-3	3	3	3	3	3-4
Turmeric	4	4-5	4-5	4	3-4	4	4	4-5	4-5	4	3-4	4
White onion peel	4-5	5	5	5	4-5	4-5	4	5	5	5	3-4	4

turmeric is considerably lower than these dyes. However, pomegranate peel and white onion peel do not have any cost as they are waste of a food industry.

As the indigo dye needs to be reduced in a basic medium in order to be dissolved, it is not possible to use this dye in combination with other natural dyes in the same bath. In other words, it is not possible to make trichromatic dyeings (yellow-red-blue mixture) with natural dyes in cotton dyeing. It would be possible to obtain secondary colors (green, orange, and purple) by dyeing blue with indigo in the first step and then dyeing red or yellow with other plants in the second step. For example, green color will be obtained by dyeing blue color with indigo in the first step and then dyeing yellow color with turmeric in the second step.

As can be seen from the photographs given in Table 2, the important result gained within the scope of the study is that a bluish tone can be obtained directly on the cotton fabrics with bugloss. Dyeing with bugloss is carried out in the same way as other plants, i.e. without the need of vatting process. In this respect, bugloss is an important opportunity over indigo dye. By using bugloss for blue color with the plants giving yellow and red colors, trichromatic dyeings can be done in a single step in the same bath. However, color yield obtained with bugloss on cotton is very low. The color strengths of yellow, red, and blue dyes used in trichromatic dyeings should be similar. Otherwise, if there is a big difference between the color strengths of dyes, the desired color tone will not be obtained and the color of the dye plant with high color strength will be dominant. For example, if bugloss and turmeric are mixed in equal amounts for the green color, the turmeric will give a color yield of about 5 times higher than bugloss, and not an exact green, but a yellowish green will be obtained. From this point of view, it is necessary to choose dye plants giving yellow and red colors whose color strength is similar to that of bugloss, in order to perform trichromatic dyeings in pale shades. There are two alternatives for red color: quince and madder. On the other hand, the most suitable alternative for yellow color is safflower.

In summary, in order to obtain pale shades on cotton fabrics with natural dyes, if safflower for yellow, quince or madder for red, bugloss for blue are used it would be possible to make trichromatic dyeing. However, it is worth noting that it is not possible to obtain medium and dark shades, since the color obtained with these three plants is weak. However, if the color yield could be increased in dyeing of the cotton fabrics with these three plants, the problem of trichromatic dyeing of cotton with natural dyes in a single bath will be solved. In the following study, the results of pretreatment with chitosan in order to improve the color yield and/or the fastness properties of cotton fabrics in dyeing with natural dyes will be given.

Results Related to UV Protective Functionalization of Cotton Fabrics via Dyeing with Natural Dyes

The plants, which gave the best results in terms of color yield and fastness in dyeing of cotton fabrics, were catechu, indigo, myrobalan, pomegranate peel, turmeric, and white

Table 7. UV protection properties of undyed and dyed cotton knitted fabrics

Dye plant used in dyeing	UV protection factor	T (UVA)	T (UVB)	Critical wavelength	UV protection class
-	17.68	12.47	4.50	385	Medium
White onion peel	262.31	0.52	0.39	389	Maximum
Turmeric	73.59	1.43	1.34	390	Maximum

onion peel. A comprehensive literature search was then conducted to determine whether cotton fabrics dyed with these plants exhibited UV protection at the same time or not. Only the UV protection effects of turmeric and white onion peel have been tested in this study since it has already been determined in the previous studies [21,22] that myrobalan, indigo, catechu, and pomegranate peel have UV protection effect on the cotton fabric. Results are given in Table 7.

When Table 7 is examined, it is seen that the undyed fabric shows moderate UV protection, whereas the fabrics dyed with white onion peel or turmeric have very high UV protection effect. This further demonstrated that the fabrics dyed with natural dyes strongly blocked ultraviolet radiation. Thus, they could effectively protect skin from solar ultraviolet radiation [35]. Another important result is that the fabric dyed with white onion peel has higher UV protection ability than the fabric dyed with turmeric. As stated in the literature, the extent of upgrading the UV protection property by using natural dyes is governed by the chemical structure of the dyes and its absorption characteristics in the UV region [20]. These results demonstrate that both color and UV protection functionality can be obtained on cotton knitted fabrics with a single step process via natural dyeing.

Conclusion

In this study, the color gamut which can be obtained with natural dyes on cotton fabrics without mordant usage was determined by working with 40 dye plants. According to the results of experimental studies, it can be said that our starting hypothesis, which claims that there should be some natural dyes potentially having the ability of dyeing cotton fibers without the need of mordant usage, was confirmed. In the light of dyeings carried out with 40 different plants without mordant usage, it is possible to suggest the use of

· pomegranate peel or turmeric for yellow,
· madder or quince for red,
· indigo for blue,
· myrobalan for green,
· white onion peel for yellowish brown and
· catechu for reddish brown

colors on cotton fabrics. Furthermore, it was determined that washing, rubbing, and light fastness values of fabrics dyed with these plants (except turmeric) vary between moderate and very good. On the other hand, both acidic and alkali perspiration fastness values of these natural dyes, except catechu, are between medium to very good levels.

Besides, in this study it was determined that the cotton fabrics dyed with white onion peel or turmeric also have very high UV protection effects. As a result it can be concluded that, cotton fabrics could be dyed in saturated colors and good fastness values with natural dyes without mordant usage if dye plants having suitable chemical structure are used. In this case, UV protection functionality will also be obtained at the same time. It can be said that this situation will provide a significant advantage in terms of economic and ecologic production. It is believed that the findings of this study will help the researchers working on application potential of natural dyeing in industrial scale to solve the problems like necessity of mordant usage. Furthermore, in the future studies tri-chromatic dyeings with natural dyes on cotton fabrics could be investigated.

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