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Dyeing of Silk Fabric with Cuminum Cyminum L as a Source of Natural Dye

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Abstract: In the present study an attempt has been made to dye the silk fabric with *Cuminum Cyminum L*, commonly known as cumin seeds, as a source of natural dye which has not been exploited as natural dye by far. Optimization of natural dye extraction from cumin seeds with respect to buffer medium; acidic, neutral and alkaline and dyeing parameters viz., dyeing time, dyeing temperature, electrolyte concentration to aid exhaustion was done. Dyeing of silk fabric was carried out with the aqueous extract of cumin seeds with and without mordant. Dyeings obtained without mordants were compared with those obtained by pre-mordanting with Tannic acid and various Metallic mordants viz., Potassium aluminium sulphate, Ferrous sulphate, Copper sulphate, Stannous chloride and Potassium dichromate and their combinations. Findings show that the natural dye extracted from cumin seeds has good potential in the textile dyeing and can be exploited further.
Keywords: Cuminum Cyminum L; Natural dye; Silk; Mordants; Fastness properties.

1. Introduction

People have relied on insects, leaves and roots of plants for thousands of years to impart colour onto textiles. Today, natural dyes have almost no economical importance and are used in limited quantities by craftsmen. However, with the consumer’s growing appetite for eco-friendly apparel, it might be prudent to check-out natural dyes[1]. With the plethora of chemical dyes available and recognition of the harmful effects of these substances, natural dyes are being looked at with renewed interest. Natural dyes are seen as more eco-friendly, unlike their synthetic counterparts, as they are all derived from nature[2]. Natural dyes[3], have the ability to produce wide range of tints and shades, with the same dye material, but with the invention of synthetic dyes in 1856, the prominence of natural dyes slacked because the synthetic dyes had some advantages over natural dyes like colour fastness, good reproducibility of shades, brilliance of colour and easy to use[4]. Natural dyes may have a wide range of shades, and can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit[5]. Recently, a number of commercial dyers and small textile export houses have started looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles to overcome environmental pollution caused by the synthetic dyes[6].

The use of vegetable materials in textile colouration is a well known way of utilizing renewable raw materials according to the technical, economical, and ecological requirements of the 21st Century[7].

With this background, in this study, cumin seeds (*Cuminum Cyminum L*) had been taken as a source of natural dye for dyeing of silk fabric which has been hitherto unexplored. *Cuminum Cyminum L* is an annual plant of the family Apiaceae. Fruits of *Cuminum Cyminum L*, commonly known as *jeera* in India are consumed as condiment across the globe. The fruits are rich in estrogenic, iso-flavonoids, luteolin and apigenin[8]. Cumin is known to have been cultivated since antiquity, and is now mainly cultivated in North Africa, Iran, India, Indonesia and China. The fruit has also been used for medicinal purposes[9]. Moreover, cumin oil shows high antifungal activity against various pathogenic fungi and effective antibacterial activity. The yellow-coloured fresh oil contains cuminaldehyde and two p-menthadienals as its chief components[10].

The present research aims at optimizing extraction conditions of colouring component from the cumin seeds with environmental friendly extraction procedures and its application on silk fabric. The research work reports dyeing of silk fabric with *Cuminum Cyminum L* as a source of natural dye in presence of natural mordant like tannic acid and different metal salts like potassium aluminium sulphate, ferrous sulphate, copper sulphate, stannous chloride and potassium dichromate. The colour strength values were studied and colourfastness properties of the dyed fabrics were evaluated.

2. Experimental

2.1. Materials and Equipment

Dried cumin seeds were purchased from the local market. Formic acid, Sulphuric acid (H_2SO_4), Glauber salt and mordants like Tannic acid, Aluminium potassium sulphate (Alum), Ferrous sulphate ($FeSO_4$), Copper sulphate ($CuSO_4$), Stannous chloride ($SnCl_2$) and Potassium dichromate ($K_2Cr_2O_7$) were supplied by S D Fine Chemicals Ltd., Mumbai. Silk fabric was purchased from Piyush Syndicate, Mumbai. Rota dyer machine from Rossari Lab Tech., Computer Colour Matching System (Spectra Scan 5100+, Data colour International, U.S.A); TECHCOMP UV-Visible Spectrophotometer (UV-VIS 8500), Crock meter from Rossari Lab Tech Pvt. Ltd. and Light Fastness Tester by Q-Sun's Xenon Arch Light Fastness Tester were used for testing.

2.2. Optimization of Dye Extraction Conditions

Optimization of dye extraction conditions was done by firstly optimizing the dye extraction medium. It was done by extracting fixed quantity of cumin seeds in three different buffer mediums viz., acidic, neutral and alkaline. Extraction was carried out at 80^{o}C for 3 hours as these extraction parameters are in vogue and are considered to extract maximum dye by the end of 3 hours. The extracts obtained with different buffer mediums were analyzed for their optical density values by using TECHCOMP UV-Visible Spectrophotometer (UV-VIS 8500) and were also used to dye silk fabric at 100^{o}C keeping 50:1 liquor ratio for 1hour. In total, nine dyeings were carried out by adjusting pH of the extracts obtained from each buffer medium to 3, 7 and 9. On the basis of the optical density values of the extracts and the colour strength value obtained on the fabric, the extraction conditions were optimized.

Optimization of the quantity of dye material to be used for the extraction of dye, the solutions were prepared by extracting 10, 20, 30, 40, 50, 60, 70, 80 and 90 gms. of cumin seeds in 100 ml of optimized extraction medium at 80-90^{o}C for 3hours. All the extracts obtained were used to dye separately the silk fabric with the addition of 1% H_2SO_4 and 5% Glauber salt at 100^{o}C keeping 50:1 liquor ratio for 1 hour. The extract which showed the maximum colour strength value on fabric was further utilized to optimize the dyeing conditions.

2.3. Optimization of Dyeing Conditions

For optimizing the dyeing conditions, at first, experiments were carried out to optimize the dyeing temperature. Dyeings were carried with optimized Cuminum Cyminum extract at 40, 60 80 and 100^{o}C, keeping 50:1 liquor ratio for 1hour in presence of 1% H_2SO_4 and 5% Glauber salt to promote exhaustion. Then to study the effect of dyeing time another set of experiment was carried out at optimized temperature for 0, 30, 60 and 90 mins. keeping the liquor ratio, concentration of sulphuric acid and glauber salt as mentioned above. To study the effect of electrolyte concentration on colour strength, dyeings were carried out with 1%, 3% and 5% H_2SO_4 and 5%, 10% and 15% Glauber salt at optimized dyeing temperature and dyeing time keeping above mentioned liquor ratio. Based on the K/S and % strength values of the dyed samples, optimum dyeing temperature, dyeing time and electrolyte concentration were selected and taken for further study.

2.4. Optimization of mordant concentrations

To study the effect of different mordants and their varying concentrations on colour strength, mordanting was carried out with five metallic salts viz., alum, ferrous sulphate, copper sulphate, stannous chloride and potassium dichromate and one natural mordant viz., tannic acid with 2%, 5%, 7% and 10% o.w.f. each. Pre-mordanting was carried out at 60°C for 1hour keeping 30:1 liquor ratio. From the K/S and % strength values the concentration which gives the best result was selected as optimum mordant concentration.

2.5. Determination of colour strength value of dyed fabric

Estimation of the colour strength of dyed fabrics was carried out by determining K/S values using a Computer Colour Matching System (Spectra Scan 5100+, Data colour International, U.S.A). Kubelka-Munk K/S function is given by:

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

where "R" is the reflectance at complete opacity, "K" is absorption coefficient and "S" is the Scattering coefficient.

The shades obtained were evaluated in terms of CIELAB colour space viz., L*, a*, b* by using Computer Colour Matching System[11]. In general, higher the K/S values higher the depth of the colour on the fabric. The L* value indicates perceived lightness or darkness where value of 0 indicates black and 100 indicates white. The values of a* and b* indicates red (+a*) and green (-a*) while b* value indicates yellow (+b*) and blue (-b*). The values of C* indicates the chroma coordinates i.e. the perpendicular distance from the lightness axis whereas H* indicates the hue angle expressed in degrees, with 0° being a location on the +a* axis, then continuing to 90° for the +b* axis, 180° for –a*, 270° for –b* and back to 360° = 0° [12,13]. As a whole, a combination of these entire enables one to understand the tonal variations.

2.6. Fastness Testing

The dyed samples were tested according to ISO standard test methods. Colourfastness to washing was assessed as per ISO 105-CO2: 1989, Colourfastness to rubbing on Crock meter as per ISO 105-X12: 2001 and Colourfastness to Light on Q-Sun's Xenon Arc Light Fastness Tester as per AATCC 117.

3. Results and discussion

3.1. Optimization of dye extraction conditions

Natural dye from cumin seeds was extracted in three different buffer mediums viz., acidic, neutral and alkaline buffers. The λ_{max} and optical density values for each extract are shown in Table 1.

Table 1. a_{max} and optical density values of different extracts

Extract medium	a_{max}	Optical density
Acidic	428 nm	0.1164
Neutral	428.7 nm	0.1617
Alkaline	390 nm	0.5135

It can be seen from the table that acidic and neutral extract shows λ_{max} of 428nm with the optical density value of 0.1164 and 0.1617 respectively whereas alkaline extract has the λ_{max} of 390nm with 0.5135 optical density value.
The colour strength in terms of K/S values of the fabrics dyed with these buffer extracts are shown in Table 2.

Table 2. K/S values of the fabric dyed with different extracts and at different pH

K/S values of the dyed fabric			
Adjusted pH	Extraction medium		
	Acidic	Neutral	Alkaline
pH 3	2.1468	2.1477	2.1769
pH 7	2.4211	1.8211	1.5474
pH 9	4.3294	2.6482	1.6751

As seen from the Table 1 the optical density value is more for the alkaline extract however dying on the fabric does not reflect that as the pigment which was extracted in alkaline medium probably is not dyeable. Also distinctly for comparison purpose K/S values are in the range for all extracts dyed at pH 3 which also confirms that there is extraction of additional pigment under alkaline extraction condition having no affinity for silk fibres under experimented dyeing conditions. From Table 2 it can be seen that acidic extract seems to be giving higher dyeing depth compared to other extracts. Although the K/S value for dyeing at pH 9 of acidic extract was observed to be significantly higher than that of dyeing at pH 3 and pH 7, pH 3 of acidic extract was selected as optimum pH for dyeing of silk fabric as silk dyeing is recommended to be carried out in acidic medium as silk is sensitive to alkaline medium of dyeing. It is also reported that during dyeing of silk under acidic pH, there is an increase in the protonation of the amino ($-NH_2$) groups of amino acids in the silk protein. The anion of the dye has complex characters, and when it is bound on the fibre with ionic forces, this ionic attraction would increase the dyeability of the fibre[13].

The effect of increase in the quantity of cumin seeds in the extraction bath on relative colour strength of the fabric is shown in Figure.1. With increase in quantity of cumin seeds in the extraction bath, the colour strength value increases but up to a certain limit. Further increase in the quantity of cumin seeds in the extraction bath does not give increase in the colour strength value of fabric, rather it remains constant. This effect can be attributed to the phenomenon of dye getting saturated in limited quantity of water which is used for extraction, thus dye solution achieving a state of equilibrium. It can also be said that, higher the quantity of cumin seeds in the extraction bath, higher is the colouring component extracted and higher is the colour strength value on the fabric dyed with these extracts until the dye exhaustion on fabric attains equilibrium i.e. equilibrium between the dye in solution and dye on fabric. As the fibre surface has limited adsorption capacity for dye molecules, when the dye concentration in the bath increases the surface gradually gets saturated keeping K/S values almost constant.

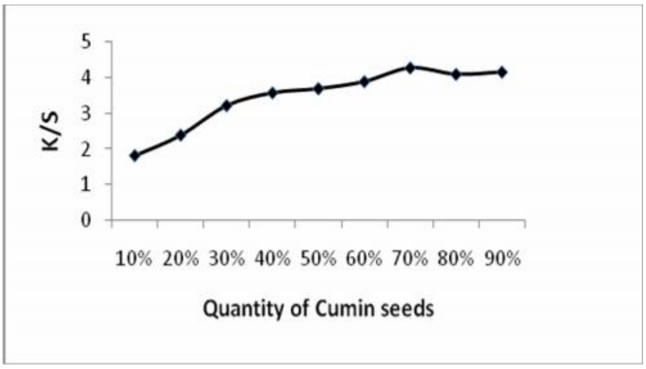

Figure 1. Effect of quantity of cumin seeds (gm/100ml of Buffer 3) on K/S value of fabric

3.2. Optimization of dyeing parameters
3.2.1. Effect of electrolyte concentration

Figure. 2 shows the effect of salt concentration on the colour strength obtained for the dyed fabrics. It is seen that as the salt concentration increases the colour strength increases and then decreases. The difference in colour strength value obtained for 1% H_2SO_4+10% Glauber salt and 3% H_2SO_4+15% Glauber salt was marginal and hence, 1% H_2SO_4+10% Glauber salt was taken as optimal electrolyte concentration.

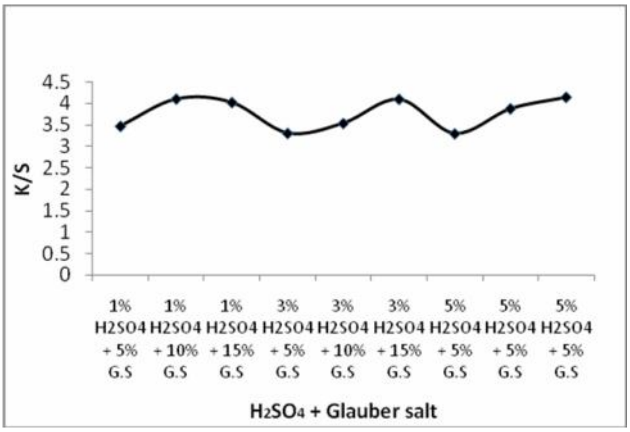

Figure 2. Effect of electrolyte on K/S value of fabric

3.2.2. Effect of temperature

The effect of temperature on the dyeability of silk fabrics with Cuminum Cyminum dye was conducted at different temperatures (40-100^{o}C). As shown in Figure. 3, it is clear that the colour strength increases with the increase of dyeing temperature and reaches a maximum value at 100^{o}C.

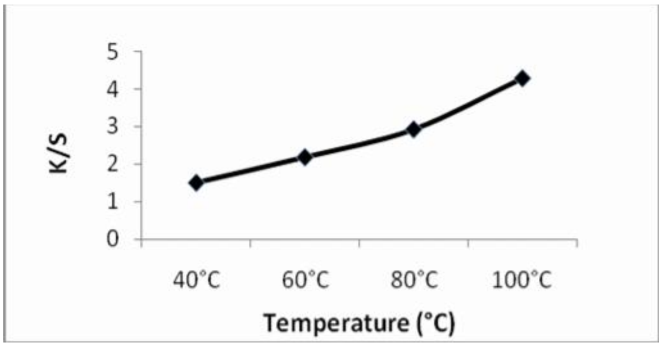

Figure 3. Effect of dyeing temperature on K/S value of fabric

3.2.3. Effect of dyeing time

As shown in Figure. 4, the colour strength obtained increased as the time increases up to 60 min, and then it decreases, i.e., dyeing for 60 mins. gave high colour strength value.

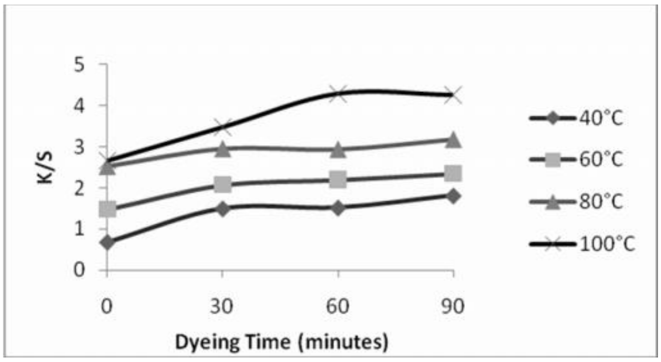

Figure 4. Effect of dyeing time on K/S value of fabric

3.3. Optimization of concentration of mordants

The silk fabrics were first treated with tannic acid which is a natural mordant and then mordanted with all the five metal mordants taken under study i.e. (Alum, $FeSO_4$, $CuSO_4$, $SnCl_2$, $K_2Cr_2O_7$) in different concentrations. The results are shown in Figure.5.

The concentration which gives maximum dye uptake value was selected as optimum and the optimized values are given as follows.

- Tannic acid : 7 % o.w.f.
- Potassium Aluminum Sulphate : 7 % o.w.f.
- Ferrous Sulphate : 2 % o.w.f.
- Copper sulphate: :10 % o.w.f.
- Stannous chloride : 7 % o.w.f.
- Potassium Dichromate : 7 % o.w.f.

3.4. Colour strength values

Table 3 shows L a b values for silk fabric dyed with Cuminum Cyminum dye extracted in acidic buffer. The L* values were higher in case of potassium dichromate mordanted samples corresponding to lighter shades whereas the L* values were found to be lower in case of ferrous sulphate mordanted samples corresponding to darker shades. C* values shows copper sulphate mordanted samples in brighter shades whereas ferrous sulphate increase dullness of shade. Also the mordanted samples shows increased dye uptake leading to higher K/S values than un-mordanted ones.

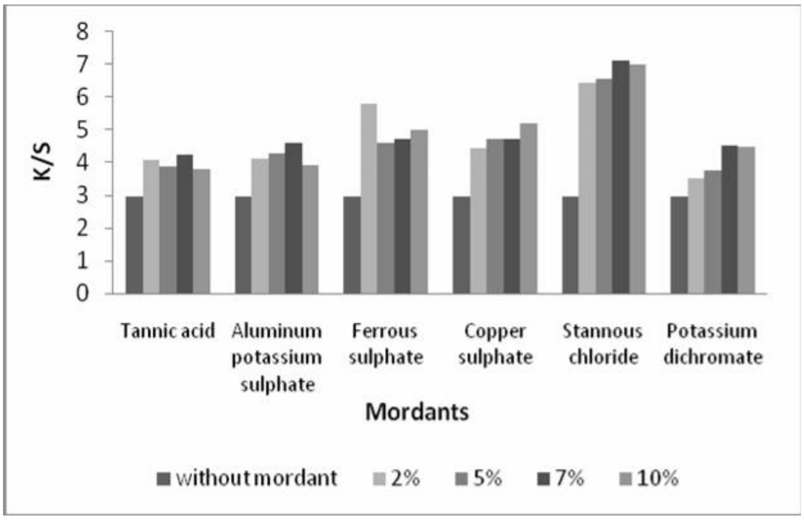

Figure 5. Effect of mordant concentration on K/S value of fabric

Table 3. Colour strength value of silk fabric pre-mordanted and dyed with Cumin dye

Samples	**L***	**a***	**b***	**dE***	**K/S**	**%**
TA + CD	66.757	3.333	33.66	------	4.2817	100
TA + Alum + CD	64.622	2.801	30.416	3.92	3.4663	80.955
TA + $FeSO_4$ + CD	46.745	3.012	9.033	31.734	9.5878	223.924
TA + $CuSO_4$ + CD	65.066	2.658	30.711	3.466	4.5406	106.046
TA + $SnCl_2$ + CD	68.811	1.325	33.278	2.898	3.1262	73.013
TA +$K_2Cr_2O_7$ + CD	72.119	0.649	41.944	10.226	12.3273	287.905

CD : Cumin dye ; **TA** : Tannic acid
L*= 0 yields black and **L*** = 100 indicates diffuse white
a* : negative values indicate green while positive values indicate magenta/red
b* : negative values indicate blue and positive values indicate yellow
C* : Chroma is a component of a colour model. There's a blue-yellow and a red-green chroma component
H* : Hue defines pure colour in terms of "red", "green" or "magenta"
dE* : Colour Difference

Table 4. Various shades obtained with cumin dye

Sr.no.	**Treatment**	**Samples**	**Shades obtained**
1	Fabric dyed with 70% cumin seeds extract (without mordanting)		**Golden Brown**
2	Fabric treated with 7% Tannic Acid followed by dyeing with Cumin Dye		**Golden Brown**
3	Fabric treated with 7% Tannic Acid and 7% Alum followed by dyeing with Cumin Dye		**Khaki**
4	Fabric treated with 7% Tannic Acid and 2% $FeSO_4$ followed by dyeing with Cumin Dye		**Coffee Brown**
5	Fabric treated with 7% Tannic Acid and 10% $CuSO_4$ followed by dyeing with Cumin Dye		**Khaki**
6	Fabric treated with 7% Tannic Acid and 7% $SnCl_2$ followed by dyeing with Cumin Dye		**Dull Brown**
7	Fabric treated with 7% Tannic Acid and 7% $K_2Cr_2O_7$ followed by dyeing with Cumin Dye		**Dark Yellow ochre**

Various shades viz., dull brown, golden brown, coffee brown, khaki, dark yellow ochre were obtained on silk fabric dyed with cumin dye without and with various metal mordants and the shade card of the same is shown below in Table 4.

3.5.Fastness properties

The colour fastness values of the fabrics dyed with cumin dye are presented in Table 5. Washing and rubbing fastness results were assessed with respect to grey scale and results for light fastness were assessed with respect to blue wool scale. Washing and rubbing fastness values of the samples dyed with and without mordant shows comparable results. The light fastness result indicates that the use of a mordant was advantageous for silk fabric dyed with cumin dye. Mordanting not only increase the dye uptake for fabric but also form metal dye complex which is more stable than colouring component itself.

4.Conclusion

In order to satisfy the demand of green minded consumers, the present study was planned, to be look out for safer alternative for dyeing with natural dyes. It was found from the study that cumin dye can be successfully used for dyeing of silk fabric to obtain wide range of soft and pastel shades with natural and synthetic mordants. The process of extraction is simple and environmental friendly. The overall fastness properties of printed fabrics ranged from good to very good to excellent. The results have shown the potential of cumin seeds as a source for dyeing of silk in yellow shades. Various shades of yellow and good fastness properties exhibited by the dyed clothes are because of the mordants used. There is a tremendous scope to use cumin dye for obtaining various color shades using safe mordants under eco-friendly textile dyeing.

Table 5. Fastness properties of silk fabric pre-mordanted and dyed with Cumin dye

Samples	Fastness properties					
	Rubbing fastness		Washing fastness			Light fastness
			Colour change	Colour staining		
	Dry	Wet		Cotton	Wool	
TA + CD	4 – 5	3 – 4	3	3	3	4 – 5
TA + Alum + CD	4 – 5	3 – 4	3 – 4	3 – 4	4	5 – 6
TA + $FeSO_4$ + CD	4 – 5	3	3 – 4	3 – 4	3 – 4	7 – 8
TA + $CuSO_4$ + CD	4 – 5/ 5	3 – 4	3	2 – 3	4	7 – 8
TA + $SnCl_2$ + CD	4 – 5	3	4	3 – 4	4	6 – 7
TA + $K_2Cr_2O_7$ + CD	4 – 5	3	4 – 5	3 – 4	4	7 – 8

References

1. Kim Anderson, Ph.D., Natural Dyes, writer/reporter for [TC]², August 2009.
2. http://www.agriculturalproductsindia.com/other-agro-products/other-miscellaneous-natural-dyes-pigments.html
3. Gulrajani M L & Gupta D, Introduction to Natural Dyes (Indian Institute of Technology, Delhi), 1992.
4. Anderson, B., Creative Spinning, Weaving and Plant Dyeing, Angus and Robinson, Singapore, 1971, 24-28.
5. Nattadon Rungruangkitkrai1, Rattanaphol Mongkholrattanasit, RMUT*P* International Conference: Textiles & Fashion 2012; July 3-4, 2012, Bangkok Thailand
6. Glover, B. and Pierce, J. H. Are natural colorants good for your health?, *Journal of the Society of Dyers and Colourists*, Vol. 109 (1993) No. 1, pp. 5-7, ISSN 1478-4408.
7. http://www.fabrikderzukunft.at/results.html/id4117.
8. Sarika S. Shirke, Aarti G. Jagtap, Effects of methanolic extract of Cuminum Cyminum on total serum cholesterol in ovariectomized rats, Indian J Pharmacol., April 2009, 41(2): 92-93.
9. Toru ISHIKAWA, Tomomi TAKAYANAGI, and Junichi KITAJIMA, Water-Soluble Constituents of Cumin: Monoterpenoid Glucosides, *Chem. Pharm. Bull.*, November 2002, 50(11) 1471-1478.
10. Yüksel KAN et al., Composition of Essential Oil of Cuminum Cyminum L. According To

Harvesting Times, Turkish J. Pharm. Sci., 2007, 4 (1) 25-29.
11. Ali S et al., Optimization of alkaline extraction of natural dye from heena leaves and its dyeing on cotton by exhaust method, J Clean Prod (2008), doi : 10.1016/j.jclepro.2008.03.002
12. http://www.colourphil.co.uk/lab_lch_colour_space.html
13. http://en.wikipedia.org/wiki/Lab_color_space
14. Montra Chairat et al., An adsorption and kinetic study of lac dyeing on silk, Dyes and Pigments, 64(2005) 231-241.

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