Nat. Volatiles & Essent. Oils, 2021; 8(4): 14255-14268

NVEO
Natural Volatiles &
Essential Oils

Natural Black Dyeing: A Sustainable Way Ahead

Dr. Sabrina Sareen

Associate Professor**,** Fabric and Apparel Science, Department of Home Science**,** Lakshmibai College, University of Delhi, Delhi

ABSTRACT

Traditionally, the methods used for natural black dyeing, have been riddled with problems due to complexities of procedures involved, low colour yield and poor fastness properties. In the present study, an attempt was made to produce a good black hue on Cotton, Woollen and Silk fabrics using a single or a suitable combination of Natural dyes of primary colours - Red, Blue, and Yellow along with mordanting. The dyed samples were analysed for their colour value in terms of their L*a*b* and K/S measurements and fastness properties to light and washing. Among all the dyes samples the ones within the 'Circle of Tolerance Limits' were selected as close to ideal black. This research work has been awarded as The Best Project Award in Natural Dyes by Alps Industries Ltd.

Keywords: Complexities, Fastness, Hue, Mordanting

INTRODUCTION

An interesting colour black, has a sophisticated appeal, which makes it appropriate for select quality merchandise. It epitomizes authority, sophistication and has overtones of sensuality (EraGem, 2020).The colour is associated with Hi-Fashion –The Haute Couture, Chic Packaging and Avant-Garde designs (Bane, 2018)

Since the classical age, admiration for black colour, has seen it being extracted from natural sources like pepper, blackberries, pomegranate and logwood (Mohanty, et.al., 1987). It's use in the more popular Madhubani and Kalamkari paintings, has had black being produced from Iron acetate of sugarcane and palm jaggery in combination with Myrabolan (Cardon,D, 2007). However, traditional methods of natural black dyeing have been riddled with problems (Zollinger, 2004). This is due to the complexity of procedures involved, poor fixation of dye stuffs

(Arora, et.al., 2017) leading to poor fastness properties (Vankar, P.S., et.al., 2001) and very low colour yield, making the process highly uneconomical (Saxena, et.al.,2001) and commercially unviable (Gulrajani & Gupta 1992). Hence, in the present study, an attempt was made to produce a good black hue on cotton, wool and silk using a single or a suitable combination of dyes of primary colours - Red, Blue and Yellow along with mordanting. Dyeing had been carried out using the Exhaust and Dip Dyeing methods in a three-step dyeing process.

OBJECTIVES

1. To standardize the dyeing procedure of developing black colour on cotton, wool and sil, using natural dyes in combination with mordant.
2. To measure colour value of the dyed samples in terms of their L*a*b* and K/S values.
3. To test wash fastness and light fastness of the dyed samples

MATERIALS AND METHODS

- Three **Natural fibres** were used for the study, which were, 100% cotton yarn (leas), 100% wool yarn (leas) and 100% mulberry silk fabric (plain weave) respectively.
- Various **natural dyes** selected were -
  Acacia catechu (Thar), Coccus laccae (Lac), Indigofera tinctoria (Indigo), Punica granatum (Pacific) & Termenalia chebula (Kongo)
- **Chemicals used** were -
  -- Oxalic acid $(COOH)_2, 2H_2O$
  -- Sodium Hydroxide (NaOH)
  -- Sodium Hydro-sulphite ($Na_2S_2O_4$)
  -- Sodium Carbonate (Na_2CO_3)
- **Mordant Used**
  -- Ferrous sulphate ($FeSO_4, 7\ H_2O$)

For the study, natural dyes, mordants and pre-treated cotton leas that had been scoured, bleached and desized were provided by the Alps Industries. The Woollen leas were given scouring treatment at 60°C for 1/2 hour using Lissapol solution. The M.L.R (Material To Liquor Ratio) was 1:30. The silk fabric had been degummed and bleached, to remove all impurities present. The Degumming operation was carried out in a liquor containing 1 g/l of Lissapol, 0.4% o.w.f concentration of Na_2CO_3 & 0.5% NaOH at 90°C for 30° minutes.

- **Dyeing Methods**

The dyeing was carried out on Cotton, Wool & Silk using either a single or a suitable combination of Natural dyes of primary colours - Red, Blue & Yellow along with mordanting with $FeSO_4$, at 2% o.w.f concentration. The procedures used are as follows:-

a) Dyeing with Acacia catechu (Thar):

The dye bath was prepared at an M.L.R (Material To Liquor Ratio) of 1:30 which was heated to a temperature of 80°C. The goods were entered and dyeing was carried out for 30 minutes. The pH was noted as 6.

Post-mordanting of the Thar dyed materials was carried out with Ferrous sulphate at 2% concentration owf. The mordanting was done for 20 minutes at 40°C.

b) Dyeing with Indigofera tinctoria (Indigo):

Dyeing with Indigo was carried out in an Indigo vat, where the dye was pasted with a few drops of water. Sodium Hydro-sulphite (same quantity as Indigo dye concentration) was added to the vat, followed by the addition of 20 ml of water, Lastly, Sodium hydroxide pellets (1/4 of Indigo dye concentration) were added to the Indigo vat. The material was added to the vat and the dyeing was done at room temperature. After dipping for 15 minutes, the material was taken out, squeezed and oxidized by exposure to the air for 10 minutes. Goods were then re-dipped in the Indigo vat for another 15 minutes, taken out and squeezed and exposed to air. The chemical oxidation of the Indigo dyed material was done using 2 g/l Hydrogen peroxide for 10 minutes at room temperature. The M.L.R. for dyeing was 1:30. Note: For wool and silk, the dyeing pH was kept at 9 and for cotton, the pH was 10.5-11.5.

c) Dyeing with Punica Granatum (Pacific) and Terminalia Chebula (Kongo) -

The dye bath was prepared, by taking required M.L.R of 1:30 and was heated to 80°C. The goods were entered and dyeing was done for 30 minutes. The pH was noted as 6.

Post-mordanting of the Pacific and Kongo dyed samples was done using Ferrous sulphate at 2% owf concentration at 40° C for 20 minutes.

d) Dyeing with Coccus laccae (Lac dye)

Woollen and silk materials were dyed with the Lac dye. The dyeing was carried out at 70°C for 30 minutes.

The pH of the dye bath was maintained between 2-3 using oxalic acid. The M.L.R. was maintained at 1:30. Mordanting treatment given to Lac dyed samples were:

(a) Simultaneous mordanting with Ferrous sulphate at 2% concentration o.w.f was done where black was produced using only Lac dye. Subsequent to this dyed, mordanted samples were treated with Sodium carbonate for 30 min. in an M.L.R of 1:30. The temperature was maintained at 40°C.

(b) Post mordanting of Lac dyed wool and silk samples with Ferrous sulphate at 2% concentration o.w.f was done at 40°C for 20 minutes (for 3 step dyeing procedure using Lac dye).

Black colour was achieved on the woollen leas (by a one stage application of the mordant either-simultaneous or post mordanting) whereas on silk, only a bluish black colour could be obtained by simultaneous mordanting.

Therefore a further post mordanting was carried out for a satisfactory black.

e) Dyeing using Dip method:

The materials were dyed, with the procedures given above, using Thar, Indigo and Pacific/ Kongo dyes. In the dip method, dyeing was carried out in two cycles. The dye baths from the first dyeing cycle were retained and the materials were re-dipped for the second cycle in the same dye baths. The 1st dyeing cycle was for 30 minutes and 2nd cycle was 15 minutes.

For post-mordanting with Ferrous sulphate at, 2 % concentration, the mordant baths were prepared fresh for both the dyeing cycles (1st and 2nd).

Table -1 : Dyeing on Cotton

Dyeing on Cotton	Code No.	THAR	INDIGO	KONGO	PACIFIC	LAC
		(Mordant: FeSO4 at 2% concentration)				
a. Using Pacific						
	L	6%	4%	-	13%	-
	U	6%	6%	-	13%	-
	G	6%	6%	-	15%	-

	B-1	10%	10%	-	15% ,	-
	R-1	10%	10%	-	15%	-
	T	10%	10%	-	20%	-
	N	15%	10%	-	20%	-
b. Using Kongo	1	6%	6%	15%	-	-
2. **Dip Method Dyeing**:						
a. Using Pacific	A-1	10%	6%	-	15%	-
	R-2	10%	10%	-	15%	-
	V	15%	10%	-	20%	-
b. Using Kongo	1-2	6%	6%	15%	-	-

Table -2: Dyeing on Wool

Dyeing on Wool	Code No.	THAR	INDIGO	KONGO	PACIFIC	LAC
1. **3 Step Dyeing Procedure**						
Exhaust Method:						
a. Using Pacific	P-1	6%	6%	-	13%	-
	P	6%	6%	-	15%	-
b. Using Kongo	X	6%	6%	15%	-	-
Dip Method Dyeing:						
a. Using Pacific	D-P	6%	6%	-	15%	-
b. Using Kongo	D-X	6%	6%	15%	-	-
3 Step Dyeing Procedure:						
a. Using Lac	Z-2	-	4%	-	13%	6%
	Z-1	-	6%	-	13%	6%
	Z	-	6%	-	15%	6%

Dyeing on Wool		**Lac**		**Sodium Carbonate**
2. **Single Step Dyeing procedure**				
Simultaneous mordanting using FeSO4 at 2% concentration	B	7%		10%
	Y	10%		10%
	W	10%		13%

Table-3 Dyeing on Silk

Dyeing on Silk	Code No.	THAR	INDIGO	KONGO	PACIFIC	LAC
	(mordant: $FeSO_4$ at 2% concentration)					
1. **3 Step Dyeing Procedure** **Exhaust Methods**:						
a. Using Thar	A	6%	6%	-	15%	-
b. Using Lac	B	-	6%	-	15%	6%
Dyeing on Silk		**Lac**		**Sodium Carbonate**		
2. **Single Step Dyeing Procedure** Simultaneous mordanting using $FeSO_4$ at 2% concentration						
	C	7%		10%		
	F	10%		10%		
	E	10%		13%		

Table- 4: L* Values of Cotton

Dyeing methods		Sample (Code No.)	L*
1.	**Exhaust Method:**		
a.	Using Pacific	L	25.43
		U	19.51
		G	17.35

		B-1	14.16
		R-1	16.24
		T	14.81
		N	15.70
b.	Using Kongo	I	16.00
2	**Dip Method:**		
a.	Using Pacific	A-1	13.12
		R-2	13.08
		V	12.11
b.	Using Kongo	1-2	16.82

Table -5: L* Values of Wool

Dyeing methods		Sample (Code No.)	L*
1.	**Exhaust Method:**		
a.	Using Pacific	P-2	12.92
		P-1	12.89
		P	12.69
b.	Using Kongo	X	13.74
2.	**Dip Method**		
a.	Using Pacific	D-P	12.60
b.	Using Kongo	D-X	13.80
		Z-1	11.82
3.	**Exhaust Method**		
b.	Using Lac	Z -2	11.90
4.	**Using Lac Dye after treatment with Sodium Carbonate**		
		B	11.96
		Y	12.29
		W	11.30

Table -6: L* Values of Silk

Dyeing methods		Sample (Code No.)	L*
1.	**Exhaust Method:**		
a.	Using Pacific	A	27.34
b.	Using Lac	B	26.48
2.	**Using Lac Dye after treatment with Sodium Carbonate**		
		C	26.85
		F	28.01
		E	24.18

- **Testing**:

The dyed samples were analysed for their colour value in terms of their L*a*b* & K/S measurements and fastness properties to light and washing.

The ACS spectrophotometer interfaced with an IBM. PC was used to analyse the K/S values of samples.

The values of CIELAB co-ordinates L*a*b*, a measure of colour quantity, type and amount of colour in a specimen was measured using a spectrophotometer interfaced with an IBM computer. In the present study, for the black dyed samples, central point (O, O) on the CIE co-ordinates in the Anlab Colour Space was considered as standard pure black and a specified area around the centre indicated by circle was considered as acceptable limits for black dyed limits for black dyed samples. Hence, in the study, “Circle of Tolerance Limits” which defines the acceptability standards for a black dyed sample was used.

The wash fastness of the samples was tested according to ISO105/ E-1978 specifications in the Paramount Launderometer.

The light fastness of the samples was tested in the Sun test CPS+(Atlas) Light fastness tester with Xenon lamp.

Table -7: K/S Values of dyes Cotton samples

Dyeing Methods	Sample (Code No.)	K/S
1. **3 Step Dyeing Procedure**		

a. Using Pacific		
	L	15.62
	U	15.93
	G	16.19
	B-1	21.03
	R-1	18.05
	T	19.58
	N	24.26
b. Using Kongo	1	16.54
2. **Dip Method Dyeing:**		
a. Using Pacific	A-1	22.05
	R-2	22.00
	V	25.17
b. Using Kongo	1-2	18.25

Table -8: K/S Values of dyed Woolen samples

Dyeing methods		Sample (Code No.)	L*
1.	**Exhaust Method:**		
a.	Using Pacific	P-2	23.05
		P-1	23.10
		P	23.16
		X	23.40
b.	Using Kongo		
2.	**Dip Method**		
a.	Using Pacific	D-P	23.08
b.	Using Kongo	D-X	23.38
3.	**Exhaust Method**		

b.	Using Lac	Z-1	25.72
.		Z -2	25.58
		Z	25.89
4.	**Using Lac Dye after treatment with Sodium Carbonate**		
		B	25.89
		Y	24.13
		W	25.99

Table– 9: K/S Values of dyed Silk samples

Dyeing methods		Sample (Code No.)	L*
1.	**Exhaust Method:**		
a.	Using Thar	A	9.04
b.	Using Lac	B	9.64
2.	**Using Lac Dye after treatment with Sodium Carbonate**		
		C	8.23
		F E	7.78 9.77

RESULT AND DISCUSSION

The results of L*a*b*, K/S, Wash and Light Fastness tests for Cotton, Wool and Silk samples were as follows:

(a) Cotton:

In the exhaust method of dyeing using Pacific, Indigo and Thar dyes, there was one sample in the Circle of Tolerance Limits (CTL). This had been dyed with maximum concentrations of the 3 dyes (Sample N) (Refer to Fig.1).

Visually, amongst all the sample, the darkest was sample B-1 which was on the borderline of the circle. This sample had lowest value of L* probably due to a higher Indigo concentration. It was seen that as Indigo concentration was increased the samples became more intensely black, gradually moving towards the circle.

Cotton leas, were also dyed with the dip method of dyeing. Most of the samples obtained were good blacks & were found to be within the CTL. The darkest sample achieved by this process was samples V, with the lowest L* value of 12.112. Hence, amongst all the methods tried on cotton, the dip method using pacific gave best results. These samples also gave maximum values of K/S, followed by the exhaust-Pacific dyed samples (Refer to Tables 4 & 7).

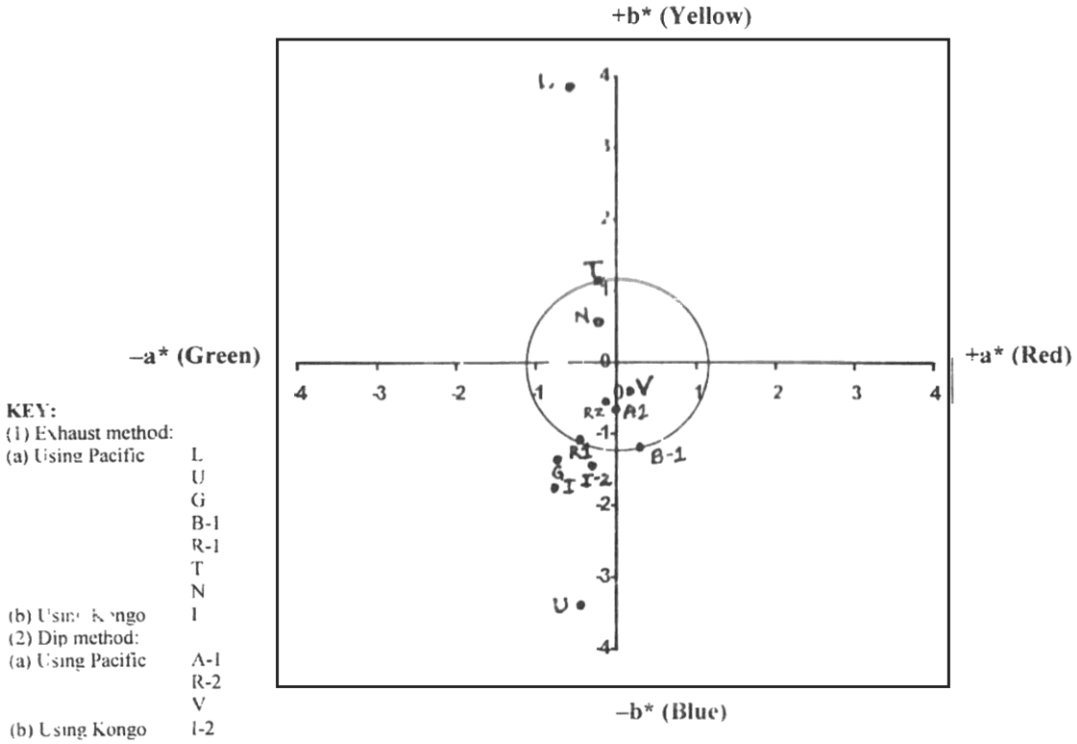

Figure 1: Plot of a*b* values of Cotton

(b) Wool:

The a*b* plot shows that 8 woollen samples were within the CTL, close to ideal black colour. In case of the exhaust method of dyeing using Pacific, Indigo and Thar dyes there were two samples within the circle (sample P&P-1). The sample P was closest to the centre point with L* value of 12.69. In case of wool, too, as the concentrations of Indigo was increased, the samples

became more intensely black. However, unlike cotton, in case of wool, the exhaust method was able to achieve darker blacks when compared with dip method of dyeing (Refer Fig 2).

The woollen leas (sample Z, Z-1, Z-2) dyed with exhaust method using Lac, Indigo and Pacific dyes were also found to have low L* values. The best blacks were achieved with a combination of Lac dye and Sodium carbonate. These samples (sample W) had lowest L* values & were found to be within the circle (Refer Table 5).

As regards the K/S values, sample W, had the highest value of 25.99, closely followed by sample Z at 25.89.

The Exhaust - That dyed sample (sample P) had lower K/S value than sample Z (Refer Table 8).

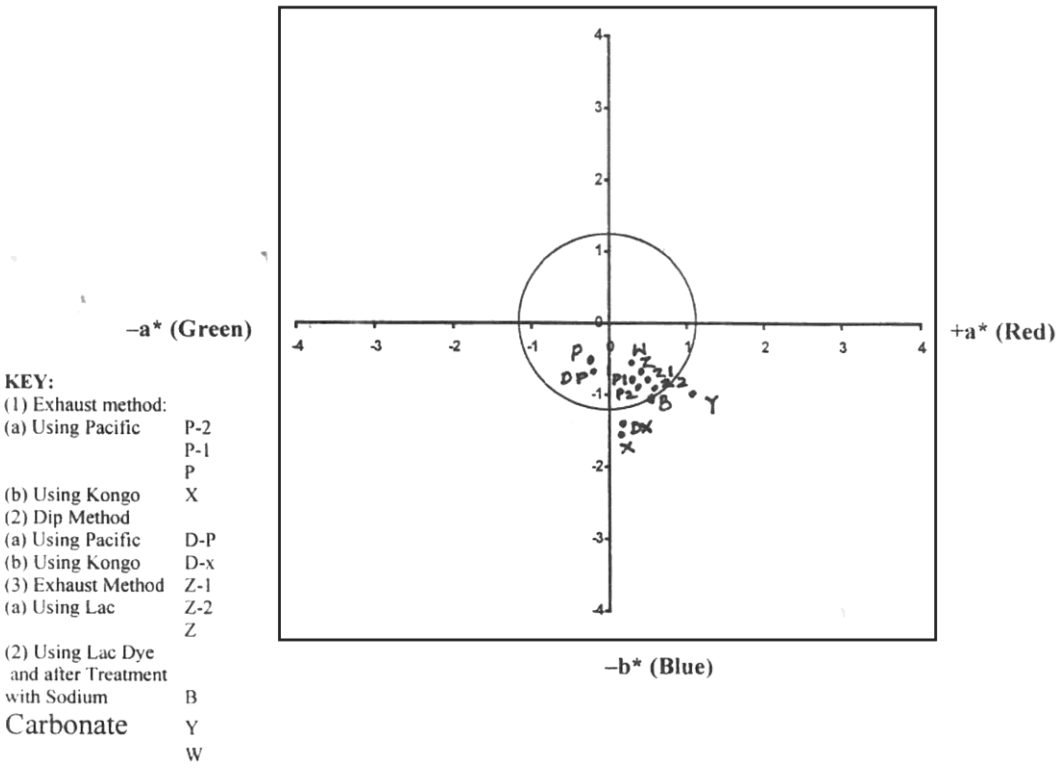

Figure 2: Plot of a*b* values of Wool

(c) Silk:

It was seen that the best black in terms of the L*a*b* values had been achieved using Lac dye & sodium carbonate (sample E). Sample B was also found to lie inside the circle (Refer to Fig 3). This had been dyed using Exhaust Lac method. The Exhaust - Thar dyed sample (sample A), also gave a satisfactory black, the highest K/S values were achieved for sample E the Exhaust - Lac & Exhaust - Thar dyed samples showed slightly lower K/S values (Refer to Table 9).

The light fastness of cotton, and wool samples were excellent, showing a rating ranging between 5-6. In case of silk samples. Light fastness was observed as ranging between 4*5.

The wash fastness of all the dyed samples was found to be excellent. The rating of staining was observed to be 5 and that of colour change as 4-5.

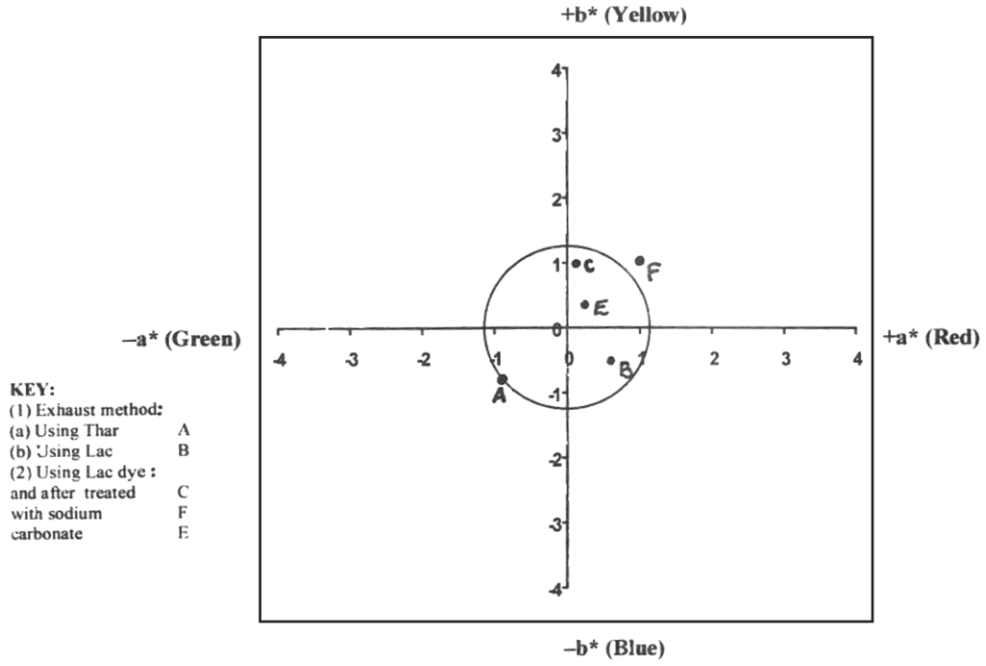

Figure 3: Plot of a*b* values of Silk

CONCLUSION

From the result of the present study, it was possible, to achieve a good black on cotton, wool & silk, using a single or a suitable combination of dyes of primary colours - Red, Blue & Yellow along with mordanting.

For the three materials, post-mordanting with Ferrous sulphate at 2% Concentration o.w.f was found to yield the best black colour. It was seen that as Indigo concentrations were increased, the samples became more intensely black and showed lower L* values. The samples dyed with Lac dyes and treated with Sodium Carbonate showed highest K/S values on Woolen and Silk fabrics. The exhaust method of dyeing, using Pacific, on cotton gave a good black. The light fastness of Cotton and Wool samples were excellent, ranging between 5-6. The wash fastness of all dyed samples was found to be excellent.

SCOPE FOR FURTHER WORK

- Development of black colour can be worked on synthetic fibres on the same lines as this study
- Further studies can be undertaken with other natural dyes, yielding Red, Blue and Yellow colours, to produce black colour on natural fibres.

REFERENCE

- Arora, J., Aggarwal, P. and Gupta, G.(2017). Rainbow of Natural Dyes on Textiles Using Plants Extracts: Sustainable and Eco-Friendly Processes. Green and Sustainable Chemistry, 7(1).Article ID:74365. 10.4236/gsc.2017.71003
- Bane, Marc. (2018, February 4). Only Black is the New Black: A Cultural History of Fashion's Favourite Shade. Quart. Retrived from: www.qz.com
- Cardon, Dominique. (2007). Natural Dyes: Sources, Tradition, Technology and Science. Archetype Publications. London.
- EraGem. (2020 September 20), The Colour Black Psychology and Meaning. Retrived from : www.eragem.com
- Gulrajani, M.L. and Gupta, D. (1992). Natural Dyes and Application to Textiles, Department of Textile Technology, Indian Institute of Technology, New Delhi, India.
- Mohanty B.C., Chandramouli K.V., and Naik H.D. (1987). Natural Dyeing Processes of India, Calico Museum of Textiles, Ahmedabad.
- Saxena, S., Varadarajan, P.V. and Nachane, N.D. (2001). Proceeding of Convention of Natural Dyes. Gupta, D. and Gulrajani, M.L., Eds., Department of Textile Technology, IIT, Delhi, 185.
- Vankar, P.S., Tiwari, V. and Ghorpade, B. (2001) Proceeding of Convention of Natural Dyes. Gupta, D. and Gulrajani, M.L., Eds., Department of Textile Technology, IIT Delhi.
- Zollinger, Heinrich, (2004). Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments, Zürich, 3rd Edition