Indian Journal of Fibre & Textile Research
Vol. 47, December 2022, pp. 450-463
DOI: 10.56042/ijftr.v47i4.47319

Optimization of extraction and dyeing parameters for dyeing of khadi cotton fabric using waste/used marigold flower petals (*Tagetes erecta*)

H D Sinnur[a], D K Verma & Tapas Ranjan Kar

Khadi & Textile Division, Mahatma Gandhi Institute for Rural Industrialization, Maganwadi, Wardha 442 001, India

Received 10 March 2021; revised received and aceepted 4 March 2022

The aim of the present study is to standardize a protocol for optimization of pre-treatment, mordanting and dyeing of cotton khadi fabric with waste marigold flower petals. The effects of different single and combined double mordanting on dye-ability and colour fastness properties have been studied after optimization of aqueous extraction of marigold flower as natural dye. Mordants used are potash alum, aluminium sulphate, stannous chloride as metallic salt mordant and harda (myrabolan) from natural source as mordant assistant. After finalizing the mordants, dyeing process variables are standardized for dyeing cotton khadi fabric with waste marigold flower extract as selective natural dye applied on 3% H_2O_2 (30%) bleached cotton khadi fabric. Dyeing process variables studied are dyeing time, temperature, MLR, *p*H, mordant concentration, dye concentration and salt concentration for dyeing with prefixed mordant. Colour fastness to washing, rubbing, light and perspiration against use of different mordants and also against different dyeing process variables are also investigated. The results indicate that, this particular natural dye renders better appreciation of colour yield by pre mordanting with 15% aluminium sulphate and harda (50:50) as compared to other single mordants (potash alum and stannous chloride) and double mordants used. Use of double mordant in 15 % application level, shows maximum *K/S* value with overall good colour fastness than others.

Keywords: Cotton khadi fabric, Fastness properties, Marigold, Harda, Potash aluminium sulphate, *Tagetes erecta*

1 Introduction

Eco-friendly and non-toxic bio-resource products are regaining popularity in different spheres of our lives due to enhanced public cognizance to eco-safety and health concerns. Natural dyes, obtained from different sources of nature such as plants, animals and minerals, are renewable. These are sustainable bio-resource products with minimum environmental impact and known since antiquity for their use, not only in coloration of textiles but also as food ingredients/ cosmetics [1-3]. In many of the world's developing countries, however, natural dyes can offer not only a rich, varied source of dyestuff, but also the possibility of an income through sustainable harvest and sale of these dye plants. Many dyes are available from tree waste or can be easily grown in market gardens[4]. In areas where synthetic dyes, mordants [fixatives], other additives are imported and are therefore relatively expensive, natural dyes can offer an attractive alternative[5]. Presently, there is an excessive use of synthetic dyes, estimated at around 10,000,000 tons per annum[6], the production as well as application of which release vast amounts of waste and unfixed colorants. This causes serious health hazards and disturbs the eco-balance of nature. Currently, ecological considerations are becoming important factors in the selection of consumer goods all over the world. Since the mid-1980s, more interest has been shown in the use of natural dyes and a limited number of commercial dyes. Small businesses have started looking at the possibility of using natural dyes for coloration[7]. Recently, a few studies[8-11] have been reported for the application of few selective natural dyes on cotton and other cellulosic natural fibres. But still the study on optimization of dyeing process variables for dyeing of cotton fabric with waste marigold flower petals is not reported anywhere to the best of our knowledge.

Khadi & Village Industries (KVI) sector is one of the strongest links in bridging India's economic growth with socio-economic transformation. Due to declining trend in involvement of rural youth in the agriculture sector, who generally tend to migrate to bigger towns and cities in search of employment, Khadi & Village Industries Commission (KVIC) stands as one of the attractive tools for employment generation and reverse migration. The importance of

[a]Corresponding author.
E-mail: hdsinnur.gouda@gmail.com

khadi lies in its ability to provide livelihood to around five lakh artisans who are engaged as spinners, weavers and dyers spread across the country. In such context the research work currently undertaken directly helps artisans working in KVI sector for using natural dye to dye khadi fabric under standardized conditions of extraction and dyeing without wasting either the dye source or the mordant/s or the khadi fabric. In this research work, efforts have been made to standardize the procedure for extraction and dyeing parameters for dyeing of cotton khadi fabric using wastemarigold flower petals.

2 Materials and Methods

2.1 Materials

Plain weave cotton khadi (hand-spun yarn woven in handloom) fabric, having 73 Nm warp, 70 Nm weft, 76 ends per inch, 53 picks per inch, 73.5 g/m^2 area density and 0.075mm thickness, was obtained from Gram Sewa Mandal, Gopuri, Wardha after bleaching with 3% H_2O_2 (30%) and used in this study.

Laboratory reagents (LR) grade aluminium sulphate, potash aluminium sulphate, stannous chloride, Turkey red oil, Green-zyme DSZL (Enzymatic desizing agent), Green scour RW (low foaming rewetting agent), Green Scour FC (Conc. scouring agent), sodium hydroxide, sodium carbonate, hydrogen peroxide, Pero-stab S.F (phosphate based non silicate peroxide stabilizer), Green-zyme POK (enzymatic peroxide killer), Commercial grade acetic acid obtained from local suppliers are used. Here, a natural mordanting assistant like myrabolan (harda, botanically known as *Terminalia chebula*) powder was also used as one of the mordant assistants for the study. Waste/used marigold flower (*Tagetes erecta*) petals after sun drying and crushing to dry powder was used as a natural dye for dyeing cotton khadi fabric.

Marigold is one of the widely used flowers in many of the Indian festivals, rituals and traditions. Most of the flowers are discarded after use, and hence, this wasted biomass can be used as natural dye alternative. Marigold flowers are rich in bio active components especially the carotenoid pigment (lutein). Natural tannin rich sources are used for pre-treatments that influence dye uptake and are preferable over metallic salts.

Many varieties of Marigolds have been cultivated all over the world, but two of them, namely *Tagetes erecta* and *Tagetes patula*, are most important. Marigold plants are chubby, branching and can grow up to 60 cm tall [4,12]. The Marigold flowers bloom from the beginning of summer up to autumn. Marigold flowers contain compounds called carotenoids. Lutein ($C_{40}H_{56}O_2$) is a natural dye that belongs to the carotenoid family[12]. Lutein and its isomer zeaxanthin are also known as oxy-carotenoids or xanthophylls (Fig. 1). These xanthophyll's are the basic element in the marigold flowers and present in high concentration than in other plants[13]. The xanthophylls, because of their yellow to orange- red coloration and natural occurrence in human foods, can be used as a food colorant. Therefore, there exists a high demand for the significantly pure xanthophyll's that can be used as a food colorant and a nutrient supplement. Marigold extract also finds application in coloring foods, like edible oils, mustard, other salad dressings, cakes, ice cream and dairy products.

2.2 Methods

2.2.1 Extraction of Color Component and Optimization of Extract Conditions

The petals from the waste/used Marigold flower of similar color are collected and dried in sun light. Dried flower petals are grinded to powder and taken in hot water for extraction of its color component under varying extract conditions, such as *p*H 4 – 12, MLR 1:30 – 1:80, time 15 – 90 min and temperature 60 – 90^0 C in order to optimize the conditions of extraction. Optical density at a particular maximum absorbance wavelength (λ_{max}. 423 nm) for the aqueous extract of the waste Marigold was estimated using Shimadzu –UV 2450 UV-VIS absorbance spectrophotometer. The usual *p*H of aqueous extract of waste Marigold was found to be 9, which, as per necessity, was alkalified with caustic soda solution for altering or varying the *p*H from 4 to 12.

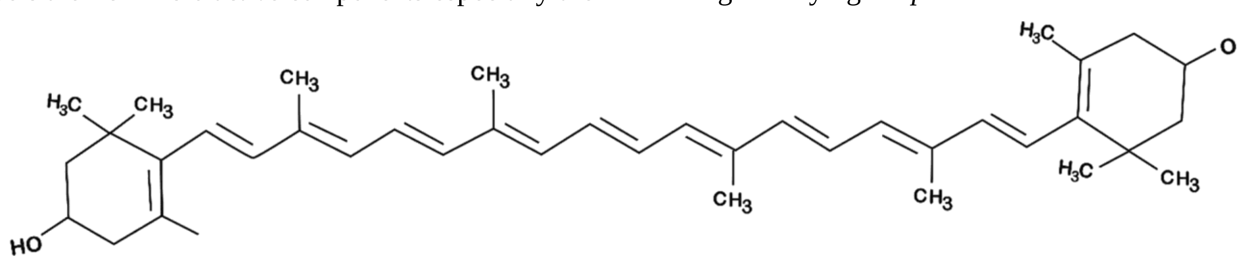

Fig. 1 — Chemical structure of lutein (colouring component of Marigold flower extract)

2.2.2 Mordanting of Cotton Khadi Fabric with Harda (Myrabolan)

Dried harda was crushed into powder and this powder was converted to gel by soaking in water (1:10 volume) for overnight (12h) at room temperature of 20 -30^{0}C. This harda gel was then mixed with a known volume of water and heated at 80^{0}C for 30 min. The solution was then cooled and filtered in a 60-mesh nylon cloth. This filtrate was used as final mordanting solution (10-40%) –as an additional mordanting assistant (with other metallic mordant used) using MLR of 1:20. Prewetted conventional H_2O_2 bleached khadi cotton fabric was treated with the filtered myrabolan (harda) gel solution in separate bath initially at 40-50^{0}C and then temperature was raised to 80^{0}C. Mordanting was continued for 30 min. After 1st mordanting with harda solution, fabric samples were dried in air without washing to keep it ready for either subsequent dyeing or for subsequent second mordanting.

2.2.3 Mordanting of Cotton Khadi Fabric with Metallic Salts

Peroxide bleached khadi cotton fabric was pre-mordanted prior to dyeing using 5-20% aqueous solution of aluminium sulphate [$Al_2 (SO_4)_3$], potash alum [$KAl (SO_4)_2$], and stannous chloride [$SnCl_2$] separately at 60^{0}C for 30 min using material-to-liquor ratio of 1:20 for both single mordanting and said double mordanting in sequence. After this single or double mordanting, the fabric samples were finally dried in air without washing to make them ready for subsequent dyeing. All single mordanted [Harda, $Al_2 (SO_4)_3$, $KAl (SO_4)_2$ and $SnCl_2$] samples and all combination of sequential double mordanted [$Al_2(SO_4)_3$+ $KAl(SO_4)_2$,$Al_2(SO_4)_3$+ $SnCl_2$, $Al_2(SO_4)_3$+ Harda, $KAl(SO_4)_2$+ $SnCl_2$, $KAl (SO_4)_2$+ Harda, $SnCl_2$+ Harda,] cotton khadi fabric samples were used for the further study.

2.2.4 Testing of Tensile, Bending and Elongation Properties of Untreated and Treated (mordanted) Cotton Khadi Fabric

Warp-way breaking tenacity (cN/tex) and breaking extension (%) values of the selective mordanted fabrics were comparatively measured (after prior conditioning of the samples at 65± 2% RH and 27± 2^{0}C temperature for 48 h as per the IS: 6359-1971) as per ASTM: D 5035-11,2015 cut strip method of tensile strength testingusing Paramount Digi strength (Model no. 16509 2004T) tester.

2.2.5 Measurement of Fabric Stiffness

Paramount fabric stiffness tester was used to measure the stiffness of the selective mordanted fabric as per IS: 6490 – 1971(Cantilever test) method.

2.2.6 Dyeing of Pre-mordanted Cotton Khadi Fabrics

Dyeing of bleached and differently pre-mordanted (single and double) cotton khadi fabrics was carried out using the aqueous color extract of waste Marigold flower powder either at specific or varying conditions of dyeing. In the first phase, the study was carried out with varying concentrations (5-20 %) of single mordants, then with overall 15% combination of varying ratio of double mordants and finally with 15% of Harda + $Al_2(SO_4)_3$ combination (50 :50 ratio). All these samples were dyed with aqueous extract of specific concentration of waste marigold dye-liquor [20 % on the weight of dye source material of marigoldpowder using MLR 1:20; common salt 5% owm; *p*H5 (with requisite amount of acetic acid); dyeing temperature 60^{0}C and dyeing time 60 min, unless otherwise mentioned] until it was optimized.

Study of the effects of dyeing process variables on color yield for optimizing the dyeing conditions was undertaken in the second phase, in which the dyeing process variables /parameters were varied as dyeing time 15-120 min, dyeing temperature 50-95^{0}C, material to liquor ratio 1:10 – 1:50, conc. of aqueous extract of waste Marigold flower powder (as natural dye) 10 – 50%, common salt conc 5-20gpl and *p*H 3-13. The mordant system was finally selected.The selected system was double pre-mordanted with 15% overall concentration of the combination of harda as first mordant + $Al (SO_4)_3$ assecond mordant(50: 50) and applied in sequence on cotton khadi fabric. After the completion of dyeing, the dyed cotton khadi fabric samples were repeatedly (thrice) washed with hot and cold water followed by drying in air. Finally, the dyed samples were subjected to soaping with 2 gpl soap solution at 50^{0}C for 30 min, followed by repeated water wash (thrice) and drying under sun. Unless otherwise stated, after optimization of the dyeing process variables, all other experiments of dyeing with waste marigold flower extract were carried out at optimum dyeing conditions observed.

2.2.7 Measurement of Surface Color Strength, Dyeing Uniformity and other Color Interaction Parameters

X-rite (Gretag Macbeth) portable spectro-photometer was used for determining the K/S values of mordanted /undyed and dyed khadi cotton fabrics by measuring surface reflectance of the fabric samples, following Kubelka Munk[14] equation with the help of relevant computer- aided colour measurement software.

The total color difference (ΔE), Chroma, (psychometric chroma), CIE 1976 metric hue-difference (ΔH) and general metamerism index (MI) values are measured by using the computer-aided reflectance spectrophotometer along with associated Color-Lab plus software using CIE-Lab equations as per CIE standard-1976.General metamerism index (MI) was calculated using the following LABD equation:

$$MI = \frac{\sum(\Delta RX_o)^2}{X^2} + \frac{\sum(\Delta RY_o)^2}{Y^2} + \frac{\sum(\Delta RZ_o)^2}{Z^2}$$

where X_o, Y_o and Z_o are the tri-stimulus values of a standard white surface of MgO (or equivalent surface of standard white tile) and *X*, *Y* and *Z* are the tri-stimulus values of the corresponding samples.

Brightness index (BI) was measured using following relationship as per ISO-2469 and 2470 method[15]

Brightness index =

$$\frac{\text{Reflectance value of sample at 457 nm}}{(\text{Reflectance value of standard diffuser (white tile) at 457 nm})} \times 100$$

2.2.8 Determination of Color Difference Index Value (CDI)

After application of selective natural dyes, the magnitudes of respective ΔE, ΔC, ΔH and MI values irrespective of their sign and direction may be utilized to obtain a single index called as Color Difference Index (CDI) values for indicating overall color variation and its dispersion against any varying parameters of a particular process variable, using the following empirical relationship[16]:

$$\text{Color difference index (CDI)} = \frac{\Delta E \times \Delta H}{\Delta C \times MI}$$

where ΔE, ΔC, ΔH and MI indicate corresponding color interaction parameters, as given above.

2.2.9 Evaluation of Fastness Properties

The wash fastness properties of dyed cotton khadi fabrics were evaluated according to IS: 3361-1979 method The light fastness of dyed cotton khadi fabric was evaluated as per IS: 2454-1985 methodRA 2013 method. Dry and wet rub fastness of the dyed cotton khadi fabric was evaluated as per IS: M766-1988 method. Perspiration fastness tests for dyed cotton khadi fabric samples were carried out as per IS method 971-1983: RA 2009 methodat two different *p*H levels (5.5 and 8) using freshly prepared perspiration liquor as per standard recipe and method.

2.2.10 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) of untreated, pre-mordanted and dyed cotton khadi fabric samples were examined in a FTIR spectrophotometer (Make: Perkin Elmer Pvt Ltd andModel: Spectrum-II) using the KBr disc technique. FTIR spectral scans obtained were analyzed following FTIR spectroscopic table[16].

3 Results and Discussion

3.1 Optimization of Conditions of Aqueous Extraction of Waste Marigold

Optimal conditions for aqueous extraction of the color components from dried wasteMarigold flower powder has been determined prior to dyeing bleached cotton khadi fabric (control). Aqueous extraction of colored solution was made from dried waste marigold flower powder under varying extraction conditions, viz, MLR 1:30 – 1:80, *p*H 4 – 10, time 15 – 90 min and temperature 60 – 90^{0}C. The optical densities or absorbance value of the filtered aqueous extracts of the waste marigold flower were estimated at maximum absorbance wavelength (λ_{max}) of 423 nm using Shimadzu –UV 2450 UV-VIS absorbance spectrophotometer.

Table 1 shows the results for optical density of colored solution after aqueous extraction of color

Table 1 — Optical density of aqueous extract of Marigold flower under various conditions of extraction

Extraction variables	Absorbance/optical density of Marigold flower extract at λ_{max} 423 nm
Material-to-liquor ratio (MLR)	
1:30	0.262
1:40	0.244
1:50	0.226
1:60	0.244
1:70	0.316
1:80	0.137
Temperature, ^{0}C	
50	0.173
60	0.173
70	0.155
80	0.137
90	0.262
Time, min	
15	0.048
30	0.084
45	0.102
60	0.084
75	0.084
90	0.066
*p*H	
4	0.102
5	0.102
6	0.084
7	0.066
8	0.280
9	0.298
10	0.191

component from waste marigold flower. The maximum values obtained for optical density at maximum absorbance wavelength ((λ_{max}= 423 nm) are identified and marked in bold letters for corresponding extraction conditions.The data shown in bold (Table 1) are considered as optimum extraction conditions respectively.

It may be noted that the aqueous extraction of color components from dried waste marigold flower powder gives maximum color yield when extraction is done under MLR at 1:30, *p*H at 9, temperature at 90^0C and time for 45 min.

3.2 Effects of Different Single Pre-mordanting

Table 2 shows the effects of varying percentage (5-20%) of aqueous solution of different single mordants, i.e aluminium sulphate [$Al_2(SO_4)_3$], potash alum [$KAl(SO_4)_2$], stannous chloride [$SnCl_2$] and harda/myrobolan applied separately at 60^0C for 30 min using material-to-liquor ratio of 1:20 followed by dyeing with wastemarigold flower extract. A standard pre-fixed conditions of dyeing (20 % extract based on the weight of dye source material using MLR 1:20, common salt 15% owm, *p*H 11.00 (with requisite amount of caustic soda/Na_2CO_3), dyeing temperature 80^0C and dyeing time 30 min, unless otherwise mentioned) are used to determine effects of different single mordants on changes in tensile strength/tenacity, breaking elongation, stiffness (bending length) of the corresponding fabric sample after pre- mordanting. The changes in surface color strength (K/S values, along with CV% of K/S values) and other color interaction parameters (ΔE, ΔL, Δa, Δb, ΔC,ΔH, BI, MI and CDI values) after dyeing the pre-mordanted cotton khadi fabric for different mordant types and concentrations are mentioned in Table 2.

It is revealed that there is a reasonable increase in the *K/S* values of the dyed sample when pre-mordanted with 5 - 10 % aluminium sulphate separately or 5-10 % potash alum separately(single mordant) as compared to the same per application of harda and stannous chloride [$SnCl_2$] under comparable conditions of treatment. Application of mordant with >10% concentration decreases the *K/S* values significantly for harda and metallic salts in comparison to that for other two mordants.Hence, considering an overall balance in all the factors, including costs etc, pre-mordanting with 5% aluminium sulphate renders a better option

Table 2 — Effects of selective single pre-mordanting for dyeing of cotton khadi with waste Marigold flower extract

Mordant and its concentration, %	Warp-way tenacity cN/tex	Warp-way breaking elongation %	Warp - way bending length, cm	*K/S* at λmax	ΔE	ΔL	Δa	Δb	ΔC	ΔH	BI	MI	CDI	CV% of *K/S*
Control fabric[a]	1.58	11.52	1.43	0.14	-	-	-	-	-	-	66.04	-	-	-
Alum $KAl_2(SO_4)_3$[a]														
5	1.55	16.37	1.32	4.55	42.34	-20.75	7.82	26.06	36.78	-3.05	13.79	7.23	0.485	58.52
10	1.36	16.05	1.30	3.77	40.22	-19.22	7.82	34.45	35.19	-3.11	15.54	7.02	0.506	34.46
15	1.29	14.28	1.36	3.50	41.26	-18.28	8.29	36.05	36.86	-3.18	15.66	7.30	0.487	73.20
20	1.33	15.52	1.40	3.20	38.62	-18.63	8.10	32.85	33.68	-3.24	16.79	6.89	0.539	66.91
Aluminium Sulphate ($Al_2(SO_4)_3$)[b]														
5	1.35	12.30	1.21	5.45	44.63	-22.38	9.11	37.52	38.46	-3.38	12.04	7.47	0.525	47.25
10	1.02	11.43	1.14	5.06	44.69	-21.94	9.14	37.84	38.78	-3.44	12.19	7.54	0.525	74.79
15	1.41	14.78	1.38	3.65	39.95	-19.37	8.12	33.98	34.80	-3.13	15.53	7.01	0.512	57.12
20	1.31	12.67	1.36	2.76	35.44	-17.27	6.99	30.15	30.81	-2.90	18.80	6.93	0.522	52.44
Stannous Chloride ($SnCl_2$)[b]														
5	1.54	15.69	1.62	2.46	47.72	-10.21	6.71	46.13	46.55	-2.48	16.89	7.51	0.338	80.46
10	1.27	14.54	1.52	1.75	41.51	-6.73	4.39	40.73	40.93	-1.72	22.37	6.71	0.259	55.39
15	1.28	12.70	1.41	2.80	47.90	-9.53	6.30	46.52	46.89	-2.31	17.12	7.64	0.308	78.17
20	0.92	13.81	1.25	2.58	42.32	-9.79	5.77	40.76	41.11	-2.23	19.89	7.33	0.313	57.75
Harda (Myrabolan)														
5	1.44	14.60	1.24	0.78	14.38	-12.31	2.04	7.15	7.31	-1.40	39.06	2.62	1.051	8.816
10	1.40	12.10	1.28	0.83	15.09	-12.57	2.14	8.07	8.23	-1.44	38.27	2.83	0.932	11.86
15	1.28	11.63	1.29	0.88	15.58	-13.14	2.15	8.10	8.26	-1.39	37.13	2.87	0.913	14.15
20	1.31	11.18	1.31	0.91	16.11	-11.88	0.93	10.85	10.87	-0.53	37.36	3.40	0.231	35.97

[a]Without dyeing and [b] with dyeing with 20% Babool bark at *p*H 11. ΔE-Total color difference, ΔL- lightness/darkness difference, Δa– greenness/redness difference, Δb-blueness/yellowness, Δ-H change in hue, ΔC-change in chroma, BI-brightness index, MI-metamerism index, CDI-colour difference index, and CV% coefficient of variation of *K/S* value.

towards best color yield than all other single mordants used in this work.

3.3 Effects of Selective Double Pre-mordanting Applied in Sequence

Table 3 reveals the changes in tensile strength/tenacity, breaking elongation, stiffness (bending length) of the fabric sample after pre-mordanting and changes in surface color strength values after dyeing the pre-mordanted cotton khadi fabric for each set of combination and concentrations of double mordanting system used.Results of surface color strength and other color interaction parameters after dyeing with 20% (based on dry solid source material weight) aqueous extract of waste marigold flower is also shown in Table 3. Double pre-mordanting with 15% overall combination of any two mordant concentrations applied in sequence with varying ratio (0: 100, 25 : 75, 50 : 50 , 75:25. and

Table 3 — Effects of selective double pre-mordanting applied in sequence for dyeing of cotton khadi with waste Marigold Flower as natural dye

Mordant and its proportion, %	Warp way tenacity cN/tex	Warp way breaking elongation, %	Warp way bending length, cm	*K/S* at λmax	ΔE	ΔL	Δa	Δb	ΔC	ΔH	BI	MI	CDI	CV% of *K/S*
Control fabric[a]	1.58	11.52	1.43	0.142	-	-	-	-	-	-	66.00	-	-	-
$KAl(SO_4)_2$ +$Al_2(SO_4)_3$ 15% Combination														
0:100	1.41	14.78	1.38	3.65	39.95	-19.37	8.12	33.98	34.80	-3.13	15.53	7.01	0.512	57.12
25:75	1.35	10.06	1.53	1.00	24.21	-7.47	4.93	22.49	22.92	-2.25	33.41	4.79	0.496	73.24
50:50	1.31	10.69	1.43	0.89	22.25	-7.21	4.56	20.55	20.94	-2.15	35.15	4.45	0.513	72.16
75:25	1.39	9.75	1.53	0.75	20.89	-5.94	3.71	19.68	19.95	-1.77	37.48	4.14	0.447	29.92
100:0	1.29	14.28	1.36	3.50	41.26	-18.28	8.29	36.05	36.86	-3.18	15.66	7.30	0.487	73.20
$Al_2(SO_4)_3$+$SnCl_2$, 15% Combination														
0:100	1.28	12.70	1.41	2.80	47.90	-9.53	6.30	46.52	46.89	-2.31	17.12	7.64	0.308	78.17
25:75	1.19	10.58	1.34	1.02	30.13	-4.41	1.79	29.76	29.80	-0.67	32.06	5.34	0.126	63.38
50:50	1.15	9.87	1.26	0.88	27.13	-4.29	1.27	26.76	26.79	-0.49	34.41	4.92	0.100	47.75
75:25	1.40	9.73	1.28	1.28	31.12	-6.29	2.70	30.36	30.46	-1.05	29.51	5.64	0.190	55.21
100:0	1.41	14.78	1.38	3.65	39.95	-19.37	8.12	33.98	34.80	-3.13	15.53	7.01	0.512	57.12
Harda+ $Al_2(SO_4)_3$, 15% Combination														
0:100	1.41	14.78	1.38	3.65	39.95	-19.37	8.12	33.98	34.80	-3.13	15.53	7.01	0.512	57.12
25:75	1.43	13.90	1.53	1.88	30.39	-13.67	6.13	26.44	27.01	-2.62	24.06	5.73	0.515	71.33
50:50	1.46	13.73	1.31	3.13	35.31	-17.45	6.17	30.07	30.60	-2.50	18.82	6.39	0.451	38.47
75:25	1.64	13.73	1.31	2.69	33.48	-15.65	6.04	28.97	29.49	-2.48	20.87	6.15	0.457	59.19
100:0%	1.28	11.63	1.29	0.88	15.58	-13.14	2.15	8.10	8.26	-1.39	37.13	2.87	0.913	14.15
$KAl_2(SO_4)_2$ + $SnCl_2$, 15% Combination														
0:100	1.28	12.70	1.41	2.80	47.90	-9.53	6.30	46.52	46.89	-2.31	17.12	7.64	0.308	78.17
25:75	1.36	9.68	1.45	1.32	31.84	-6.27	2.38	31.12	31.20	-0.90	28.99	5.67	0.161	57.22
50:50	1.07	7.84	1.35	1.35	33.97	-5.66	2.36	33.41	33.49	-0.86	28.17	5.95	0.146	34.55
75:25	1.22	10.50	1.5	1.65	35.66	-7.31	2.93	34.78	34.89	-1.07	25.59	6.27	0.174	58.08
100:0	1.29	14.28	1.36	3.50	41.26	-18.28	8.29	36.05	36.86	-3.18	15.66	7.30	0.487	73.20
Harda+ $KAl_2(SO_4)_2$, 15% Combination														
0:100	1.29	14.28	1.36	3.50	41.26	-18.28	8.29	36.05	36.86	-3.18	15.66	7.30	0.487	73.20
25:75	1.08	14.36	1.38	2.00	30.24	-13.87	5.49	26.30	26.77	-2.35	24.01	5.65	0.469	34.26
50:50	1.24	17.86	1.73	2.37	33.39	-14.76	6.77	29.18	29.82	-2.78	21.57	6.27	0.496	41.32
75:25	1.47	13.90	1.36	3.00	34.78	-17.16	5.75	29.70	30.17	-2.34	19.32	6.41	0.420	62.08
100:0	1.28	11.63	1.29	0.88	15.58	-13.14	2.15	8.10	8.26	-1.39	37.13	2.87	0.913	14.15
Harda+ $Sncl_2$, 15% Combination														
100:0	1.28	11.63	1.29	0.88	15.58	-13.14	2.15	8.10	8.26	-1.39	37.13	2.87	0.913	14.15
25:75	1.15	16.16	1.5	4.24	43.66	-13.46	5.17	41.21	41.49	-1.80	16.81	7.68	0.246	62.70
50:50	1.19	13.70	1.41	3.01	49.99	-14.66	6.71	47.32	47.74	-2.21	13.21	8.21	0.281	46.92
75:25	1.41	15.60	1.33	2.96	49.23	-13.56	6.11	46.93	47.28	-2.01	14.13	8.11	0.258	49.11
0:100	1.28	12.70	1.41	2.80	47.90	-9.53	6.30	46.52	46.89	-2.31	17.12	7.64	0.308	78.17

[a]Without dyeing & bWith dyeing with 30% at *p*H 11, ΔE-Total color difference, ΔL-lightness/darkness difference, Δa–greenness/redness difference, Δb-blueness/yellowness, Δ-H change in hue, ΔC-change in chroma, BI-brightness index, MI-metamerism index, CDI-colour difference index, and CV% coefficient of variation of *K/S* value.

100:0) for all combination of sequential double mordanting with $Al_2(SO_4)_3$ + $KAl(SO_4)_2$, $Al_2(SO_4)_3$ + $SnCl_2$, Harda + $Al_2(SO_4)_3$, KAl $(SO_4)_2$+ $SnCl_2$, Harda + KAl $(SO_4)_2$ and Harda + $SnCl_2$ applied on cotton khadi fabric samples are further studied and subsequently dyed with aqueous extract of marigold flowers at comparable conditions of dyeing.

Among all the double pre-mordanting carried out, combination of 15 % overall application of harda and aluminium sulphate (50:50) perhaps satisfies the most desirable required stoichiometric ratio (as most effective for " Fiber-Harda mordanting assistant – aluminium sulphate Metallic Mordant-Dye" giant complex formation),showing maximum surface color depth (*K*/*S* value) than using either of the above said single pre-mordants or other double pre-mordants.

After dyeing of differently pre-mordanted cotton fabric with waste marigold flower extract, harda alone as a single mordant renders grey tone shade, whereas potash alum and aluminium sulphate as single mordant give bright shades of varying color ranging from light to medium orange shades.Double pre-mordanting with harda and aluminium sulphate (15% overall concentration with 50:50 ratio)shows medium yellowish pink shade (for use of 20 % extract of marigold dye). Shades obtained with all single and double mordants (15% overall concentration with 50:50 ratio) and dyed with 20 % extract of waste marigold dye are shown in Fig. 2.

3.4 Effect of Different Single and Double Mordants on ColorFastness Properties

Table 4 reveals the data on fastness properties of dyed cotton khadi fabric samples pre-mordanted with varying types of single mordant and different ratio of double pre-mordanted samples (with Overall 15 % mordant application) subsequently dyed with waste marigold flower extract.

It is evident that the fabrics treated with all mordant concentrations subsequently dyed with 20 % wastemarigold flower extract show reasonably acceptable grade of color fastness to wash, but corresponding light fastness ratings are much poor for MBTF-UV light exposure. Fastness to dry crocking of the corresponding marigold dyed samples though appears to be good, but color fastness to wet crocking always become a bit lower, irrespective of the concentration of mordants used in pre–mordanting.

Moreover, there is hardly any significant difference in color fastness to washing, light and rubbing for use of the different single mordants, but there are some clear differences in color fastness ratings to washing, light and rubbing, when the double mordanting system is used. Amongst different combinations of double mordanting systems used, 15% overall application of harda followed by aluminium sulphate

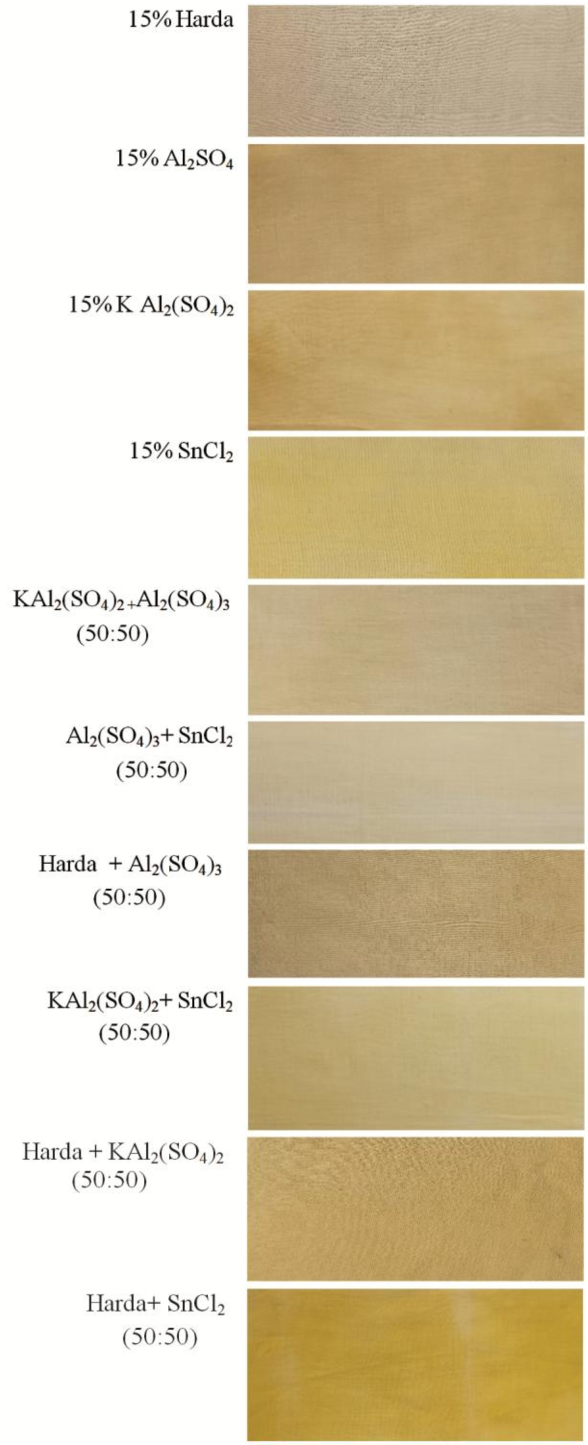

Fig. 2 — Shades obtained with various mordants (single & double) when dyed with 20% waste Marigold flower extract

Table 4 — Effect of different single and double mordants on colour fastness properties of waste marigold flower dyed khadi cotton fabric

Mordant and its proportion	Colour of dyed sample	Colour fastness						
		Washing		Light	Rubbing		Perspiration (LOD)	
		Loss of depth	Staining		Dry	Wet	Acidic	Alkali
15% Harda	Grey	2	4-5	3	5	4-5	3-4	3-4
15% $Al_2(SO_4)_3$	Light orange	1	4-5	2	5	4	3	4
15% $KAl_2(SO_4)_2$	Medium orange	1	4-5	1-2	5	4-5	2-3	4
15% $SnCl_2$	yellowish pink	1	4-5	1	4-5	4	4	4
$KAl_2(SO_4)_2$ + $Al_2(SO_4)_3$ Overall 15% application								
25:75	Yellowish pink	1	4-5	2	5	5	3	4
50:50	Medium Orange	1	4-5	2	5	5	3	3-4
75:25	Light Orange	1	4-5	2	5	5	3-4	3
$Al_2(SO_4)_3$+ $SnCl_2$ Overall 15% application								
25:75	Light yellow	1	4-5	1	5	4-5	3-4	3-4
50:50	Medium yellow	1-2	4-5	1	5	4-5	3	2-3
75:25	yellow	1-2	4-5	1-2	5	4-5	2-3	2-3
Harda + $Al_2(SO_4)_3$ Overall 15% application								
25:75	Light yellowish pink	2	4-5	1-2	5	4-5	3	4
50:50	Medium yellowish pink	3-4	4-5	1-2	5	4-5	3	4
75:25	Yellowish pink	2-3	4-5	1-2	5	4	2-3	4
$KAl_2(SO_4)_2$+ $SnCl_2$ Overall 15% application								
25:75	light Pink	1-2	4-5	1	5	4-5	3	2-3
50:50	Light Pink	1	4-5	1	5	4	2-3	2-3
75:25	light Pink	1-2	4-5	1-2	5	4	3-4	4
Harda + $KAl_2(SO_4)_2$ Overall 15% application								
25:75	Light yellowish Brown	2	4-5	2	5	4-5	3	4
50:50	Yellowish orange	1-2	4-5	2	5	4-5	2-3	3-4
75:25	Yellowish orange	2	4-5	2	5	4-5	3	4
Harda+ $SnCl_2$ Overall 15% application								
25:75	Light yellowish Cream	1-2	4-5	1	5	4	3-4	3-4
50:50	Medium yellowish Cream	1	4-5	1-2	4-5	3-4	3-4	3-4
75:25	Yellowish Cream	1-2	4-5	1-2	5	3-4	3-4	3-4

(Hard **+** aluminium sulphate in 50:50 ratio) applied in sequence shows reasonably better color fastness rating to washing, light and rubbing. This may be due to some synergistic effect of the combination of aluminium sulphate with harda, where the latter is used as mordanting assistant having additional high coordinating power of –OH and –COOH groups of chebulinic acid of harda facilitating formation ofhuge number of giant and strong complex amongst the said fib-mordants-dye system.

For use of single mordant, perspiration fastness results in terms of the loss in depth of shade is average togood for both acidic and alkaline perspiration.For use of potash aluminium sulphate as mordant,the same is poorer while good for the use of only harda or only aluminium sulphateas single mordant. Perspiration fastness with respect to loss of depth of shade is extremely good for the dyed cotton khadi fabric samples pre-mordanted with 15% overall application of harda + aluminium sulphate (50:50) applied in sequence.This facilitates better anchoring/ fixing of thecolor components (Lutein and zeaxanthin) ofwasteMarigold flower extract to the cotton khadi fabric due to formation of insoluble and strong complex (cotton fib-harda- aluminium sulphate –Marigold)bigger size metal tannate based insoluble dyed complex on cotton.

3.5 Effects of Dyeing Process Variables on ColorYield and ColorFastness Properties

The effects of dyeing process variables on surfacecolor strength (*K*/*S*value) and uniform color distribution (CV % of K/S values) and other color interaction parameters are shown in Table 5 and corresponding color fastness rating properties are shown in Table 6. Effect of different dyeing process variables have been studied to standardize /optimize the dyeing conditions for maximum surface color strength (in terms of *K*/*S*value) and uniform color distribution (in terms of CV % of K/S values) for 15% Harda + Aluminium Sulphate (50:50) double

Table 5 — Colour strength and related colour parameter for variation in dyeing process variables

Dyeing conditions	*K/S* at λmax	ΔE	ΔL	Δa	Δb	ΔC	ΔH	BI	MI	CDI*	CV%	CDI_{max}-CDI_{min}
Control (mordanted)	0.13	0.00	0.00	0.00	0.00	0.00	0.00	66.84	0.00	0.00	0.00	
Time, min												
15	4.53	43.23	-20.03	8.23	37.41	38.19	-2.97	13.79	7.23	0.46	47.78	0.06
30	4.16	41.88	-19.73	7.99	36.07	36.82	-2.93	14.54	7.04	0.47	20.93	
60	4.62	43.49	-20.80	8.90	37.15	38.06	-3.24	13.34	7.25	0.51	57.93	
90	4.54	43.00	-20.78	9.16	36.52	37.50	-3.36	13.61	7.27	0.52	55.91	
120	4.01	40.98	-20.10	8.57	34.66	35.56	-3.21	14.85	6.98	0.50	44.29	
Temp, ^{0}C												
50	5.05	44.75	-19.99	7.47	39.34	39.95	-2.62	13.12	7.42	0.41	22.62	0.10
65	4.25	42.29	-19.91	7.22	36.60	37.22	-2.61	14.20	6.96	0.42	16.75	
80	4.49	43.59	-19.80	8.09	37.99	39.73	-2.90	13.70	7.18	0.45	36.41	
95	4.75	44.98	-20.31	9.58	38.97	39.98	-3.42	12.93	7.43	0.51	42.59	
***p*H**												
3	4.64	38.29	-18.59	1.96	33.41	33.47	-0.62	17.01	6.92	0.10	12.85	0.34
5	5.48	42.69	-22.58	6.24	35.69	36.16	-2.27	12.88	7.02	0.38	98.31	
7	5.14	43.73	-21.09	7.79	37.51	38.21	-2.80	13.10	7.28	0.44	36.09	
9	2.06	31.60	-13.98	4.74	27.94	28.28	-1.90	23.47	5.87	0.36	26.79	
11	0.47	10.66	-4.86	0.75	9.46	9.48	-0.40	48.97	2.58	0.17	41.47	
13	0.94	19.12	-8.39	2.02	17.06	17.15	-0.95	37.42	4.17	0.25	15.30	
MLR												
1:10	4.49	40.67	-21.13	7.10	34.01	34.65	-2.66	14.50	6.90	0.45	23.63	0.04
1:20	5.22	42.73	-22.56	8.10	35.37	36.16	-3.00	12.94	7.13	0.49	54.25	
1:30	4.19	40.44	-20.30	7.47	34.17	34.86	-2.80	15.01	6.97	0.46	16.11	
1:40	4.08	40.43	-20.07	7.28	34.34	35.00	-2.72	15.08	6.91	0.45	25.72	
1:50	4.33	41.48	-19.94	7.61	35.56	36.26	-2.80	14.67	7.10	0.45	38.35	
Varying overall total concentration of harda and aluminium sulphate applied in sequence in (50:50) before dyeing												
Mordant conc., %												
5	4.22	40.44	-20.28	7.79	34.12	34.87	-2.93	15.03	6.92	0.49	34.53	0.05
10	4.54	43.88	-21.92	9.30	36.86	37.86	-3.40	12.68	7.24	0.54	53.18	
15	4.93	42.46	-21.37	8.93	35.58	36.53	-3.32	13.57	7.11	0.54	49.11	
20	4.65	42.20	-21.45	8.57	35.32	36.20	-3.19	13.66	7.09	0.52	40.75	
Dye conc., %												
10	2.45	33.92	-15.75	4.90	29.64	29.98	-1.91	20.85	6.05	0.35	27.14	
20	2.80	37.43	-16.10	6.53	33.15	33.70	-2.47	18.68	6.55	0.41	33.08	0.21
30	4.31	43.54	-19.75	9.20	37.70	38.66	-3.33	13.80	7.31	0.51	50.21	
40	5.87	46.08	-22.35	9.75	39.09	40.14	-3.48	11.63	7.56	0.52	56.48	
50	7.81	48.02	-25.85	10.08	39.19	40.31	-3.60	9.60	7.60	0.56	29.50	
Salt conc., %												
0	2.69	35.29	-16.88	6.13	30.38	30.90	-2.41	19.43	6.29	0.43	26.05	0.14
3	2.75	35.43	-17.18	6.64	30.26	30.87	-2.62	19.22	6.36	0.47	41.67	
5	2.90	35.75	-17.84	6.43	30.31	30.88	-2.53	18.66	6.35	0.46	22.47	
10	3.54	39.13	-19.68	8.06	32.85	33.68	-3.09	15.94	6.78	0.52	37.12	
15	4.07	40.74	-21.47	8.79	33.49	34.46	-3.36	14.33	6.94	0.57	30.10	

pre-mordanted and 20% wasteMarigold flower extract dyed cotton khadi fabric.

It is observed that when all other dyeing variables are kept constant, with the increase in time of dyeing (15-120 min), *K/S* value initially decreases up to 30 min dyeing time and then starts increasing on further increase in dyeing time up to 60 min. After that it starts decreasing from 60 min to 120 min. This may be explained by the possibility of achieving dyeing equilibrium at 60 min, by quicker absorption of highly an-ionizable waste marigoldflower extract and thereafter it is reduced due to start of desorption of dyes after 60 min and up to 120 min dyeing time.

On comparing corresponding results of observed color fastness properties (Table 6), it is observed that 60 min dyeing time renders the dyed fabric overall

Table 6 — Colour fastness data against changes of dyeing process variables

Dyeing conditions	Colour fastness at 50^0C					Perspiration	
	Washing		Light	Rubbing			
	Loss of depth	Staining		Dry	Wet	Acidic	Alkaline
Time, min							
15	1-2	4-5	1	4-5	4	1-2	2
30	1-2	4-5	1	4-5	4	1-2	4
60	1-2	4-5	1	4-5	4	1-2	2-3
90	2-3	4-5	1	4-5	4	1-2	2-3
120	1-2	4-5	1	4-5	3-4	1-2	2
Temperature,^{0}C							
50	1-2	4-5	1	4-5	4	1-2	1-2
65	1	4-5	1	4-5	4	2-3	2
80	1	4-5	1	4-5	4	1-2	2-3
95	2	4-5	1-2	4-5	4	1-2	2-3
***p*H**							
3	1-2	4-5	1	4-5	4	2	2
5	1-2	4-5	1	4-5	3-4	2	2-3
7	1-2	4-5	1	4-5	3-4	1-2	2-3
9	1-2	4-5	1	4-5	4	1-2	2
11	2-3	4-5	3-4	5	4-5	4-5	4-5
13	2-3	4-5	2	4-5	4-5	4	4-5
M L R							
1:10	1-2	4-5	1	4-5	4	1-2	2-3
1:20	1-2	4-5	1	4-5	4	2	2-3
1:30	1-2	4-5	**1**	4-5	**4**	1-2	2-3
1:40	1-2	4-5	1	4-5	4	1-2	2
1:50	1-2	4-5	1	4-5	4	1-2	1-2
Varying overall total concentration of harda and aluminium Sulphate applied in sequence in (50:50) before dyeing							
Mordant conc., %							
5	1-2	4-5	1	4-5	4	1-2	2-3
10	1-2	4-5	1	4-5	4	1-2	2-3
15	1-2	4-5	1	4-5	4	1-2	3
20	1-2	4-5	1	4-5	4	2	3
Dye conc., %							
10	1-2	4-5	1	4-5	4	1-2	2-3
20	1-2	4-5	1	4-5	3-4	1-2	2-3
30	1-2	4-5	1	4-5	3-4	1-2	3
40	1-2	4-5	1	4-5	3-4	2	2
50	1-2	4-5	1	4-5	4	2	3
Salt conc., %							
0	2-3	4-5	1	4-5	4	2	2-3
3	1-2	4-5	1	4-5	4	1-2	2-3
5	1-2	4-5	1	4-5	4	1-2	2-3
10	1-2	4-5	1	4-5	4	1-2	2
15	1-2	4-5	1	4-5	3-4	2	3

better-balancedcolor fastness to wash, light, rubbing and perspirations.Dyeing time higher than 90 min offers lesser or at par color fastness grade for wash, light, rubbing and perspiration fastness. Hence, 60 min dyeing time may be considered as the best / standardized result out of all experiments of varying dyeing time.

On increasing the dyeing temperature (40^0 – 95^0C), keeping all other variables constant, the surface color strength (*K*/*S* values) is found to show a rapid increase from 40^0 to 50^0C. This value decreases when temperature is increased from 50^0 to 65^0C. A gradual increase in surface color strength can be noticed during increase of temperature from 65^0C to 95^0C. While comparing the corresponding color fastness data in Table 6, it is observed that overall color fastness data for different agency show a better balance for dyeing temperature at 95^{0}C than those obtained for 50^{0}C or 65^{0}C as dyeing temperature. Hence, considering *K/S* value and also color fastness properties, 95^{0}C temperature may be considered as better choice for fixing optimum dyeing temperature for this fibre-mordant-dye for waste marigold flower extract.

Corresponding data in Table 5 show almost increasing level of dye up take in terms of surface colorstrength (*K/S* value) with the variation of *p*H (keeping other dyeing process variables constant) from 3 to 5. While increasing *p*H from 5 to 7, the surface color strength (*K/S* value) values start slowly reducing and it further shows a decrease at *p*H 9. Consequently, the *K/S* value drastically reduces with the increase in *p*H above 9. Thus, *p*H may be considered as critical variables as it gives maximum dispersion of CDI value showing highest differences of maximum CDI and minimum CDI amongst varying *p*H of dye bath. Considering color fastness data as shown in Table 6, it is further understood that *p*H 5 renders better balance of overall all types of color fastness results. So, *p*H 5 may be considered as optimum value in this case of said fib-mordant –dye (marigold) system. It may be presumed that at lower *p*H (*p*H 5), there is higher chances of ionization of hydroxyl groups of color component of marigold (carotenoids) and hence better chances of complex formation with both harda and aluminium sulphate as double mordants forming giant insoluble metallic tannate complex helping not to leach out color,i.e. more anchoring of mordant-1-mordant-2-dye complex formation with fibre (cotton) in this case, as schematically shown in Fig. 3.

Keeping other variables constant, with the variation in material-to-liquor ratio (MLR) from 1:10 to 1:50 (Table 5), initially the *K/S* value shows an increase from MLR of 1:10 to 1:20 and then there is a slow decrease from MLR 1:20 onwards till MLR 1:50. MLR 1:20 shows highest *K/S* value as compared to any other MLR used and gives more uniformity of color in terms of CV % of *K/S* values. Hence, the optimum MLR may be considered as 1:20. Comparing corresponding color fastness data in Table 6, it is observed that MLR 1:20 shows medium to good overall all types ofcolor fastness data tested. Overall color fastness data for all types of color fastness properties are more or less found to be acceptable for MLR 1:10, 1:30 and 1:40. But considering both color yield and color fastness data, MLR 1:20 gives a better balance having more uniform dyeing (CV% data of *K/S* values) and this may be considered as optimum dyeing conditions with respect to MLR.

Table 5 shows a gradual increase in *K/S*value with the increase in mordant concentrations for overall varying percentages of harda (Myrabolan) and aluminium sulphate in sequence keeping total concentrations of these two mordants/ mordant assistants in between 5% and 20%. *K/S* value is found to be increased with increase in mordant concentration from 5% to 15%. *K/S* value starts slowly decreasing from 15% to 20% and it is observed that 5 % mordant concentration shows lowest *K/S* value as compared to other percentages of overall concentration of double mordants used. Also, considering corresponding color fastness properties (Table 6), it may be observed that 15 % overall concentration of the said double mordants (harda and aluminium sulphate in 50:50 ratio) applied in sequence, show overall balanced color strength and all types of color fastness properties are studied. Thus, considering all the above facts, the optimum

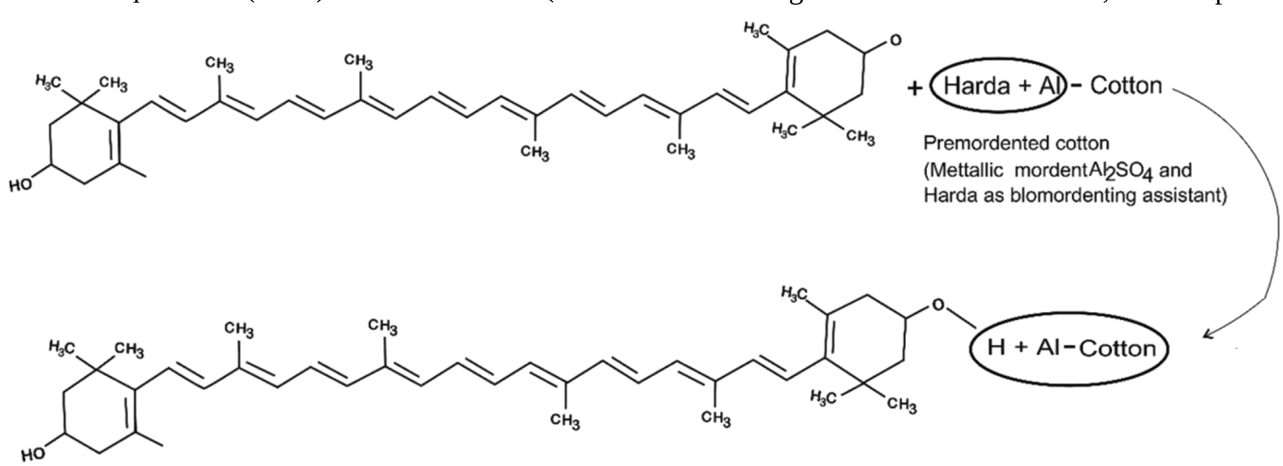

Fig. 3 — Reaction showing complex formation amongst (harda + aluminium sulphate mordant)- cotton - lutein present in Marigold flower

concentration of the mordant be selected as 15% overall application of double pre mordanting with Harda plus aluminium sulphate (applied in sequence with 50: 50 ratio).

Keeping other dyeing process variables constant, relevant results of *K/S* value and other color parameters for use of varying percentage of dye concentration for selective marigold dye from 10 % to 50% (based on oven dry weight of source dye materials) are shown in Table 5. There is a gradual increase in *K/S* value with the increase in dye conc. from 10 % to 50% waste Marigold dye extract concentration (based on weight % of dry marigold flowerpowder). Increase in *K/S* value with the increase in dye concentration up to 50% is obvious, and with the use of waste Marigold dye at 50 % concentration, the observed levelling off trend of *K/S* value maybe viewed as an effect of reaching saturation of dye sites achieving dyeing equilibrium. Considering *K/S*value, CV % of *K/S* value and all types of color fastness data studied in this case, the use of aqueous extract of 50 % Marigold dye concentration shows overall good results and may be considered as an optimal result. Dye-mordant-fibre complex formed within fibre matrix also depends upon stoichiometric ratio of complex forming entities. Thus, in this case, it may be presumed that stoichiometric ratio required for dye-mordant-fibre complex forming entities better matches for use of 50 % concentration of waste Marigold dye extract and thus renders a better overall color fastness result. Hence, 50% dye conc. may be considered as the optimum value for dye concentrations as one of the important dyeing process variables.

From the relevant data in Table 5, it is observed that with the increase in salt/electrolyte concentration from 0% to 15%, the color yield in terms of *K/S* value increases for use of 0-15% salt concentration. *K/S* value reaches its peak/highest value during usage of salt concentration of 15%. However, on comparing overall color fastness properties for corresponding part, the overall all-roundcolor fastness properties are also found the best for 15 % salt concentrations. Considering all the above matter, optimum concentration of common salt for waste marigold dyed cotton khadi fabric is selected to be 15% as the *K/S* values are found to be maximum at this conc. level, with moderate to good all-round color fastness properties.

From this study, it may be summarized that the optimum conditions of dyeing of harda and aluminium sulphate double pre-mordanted (with overall 15% concentration of harda and aluminium sulphate in 50:50 ratio in sequence) bleached cotton khadi fabric with aqueous waste marigold flower extract are: dyeing time 60 min, dyeing temperature 90^0- 95^0C, MLR 1:20, *p*H at 5, mordant concentration 15% (harda + aluminium sulphate in 50 : 50 ratio) for pre-mordanting, Marigold dye concentration 50 % (on weight percentage of dried source material) and common salt concentration 15%.

Besides wash fastness, the wet and dry rub fastness rating of bleached and pre-mordanted cotton khadi fabric dyed with waste marigold flower extract in different conditions of dyeing are found to be good for cotton khadi fabrics being rated as 4/5 for dry rubbing and 4 for wet rubbing (except few odd cases) and may need no further after treatment. This good rub fastness (fastness to crocking) property confirms that almost no superficial loosely held dyes are attached at the fibre surface after thorough washing and soaping at 50^0C for 15 min.

Its light fastness is somewhat fair to medium, and it can be improved by suitable aftertreatment with suitable wash fast UV-absorber for cotton. Hence, there is scope to improve the light fastness properties of waste marigold dyed cotton khadi fabrics, with suitable UV-absorber agents.

3.6 Analysis of Color Differences and Related Color Interaction Parameters

Table 5 also shows the effects of different process variables on *K/S* values along with other color interaction parameters, including total color difference (ΔE), change in hue (ΔH), change in chroma (ΔC), general metamerism index (MI), brightness index (BI) and color difference index (CDI) values. It is interesting to observe that among the dyeing conditions (time, temperature, *p*H, MLR, mordant, dye concentration, and salt concentration) the most important and predominating variables are identified as dye concentration and pH of dye bath as indicated by wide dispersion of CDI values (higher value of differences of $CDI_{maximum}$ and $CDI_{minimum}$ i.e the ranges of CDI values), which are either equal to or more than 0.20 (for varying dye concentration it is 0.21 and for *p*H, it is 0.34).For all other dyeing process variables studied here, the range of dispersion of CDI is ≤ 0.14. The order of increasing CDI values for different dyeing conditions, therefore, appears to be as follows:

MLR< Mordant concentration < Time < Temperature < Salt < Dye concentration < *p*H

Therefore, for uniform dyeing of cotton khadi fabric using waste marigold flower extract, special care is to be taken for control of dye concentration and *p*H The other color parameters, such as ΔE, ΔL, Δa and Δb indicate the differences in color yield or surface color strength for varying dyeing condition in each case, as compared to standard undyed pre-mordanted control cotton khadi fabric. The higher range of ΔE values (>42) is observed for the variation in dyeing temperature and dye concentration, indicating that these two are also the next level of important controlling parameters responsible for uniform dyeing. So, next level of care is also required for temperature and dye concentration variation.

Changes in hue for all cases are found to be negative (Table 5), indicating that there is minor change in predominating hue. However, the maximum ΔH value is observed in case of the variation in dye concentration from 10% to 50%, which further indicates the high sensitivity of color yield for this particular natural dye for dye concentration during dyeing.

Brightness index of dyed products depends on reflectance value of dye and its orientation along the fibre axis after fixation. No appreciable reduction in brightness index is observed for marigold dyed cotton khadi fabric after dyeing, irrespective of dyeing conditions used. However, it may be noted that at lower *p*H of 5, lower MLR (1:20), lower mordant concentration (10%) and higher dye concentration (40-50%), the reduction in brightness index is much higher than that observed in other conditions.

The general metamerism index (MI) indicates the metameric effect on the waste marigold dyed cotton khadi fabric for different conditions of dyeing. In all these cases, the MI varies from 4.17 to 7.60 (Table 5) and data are not much widely dispersed within a particular condition being varied but varies to a noticeable degree from one condition to other, indicating its potent metameric nature from one condition to other. Therefore, use of standardized conditions of dyeing is must to minimize metamerism for achieving least metameric dyed products for this fibre-mordant -dye system.

3.7 FTIR Analysis

FTIR spectra for (a) bleached control khadi cotton fabric (b) mordantedkhadi cotton fabricand (c) mordanted and dyed khadi cotton fabric are shown in Fig. 4. The spectra show the following common peaks and trough (FTIR peak position in cm^{-1}), mentioning specific peak positions and corresponding chemical functioning groups/ bonds vibration/stretching, etc.

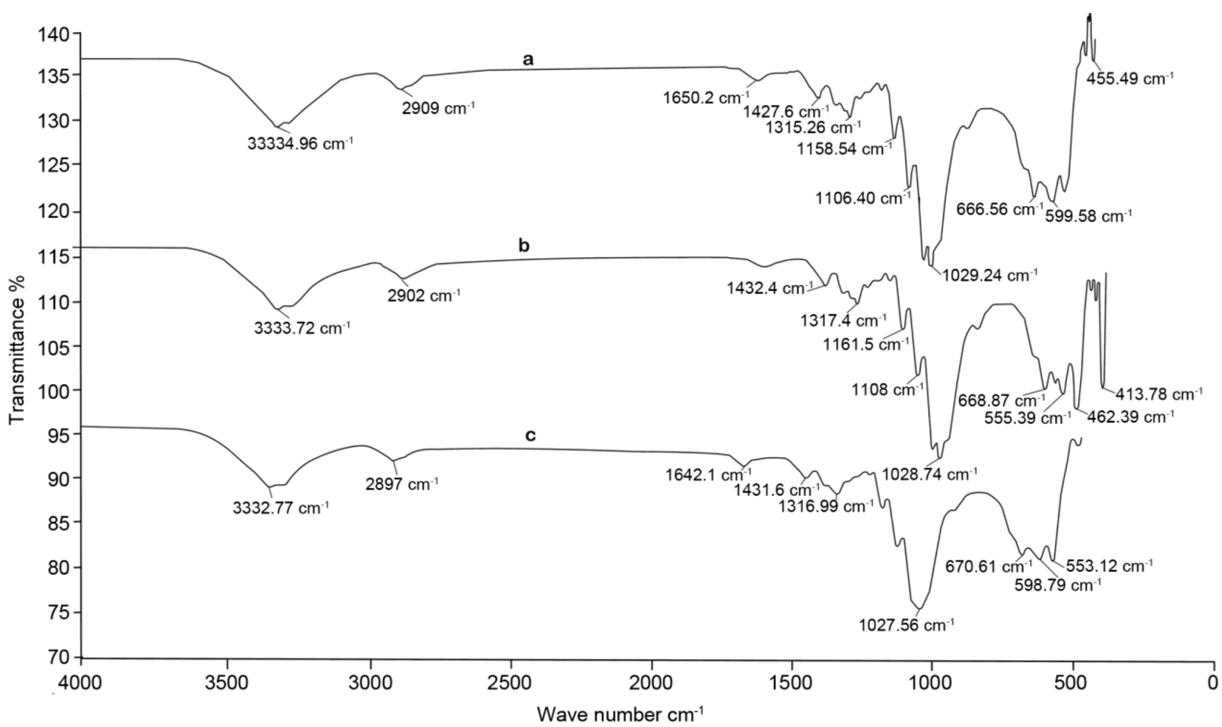

Fig. 4 — FTIR spectra for (a) bleached control cotton khadi fabric, (b) mordanted cotton khadi fabric and (c) mordanted & dyed cotton khadi fabric

Control cotton shows common peaks in all the FTIR curves [Figs 4 (a), (b) & (c)] at 3332-3334 cm^{-1} for free hydroxyl stretching, 2897 – 2909 cm^{-1} for C-H stretching, 1427 – 1432 cm^{-1} ford(C-H); d(C-OH) primary/ secondary alcohol and for some d(C-H) stretching, 1317 cm^{-1} for d(C-H) stretching.

The peak at 1630 cm^{-1} is more pronounced due to prime of mono substituted alkene (C=C) bonding, indicating presence of aluminium sulphate and harda in dyed fabric. The peak at 1432 cm^{-1} is attributed to d(C-H), d(C-OH) primary and secondary alcohols and some d(C-H) stretching. The peak at 1027 cm^{-1} is less prominent due to absorption of dyes in spectra [Fig. 4 (c)].

4 Conclusion

4.1 The optimized conditions for aqueous extraction of color component from waste marigold flower petals are: MLR 1:30, *p*H 9, temperature 90^0C and time 45 min.

4.2 The observed optimum conditions for dyeing of the double pre-mordanted (with overall 15% concentration of harda and aluminium sulphate in 50:50 ratio in sequence) for bleached cotton khadi fabric with aqueous waste marigold flower extract are dyeing time 60 min, dyeing temperature 95ºC, MLR 1:20, *p*H at 5, mordant concentration 15%, dye concentration 50 % (on weight percentage of dried source material) and common salt conc. 15gpl.

4.3 Interpretation from color difference index (CDI) values clearly reveals that dye concentrationand *p*H of dye bath are the two most critical dyeing process variables in this case, amongst all other parameters of dyeing process variables studied in this case.

Acknowledgement

Authors express thankfulness to the Ministry of Micro, Small & Medium Enterprises (Govt. of India) for the relevant R&D project grant-in-aid to carry out this study.

References

1 Dweck AC, *Int J Cosmet*, 24 (2002) 287.
2 Frick D, *Rec Prog Color*, 33 (2003) 15.
3 Kadolph SJF, *Delta Kappa Gamma Bull*, 75 (2008) 74.
4 Heo BG, Jang HJ, Kim SH, Kim HY, Yoo YK, Cho J Y & Park YJ, *Korean J Horticult Sci Technol*, 3(2004) 22.
5 Bosma TL, Dole JM & Maness NO, *Crop Sci*, 43 (2003) 2118.
6 Shenai VA, *Technology of Textile Processing*, Vol. 2 (Sevak Publications, India), 1997, 159.
7 Samanta AK, Agarwal P & Datta S, *Indian J Fibre Text Res*, 32 (12) (2007) 466.
8 Senthilkumar P, Umashankar P & Sujata B, *Indian Text J*, 112 (6) (2002) 15.
9 Sinnur H D, Samanta A K, Verma D K & Kaware Runali *J. IE (I) Ser E*, 99 (1) (2018) 9.
10 Sinnur H D, Verma D K, Kaware Runali & Samanta A K, *Indian J Natural Fibre*, 4 (1) (2017) 21.
11 Bosma T L, Dole J M & Maness N O, *Crop Sci*, 43 (2003) 2118.
12 Valianou L, Karapanagiotis I, & Chryssoulakis Y, *Anal Bio-analytical Chem*, 395(7) (2009)2175.
13 Sivakumar V, Vijaeeswarri J & Anna JL, *Industrial Crops Products*, 33(1) (2011) 116.
14 Shah H S & Gandhi R S, *Instrumental Colour Measurements and Computer Aided Colour Matching for Textiles* (Mahajan Brothers, Ahemdabad, India), 1990, 76.
15 Vankar P S, Shanker R & Wijayapala S, *Pigm Resin Technol*, 38 (4) (2009) 242.
16 Vasi I G & Shah PR, *Spectroscopic Data Tables* (Mahajan Brothers, Ahmedabad), 1980, 4-11.