Investigating the Impact of Hard Water on Natural Dyeing of Cotton Fabric by *Tagetes erecta* Flowers

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Summary: Ground water is commonly used media for most of textile processing treatments and it is often inherent with significant degree of hardness. This study is undertaken to evaluate the influence of water hardness on dyeing of cotton fabric by natural colorant extracted from flowers of *Tagetes erecta*. Response Surface Methodology (RSM) was applied for optimization of extraction and application of the natural colorant. Results were examined by Analysis of variance (ANOVA). In the present study, effect of process parameters viz. time (30–90 min), temperature (60–90ºC) and concentration of hard water (250–1250 ppm) on natural dyeing process (*K/S* value) were modelled by employing RSM based central composite design. For the applications of natural colorants, mordanting technique was employed wherein the results of pre-mordanting and post-mordanting were studied comparatively. The dyed fabric was evaluated for colour strength (*K/S*) and CIE*Lab* values. It was observed that increase in water hardness adversely influenced the colour strength and it also adds to significant degree of unevenness in cotton dyeing using natural colorant.

Keywords: Natural dyeing, Cotton; Extraction optimization; Marigold flowers; *Tagetes erecta*; Response surface methodology.

Introduction

Most of the wet-processing of textile industry is carried out in water as a medium for application of concerned chemicals and auxiliaries. For this purpose, huge amount of good quality water free from dissolved impurities is needed all around the year. Availability of this water is becoming a challenge due to scarcity of natural water resources. Moreover suitable infrastructure is also required to maintain water quality as per required parameters of a process. All these approaches of good quality water supply for wet-processing contribute to a significant increase in cost. Quality of water is largely influenced by various types of dissolved impurities including dissolved metallic cations of calcium, magnesium, iron, copper, manganese, aluminum etc. along with miscellaneous types of anions like sulphide, chloride, fluoride etc. These impurities may cause a plenitude of processing defects. The major contributors that cause water hardness are divalent cations especially Ca^{2+} and Mg^{2+} [1-3]. Keeping in view the conditions of water quality, the present study was undertaken to find out the influence of water hardness on dyeing of cotton fabric by natural colorant extracted from flowers of *Tagetes erecta*.

Use of natural colorants for dyeing of textile products is increasing continuously to overcome environmental concerns caused by synthetic dyes. Many organizations such as, environmental protection agency (EPA), global organic textile standards (GOTS) and food and agriculture organization (FAO) are also putting pressure to seek for the alternatives of synthetic dyes to curtail water pollution and to withstand the global eco-balance [4-6_ENREF_6].

Marigold (*Tagetes erecta L*) is a widespread ornamental plant bearing many medicinal and commercial values [7]. It has good antioxidant, antifungal and antiseptic properties which can be harnessed in both the food and textile sector but especially in textile as it is also capable of imparting color to the substrate along with medicinal attributes [8]. Its major coloring component is lutein (Fig 1) along with many other flavonoids [9].

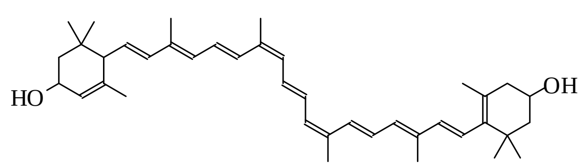

Fig. 1: Molecular structure of lutein.

Hardness produces a lot of undesirable effects during wet processing of textile substrates

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including not only excessive shade changes but also uneven dyeing and precipitated deposits onto the fibers [10]. Although a number of studies have been published [11-13] exploring the extracts of marigold as a natural coloring source for textiles but these are lacking to show the effect of water hardness on dyeing parameters. So this study is undertaken to evaluate the influence of water hardness on the dyeing of cotton fabrics with marigold flower extracts.

Design of experiment (DOE) is an effective statistical tool to design experiments and to analyze output variable with the simultaneous change in the input variables. DOE helps in finding the combination of optimum settings of the process parameters that are liable for the optimum response over a region of interest [14]. Response surface methodology originated by Box and Wilson in 1951, is an efficient tool for planning, statistical modelling, analyzing and interpreting the scientific and engineering problems [15]. In this study, RSM based central composite design (CCD) has been successfully employed to investigate the adverse effect of concentration of hard water on the natural colour strength (*K/S*). ANOVA was also employed to investigate the percentage contribution of the process parameters in the process of natural dyeing of cotton fabric. The observed negative effect was then rationalized by sequestering agent having chelating powers, mitigating the unevenness and shade variation due to the hardness of water

Experimental

The choice of factors

To investigate the effect of concentration of hard water in natural dyeing of cotton fabric, three input variables, i.e. time of dyeing, temperature and concentration of hard water were considered. The relationship between *K/S* values and the process parameters was postulated to be non-linear (quadratic).

Design of experiment (DOE)

DOE is an efficient technique to investigate the important process parameters that affect the process under consideration resulting in statistical model for the output variable. With the virtue of DOE several process variables may vary simultaneously to identify the important factor(s) that have significant impact on the process of interest resulting in an estimated model based on ANOVA [16].

Response surface methodology (RSM) is an assembly of mathematical and statistical tools helpful for experimental planning, modelling, analysing and optimization of scientific, modern mechanical and engineering problems [17]. The purpose of RSM is to obtain an optimized response variable influenced by number of process parameters. RSM is efficiently used in determining the mathematical relationship, usually quadratic using given below equation between process parameters and the estimated responses.

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{\substack{i=1 \\ i<j}}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \epsilon \tag{1}$$

where, y is response variable, βs are regression coefficients, which are obtained by least square method, and ϵ is the error term.

RSM gives a graphical representation of the relationship between the process parameters and the identified response. If there are three or more process parameters involved in the process of interest then solid surface of the response in three dimensional space (3D) is obtained by varying the levels of two process parameters and taking level of the remaining process parameters constant.

Analysis of variance

The analysis of variance (ANOVA) is an effective statistical tool to analyse and estimate the important process parameters with respect to the optimized response variable. ANOVA is used to evaluate the percentage contribution of the process parameters in the optimized process of interest. Significance of model and the process parameters are judged by determining the p-values less than level of significance (α), usually 5%.

Materials

Desized, bleached and scoured 100% cotton fabric (plain weave) with gsm 180 g/m^2, average thread density of 68 ends per inch and 52 picks per inch (PPI) was used. All the chemicals used in this study were purchased from Merck and used without further purification.

Preparation of hard water

Hardness in reverse osmosis (RO) water was artificially imparted for various concentrations by adding inorganic salts including anhydrous $CaSO_4$, $MgSO_4$ and verified by titrating against 0.01M EDTA solution. Total hardness was expressed as $CaCO_3$ equivalent in ppm and concentrations of 250, 750 and

1250 ppm were prepared by dilution formula. RO water was taken as control for comparison.

Sample collection and dye extraction

Marigold (*Tagetes erecta L*) flowers were collected from botanical garden of University of Agriculture, Faisalabad (UAF) and further authenticated from Department of Botany, UAF. Collected flowers were washed with distilled water, dried in shade and ground to fine powder which was employed for extraction of natural colorant in reflux apparatus using RO water and hard water. Three samples of water having hardness of 250, 750 and 1250 ppm were used to optimize the extraction yield by varying extraction time and temperature [18].

Dyeing

Mercerized 100% woven cotton fabric was exhaust dyed with the above stated extracts employing Na_2SO_4 as exhausting agent, varying three parameters including time, temperature and concentrations of hardness using the reported method [18, 19].

Application of mordanting agents

Pre and post mordanting was carried out with 5% alum and ferrous sulphate at optimized conditions according to the reported method [20]. Phosphate based sequestering agent (Texassist ECS) was also employed to investigate the influence on water hardness.

Quality assurance test

Spectraflash SF-650 with an illuminant of D-65 observer was used for the investigation of colorimetric properties of all treated and controlled fabric samples. The samples were also subjected to some other colorfastness tests. The colorfastness to rubbing, light and washing fastness were measured using AATCC 8-2007, ISO 105 B02: 1994 and ISO 105 C06: 2010 (A2S) respectively [21_ENREF_13].

Table-1: Process parameters and their levels for natural dyeing process.

Independent Variables	Short Name	Unit	Code	Range and level		
				Low (-1)	Centre (0)	High (+1)
Time	Time	min	A	30	60	90
Temperature	Temp	°C	B	60	75	90
Hard Water Concentration	HW conc.	ppm	C	250	750	1250

Table-2: Central composite design and experimental responses.

Std	Run	Coded			Actual			Response: Colour strength (*K/S*) and CIE*Lab* values					
		A	B	C	Time (min)	Temp (ºC)	HW Conc. (ppm)	*K/S*	*L**	*a**	*b**	*C**	*h*
1	1	-1	-1	-1	30	60	250	3.20	6.05	-1.42	0.57	1.52	6.02
2	10	1	-1	-1	90	60	250	5.80	0.45	-1.17	3.90	1.21	0.30
3	7	-1	1	-1	30	90	250	3.80	0.29	-0.57	2.50	0.60	0.21
4	17	1	1	-1	90	90	250	5.80	0.32	-1.88	5.17	1.91	0.08
5	9	-1	-1	1	60	75	250	4.90	3.88	-4.29	2.35	4.51	3.62
6	18	1	-1	1	30	75	750	4.20	5.03	-0.63	-2.98	0.82	5.00
7	11	-1	1	1	90	75	750	4.80	4.79	-2.53	-2.31	2.73	4.68
8	3	1	1	1	60	60	750	4.50	3.88	-4.29	2.35	4.51	3.62
9	12	-1	0	0	60	90	750	4.70	3.88	-4.29	2.35	4.51	3.62
10	6	1	0	0	60	75	750	4.80	0.59	-3.86	-4.58	3.73	1.16
11	13	0	-1	0	60	75	750	4.70	0.72	-2.07	1.50	2.14	0.47
12	5	0	1	0	60	75	750	5.00	3.88	-4.29	2.35	4.51	3.62
13	15	0	0	-1	60	75	750	5.20	3.88	-4.29	2.35	4.51	3.62
14	4	0	0	1	60	75	750	4.30	0.46	-1.73	-3.75	1.78	0.25
15	20	0	0	0	60	75	750	5.50	0.37	-6.53	5.52	6.39	1.36
16	8	0	0	0	30	60	1250	2.50	0.61	-1.49	2.35	1.39	0.82
17	14	0	0	0	90	60	1250	4.20	0.88	-1.04	5.84	1.13	0.76
18	2	0	0	0	30	90	1250	3.50	5.03	-0.57	2.35	1.78	0.21
19	16	0	0	0	90	90	1250	3.80	4.79	-4.29	5.17	2.73	3.62
20	19	0	0	0	60	75	1250	4.20	0.46	-1.88	-2.98	4.51	1.16

Table-3: Analysis of variance (ANOVA) for the natural dyeing process.

K/S values						
Source	SS	DF	MS	F-value	p-value	
Model	11.46	7	1.64	9.6	0.0004	significant
A-Time	5.18	1	5.18	30.4	0.0001	
B-Temp	0.2	1	0.2	1.15	0.3047	
C-HW conc.	2.81	1	2.81	16.48	0.0016	
AB	0.5	1	0.5	2.93	0.1125	
AC	0.84	1	0.84	4.96	0.0459	
A^2	1.92	1	1.92	11.27	0.0057	
Residual	2.05	12	0.17			
Lack of Fit	1.18	7	0.17	0.97	0.5334	not significant

$$R^2 = 85\%, \ \& \ \ adjusted\ R^2 = 76\%$$

Results and Discussion

Statistical analysis using RSM

In this study, three factors: time for extraction (A), temperature of extraction (B) were optimized to minimize effect of water hardness (C) using Response surface methodology (RSM) with central composite design (CCD). The CCD is more efficient than other response surface designs when optimization is required within the given range of chosen levels of factors of interest. Time of extraction (A) has three levels: 30, 60 and 90 minutes. Temperature of extraction (B) is also studied at three levels: 60°C, 75°C and 90°C. Third factor C is water hardness (ppm) at three concentration levels 250, 750 and 1250 (Table-1). RSM based CCD design with 20 experimental runs along with the corresponding response colour strength (*K/S*) and CIE*Lab* values are given in Table-2. Statistically significant linear and quadratic model terms for the natural dyeing process with estimated *p*-values are shown in Table-3. The model term with least *p*-value have more significant effect on the process.

The objective was to get maximum yield of natural colorant from marigold plant. The second order response surface model seems better fitted (Eq. 2). The adequacy of the fitted model is judged by determining the coefficient of determination, adjusted R^2, mean square sum of squares. Statistical significance is judged by Fisher value (F-value) and the probability value (p-value). The terms of the model are considered significant if *p*-value is less than level of significance (α) [22]. In this perspective and based on ANOVA results, the linear terms of dyeing time (A) (*F*-value = 30.4, *p*-value = 0.0001), temperature (B) (*F*-value = 1.15, *p*-value = 0.3047), HW concentration (C) (*F*-value = 16.48, *p*-value = 0.0016), and the interaction terms AB (*F*-value = 2.93, *p*-value = 0.1125), AC (*F*-value = 4.96, *p*-value = 0.0459) and A^2 (*F*-value = 11.27, *p*-value = 0.0057) have significant effect on the natural dyeing process. Lack of fit with *F*-value = 0.97, *p*-value = 0.5334) was not significant relative to the pure error which proved the adequacy of the fitted model. The value of coefficient of determination (R^2) is 85% and adjusted R^2 is 76% (Table-3) shows an agreement between predicted and actual extraction yield of natural dye of marigold flowers.

$$Y\ (K/_S\ \text{value}) = 4.78 + 0.72\,X_1 + 0.14\,X_2 - 0.00024\,X_3 - 0.00056\,X_1X_2 - 2.2E - 5\,X_1X_3 - 1.4E - 19X_2X_3 - 0.00069X_1^2 + \epsilon \quad (2)$$

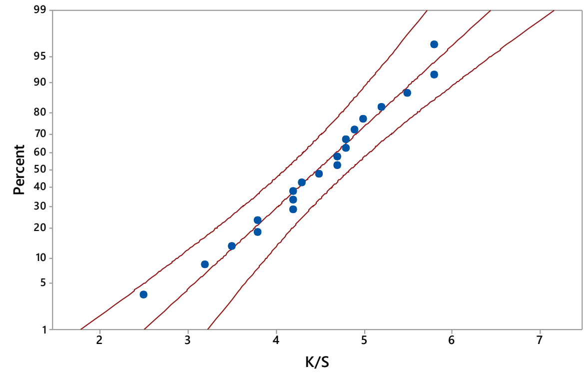

Fig. 1: Normal probability plot of *K/S* values.

Straight line obtained from normality plot further robust the model shown in Fig 2, validation of fitted RSM model is shown in Table-2. This table shows the estimates of studied parameters related to colour strength of fabric (*K/S*), dyed with natural dye extracted from the marigold flowers. The colour strength is significantly affected by direct proportion with temperature and extraction time of marigold dye. The interaction effect of the process parameters including dyeing time, temperature and HW concentration on the response variable colour strength of fabric (*K/S*) in the natural dyeing process was visualized with the help of 3D graphs. The interaction can be understood from Fig 3, three dimensional interactions of time and concentration of water hardness. Low concentration of water hardness and higher dyeing time imparted better colour strength values.

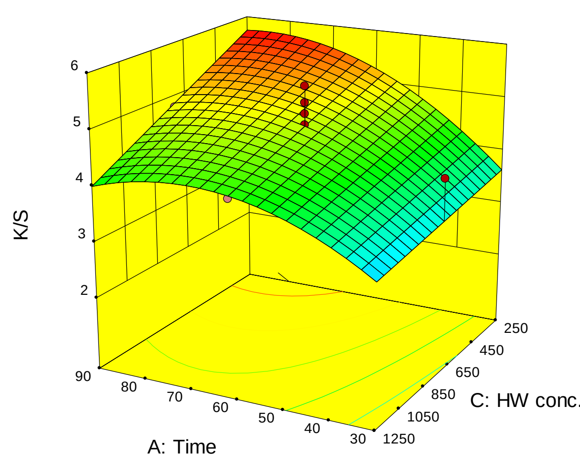

Fig. 2: Effect of time (min) and hard water concentration (ppm) on *K/S* values.

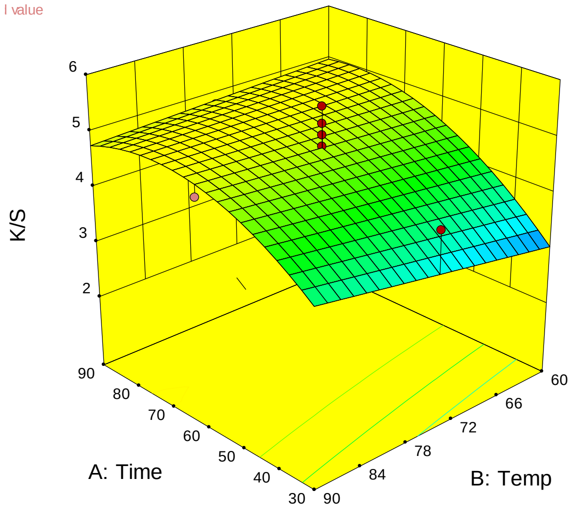

Fig. 3: Effect of time (min) and temperature (°C) on *K/S* values.

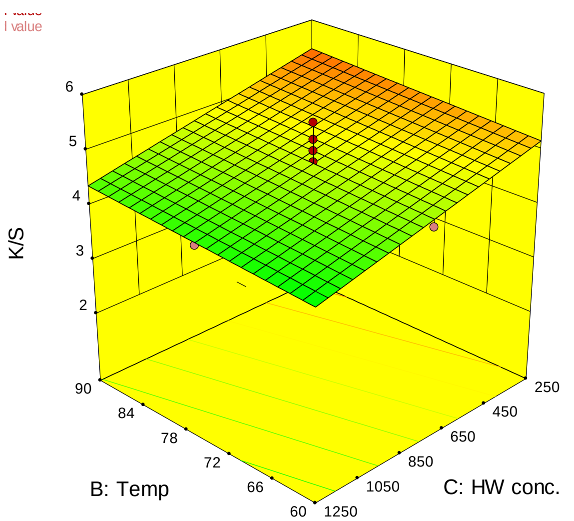

Fig. 4: Effect of temperature (°C) and hard water concentration (ppm) on *K/S* values.

Fig 3 shows the interaction effect of time and temperature on *K/S* values and similarly Fig 4 represents the interaction effect of temperature and HW concentration on *K/S* values. It is obvious from three 3D Figs that higher HW concentration inhibits the natural dyeing process. Moreover the effect of increase in dyeing time and temperature is the same as reported by earlier researchers.

Effect of hard water on extraction process

The effect of water hardness on extraction of dye is given in Table-4. It is obvious that higher concentration of water hardness exhibit negative effect on extraction process. The increase in extraction time significantly affect the process. Higher extraction time delivered lower *K/S* values and the trend was same at 250 and 750 ppm hard water concentration while higher extraction time with 1250 ppm water hardness exhibit positive trend in terms of increase in *K/S* which may be attributed to the partitioning behaviour of dye molecules in different phases of the metallic ions strength. The detailed CIE*Lab* and *K/S* values are given in Table-4.

Table-4: Effect of hard water on extraction of dye.

HW (ppm)	Time (min)	*K/S*	*L**	*a**	*b**	*C**	*h*
	30	6	3.99	0.37	0.63	0.15	4.01
250	60	5.4	1.98	1.83	3.38	1.64	2.13
	90	5.3	4.56	1.45	3.72	1.25	4.62
	30	5.8	4.99	-4.79	-5.58	4.97	4.81
750	60	5.2	5.04	-2.95	-4.55	3.13	4.93
	90	5.6	1.58	-1.45	0.22	1.61	1.43
	30	5.4	1.19	-0.79	4.91	0.92	1.09
1250	60	5.5	0.96	-1.08	2.76	1.18	0.83
	90	5.9	1.20	-1.06	4.81	1.19	1.2

Effect of mordants on dyeing behaviour

In this case, dyeing behaviour was studied by pre-mordanting and post-mordanting techniques

Pre-mordanting

The fabric was firstly pre-treated with two mordants ($FeSO_4$ 5% and alum 5%) individually at optimized condition of 60°C, for 45 minutes. The pre-mordanted fabric was dyed with extract of marigold flowers and effect was observed on *K/S* values and other colorimetric data. Ostensibly, there was subtle difference of the mordanting agent on colour strength but an obvious variation in colorimetric coordinates was observed as in Table-5. Overall *K/S* was in the range of 6-9 for $FeSO_4$ and 12-14 for alum. The Table-5 also indicates that both mordants have positive effect on hard water but alum is a better choice in improving colour fastness and quality of the substrate fabric as compared to $FeSO_4$. This might be attributed to low reduction potential of Fe^{2+} and Al^{3+} that emanate fixation onto modified cotton as compared to non-mordanted fabric. This improvement in colour strength might be due to presence of empty d orbitals in ferrous ions, which would be utilized for coordinate bonding with hydroxyl groups of lutein present in marigold dye [23]. Aluminium in the alum is also transition metal containing empty d orbitals and contribute to dye exhaustion in the same trend as iron in $FeSO_4$. In short, mordanting agents surprisingly improved the colour strength and diminished the adverse effect of hard water on dyeing behaviour.

Table-5: Colorimetric data of effect of mordants on dyeing process.

Process	Mordant (5%)	Water hardness (ppm)	*K/S*	*L**	*a**	*b**	*C**	*h*
Control	None	RO	6	23.05	3.2	-6.5	4.8	5.4
Pre-mordanting	$FeSO_4$	250	9	12.67	5.20	0.77	0.45	5.23
		750	7.2	15.03	5.67	-2.67	2.94	5.53
		1250	6.9	15.19	5.73	0.26	0.02	5.74
	Alum	250	16	2.85	5.85	12.46	12.16	6.45
		750	11	3.23	7.48	15.93	15.74	7.87
		1250	12	3.20	6.43	10.94	10.68	6.85
Post-mordanting	$FeSO_4$	250	8.5	20.77	4.82	-11.11	11.43	4.01
		750	7	20.31	4.95	-10.58	10.89	4.22
		1250	6.5	22.04	5.46	-10.12	10.37	4.96
	Alum	250	13	3.49	10.40	10.16	10.45	10.10
		750	10	4.79	10.45	11.52	11.80	10.13
		1250	8	4.46	10.97	12.45	12.81	10.54

Table-6: Effect of sequestering agent on extraction and dyeing behaviours.

Process	Water hardness (ppm)	*K/S*	*L**	*a**	*b**	C*	*h*
Extraction	250	12.8	1.24	4.98	4.48	4.15	-5.26
	750	11	0.74	5.08	1.95	1.62	-5.19
	1250	10.2	4.00	5.58	5.41	5.10	-5.86
Dyeing	250	14.5	57.82	-3.93	21.55	21.91	100.34
	750	11.9	52.28	-0.41	21.84	21.87	-0.1
	1250	10.2	56.72	-1.98	21.66	21.64	-2.78

Table-7: Colorfastness measurements.

Process	Mordant (5%)	Water hardness (ppm)	Fastness to light	Fastness to washing	Fastness to rubbing
Control	None	RO	3-4	3	3
Pre-mordanting	$FeSO_4$	250	6	4-5	4-5
		750	5	4-5	4-5
		1250	5	4-5	4-5
	Alum	250	7	4-5	4-5
		750	5-6	4-5	4-5
		1250	5	4-5	4-5
Post-mordanting	$FeSO_4$	250	5	4-5	4-5
		750	4	4-5	4-5
		1250	4	4-5	4-5
	Alum	250	5	4-5	4-5
		750	4	4-5	4-5
		1250	4	4-5	4-5

Post-mordanting

In this method, fabric was dyed using marigold extract for 60 minutes at 90°C temperature, M:L ratio was 1:20, and then mordants were applied with same concentrations as in pre-mordanting at all three levels of hardness. The Table-5 indicates that iron and aluminium in $FeSO_4$ and alum respectively, as post mordants, was the optimal choice for the achievement of good colour strength values. Literature reported the use of copper as metallic mordant for the achievement of better dyeing results. It was found that copper was good mordant for levelled dyeing, that might be due to interaction of dye with copper metal through coordinate covalent bond, the dye was appeared in darker shades with high tinctorial strength [24].

Effect of sequestering agents on extraction and dyeing

Sequestering agent, Texassist ECS, was employed to overcome the water hardness in the both extraction and dyeing process. The influence of this effect using water of three scales of synthetically produced hardness was monitored by *K/S* parameter. It was found that *K/S* value was remarkably affected by sequestrate in the both extraction and dyeing process. Results explored that the elevation in water hardness adversely affected the extraction yield of dye However, on application of sequestering agents, this hardness effect can be controlled. Sequestering agent successfully improved the extraction yield of colorants. It was observed that yield was highest at water hardness (250 ppm) under the applications of sequestering agent that improved from 6 (control) to 12.8 as shown in Table-6. The trend was survived at other hardness scales and in this way a significant change was observed on different colorimetric parameters. The unevenness of shade was substantially minimized by the consequent chelation of heavy metals and dispersing impurities.

Our work is in agreement with various studies that reported the improvement of dyeability with the use of sequestering agents that also improved the absorbance ability of the fabric [25]. ECS is also a widely known chelating agent which is capable for complexation with cations of hard water to remove spot formation for an even and uniform coloration.

Evaluation of colorfastness

Thus mordanting with sulfates of iron and aluminium improved the exhaustion and overall color strength along with washing and rubbing fastness as shown in Table-7. The improvement in fastness and fixation of dye might be associated with strong intermolecular interaction between dye and fabric with iron and aluminium. However the increase in water hardness slightly decreases the light fastness values. Water hardness doesn't show any obvious change in the washing and rubbing fastness values.

Conclusion

Extraction and dyeing behaviour of cotton fabric was characterized and analyzed using floral extract of *Tagetes erecta* under the influence of hard water. Different concentrations were applied and optimized through statistical calculations using RSM (respond surface methodology) for maximum extraction and colour strengths. It was found that the hard water has negative effect on natural dyeing and extraction. Different mordanting and sequestering agents were employed to combat the adverse effect of hard water. The applied mordants were alum and ferrous sulphate and both have shown positive effect on dyeing and fastness properties. However comparatively, alum has shown better results than $FeSO_4$. Phosphate based sequestering agent was applied which successfully improved extraction yield of colourants and dyeing parameters and also helped in minimizing the unevenness of the colour shade.

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