



Dyeing of cotton yarn with marigold (*Tagetes erecta*) petals: An emphasis on pre-treatments and mordants

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Abstract: Natural dyes and eco-friendly finishing of textile fabrics is gaining popularity because of the consciousness of people in saving the ecology. Widely available resources in India have encouraged researchers in experimenting on extraction and application of dyes for textile coloration. The aim of the present experiment was to standardize a protocol for optimization of pre-treatment, mordanting and dyeing of cotton yarn with African marigold flower petals. Myrobalan, pomegranate rind and tamarind hull were utilized in different concentrations for pre-treatment. Effect of different mordants and pre-treatment concentrations on colour strength (K/S, L, a* and b*) parameters of the cotton yarn is studied. Optimised pre-treatment concentrations, mordants and dyeing techniques on colourfastness parameters are also presented. Myrobalan followed by pomegranate rind pre-treatment produced darker and even shades on cotton yarns. Metallic salts viz., Stannous Chloride, Copper Sulphate and Ferrous Sulphate proved to produce shades with good to excellent colourfastness properties.

Keywords: Eco-friendly finishing, Marigold, Mordants, Natural dyeing, Pre-treatments

INTRODUCTION

Marigold is one of the widely used flowers in many of the Indian festivals, rituals and traditions. African marigold is known for their large flower sizes with very bright orange colour. Most of the flowers discarded after use and hence natural dyeing is an alternative to use this wasted biomass. Marigold flowers are rich in bio active components especially the carotenoid pigment, lutein. Natural tannin rich sources are used as pre-treatments that influence dye uptake and preferable over metallic salts. African marigold (*Tagetes erecta*) is a hardy annual plant about 90 cm tall, erect and branched. Florets are either 2 lipped or quilled. Flower colour varies from lemon yellow to golden yellow and orange. It is grown as a cut flower and a garden flower, in addition to being grown for its medicinal values. Marigold flowers, which are yellow to orange red in colour, are a rich source of lutein, a carotenoid pigment. Nowadays, Lutein is becoming an increasingly popular active ingredient used in the Food Industry and Textile coloration. This pigment has acquired greater significance because of its excellent colour value. In 1972, Quackenbush and Miller separated lutein and 16 common lutein fatty acid esters which, on the whole, represented over 95% of the pigments identified in the petals of the marigold.

Although marigold flower extract has been used in veterinary feeds, the potential use of marigold as a natural textile colorant has not been exploited to its full

extent. This is due to the lack of information on its safety, stability, and compatibility in textile coloration (Jothi, 2008). Natural dyes are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fibre. Marigold is one of the plants of medicinal value with wide applications in ayurvedic formulations for the treatment of skin problems, inflammation of the skin, either due to infection or any physical damage. Phytochemical screening of the *Tagetes erecta* have proved to contain flavonoid, alkaloid, quinones, Phenols, triterpenoid and coumarins bioactive compounds which are of medicinal value and have a definite physiological action on the human body (Devika and Koilpillai, 2015) reported potential benefits include Age-Related Macular Degeneration (AMD) (Landrum and Bone, 2001), enhanced immune function, and protection against oxidant induced cell damage (Olmedilla *et al.*, 2001). Natural dyes are known for their use in colouring of food substrate, leather as well as natural protein fibres like wool, silk and cotton as major areas of application since pre-historic times. The use of non-allergic, non-toxic and eco-friendly natural dyes on textiles has become a matter of significant importance due to the increased environmental awareness in order to avoid some hazardous synthetic dyes (Ashis and Priti, 2009). Recent resurgence in research and development on natural dye production and application is observed due to increasing popularity of more natural lifestyle based

on naturally sustainable goods (Jha *et al.*, 2015). At present there is an excessive use of synthetic dyes, the production and application of these dyes release vast amounts of waste and unfixed colorants, causing serious health hazards and disturbing the ecological balance of nature (Ghorpade *et al.*, 2000; Jyoti, 2008; Adeel *et al.*, 2009; Singh and Purohit, 2012). A number of commercial dyers and small textile export houses have started looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles to overcome environmental pollution caused by the synthetic dyes (Glover and Pierce, 1993). Mordanting can be achieved by either pre-mordanting, simultaneously mordanting and post-mordanting. Different types and selective mordants or their combination can be applied on the textile fabrics to obtain varying colour/shade, to increase the dye uptake and to improve the colour fastness property of any natural dye, several researchers have reported on this study (Paliwal, 2001; Paul *et al.*, 2002).

Thousands of flowers used are thrown into the pits on drying. It would be worthwhile if the waste that is rich in phenolics can be used for value addition. Textile colouration is one of the technologies that is averting towards eco-friendly procedures. Clothing being one of the basic necessities then is now considered as symbol of status that defines the socio-economic status of an individual. Fashion and style are the next concerns among people with a flare for self grooming. Growing consciousness of the consumers to save mother earth is propagating the use of eco-friendly biodegradable products. For successful commercial use of natural dyes, the appropriate and standardized dyeing techniques need to be adopted without sacrificing required quality of dyed textile materials (Ashis and Priti, 2009). Owing into the advantages of natural dyes of not only being eco-friendly but also antimicrobial, the present study was undertaken to standardize a protocol for dyeing of cotton yarn with marigold dye extract and to know the effect of various pre treatments and mordants on the colour parameters of marigold dyed cotton yarns.

MATERIALS AND METHODS

Source of raw material: Fully bloomed marigold flowers of Orange double variety freshly harvested were procured from the experimental plots of the Department of Horticulture, University of Agricultural Sciences, Dharwad. Myroblan, pomegranate rind powder and tamarind hull powder were sourced from one of the Ayurvedic Bhashaks at Belgaum. Grey cotton yarn of 2/60s was procured from a local yarn merchant.

Chemicals: Metallic salts *viz.* Potash Alum (AlK(SO₄)₂.12H₂O), Copper Sulphate (CuSO₄), Aluminium Acetate (Al(C₂H₃O₂)₃), Lead Acetate ((CH₃.COO)₂Pb.3H₂O), Ferrous Sulphate (FeSO₄.7H₂O), Stannous Chloride (SnCl₂.2H₂O) and Zinc Chloride (ZnCl₂)

were procured from Merck, Mumbai were used as mordants.

Processing and preparations: Yarn of 2/60s was desized by boiling in 2gpl detergent for 30 minutes with Material to Liquor Ratio of 1:30. The desized yarn was rinsed thoroughly and dried.

Marigold petals were removed from the calyx without pulling out the seeds, dried in a hot air oven at 50°C±2°C. Dried petals were powdered in a laboratory blender, packed and refrigerated.

Optimization of pre-treatment type and concentration:

Pre treatment agent : Myroblan, pomegranate rind, tamarind hull

Concentration : 1%, 2% and 3% each

Material to Liquor Ratio MLR : 1:10

Calculated amounts of the pre-treatment agents were soaked overnight with the Material-to-liquor ratio of 1:30. Scoured cotton yarns pre-soaked in water containing a surfactant like Turkey Red Oil were dipped in the pre-treatment agents for three hours. The yarn were squeezed and dried in sunlight. The pre-treated yarn was later dyed in 1 per cent concentration of marigold dye with an MLR of 1:20 for 30 minutes at boiling temperature. The dyed samples were squeezed and line dried in shade for oxidation reactions if any to occur and later rinsed in plain water twice and dried completely in shade.

The pre-treated and dyed samples were assessed for Colour Strength (K/S) values at 400nm using a Spectrophotometer with Premier colour scan software. K/S value denotes the fabric color strength. This method also involves Kubelka-Munk K/S equation, which indicates that the production of reflected light involves absorption and scattering. Based on the % reflectance (R), K/S can be calculated by the following formula:

$$K/S = (1-R) / 2R \quad \dots \dots \dots \text{eq. 1}$$

where K is the absorption coefficient and S is the Scattering coefficient. (Jha *et al.*, 2015) Samples recording the highest K/S values and the concentration were selected for optimization of Dye concentration.

Optimization of dye and mordant concentration:

Cotton yarn pre-treated with selected pre-treatment type and concentration were dyed with various combinations of mordant and dye concentrations with the recipe given below:

Mordanting

Mordant : Potash Alum

Concentration : 0.5, 1, 1.5 and 2 % (owf)

MLR : 1:10

Treatment time : 20min+10min

Dyeing

Concentration : 0.5, 1.0, 1.5, 2.0 and 2.5%

MLR : 1:30

Dyeing time : 20+10 minutes

Temperature : Boiling

Samples were dipped in luke warm mordant solution

for 20 minutes, squeezed and put into the boiling dye liquor for 20 minutes. As an intermediate treatment, the cotton yarn was re-dipped in the mordant solution for 10 minutes and later was again dyed for 10 minutes. Dyed yarn was allowed to partially dry under shade and later rinsed and dried. The optimization of mordant and dye concentration was done based on the Colour Strength (K/S) values.

Optimization of pre-treatment and mordant combinations: An effort was made to study the effect of different pre treatment concentrations and mordants on K/S of the marigold dyed fibres by keeping the mordant concentration constant at 1 per cent. Samples pre-treated with various concentrations (1, 2 and 3%) of myrobolan, pomegranate rind and tamarind hull were dyed in 1 per cent each mordant and dye concentrations. Optimization of the pre treatment and mordant concentrations were done referring to the K/S values measured at 400nm. In a similar study, which reported the use of Potash Alum in the mordanting of cotton fabrics dyed with natural dyes Wanyama *et al* (2011).

Quality assessment

Colour strength: Colour strength parameters *viz.*, Colour Strength (K/S), Lightness/Darkness values (L), Redness/greenness values (a*) and yellowness/blueness values (b*) were assessed using Spectrophotometer (SS5100A) with Premier Colour scan software (Colorlab+). The Colour Strength for the integrated wavelength option available in the software was recorded. However the instrument measures reflectance and transmission of the given samples at 360nm to 740nm. Differences in colour parameters (δE , δL , δa , δb) were also recorded. The readings of the instrument and the principle of the equipment is in accordance with CIE L*a*b* standards.

Colourfastness: Colourfastness studies to various agents *viz.*, Sunlight, washing, wet and dry rubbing and acid and alkaline perspiration were tested using standard test methods (IS: 971-1983 for Colour fastness to perspiration; IS: 686-1985 for Light; IS: 687-1979 for Wash; IS: 766-1988 for Rubbing). Ratings for sunlight fastness were assigned as per the blue wool standards and those for washing, rubbing and perspiration as per grey scale.

RESULTS AND DISCUSSION

Characterization and quantification is one of the preliminary requirements of optimization process. Optimi-

Table 1. Colour Strength (K/S) values of the marigold dyed cotton yarn with different pre-treatment types and concentrations.

Pre-treatment type	Concentration		
	1%	2%	3%
Myrobolan	31.931	43.598	47.427
Pomegranate rind	6.825	8.360	9.942
Tamarind hull	34.892	36.580	43.189

zation is standardization of the source processing, auxiliaries, pre-treatments, mordants, concentrations, treatment time, temperature, pH, *etc.* (Vastrad *et al.*, 2016).

Optimization of pre-treatment type and concentration: Irrespective of the pre-treatment type an increase in the K/S was observed with increase in the concentrations. Myrobolan 2 per cent was selected for further studies. Myrobolan (*Terminalia chebula*) also known as *haritaki* in Sanskrit and hindi, belongs to the family Combretaceae. The tree is found in the western ghat forests of Karnataka. (Vastrad *et al.*, 2016) The fruit contains several phytoconstituents like tannins, flavonoids, sterols, amino acids, fructose, resin, *etc.* It is fairly rich (32%) in tannins that is largely dependent on its geographic location. (Kumar *et al.*, 2006). On the other hand rind of pomegranate also known for its phenolics is said to contain tannins about 19 per cent with pelletierine (Tiwari *et al.*, 2010).

Optimization of mordant (PA) and dye concentrations: It was observed that an increase in the dye concentration increased the K/S value. However, the reading at 2.00 and 2.50 per cent concentration of the dye was found to be on par with each other. Similarly an increase in the mordant (PA) concentration from 0.50 to 1.00 per cent brought in significant increase in the K/S values. However the difference between the K/S of 1.0, 1.5 and 2.00 percent mordant concentration was non-significant. In Chemical terms, mordants are defined as polyvalent metallic compounds which can develop co-ordinate and covalent complexes with dyes and fibres (Baker, 1958). However, typically metallic atom forms covalent bond with hydroxyl/carboxyl oxygen on the dye/fibre and a co-ordinate bond with adjacent long pair of electrons on double bonded oxygen. Mordants can chelate several dye molecules together creating a larger complex and provide link between the dye and fibre. They also assist fibre to retain colour, increasing depth of shade, fastness to wet and mechanical treatments (Gordon and Gregory, 1983). Based on the readings in the Table 2, mordant concentration of 1 per cent and dye concentration of 2 per cent was selected for bulk dyeing.

Optimization of pre-treatment and mordant combinations: It is clear from the table 3 that the K/S values were higher with the samples pre treated with myrobolan and mordanted using different metallic salts. With Aluminium Acetate, Ferrous Sulphate, Lead Acetate

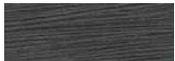
Table 2. K/S of the cotton yarn samples dyed with different concentrations mordant (PA) and Dye.

Dye Concentration (%)	Mordant (PA) concentrations (% owf)			
	0.50	1.00	1.50	2.00
Control	22.418	44.343	43.717	45.391
0.50	25.799	31.262	30.662	32.967
1.00	37.139	77.042	79.021	81.564
1.50	70.171	138.788	141.002	143.201
2.00	104.662	282.240	285.128	287.026
2.50	113.762	289.410	291.180	293.526

Table 3. K/S values of the cotton yarn samples pre-treated with different agents and mordants

Mordant	Myrobolan			Pomegranate rind			Tamarind hull		
	1%	2%	3%	1%	2%	3%	1%	2%	3%
Aluminium Acetate	47.498	63.790	64.718	9.581	16.376	22.480	29.29	48.744	40.696
Copper Sulphate	79.197	371.74	212.13	88.63	77.566	110.339	24.356	53.361	57.574
Ferrous Sulphate	184.739	233.976	309.49	271.628	241.190	182.266	55.001	87.347	163.031
Lead Acetate	53.268	97.611	257.028	92.626	90.004	103.134	26.949	51.142	61.226
Potash Alum	99.399	181.261	174.472	163.486	131.873	123.540	49.083	100.977	110.509
Stannous Chloride	94.306	450.413	759.488	353.697	213.134	262.625	68.179	169.659	129.546

Table 4. Colour measurement value for dyed marigold sample pre-mordanted with different mordants

S. N.	Sample	Myrobo-lan conc.	Particulars	K/S	L	A	b	c	H
1		-	Control	81.403	50.097	5.201	34.813	35.199	81.470
2		3%	Ferrous Sulphate	680.991 (48.603)	38.400 (-12.280)	-1.917 (-7.118)	8.914 (-25.899)	9.118 (-26.082)	102.168 (6.417)
3		2%	Copper Sulphate	402.158 (20.532)	53.315 (2.635)	6.874 (1.673)	42.455 (7.642)	43.008 (7.809)	80.770 (0.476)
4		3%	Stannous Chloride	736.266 (55.932)	75.771 (25.091)	16.379 (11.178)	83.269 (48.456)	84.865 (49.665)	78.840 (-2.509)
5		3%	Lead Acetate	283.393 (14.866)	54.170 (3.490)	5.019 (-0.182)	43.500 (8.687)	43.789 (8.589)	83.385 (1.312)
6		3%	Aluminium Acetate	47.752 (8.504)	51.097 (0.417)	5.096 (-0.105)	36.632 (1.819)	36.985 (1.785)	82.047 (0.364)
7		2%	Potash Alum	270.980 (24.019)	66.965 (16.285)	4.910 (-0.291)	61.788 (26.975)	61.983 (26.783)	85.422 (3.222)

(Figure in parenthesis indicate the ΔE, ΔL, Δa and Δb respectively), ΔE=colour difference, ΔL=Lightness/Darkness, Δa=Redness/Greenness, Δb= Yellowness/Blueness, Δc=Chroma.

Table 5. Colour fastness of cotton yarn dyed with marigold.

Mordant	Light fastness	Wash fastness			Rubbing (SC)		Perspiration					
		CC	SC	SW	Dry	Wet	Acid			Alkali		
							CC	SC	SW	CC	SC	SW
Ferrous Sulphate	4	4-5	4-5	4-5	4	5	4-5	3-4	3-4	4-5	5	5
Copper Sulphate	4-5	4-5	5	5	4-5	4-5	4-5	3-4	3	4	4-5	5
Stannous Chloride	5	5	5	4-5	4-5	4	5	5	5	5	5	5
Lead Acetate	4	4	4	4-5	4	3-4	4	3-4	3-4	4	4	4
Aluminium Acetate	3	3	3	3-4	3	3-4	3	3	3	3-4	3-4	3-4
Potash Alum	3-4	3-4	3-4	3-4	4	4	3-4	4	4	4	4	4

CC- Change in color, SC- Stain on cotton, SW- Stain on wool

and Stannous Chloride mordants the K/S was maximum at 3 per cent myrobolan concentration. Whereas for Copper sulphate and Potash Alum mordants the K/S was maximum at 2 per cent myrobolan concentration.

Colour assessment of the samples dyed using optimized methods: Cotton yarns pre treated with 2 per cent myrobolan were mordanted with CS and PA; Yarn pre-treated with 3 per cent myrobolan were mordanted with AA, FS, LA and SC. Dyeing was carried out with 2 per cent concentration with redipping technique for even and efficient dyeing. Samples exhibited better Colour Strength values over control. Ferrous Sulphate mordant produced the darkest shade indicat-

ed by the L value (38.400) whereas lightest colour was obtained by Stannous Chloride (75.771) with the K/S of 736.266. All the samples were towards the yellower shade as indicated by the b* values but samples mordanted with Ferrous Sulphate were towards the greener tinge. The coordination of the mordants with the pre-treatments and the dye molecules may propagate formation of complexes to facilitate better dye uptake with enhancement in the colour.

Colourfastness of dyed cotton samples: The ultimate performance expected of dyes and pigments was their fastness to various agents. Sustainability of the dye/pigment to sunlight is of utmost importance. However, the colourfastness test authenticated the procedures

followed for dyeing especially with the natural resources. Mordants proved to have affinity for the dye and the fibre, that aided in forming insoluble complexes within the fibre imparting good colourfastness performance to the fabric. The FS, CS, SC, and LA mordanted samples dyed with marigold dye exhibited fair to good colourfastness properties. This is due to the formation of a complex with transition metal (mordant CS, FS) which protects the chromophore from photolytic degradation and the photons sorbed by the chromophoric group dissipate their energy by resonating within the six member ring thus formed and hence protecting the dye (Jothi, 2008). Wash fastness is influenced by the rate of diffusion of dye and the state of the dye molecule inside the fibre. Cotton yarn mordanted with FS and SC exhibited very good to excellent wash, rubbing and perspiration fastness. The same can further be experimented for the biochemical composition through analytical techniques. Different constituents have different degrees of solubility in different types of solvents. The mode of action of plants producing dyeing effects on selected textile material can be better investigated if the active ingredients are identified and characterized (Vastrad and Goudar, 2016).

Conclusion

The present work indicated that 3% myrobolan pretreatment imparted darker hues, even shades and good to excellent colour fastness compared to 1% and 2% myrobolan followed by the pomegranate rind and tamarind hull powder. Myrobolan rich in tannins are proven to improve the dye uptake and dye performance. Various shades were obtained using different pretreatments and mordanting. Mordant concentration of 1% for Stannous Chloride, Copper Sulphate and Ferrous Sulphate and dye concentration of 2% were optimized for bulk dyeing. There is a need to commercialize natural dye not only to protect the ancient and traditional folklore but also to save and protect the ecology.

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