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Sonicator Dyeing of Cotton, Wool and Silk with the Leaves Extract

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ABSTRACT

Malus sikkimensis. (Local name- Chap shaw sheng) belongs to family Rosaceae is being primarily used for preparing tea by Monpas tribes of Arunachal Pradesh. In the present study sonicator dyeing with Malus extract has been demonstrated. Pretreatment with 1-2 % metal mordant and using 5 % of plant extract (owf) was found to be optimum and showed very good hue colors for cotton, wool and silk dyed fabrics. We have demonstrated that the use of sonication in conjunction with metal mordanting has a synergistic effect on better dye uptake, dye adherence and eventually on good fastness properties of the dyed swatches of cotton, silk and wool.

Keywords: Malus sikkimensis, natural dye, cotton, wool, silk, commercial dyeing

1. Introduction: *Malus sikkimensis,* belongs to family *Rosaceae,* is an evergreen woody tree with a maximum height of 40 m and diameter 2.3 m. It occurs in humid valley forest of Arunachal Pradesh. In the present study *Malus* leaves (figure-1) have been used as natural dye-stuff, which is primarily used as a substitute for tea by the local Arunachalees. The crude aqueous extract has been shown to dye cotton, silk and wool samples as shown in figures 5-7.

Traditional Knowledge of its use: Stem and leaves of the plant locally known as "Chapshaw sheng" (*Malus sikkimensis*) has been mainly used for the preparation of tea by the Monpas –one of the tribe of Arunachal Pradesh. Since Malus grows in the Tawang and West Kameng Districts, 2500-3500 m, in open forests of Arunachal Pradesh [1].

Figure-1 Leaves of *Malus sikkimensis*

2. Experimental

2.1. Materials:

The cotton fabric of 105 g/m^2 (warp-30 , weft-20) was scoured with a solution containing 5 g/l of sodium carbonate and 3 g/l of non-ionic detergent (Labolene) under the boiling condition for

4 h, after which time it was thoroughly rinsed and air dried at room temperature.

The munga silk of GSM-45 fabric was scoured with solution containing 0.5 g/L sodium carbonate and 2 g/L non-ionic detergent (Labolene) solution at 40-45° C for 30 min, keeping the material to liquor ratio at 1:50. The scoured material was thoroughly washed with tap water and dried at room temperature. The scoured material was soaked in clean water for 30 min prior to dyeing or mordanting.

The pure new wool(J sagar) 60 gm was scoured with solution containing 2 g/L non-ionic detergent (Labolene) solution at 30-35° C for 30 min, keeping the material to liquor ratio at 1:50. The scoured material was thoroughly washed with tap water and dried at room temperature. The scoured material was soaked in clean water for 30 min prior to dyeing or mordanting.

Dye used —*Malus sikkimensis* leaves

Pretreatment—Tannic acid (in the case of cotton only)

Mordant used –Alum, ferrous sulphate, stannic chloride, stannous chloride, copper sulphate and potassium dichromate. All other chemicals used were laboratory grade reagents.

2.2. Methods:

2.2.1 Extraction of the dye: Dry leaves from plant source were crushed and dissolved in distilled water and heated to (70^{0}C) in a beaker kept over water bath for quick extraction for 1.5 hours. All the color was extracted from leaves by the end of 1.5 hours.

Optimization of extraction condition: Malus leaves were completely dried at room temperature. The dry leaves were crushed and ground to make powder.

Extraction amount and time required: The dried-ground leaves (2.5,5,7.5,10 and 12.5 gm each) were soaked in sufficient water (app. 200-250ml) at 70-75°C for 0.5,1.0,1.5 and 2.0 hours. After extraction the extract was filtered through ordinary filter paper and the filtrate was collected, and absorbance was recorded for determination of concentration.

Extraction temperature: The dried-ground leaves (10 gm each) were soaked in sufficient water at 50, 60 70 and 80°C for specified period of time.

pH of extraction medium: The ground leaves (10 gm each) were soaked in beaker which contain water (app. 200-250 ml) and the pH was determined.

Mass to liquor ratio: The ground leaves 10 gm were soaked in four beaker having 100, 200, 300 and 400 ml at 70°C for 1.5 hrs.

2.2.2. Treatment of fabric before dyeing: After removing the impurity of cotton fabric then it was treated with 4 % (owf) solution of tannic acid in water. The fabric should be dipped in tannic acid solution for at least 4-5 hours. It is squeezed and dried. Pre-mordanting was used for this study, fabric which was already treated with tannic acid was dipped, in mordant (2% for alum and 1% for stannous chloride, stannic chloride, ferrous sulphate, copper sulphate and potassium dichromate separately) solution and was kept on water bath at 40°C for one hour. It was squeezed and dried. Silk and wool were directly premordanted with metal salts, no tannic acid treatment was required in the latter case.

Pretreatment: Cotton fabrics have been reported to be pretreated with tannic acid[4] that provide carboxylic acid (-COOH) groups to the fabric.

2.2.3. Sonicator dyeing: Sonicator dyeing has been used for dyeing of cotton, silk and wool by various types of natural dye extracts by us [2, 3 and 4]. The ultrasound energy gives rise to acoustic cavitations in the dye bath. The cavitations occurring near to a solid surface generate microjets, which facilitates the liquid to move with a high speed and give rise to an increased diffusion of dye molecules inside the fabric's pores. In the case of sonication, an enhancement in the localized temperature and pressure induces swelling effects in the fiber, thus causing improved diffusion of the dye.

The cavitations bubbles oscillate and implode, thus enhancing molecular motion and stirring effect in the dye bath. In case of cotton dyeing, the effects produced due to stable cavitations may be realized at the interface of the fabric and the dye molecules in the solution. Dye uptake was studied during the dyeing process for a total treatment time of 1-3 hrs in the presence or not of ultrasound.

2.3. Measurements and analysis

2.3.1. Color measurements: The relative color strength of dyed fabrics expressed as *K*/*S* was measured by the light reflectance technique using the Kubelka–Munk equation [5,6]. The reflectance of dyed fabrics was measured on a Premier Colorscan.

$$K/S = (1-R)^2/2R$$

Where K is the sorption coefficient, R is the reflectance of the dyed fabric and S is the scattering coefficient.

The CIE lab values were also recorded for all dyed samples along with controlled sample.

2.3.2. Fastness Testing of dyed samples:

Xenoster: Used to test the light fastness of the dyed fabric.
Wash wheel: Thermolab model**:** Used to test the washing fastness of the dyed fabric.
Perspirometer: Sashmira Model***:*** Used for the testing of perspiration fastness of the dyed fabric.
Crock meter: Ravindra Engg. Model: Used for testing the rubbing fastness of the dyed fabric.
Color Matching system: The reflectance of dyed fabrics was measured on a Premier Colorscan.

2.4. Dyeing: Dyeing was carried out in the following manner: A two step dyeing (in the ratio of 1 or 2 % mordant, owf) was used as pretreatment and then dyeing with *Malus* leaves extract was carried out for 1 hour at temperature 30-40^{0}C[5]. The dyed fabrics were dipped in saturated brine solution (15 mins) acting as dye-fix and then rinsed thoroughly in tap water and allowed to dry in open air. The colorimetric data obtained from dyed fabrics and yarn which had been pretreated with tannic acid/metal mordants in the case of cotton and only metal mordants in the cases of silk and wool reveal that pretreatment markedly improved the wash fastness, in terms of change of shade of the dyed fabrics with respect to controlled samples. It also increased the color strength and flattened the shade of the dyeings. In each experiment controlled dyed samples were also prepared.

2.5. Color measurements: K/S were measured for cotton, silk fabrics and wool yarn as shown in figures- 2, 3 and 4 and CIE lab values are shown in table 2-4.

3. Results and Discussions:

3.1. Optimization of extraction condition: The optimization conditions were carried out as per the method described in 2.2.1. Aqueous extract prepared from dried Malus leaves was used for the study in table-1:

Table-1 showing Optimization of extraction condition for Malus

Parameters for optimization for dyeing samples with Malus leaves	Trial	Selected
1. Dye material concentration	2.5,5.0,7.5,10.0 and 12.5 g	10.0 g
2. Dye extraction time	0.5, 1.0,1.5 and 2.0 hours	1.5 hours
3. Dye Extraction temperature	50, 60, 70 and 80°C	70 °C
4. pH of the Extract	4.34	Stable at pH 4-9
5. Dyeing time (Sonicator) (Conventional)	0.5, 1.0, 1.5, 2.0 and 3 hours	1 hour 3 hours
6. Dyeing Temperature	30, 40, 50, 70 °C	30-40°C
7. Mordanting time	30, 45, 60, 90 mins	60 mins
8. Mass to liquor ratio	100, 200,300 and 400 ml	10gm/200 ml

3.2 Color measurements: K/S were measured for cotton, silk fabrics and wool yarn as shown in figure -2,3 and 4 as well as CIE lab values are shown in table 2-4.

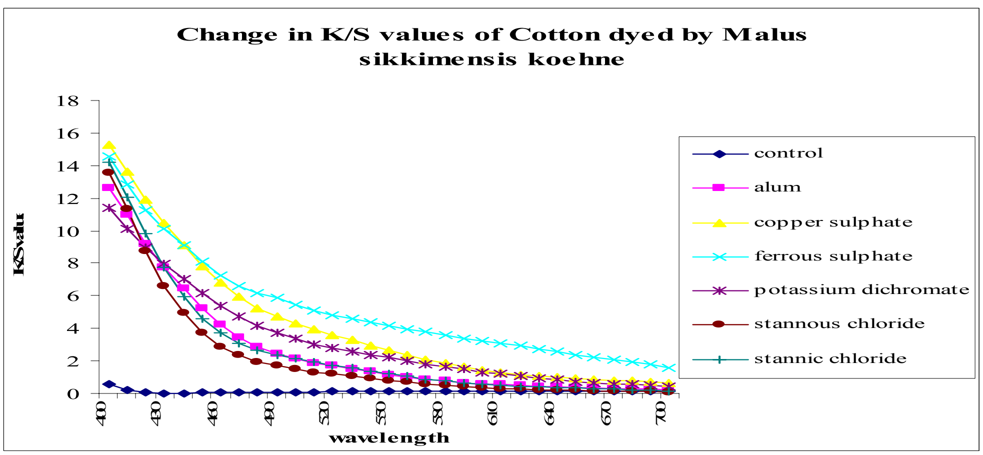

Figure-2 Change in K/S value for Cotton fabrics

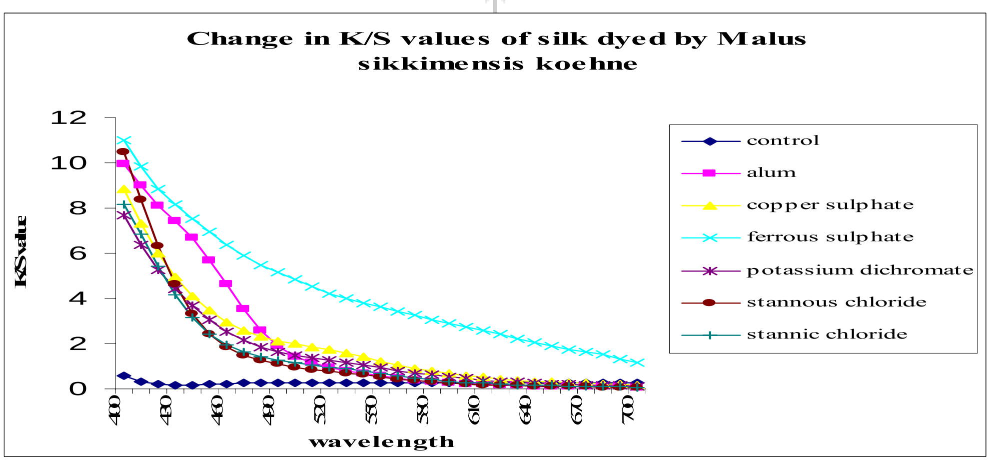

Figure-3 Change in K/S value for Silk fabrics

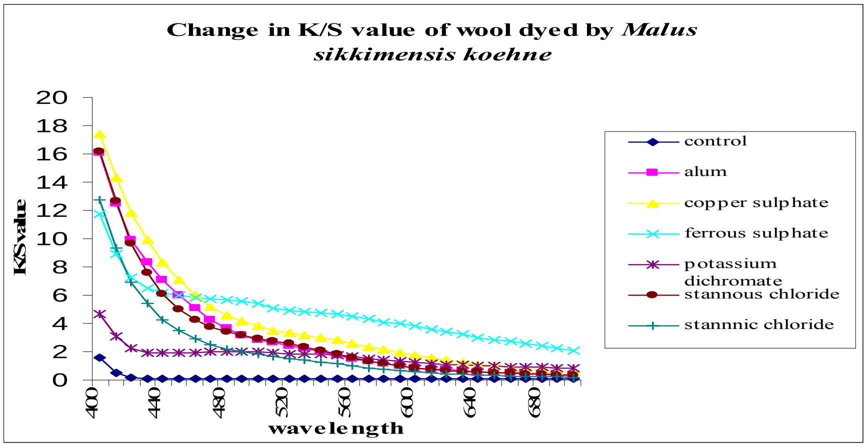

Figure-4 Change in K/S value for Wool yarn

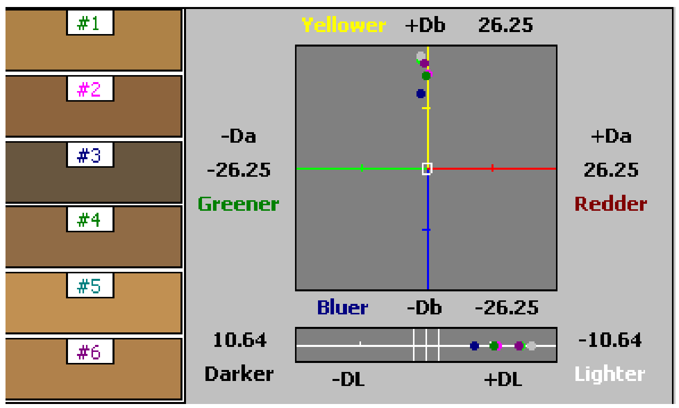

Figure-5 shows the colorimetric values of dyed cotton fabric with Malus

Fig-5 shows the colorimetric values of dyed cotton fabric with Malus after pretreatment with different metal mordants(#1-6 in the order of alum, copper sulphate, ferrous sulphate, potassium dichromate, stannous chloride and stannic chloride). The dyeings with different mordants imparted a shade change from light brown to dark brown having reddish tinge. Also, the lightness value decreased for copper and iron mordanted fabrics and shade of depth retained their brightness, while the highest was obtained with ferrous sulphate having dullness.

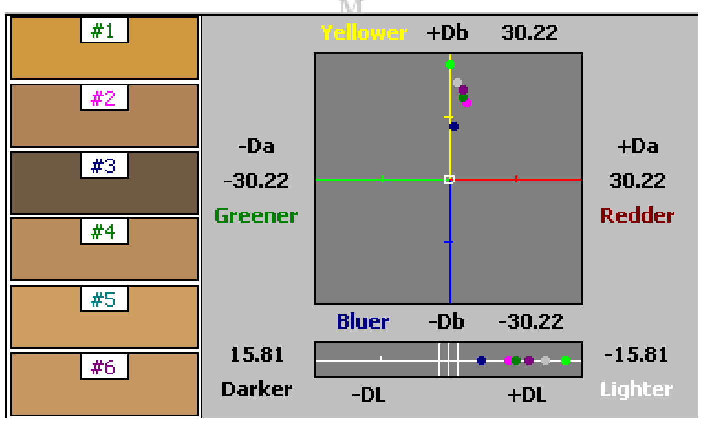

Figure-6 shows the colorimetric values of dyed silk fabric with Malus

Fig-6 shows the colorimetric values of dyed silk fabric with Malus after pretreatment with different metal mordants (#1-6 in the order of alum, copper sulphate, ferrous sulphate, potassium dichromate, stannous chloride and stannic chloride). The dyeings with different mordants imparted a shade change from pure yellow to dark brown. Also, the lightness value decreased for iron and chromium and shade of depth became dull and dark, while the highest was obtained with stannic chloride having good brightness.

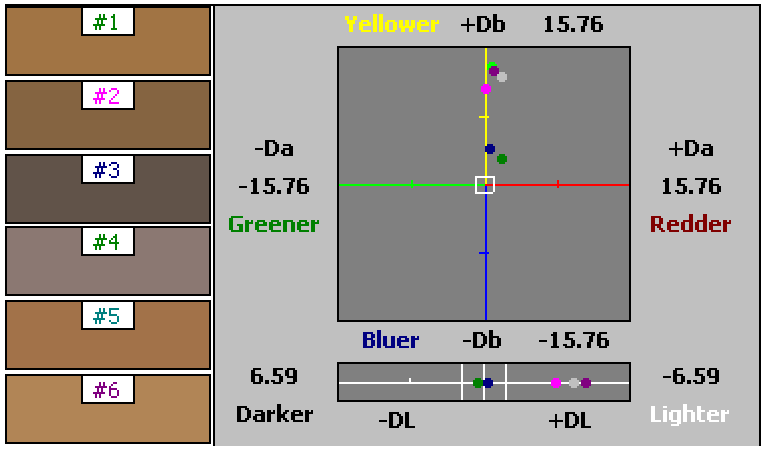

Figure-7 shows the colorimetric values of dyed wool yarn with Malus

Fig-7 shows the colorimetric values of dyed wool yarn with Malus after pretreatment with different metal mordants (#1-6 in the order of alum, copper sulphate, ferrous sulphate, potassium dichromate, stannous chloride and stannic chloride). The dyeings with different mordants imparted a shade change from light yellow to brown and grey. Also, the lightness value decreased for potassium dichromate and shade of depth became dull and dark, while the highest was obtained with potassium dichromate having good brightness.

Table-2 CIEL*ab values of cotton dyed fabrics with Malus extract

	Control	Alum	$CuSO_4$	Fe SO_4	$K_2Cr_2O_7$	$SnCl_2$	Sn Cl_4
L*	78.902	86.661	84.745	82.806	84.425	87.541	86.473
a*	1.832	0.603	1.967	0.578	1.570	0.675	1.215
b*	-9.020	14.516	11.586	7.380	10.993	15.229	13.868
C*	9.204	14.529	11.752	7.403	11.105	15.244	13.921
H*	281.512	87.586	80.332	85.487	81.839	87.427	84.959
dE*	------	24.812	21.419	16.905	20.763	25.768	24.116
K/S	1.6945	50.3341	81.2542	98.9014	64.3907	39.0197	48.7756

Table-3 CIEL*ab values of silk dyed fabrics with Malus extract

	Control	Alum	$CuSO_4$	Fe SO_4	$K_2Cr_2O_7$	$SnCl_2$	Sn Cl_4
L*	70.105	83.918	77.346	74.005	78.206	81.584	79.661
a*	0.705	0.769	4.850	1.935	3.680	2.541	3.761
b*	-3.341	24.876	15.516	9.565	16.760	20.188	18.213
C*	3.415	24.888	16.256	9.759	17.159	20.347	18.597
H*	281.947	88.194	72.613	78.532	77.585	82.793	78.301
dE*	------	31.417	20.620	13.538	21.875	26.244	23.775
K/S	4.3176	44.6756	37.0819	83.5632	31.1734	26.3359	26.1342

Table-4 CIEL*ab values of wool dyed with Malus extract

	Control	Alum	$CuSO_4$	Fe SO_4	$K_2Cr_2O_7$	$SnCl_2$	Sn Cl_4
L*	80.701	85.291	83.974	80.865	80.402	84.721	85.264
a*	0.961	1.658	1.138	1.522	2.915	2.724	1.855
b*	-0.615	13.140	10.587	3.604	2.465	11.935	12.689
C*	1.141	13.244	10.648	3.912	3.818	12.242	12.824
H*	327.396	82.775	83.831	67.078	40.203	77.112	81.650
dE*	------	14.517	11.672	4.259	3.660	13.296	14.093
DL*	------	4.590	3.273	0.164	-0.299	4.020	4.563
K/S	1.7788	60.4970	78.1461	87.6810	29.6761	56.1052	37.9418

3.3. Effect of mordanting conditions

It was observed that the pre mordanting technique with metal mordants imparted good fastness properties to the cotton and silk fabric. However in the case of cotton fabrics pretreatment with tannic acid gave better results. Therefore, the fabrics were mordanted with stannic chloride, stannous chloride, ferrous sulphate, copper sulphate, potassium dichromate and alum after tannic acid treatment.

The mordant activity of the six cases followed the sequences

The order of K/S values is as following : Fe → Cu →Cr→ Al → Sn (IV)→Sn (II) in cotton for *Malus,* the absorption of color by cotton fabric was enhanced when using metal mordants, this might be due to the maximum absorption and easy formation of metal-complexes with the fabric as can be seen figure-2.

The order of K/S values is as following: Fe →Al→ Cu → Cr →Sn (II) → Sn (IV) in silk for *Malus,* the absorption of color by silk fabric was enhanced when using metal mordants, this might be due to the maximum absorption and easy formation of metal-complexes with the fabric as seen in figure-3.

The order of K/S values is as following: Fe → Cu→ Al→ Sn(II) → Sn(IV) → Cr in wool for *Malus,* the absorption of color by wool yarn was enhanced when using metal mordants, this might be due to the maximum absorption and easy formation of metal-complexes with the fabric as seen in figure-4.

3.4 Statistical analyses

The absorbance (%) of dye uptake and *K*/*S* values of each dyeing condition were evaluated by analysis of variance and each treatment was replicated three times. The standard error of the difference SED(±) was calculated for each mordant.

3.5 Fastness testing

The dyed samples were tested according to Indian standard methods [7] and the results for alum mordanted are tabulated below in table-5.

Table-5. Fastness properties of dyed cotton, silk fabrics and wool yarn by conventional and ultrasonic conditions of alum mordanted and dyed with *Malus sikkimensis*

Dyeing methods	Wash–perspiration–rubbing–light					
	WF	Per$_{acidic}$	Per$_{basic}$	Rub$_{dry}$	Rub$_{wet}$	LF
Conventional (C)	4	4	4	4	4	4
Ultrasonic(C)	5	5	5	5	5	5
Conventional(S)	4-5	4-5	4	4	4-5	4-5
Ultrasonic(S)	5	5	5	5	5	5
Conventional(W)	4-5	4-5	4	4	4-5	4-5
Ultrasonic(W)	5	5	5	5	5	5

WF = wash fastness, LF = light fastness.

Thus table-5 shows that alum mordanting has caused improved fastness properties under sonication in all the three types of material as a representative case. Similar observations were made in the case of other five mordants as well. Marked improvement can be noticed in the case of washing and light fastness. Thus the dye can be recommended for commercial use.

Higher exhaustion of dye (*Malus*) can be achieved in 1 h dyeing time using ultrasound while in the case of conventional dyeing (in absence of ultrasound in stationary condition for the same natural dye) it takes 3 hours. Dye uptake has been calculated for all samples on the basis of dye exhaustion with respect to controlled sample, the results of mordanted cotton dyed fabrics are shown in table-6.

Table-6 Shows effect of mordant in dye uptake in different dyeing methods

Mordant	Sonicator Dyeing(1 Hr)	Conventional Dyeing(3 Hrs)
Controlled sample	**34%**	**14%**
Alum	**68 %**	**38%**
Ferrous Sulphate	**74%**	**32%**
Copper Sulphate	**55%**	**25%**
Stannous Chloride	**70%**	**32%**
Stannic Chloride	**73%**	**38%**
Pot. Dichromate	**63%**	**36%**

Similarly dye uptake was calculated for other mordants with and without sonication in order to show the beneficial effect of sonication in natural dyeing. It is very clear that as compared to the controlled samples and it is concluded that the effect of sonication is certainly advantageous. Figure-8 also depicts that at faster kinetics as in the case of sonicator dyeing (1 hour) better results are obtained, while in conventional dyeing it took 3 hours for optimum dye-uptake.

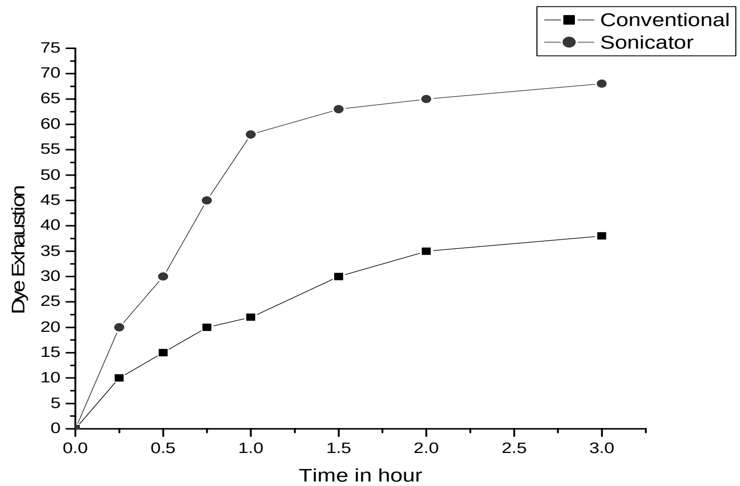

Figure-8 Ultrasonic dyeing with Malus with alum mordant

The figure-8 shows that the dye-uptake values of sonicator dyed samples are generally better than those obtained by conventional method. It is well documented in the literature [9] that dyeing process is a solid/liquid phase process, which proceeds by the movement of the dye molecules from liquid phase to the solid surface of the fabric by their force of affinity toward the fabric, and then diffuse into the fabric. Therefore, the first process probably would be a fast adsorption controlled process, once the dye molecules get into the fabric , the second slow process, which is diffusion starts to take place. Thus the influence of vibrations from sonicator on the rate of dyeing process would show higher dye-uptake in short time for ultrasonically dyed samples in comparison with conventionally dyed ones. This enhancement effect of ultrasonic power is due to the cavitation effect[8].

The data in figure-8 can be analyzed by using the derivable general form of the first order rate equation Eq-1:

$$\mathbf{A_t - A_f / A_o - A_f = e^{-kt}} \qquad \textbf{Eq-1}$$

where A_t is the absorbance at time t, A_0 is the initial absorbance, A_f is the final absorbance, t is the reaction time and k is the reaction rate. As the absorbance of dye bath solution is directly related to the concentration by Beer-Lambert's Law, therefore can be written in terms of dye uptake to give Eq. 2

$$\mathbf{D_t - D_f / D_o - D_f = e^{-kt}} \qquad \textbf{Eq-2}$$

where D_t is the dye uptake at time t, D_0 is the dye uptake at zero time, D_f is the final dye uptake, t is the dyeing time and K is the dyeing rate. The time of half dyeing $t_{1/2}$ which is the time required for the fabric to take up half of the amount of dye taken at equilibrium, is estimated from the following equation Eq.3:

$$\mathbf{t_{1/2} = \ln 2/k} \qquad \textbf{Eq-3}$$

The data for dyeing equilibria are reported as the standard affinity of dyeing, $-\Delta\mu$ [11]

It has been reported that the dyeing of cotton fabric using natural dyes follows the same mechanism as that of synthetic dyes proposed to be taking place by partition mechanism. Therefore, the standard affinity can be calculated using Eq. 4:

$$\mathbf{-\Delta\mu = RT \ln Con_{Fab} / Con_{Dyebath}} \qquad \textbf{Eq-4}$$

where R is the gas constant, T is the absolute temperature (K), Con_{fab} and $C_{dyebath}$ are dye concentrations in the fabric and the dye bath, respectively. As mentioned above, the dyeability of tannic acid treated cotton is mainly attributed to ion–ion interactions between the negative carboxylate anions and the positive cationic groups present in the metal mordanted fabric. This dyeing mechanism is similar to that reported by Kamel et al [10]. Therefore, the standard affinity can be calculated using Eq – 4. The values of dyeing rate constant K, times of half dyeing time $t_{1/2}$, standard affinity $\Delta \mu$ and amount of final dye uptake by cotton fabric under sonication effect Con_{fab1} obtained were $k \times 100$ (min^{-1}) = 2.3, $-\Delta \mu$ (kJ/mol) = 2.98 kJ /mole, $t_{1/2}$ (min) = 30.0, and Con_{fab} (mg/g) = 280 and for conventionally dyed cotton fabric Con_{fab2} obtained were $k \times 100$ (min^{-1})= 0.77, $-\Delta \mu$ (kJ/mol) =1.42 kJ /mole, $t_{1/2}$ (min) = 90.0, and Con_{fab} (mg/g) = 170

The dye extract has less affinity for cotton fibers, their fastness was often enhanced by metal mordants, which form an insoluble complex with dye molecules, which include potassium aluminum sulfate (alum) and ferrous sulfate. Metal mordant when used in conjunction with sonication for the extract of *Malus sikkemnsis* was found to enhance not only the dyeability but also the fastness properties of the dyed fabrics as compared to the controlled sample. Enhancement of dye uptake was better than unmordanted fabrics. So we have demonstrated that the use of sonication and metal mordanting are having a synergistic effect on better dye uptake, dye adherence and eventually on good fastness properties of the dyed swatches of cotton, silk and wool.

The two stage dyeing of cotton fabric with metal mordant by the natural dye *Malus sikkemnsis*, show that this process showed very good results. The dye uptake different mordants was different. The effectiveness of metal mordant-malus in better dye uptake appears to be improve process causing improved fastness properties and thus it outweighs its benefit as observed during the course of this study.

Reuse of spent baths in the case of Sonicator bath

Dyeing processes contribute more than 60% of the total effluent loading causing high TSS and COD in a typical textile dye house effluent. We tried to overcome these difficulties by using sonicator. Therefore, the possibility of reusing spent dye bath in the case of sonicator was also explored. The results were very encouraging. The vibrations occurring in the sonicator bath do not let the dye aggregates to form in one place and are in dispersed form thus patchiness on swatches were not observed in this case. Testing of dye content in spent baths in the laboratory helped to substantiate the dyebath with desired amount of fresh extract to get the required concentration for re use.

4. Conclusion

Malus sikkemnsis has been found to have good agronomic potential as a dye plant. Metal mordant when used in conjunction with sonication for the extract of *Malus sikkemnsis* was found to enhance not only the dyeability but also the fastness properties of the dyed fabrics as compared to the controlled sample. Enhancement of dye uptake was better than unmordanted fabrics. Even the fastness properties in this case show good results. The two step process of pre- mordanting- dyeing developed was for the ease of industrial application.

Acknowledgement

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