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Ultrasound Assisted Extraction of Natural Dyes and Natural Mordants vis a vis Dyeing

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Abstract: Most of the natural dyes require mordants for their fixation on textile materials. Natural mordants are thus gaining importance in order to get complete-natural dyeing. In the present work, natural dyes and mordants were extracted using conventional and ultrasound methods and comparative studies were made. The natural mordants namely harda and tamarind seed coat and natural dyes like turmeric, henna were extracted using conventional and ultrasound approaches and various extracts obtained were described in terms of their optical densities. In order to verify the extraction efficiencies, wool fabrics were dyed with extracts of various combinations of mordants/dyes and dyed fabrics were evaluated for their colour strengths and fastness properties. The extent of colour extraction was higher in case of ultrasound assisted extraction as compared to that of conventional method. The fabrics dyed using extracts of ultrasound method showed higher colour values as compared to those dyed using extracts from conventional methods thus confirming ultrasound as more efficient method of extraction.

Keywords: Natural dyes, Harda, Tamarind seed coat, Ultrasound

Introduction

Human beings are naturally attracted to colours and it is considered as one of the desirable property of textile materials. Natural dyes have been an integral part of human life since time immemorial. Natural dyes are derived from naturally occurring sources such as plants, animals, insects and minerals without any chemical treatment and beautiful natural colours can be obtained on textiles using natural dyes. Synthetic dyes offer number of advantages over natural dyes which resulted in replacement of natural dyes by synthetic ones, however during the last few decades, natural dyes are gaining importance as they are obtained from renewable resources and they present no health hazards and some of them sometimes act as health care products. Natural dyes are generally applied using mordants like metallic salts, tannins, and oils. Tannins are high molecular weight compounds containing phenolic hydroxyl groups and they enable effective cross-links between proteins and other macromolecules. Tannins, being natural, are eco-friendly mordants and various sources of tannins are available which can be used as natural mordants [1-6].

Ultrasound is considered to be efficient and energy conservative source of energy and use of ultrasound can possibly make the extraction process as well as dyeing much faster. Application of ultrasound in natural dyeing has been reported in the literature [7-13].

Even though a lot of research has been carried out on extraction and application of natural dyes, the area of extraction using ultrasound is explored to a limited extent. Apart from this, extraction of natural mordants by ultrasound method is rarely reported. In the current study, the extraction of natural dyes and natural mordants by ultrasound assisted method has been attempted and compared with conventional aqueous boil method. The dyeing of wool fabric was studied using dye extracts by both methods and the comparative colour strengths and fastness properties are discussed.

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Experimental

Materials

Wool fabric was purchased from market, Turmeric, catechu, henna, harda and tamarind seed coat were purchased from market. All other chemicals used were of laboratory grade.

Methods

Preparation of Metal Mordant Solution

The 1 % stock solution of alum mordant was made by dissolving 1 g of alum in 100 m*l* of water and the solution was used for mordanting.

Extraction of Natural Mordants

Aqueous Extraction at Boil

The 0.5 %, 1 %, 2 % stock solutions were made by boiling 0.5 g, 1 g, 2 g of mordant powder in 100 m*l* water respectively at boil (100 ^{o}C) for different time parameters till we obtained the maximum possible extraction of the mordant. The extract was filtered, made to 100 m*l* using water and used for mordanting.

Ultrasound Assisted Extraction

The 0.5 %, 1 %, 2 % stock extracts were obtained by taking 0.5 g, 1 g, 2 g of mordant powder in 100 m*l* water respectively and allowing them to get extracted in the ultrasound sonicator at 35 KHz frequency for different time parameters till we obtained the saturation point of the mordant. The extract was then filtered, made to 100 m*l* using water and used for mordanting.

Extraction of Dyes

Aqueous Extraction at Boil

The 0.5 %, 1 %, 2 % stock solutions were made by boiling 0.5 g, 1 g, 2 g of dye powder in 100 m*l* water respectively at boil (100 °C) for different time parameters till we obtained the maximum possible extraction of the dye. The extract was filtered, made to 100 m*l* using water and used for dyeing.

Ultrasound Assisted Extraction

The 0.5 %, 1 %, 2 % stock extracts were obtained by taking 0.5 g, 1 g, 2 g of dye powder in 100 m*l* water respectively and allowing them to get extracted in the ultrasound sonicator at 35 KHz frequency for different time parameters till we obtained the saturation point of the dye. The extract was then filtered, made to 100 m*l* using water and used for mordanting.

Determination of Optical Density

The filtered mordant and dye extracts were then evaluated for maximum absorption wavelength using a double beam spectrophotometer and optical density using a single beam spectrophotometer (Shimadzu, Japan). Suitable dilutions were made in order to measure the optical density accurately.

Mordanting and Dyeing of Wool Fabrics

The mordanting of wool fabric was carried out in Rota dyer (Rota Dyer machine, Rossari® Labtech, Mumbai) keeping the liquor to material ratio of 30:1. The fabrics were introduced into the mordant solution at room temperature and the temperature was raised to 90 °C at the rate of 2.5 °C/min. The mordanting was continued at this temperature for 60 min. After mordanting the fabric was squeezed and dyed. The mordanted fabrics were introduced in Rota dyer and dyeing was continued at 90 °C for 60 min. After dyeing the fabrics were squeezed and washed with cold water.

Colour Value by Reflectance Method

The dyed samples were evaluated for the depth of colour by reflectance method using 10 degree observer. The absorbance of the dyed samples was measured on Rayscan Spectrascan 5100+ equipped with reflectance accessories. The *K/S* values were determined using expression;

$$K/S = \frac{(1-R)^2}{2R}$$

where, R is the reflectance at complete opacity, K is the Absorption coefficient, S is the Scattering coefficient.

Dyed fabrics were simultaneously evaluated in terms of CIELAB colour space (L^*, a^* and b^*) values using the Rayscan Spectrascan 5100+. In general, the higher the *K/S* value, the higher the depth of the colour on the fabric. L^* corresponds to the brightness, a^* to the red-green coordinate and b^* to the yellow-blue coordinate. As a whole, a combination of all these parameters enables one to understand the tonal variations.

Fastness Properties

Washing Fastness

Evaluation of color fastness to washing was carried out using ISO II methods [14]. A solution containing 5 g/*l* soap solution was used as the washing liquor. The samples were treated for 45 min at 50 °C using liquor to material ratio of 50:1 in rota machine. After rinsing and drying, the change in colour of the sample and staining on the undyed samples were evaluated on the respective standard scales.

Light Fastness

Dyed fabric was tested for colourfastness to light according to ISO 105/B02 [15]. The light fastness was determined using artificial illumination with Xenon arc light source (Q-Sun Xenon Testing Chamber). The samples were compared with the standard scale of blue wool reading.

Results and Discussion

In order to study the comparative extraction efficiency of ultrasound with conventional extraction method (SABM), the dyes and mordants were extracted in aqueous media and the optical densities of the extracts were measured and summarized in Table 1.

The time period of the extraction was varied in order to study the maximum possible extraction of dye and thus to study the relative efficiencies of two methods. Results in Table 1 indicate the increase in optical density of extract with increase in time irrespective of the method of extraction. In case of turmeric extraction using SABM, the optical density increased with extraction time from 30 to 90 min. The extracts using ultrasound method showed higher optical densities in shorter time. In other words, if the extract of particular optical density is required ultrasound method can provide in much shorter time. The relative increase in optical density and the maximum optical density seems to be dependent on the concentration of dye and the time of extraction. However in general, the optical density of the extract obtained using SABM at boil for 60 min can be obtained in 5-15 min using ultrasound method. In case of henna, similar trends are valid but the optical density of extract obtained using SABM at boil for 60 min can be obtained in 5-10 min using ultrasound.

As far as ultrasound extraction is concerned, the time of extraction was varied the in order to get optimum extraction (leveling-off). The optical densities were found to be increasing with the increase in time of extraction reaching leveling-off after certain times (which were marked bold in Table 1). The trend was valid for all the dyes and mordants in the study; however the individual leveling off time periods vary with individual dye and mordant. Another thing to be noted is the effect of time parameter on individual dye and mordant was distinct in each case i.e. variation in colour yield with time is quite different.

The ultrasound extraction method showed higher optical densities, indicating higher extent of extraction of dyes and mordants using ultrasound, in case of all the natural mordants and dyes studied. The relative increase of optical

Table 1. Optical densities of different dye/mordant extracts by different extraction methods

Dye/Mordant	Extraction method	Parameters	Optical density (Dilution factor 100)		
			0.5 % extract	1.0 % extract	2.0 % extract
Turmeric	Simple aqueous boil method	100 °C, 30 min	0.0514	0.157	0.286
		100 °C, 60 min	**0.0627**	**0.159**	**0.284**
		100 °C, 90 min	0.0625	0.159	-
	Ultrasound extraction method	35 KHz, 5 min	0.0618	0.115	0.146
		35 KHz, 10 min	0.0784	0.121	0.184
		35 KHz, 15 min	0.0873	0.185	0.279
		35 KHz, 20 min	**0.097**	**0.248**	**0.446**
		35 KHz, 25 min	0.0975	0.247	0.444
Henna	Simple aqueous boil method	100 °C, 30 min	**0.145**	**0.203**	**0.334**
		100 °C, 60 min	0.147	0.204	0.335
		100 °C, 90 min	0.146	0.201	0.332
	Ultrasound extraction method	35 KHz, 5 min	0.104	0.213	0.487
		35 KHz, 10 min	0.163	0.263	0.508
		35 KHz, 15 min	0.194	0.282	0.523
		35 KHz, 20 min	**0.231**	**0.28**	**0.667**
		35 KHz, 25 min	0.235	-	0.544
Harda	Simple aqueous boil method	100 °C, 30 min	0.0954	0.2220	0.4120
		100 °C, 60 min	**0.1080**	**0.2250**	**0.4110**
		100 °C, 90 min	0.1050	0.2240	0.3460
	Ultrasound extraction method	35 KHz, 5 min	0.0686	0.0901	0.2350
		35 KHz, 10 min	0.0741	0.2260	0.3390
		35 KHz, 15 min	**0.1530**	**0.2660**	**0.4880**
		35 KHz, 20 min	0.1520	0.2650	0.3580
Tamarind seed coat	Simple aqueous boil method	100 °C, 30 min	0.0087	0.0198	0.0389
		100 °C, 60 min	0.0175	0.0276	0.0597
		100 °C, 90 min	**0.0245**	**0.0321**	**0.0695**
	Ultrasound extraction method	35 KHz, 5 min	0.0108	0.0176	0.0661
		35 KHz, 10 min	0.0186	0.0349	0.0922
		35 KHz, 15 min	0.0201	0.0607	0.1250
		35 KHz, 20 min	**0.0365**	**0.0605**	**0.1680**

densities is different in all the dyes and mordant and also for the different concentration of dyes/mordants used for extraction.

In case of ultrasound method extraction leveling off occurred much faster as compared to conventional aqueous extraction and the optical density values were significantly higher than those obtained using conventional method. Hence ultrasound assisted extraction can be claimed to be advantageous method for faster and efficient extraction of natural dye or mordant.

In case of natural mordant, the trends observed were similar to that obtained in case of natural dyes extend of variation however is different. In case of both the mordants, the ultrasound method showed higher optical density in shorter time indicating better and efficient extraction than SABM method. The optical density values were distinctly lower in case of Tamarind seed coat as compared to that of ultrasound irrespective of the method of extraction.

In the next set of experiments, in order to confirm the extraction results by dyeing method, wool fabric was dyed with the extracts of natural dyes using alum as a standard mordant and the results are summarized in Table 2.

In general at the constant dye concentrations, colour strength (*K/S*) values increased with the increasing concentration of alum. However since only two concentrations of alum were used in the study i.e. 5 % and 10 %, it is quite difficult to comment on leveling-off concentration (optimum) of the alum to get maximum colour values. Since the objective of the study was to compare extraction methods of natural dyes and mordants, the optimum concentration study seems to be

Table 2. Effect of extraction methods on the colour values of wool using alum as standard mordant

Dye	Extraction method	Alum (%)	Dye (%)	Colour values	CIELAB Co-ordinates		
				K/S	L^*	a^*	b^*
Turmeric	SABM (1 %, 60 min)	5	2	0.2255	28.928	10.637	46.743
		5	5	0.2444	26.666	13.814	43.467
		10	2	0.2492	29.018	11.848	47.086
		10	5	0.2574	27.289	13.75	44.439
	Ultrasound (1 %, 20 min)	5	2	0.2423	28.918	10.671	46.507
		5	5	0.296	26.947	13.587	43.589
		10	2	0.2704	28.843	11.204	46.248
		10	5	0.3018	26.795	14.068	43.282
Henna	SABM (1 %, 30 min)	5	2	0.3969	29.591	8.618	24.985
		5	5	0.7573	27.177	11.476	24.73
		10	2	0.5829	27.859	10.567	24.564
		10	5	0.7751	27.018	11.429	24.849
	Ultrasound (1 %, 20 min)	5	2	0.7988	27.275	10.706	24.539
		5	5	0.8847	27.141	11.022	24.17
		10	2	0.818	27.239	10.884	23.715
		10	5	1.0725	26.956	11.571	23.488

Table 3. Effect of extraction method of mordant on the color strength of wool using turmeric as a dye

Mordant & dye	Mordant extraction method	Mordant (%)	Dye (%)	Color values	CIELAB Co-ordinates		
				K/S	L^*	a^*	b^*
Harda & turmeric	SABM (1 %, 60 min)	5	10	0.7015	28.848	6.623	41.513
		5	20	0.7365	28.658	7.033	41.099
		10	10	0.9316	29.793	4.014	37.428
		10	20	0.934	30.422	2.573	31.068
	Ultrasound (1 %, 15 min)	5	10	0.7937	29.018	6.417	40.733
		5	20	0.928	30.042	3.685	37.261
		10	10	0.9439	28.985	5.803	39.573
		10	20	1.2197	30.074	3.332	34.097
Tamarind seed coat & turmeric	SABM (1 %, 90 min)	5	10	0.3738	27.848	10.625	42.966
		5	20	0.4296	27.433	10.184	41.626
		10	10	0.4604	29.306	6.996	40.809
		10	20	0.462	29.553	5.446	37.304
	Ultrasound (1 %, 20 min)	5	10	0.4538	27.677	10.309	41.858
		5	20	0.4651	27.333	9.649	40.802
		10	10	0.4982	28.938	6.979	39.479
		10	20	0.5397	28.695	6.699	38.479

less significant. In general, at the constant mordant concentration, the *K/S* values were found to be improving with increase in dye concentration from 10 % to 20 %. The various shades from light to deep can be obtained using the varying concentration of mordant and natural dyes. The color value in the case of natural dyes is a combined contribution of the effect of mordant and the dye. Hence the *K/S* was improved with mordant and dye concentration till the saturation point of the fibre.

The *K/S* values obtained in case of dyeing with the extracts at the leveling point parameters were higher in case of extracts obtained by ultrasound method as compared to

Table 4. Fastness properties of dyed wool using different mordants

Dye	Extraction method*	Mordant	Mordant conc. (%)	Dye conc. (%)	Washing fastness		Light fastness
					Change in colour	Staining	
Turmeric	SABM	Alum	10	20	3	3	3
	Ultrasound		10	20	3	3	3
	SABM	Harda	10	20	3	3	3
	Ultrasound		10	20	3	3	3
	SABM	Tamarind seed coat	10	20	3	3	3
	Ultrasound		10	20	3	3	3
Henna	SABM	Alum	10	20	4-5	4-5	6
	Ultrasound		10	20	4-5	4-5	7
	SABM	Harda	10	20	5	4-5	6
	Ultrasound		10	20	4-5	4-5	6
	SABM	Tamarind seed coat	10	20	5	4-5	6
	Ultrasound		10	20	5	4-5	6

*Parameters of extraction are mentioned in Table 2 and 3.

the conventional method. This trend was quite obvious as the higher optical densities of the extracts were obtained by conventional aqueous extraction method.

In order to confirm the extraction results in case of natural mordants, the wool fabrics were dyed using turmeric as a dye varying harda and tamarind seed coat by different extraction methods and the results are summarized in Table 3.

In general, the harda mordanted samples showed higher colour values as compared to that of tamarind seed coat samples indicating higher extraction of natural mordant in harda than TSC. This was quite obvious trend as the optical densities were higher in case of harda extracts compared to tamarind seed coat extracts. The wool fabrics dyed using tamarind seed coat mordant showed higher values of a^* and b^* indicating the more yellow-red tones compared to harda mordanted dyed wool fabrics.

The fastness properties of the representative samples were evaluated and are presented in Table 4. The wash and light fastness was of the grade "very good" to "excellent" for the dyes in combination with any mordant. The fastness properties were improved with increasing mordant concentrations. The wash and light fastness properties for turmeric were found to be inferior compared to that for other natural dyes.

Light fastness was found to be improving with higher *K/S* values, which in turn was dependant on higher mordant and/or dye concentration. Light fastness is dependent on the depth of shade and is generally better for darker shades than lighter ones, for the same dye and fabric combination. The darker shades were obtained with higher mordant and dye concentrations, hence the better fastness. The effect of extraction method on fastness properties was not so distinct; however the fastness properties obtained in case of wool dyed using ultrasound extracts were slightly better which seems to be dependent on colour values rather than extraction methods.

Conclusion

The use of ultrasound was found to be quite faster and efficient method of extraction of colourant from various natural sources. The superior efficiency of ultrasound extraction was confirmed using dyeing study. The role of extraction method on fastness properties was not confirmed but those values were found to be rather dependent on colour values. Therefore, the present study clearly offers efficient extraction methodology for natural dye and mordants using ultrasound.

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