Acacia Arabica-A Source Of Natural Dye For Handmade Paper Making

Saakshy[1], Madhu Agarwal [2], Ajendra [2] ,R K Jain [1], A.K Sharma [1]

[1]Kumarappa National Handmade Paper Institute, Jaipur 302019, Rajasthan, India
[2]Malviya National Institute of Technology, Jaipur 302017, Rajasthan, India

Abstract

The extracted dye from babool bark has been explored for its application in handmade paper industry. The handmade paper sector is known for its aesthetic sense and eco-friendliness. The application of natural dyes may offer the great potential for producing the colored handmade paper to retain its eco-friendly credentials by replacing the azo dyes in use extensively by handmade paper industry. The studies have been conducted on aqueous, organic solvent, microwave assisted extraction for extraction of natural dye from babool bark. The extracted natural dye was characterized for the presence of lignin, tannin, reducing sugar content etc. The strength properties of paper dyed with extracted natural dye from babool bark has been compared with direct dyed paper and it has been found that natural dyed paper has better strength properties in comparison to direct dyed paper. The studies on the light fastness of handmade paper, cotton fibre, wool fibre and silk fibre dyed with natural dye and its comparison with direct dye has also been covered.

Keywords: *babool, extraction, strength properties, mordant, light fastness*

"1. Introduction"

The history of handmade paper making in Indian goes as far back to the 3rd century BC. The handmade paper is the traditional method of making paper which even after so many years is one of potential export oriented sectors of India. The handmade paper utilizes non woody raw material and eco-friendly processes technologies. The handmade paper has niche over mill made paper for its aesthetics and eco-friendly characteristics.[1] Traditionally, the direct dyes are used for producing colored handmade paper due to its easy solubility and readily attachment to the fibres. Moreover, direct dyes have good light-fastness which made direct dyes a better choice for handmade paper manufacturers. Most of the direct dyes available in the market possess azo group which on reduction releases carcinogenic or harmful amines.

The present paper highlights the application of natural dyes in handmade paper industry which may help the manufacturers to retain the eco-friendly credentials of the product, thereby, helping to boost export of handmade paper in global market.

BABOOL, *Acacia nilotica* also known as "monkeypod" is an environment friendly hard wood that is grown all over the world and known for its beautiful grain and contrasting walnut brown to light tan colors. In northern India, the bark of *A. nilotica* forms the most important tannin yielding raw material and is very good for tanning heavier leathers. It is a common tree found in forest, wastelands, and cultivated fields throughout India. It is a large tree, up to 14 meters height, with thorns on its branches having darkish bark and yellow flowers in spherical heads. Babool tree is indigenous to Sind in Pakistan and occurs widely in India and tropical Africa. The tree yields a gum, known as babul gum.

Figure 1 Babool tree and bark

The bark of babul tree contains tannin and gallic acid and therefore, tree is planted for its bark.[2] It has great medicinal value with antioxidant activity.[3] Acacia Arabica is considered as astringent, demulcent, aphrodisiac, antimicrobial in Indian traditional medicine system.[4] An average 15-year-old plantation yields about 12.5 tons of bark. About 22,000 tons of babool bark are produced annually valued at Rs 55 million.[5]

2. Materials and Methods

2.1 Raw material preparation-Babool Bark

The babool bark was procured as waste from carpentry shop of Jaipur. The bark was initially washed with water to clean the bark of presence of any dirt particle and then dried in an air oven at 60^0 C for 24 hours. The bark was converted in to dust form with the help of laboratory mechanical crusher to give dust screened through 1 mm screen to get dust particle size of 1000 µm.

2.2 Pulp from Cotton rags

Cotton rags were beaten in laboratory valley beater to desired freeness level of 300 ml. The beaten pulp was then squeezed and allowed to dry in an air oven at 60^0 C. The dried pulp was then stored in a polythene bag and kept in freeze for further use.

2.3 Procurement of Dyes and Mordants

The commercial natural dye of babool bark was procured from Sir Naturals, Kanpur (ISO 9001 company). The direct red dye of Clariant, Mumbai was used for the comparison studies. Alum (Aluminium sulphate) was used as mordant for application of natural dye.

2.4 Apparatus

The double beam UV-VIS Spectrophotometer, Electronics Corporation of India Limited (ECIL) Hyderabad was employed for color and maxima determination of dye solutions. The laboratory mechanical crusher, UEC Saharanpur was used to convert bark in to dust form. The soxhlet apparatus was used to extract dye from the dust with water and alcohol.

2.5 Spectral analysis of commercial dye

The standard stock solution of 1 g/L was prepared with commercial dye of babool bark. The 1 g of dust of babool bark was boiled with 1L of water and filtered through fritted glass support of porosity (40-60 µm) and the accept solution was used for spectrophotometric studies . The spectral analysis of commercial dye showed two absorption maxima at 247.0 & 404.5 nm.

2.6 Extraction of natural dyes

The aqueous extraction was done by reflux of babool dust with distill water with the help of soxhlet apparatus at 90-95^0 C for 3 hours. The material to liquor ratio was kept 1:80 in boiling flask of 500 ml capacity. The extract was collected by filtering the solution through fritted glass assembly. The residual powder was reflux number of times till color in extracted solution was negligible. Then, the filtrate was dried on hot plate on petri dish, cooled and weighed. The alcoholic extraction of babool bark was done by taking babool dust along with different solvents having different polarities including isopropyl alcohol, diethyl ether, hexane, ethanol, benzene, acetone, butanol, and methanol added in the ratio of 1:1 with distill water. The reflux was carried out in water bath at 40-95 ^{0} C for 3 hours. The reflux was repeated till no trace of color in solvent. The de-solventization was conducted by distillation of extract on water bath and the traces of solvent residues were removed by applying vacuum for 30 minutes continuing heating on water bath. The residual powder was refluxed number of times till color in extracted solution was negligible.

2.7 Analysis of extracted color

The extracted color mass was evaluated with the help of Double beam UV-VIS Spectrophotometer by measuring absorbance of extracted solution at its maxima.

2.8 Mordant

Mordanting was done with alum (Aluminium sulfate). Firstly, the solution of natural dye as per requirement was added to the beaten cotton pulp and after 5 minutes of stirring of pulp slurry with magnetic stirrer at 250 rpm, alum has been added as mordant to assist fixation of dye on the fibres as well as to maintain the pH of the pulp between 6.5 to 7.5.

2.9 Analysis of physical properties of paper

The tensile strength, tear strength, bursting strength and folding endurance was evaluated as per standard testing methods. One of the most commonly used color systems in paper industry are Hunter L, a, b values. CIE tristimulus functions X (red), Y (green) and Z (blue) were developed. Effective wavelengths for the CIE functions based on illuminant C, 2^0 observer are: X (595nm), Y (557nm) and Z (445nm). The hunter co-ordinates (L, a and b) were calculated from the tristimulus values x, y, z and were converted to CIE Lab co-ordinates. **L** is a measure of lightness and varies from 100 for a perfect white to 0 for absolute black. **+a** indicates redness and **–a** indicates greenness. **+b** indicates yellowness and **–b** indicates blueness.

"3. Results and Discussion"

3.1 Proximate analysis of babool bark

The proximate analysis of dust of babool bark was done as per standard testing method and the results are depicted as Table 1.

Table 1 Proximate analysis of babool bark

Parameters	Result	Testing Methods
pH	7.42	APHA 4500 H Electrometric method
Moisture,%	6.15	T 671 cm-85
Ash,%	11.06	T 15 wd-80
Cold water solubility,%	11.49	T 207
Hot water solubility,%	20.52	T 207
Alcohol Benzene solubility,%	35.56	T 204
Acid insoluble Lignin,%	23.5	T 222
Soluble Lignin,%	2.1	Morrison method
Holocellulose, %	60.5	T 249
Reducing sugars,%	2.93	Miller method
Tannin,%	11.96	Vanillin-Hcl method
Protein,%	3.38	Lowry method

The proximate analysis showed high amount of lignin and tannin content in babool bark. The results are well in agreement with previous studies.[6]

3.2 Aqueous extraction

The concentrated color mass was obtained from babool bark after extracting with water at 90-95^{0}C. The residue after reflux was dried in oven and weighed to determine the insoluble colored mass.

3.2.1 Number of reflux obtaining maximum extracted dye

The dust of babool bark was refluxed with distill water maintaining material to liquor ratio of 80:1 with the help of soxhlet apparatus at 90-95^{0}C for 3 hours. The extract was collected by filtering the solution through fritted glass assembly. The residual powder was again refluxed with distill water at 90-95^{0}C for 3 hours. The same procedure was repeated till the color in the residue was negligible. The filtrate was dried on hot plate on petri dish. The analysis of colored mass after refluxing of residual dust is tabulated as Table 2 depicting yield of colored mass at each reflux.

Table 2 Yield of colored mass at different reflux number

Reflux number	% Concentrated mass extracted
1	20.25
2	5.45
3	1.4
4	0.65
5	0.25
6	0.09
7	0.0
Total	28.09

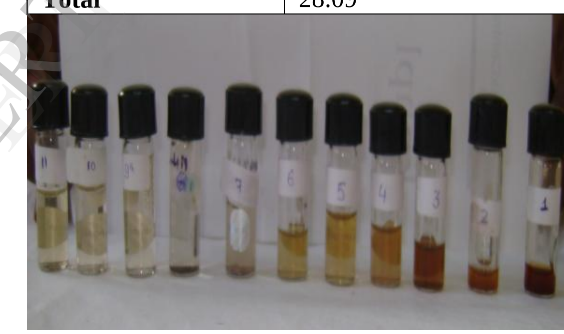

Figure 2 Colored solutions from 1st to 11th reflux(R to L)

The Table 2 and Figure 2 showed that colored mass has been extracted completely from babool bark after two times extraction and there is no significant colored mass remaining after second extraction.

3.2.2 Effect of soaking prior reflux stage

The effect of soaking of babool dust for 24 hours prior to reflux is depicted as Table 3.

Table 3 Yield of colored mass after soaking

Reflux time, hrs	Yield without soaking,%	Yield after soaking,%	Inc. in yield, %
0	0	8.52	8.52
2	18.52	25.14	6.62

4	21.63	27.26	5.63
6	22.03	28.84	6.81

The soaking stage prior to reflux stage increased the yield of colored mass by almost 6%.

3.2.3 Microwave assisted extraction techniques

The effect of microwave technology on extraction of colored mass from babool bark and the comparison with reflux method is shown as Table 4.

Table 4 Comparison of conventional reflux with microwave assisted method

Extraction time with microwave treatment, minutes	Yield, %	Extraction time with reflux method, hours	Yield,%
4	10.45	2	18.52
8	15.81	4	21.63
12	18.97	6	22.03
16	21.55	8	23.83
20	22.00	10	24.02

It has been observed that microwave is an effective method for extraction of colored mass from babool bark in fraction of time in comparison to reflux method. The same yield of extracted mass is achieved at 20 minutes of microwave treatment in comparison of 6 hours of reflux method. The studies on microwave technology was also applied to natural ingredient extraction from Amazonian fruits and butterfly pea.[7,8] However, the costing of the process has to be studied. The electromagnetic waves in microwave oven with wavelengths ranging from as long as one meter to as short as one millimeter or with frequencies ranging between 300 MHz and 300 GHz assisted in faster and efficient yield of colored mass.

3.3 Organic Solvent extraction

The yield of colored mass with different organic solvents and water is given as Table 5 and the maxima studied with alcohols and water is shown as Table 6.

Table 5 Yield of colored mass with different organic solvents

Name of chemical	Yield %	Polarity Index
Benzene	6.22	2.7
Hexane	7.54	0.1
Diethyl ether	8.02	2.8
Toluene	9.65	2.4
Chloroform	10.76	4.1
Ethyl acetate	14.00	4.4
Acetone	14.44	5.1
Ethanol	23.98	5.2
Butanol	19.43	4.0
Isopropyl alcohol	28.60	3.9
Methanol	33.12	5.1
Water	20.66	10.2

Table 6

Maxima with alcohols and water

Solvents	λ_{max}
Water	406,252
Ethyl acetate	406.5, 251.5
Ethanol	404.5,247.5
Methanol	405.5,253
Isopropyl alcohol	405.5,253.5
Diethyl ether	391.5

The high extraction yield of babool bark with organic polar solvents in comparison to non polar or less polar solvents showed that babool bark contains high amount of organic polar component. In case of babool dye also, the best solvent proved to be methanol followed by water, ethanol, isopropyl alcohol, butanol, acetone, ethyl acetate, chloroform , toluene, diethyl ether, hexane and benzene. The study conducted on extraction of natural dyes from babool bark with solution of (methanol: water = 1:1) showed better yield in comparison to extraction with water alone. The yield of colored mass extracted with methanol at different reflux is given as Table 7.

Table 7

Yield of extracted colored mass with alcohol

Reflux number	Yield, %
1	34.0
2	9.84
3	3.4
4	3.24
5	1.96
6	0.44
Total	52.88

It has been observed that most of the colored mass was achieved in two reflux in alcoholic extraction. The results are well in agreement with the study conducted by Bushra et al. 2009. The low extraction yield of babool with ether comply with the studies conducted by Angelini et al.1997 as ether was able to dissolve only free aglycones in Rubia tinctorum while he achieved better yield with ethanol and water. The ethanol was found to be the best solvent by him for extraction of alizarin followed by water, ethanol, acetone and ether. [9-11]

3.4 Comparative spectral analysis of commercial, extracted colored mass with water and methanol

The absorption spectra of 1 g/L solution of commercial dye, extracted dye with water, and extracted dye with organic solvents was recorded with the help of double beam UV-VIS spectrophotometer in the wavelength range of 200-700 nm. The maximum wavelength range from 404.5 to 405.5 nm and 252 to 254.5 nm for all the solution of dyes.

3.5 Characterization of the commercial natural dye of babool bark and extracted colored mass from babool bark

The commercial available dye of babool bark along with extracted dye with water and methanol is characterized for pH, moisture content, ash content, solubility of dye at room temperature, solubility of dye in hot water , chemical oxygen demand and λ_{max} as shown in Table 8.

Table 8.Comparison of characteristics of dye from bark of babool

Parameters	**Commercially available dye of babool**	**Extracted dye with water**	**Extracted dye with methanol**
pH of 1% solution	7.5	6.28	7.23
Moisture, %	12.29	7.69	10.64
Ash,%	27.0	24.79	30.0
Insoluble matter at room temperature,%	68.0	64.65	46.21
Insoluble matter after boiling for one hour,%	61.0	58.35	40.0
COD, ppm (of 1g/L solution)	304	289	325
λ_{max} ,nm (of 1 g/L solution)	404.5	383.0	405.5
Soluble Lignin,%	3.30	2.86	4.12
Tannin, %	19.45	11.48	23.45
Reducing sugars,%	18.46	30.63	10.83

The characterization of dye showed highest COD for dye extracted with methanol. This may be due to presence of other alcohol soluble components which have been extracted with methanol. The methanol extracted dye showed better solubility due to more purified form of colored mass.

3.6 Retention of extracted dye and commercial dye before and after addition of mordant

The 5% dosage of dye is added to the cotton pulp and the slurry was stirred for 5 minutes with magnetic stirrer at 250 rpm. 0.25% (w/w) alum has been added as a mordant to the cotton pulp. The pH of the pulp was determined and then the remaining liquor was taken after filtration of the pulp through Bucchner funnel. The remaining dye in solution was determined with spectrophotometer to study retention of dye in the pulp. The spectra was obtained of spent liquor with and without addition of mordant as Figure 3.

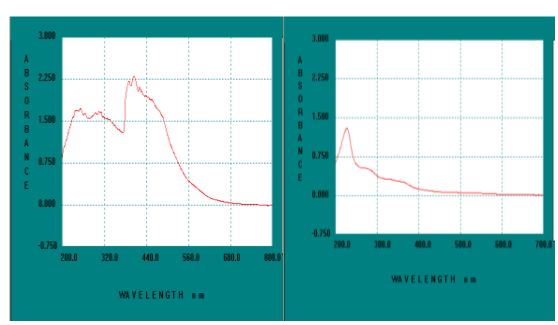

Figure 3 Spectra of spent liquor before and after addition of mordant

The results of retention with and without addition of mordant are given as Table 9 & 10.

Table 9 Retention of natural dye before addition of mordant

Natural Dye	Dosage of dye,%	Retention,%	pH
Extracted with water	5	37.64	6.86
Extracted with methanol	5	40.55	7.12
Commercial	5	35.63	7.33

Table 10 Retention of natural dye after addition of mordant

Natural dye	Dosage of alum	Retention,%	pH
Extracted with water	0.25%	69.69	6.51
Extracted with ethanol	0.25%	77.52	7.25
Commercial dye	0.25%	67.21	7.18

% Retention=(Initial absorbance-Final absorbance)/Initial absorbance X 100

The retention of natural dyes was found to be somewhat poor without mordant and has almost doubled after addition of alum as mordant. From Figure 3 also, it has been concluded that most of the natural dye has been retained on pulp and only slightly remains in spent liquor. However, best retention has been observed in case of methanol extract dye. The pH of pulp was maintained between 6.5 to 7.5 to keep paper within neutral range. The various mordants viz. tannic acid, copper sulfate, stannous chloride, ferrous sulfate & aluminium sulfate was used in previous studies.[12]

3.7 Effect on strength properties of extracted dye and commercial available natural dye

The laboratory sheets of cotton pulp were made after addition of 5% dosage of dye and 0.25% alum as mordant and then the laboratory sheets were kept for conditioning at 65% relative humidity and 27^0C for 4 hours as per standard method IS 1060 Part I 1966. The strength properties of the paper made out of pulp of cotton rags without addition of dye (control), commercial dye of babool bark, extracted dye with water, extracted dye with alcohol were evaluated and the results are given as Table 11.

Table 11(a) Effect of dye on strength

Table 11(b) Effect of dye on strength

Parameters	Control	Commercial dye	Extracted dye with water
Tensile Index, Nm/g	22.46	27.12	28.07
Tear Index,mN. m^2/g	25.96	26.00	25.86
Burst Index,Kpa . m^2/g	2.22	2.39	2.40
Double Fold, No.	625	710	750

The strength properties of paper showed increase in strength properties when dyed with natural dye.

Parameters	Extracted dye with methanol: water (1:1)	Direct Red
Tensile Index, Nm/g	30.85	21.45
Tear Index,mN .m^2/g	29.14	24.52
Burst Index,Kp a. m^2/g	2.55	2.10
Double Fold, No.	851	600

However, it has been observed that the purified dye with methanol showed best results in terms of strength properties of paper. The application of natural dye extracted from bark of Odina wodier L. was studied for garments industry in previous studies.[13]

3.8 Effect on Hunter values

The hunter co-ordinates L, a and b of the samples dyed and mordanted with different dosage of natural dye of 1% concentration and 0.25% alum respectively and direct dye were calculated from the tristimulus values x, y ,z and depicted as Table 12.

Table 12 Hunter values of handmade paper dyed with natural dye and direct dye

Dye	Dosage of dye,%	L	a	b
Extracted dye with alcohol	1	80.32	1.56	4.57
	2	72.73	1.02	8.79
	3	61.17	0.97	12.67
Direct dye	0.05	85.50	5.16	16.23
	0.10	81.20	6.72	22.94
	0.30	69.40	7.08	33.06
	0.5	68.80	8.37	31.72
	1.0	59.20	11.23	34.46

It was observed that the cotton pulp dyed with extract of babool bark showed 'L' value range from 74 to 61 , 'a' ranging from 4.97 to 8.56 and 'b' ranging from 12.5 to 22.6. D De Santis & M Moresi, 2007 determined 'L', 'a' and 'b' values of cotton and wool dyed specimen with alizarin extract. According to his study, the L value with cotton specimen range from 55.5 to 52.9, a range from 18.3 to 21.1 and b range from 7.6 to 8.5.[14,15]

3.9 Light Fastness properties of handmade paper

The light fastness properties of handmade paper dyed with extracted natural dye with methanol and water was compared with direct dye as given in Table 13.

Table 13 Light fastness of cotton cloth, wool fibre, silk fibre and handmade paper

Dye	Light fatness scale of cotton cloth	Light fastness scale of wool fibre	Light fastness scale of silk fibre	Light fastness scale of handmade paper
Extracted with water	4.0	4.0	4.0	4.0
Extracted with alcohol	4.0	4.0	4.0	4.0
Direct dye	2-3	2-3	2-3	2-3

Padfield and Landi et al., 1966 found that yellow dyes(old fustic, Persian berries) showed poor light fastness(1-2), cochineal with tin as mordant and alizarin with alum and tin as mordant showed better light fastness (3-4). As per his studies, indigo showed better light fastness (3-4) and (5-6) as per mordant used. Logwood black showed light fastness (6-7). Indigotin is a symmetrical dye molecule and therefore has superior light fastness according to D. Cristea and G Vilarem, 2006.[16-20]

3.10 Stability of dye

The degradation of the extracted dye at a particular time was determined by calculating the change in its concentration from its original concentration. The degradation of dye at different temperature is given in Table 14.

Table 14 Comparison of degradation of dye from babool bark

Dye	Degradation at 25^0C ,%	Degradation at 35^0C, %	Degradation at 45^0C ,%
Commercial	1.77	2.94	5.28
Extracted with water	2.14	3.65	6.87
Extracted with alcohol	1.12	2.23	4.65

It has been observed that increase in temperature accelerated the reaction rate and thus the degradation was more at high temperature. The results showed rapid growth of fungus in commercial dye while least growth of fungus in extracted dye with methanol: water.

3.11 Kinetics of dye degradation

The kinetics of degradation of commercial dye, extracted dye with water and extracted dye with water: methanol at different storage time is given as Table 15, 16 & 17. The commercial dye, extracted dye with water and extracted dye with methanol: water has been studied for its degradation properties.

Table 15 Degradation of commercial dye at room temperature

Days, t	Co, gL^{-1}	C, gL^{-1}	$1/C-1/C_o$,L g^{-1}
0	1	1	0
1		0.99	0.04
2		0.95	0.08
3		0.91	0.15
4		0.85	0.20
5		0.81	0.25
6		0.76	0.31
7		0.71	0.34

Table 16 Degradation of extracted dye with water at room temperature

Days, t	Co, gL^{-1}	C, gL^{-1}	$1/C-1/C_0$, Lg^{-1}
0	1	1	0
1		0.97	0.06
2		0.92	0.10
3		0.88	0.17
4		0.81	0.22
5		0.77	0.29
6		0.71	0.35
7		0.69	0.40

Table 17 Degradation of extracted dye with water: methanol at room temperature

Days, t	Co, gL^{-1}	C, gL^{-1}	$1/C-1/C_0$, Lg^{-1}
0	1	1	0
1		1	0.03
2		0.98	0.06
3		0.94	0.09
4		0.90	0.14
5		0.86	0.18
6		0.83	0.21
7		0.79	0.26

The second order kinetics was assumed for degradation as suggested by the equation.

$$-dC/dt = k_2 C^2 \quad \text{……….(1)}$$

Where C is concentration of dye at time t,
k_2 is the overall second order reaction rate constant.

On integration, the equation 1 yields

$$1/C - 1/C_0 = k_2 t \quad \text{…..…(2)}$$

Where, C_0 is initial concentration of dye,

If it is second order reaction in nature, a plot of 1/C - $1/C_0$ should be straight line.

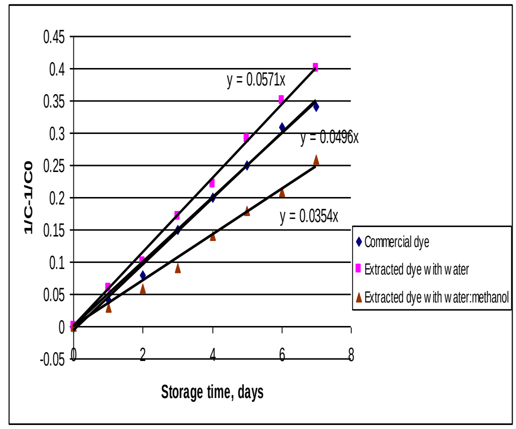

Figure 4 Plot of $1/C-1/C_0$ Vs Storage period

As can be seen from Figure 4 , the plot of $1/C-1/C_0$ is almost linear and confirms second order reaction. The plot showed that experimental data well fitted with second order kinetics. The overall second order reaction rate constant was determined from the slope of the curve. The k_2 value of babool bark for commercial dye, extracted dye with water and extracted dye with water: methanol is given in Table 18.

Table 18 k_2 values of dye degradation of dye

Dye	k_2, L/g/D
Commercial dye	4.96×10^{-2}
Extracted dye with water	5.71×10^{-2}
Extracted dye with methanol: water	3.54×10^{-2}

The results well correlate with the results achieved by K Balaswamy k_2 (second order reaction rate constant) value of 1.75×10^{-2} of bixin content in annatto at diffused day light.[21]

"4. Conclusions"

The study conducted on extraction of natural dyes from babool bark with solution of (methanol: water :: 1:1) showed better yield in comparison to extraction with water alone. However, in both cases the reflux of three hours for two times has been optimized as further reflux showed no remarkable extraction of dye. The characterization of dye showed better solubility of methanol extracted dye due to more purified form of colored mass. It was observed that retention of natural dyes has almost doubled after addition of alum as mordant. The pH of pulp was maintained between 6.5 to 7.5 to keep paper within neutral range. The strength properties of paper made by utilizing pulp of 100 % cotton fibre, when dyed with natural dye showed increase in strength properties.

The application of natural dyes further enhances the credibility of handmade paper in global market and could make it possible to retain its eco-friendliness. The extraction of natural dyes from babool waste which is available abundantly can be a potential employment generation sector for rural masses and also may help to boost its export potential in the developing and developed countries.

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