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A Study on Employing AAS to Determine Metal Absorption Capacity of Natural Dyes

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ABSTRACT : The global market for ecofriendly textiles is influencing manufacturers to increase utilization of natural dyes. Most of these dyes require excess mordants (metallic salts) for effective substantiation. In order to minimize effluent load of unused mordant that is discharged, ideal dye-mordant combinations need to be established. This research employed atomic absorption spectroscopy (AAS) to measure and compare the amount of metal retained by fabrics in the absence and presence of natural dye. Individual combinations of copper sulfate and iron sulfate with dyes derived from Acacia catechu and Acacia nilotica on cotton and wool were evaluated. Mordant concentrations of 5, 10, 15 and 20 grams per litre (g/l) of the first mordant and 3, 5, 10 and 15 g/l of the second in combination with 10 g/l of dye were investigated. Dyeing was carried out by the padding process sequence of pad → dry → steam (dye) followed by pad → steam → dry (mordant). Dyeing was done only for 15 g/l copper sulfate and 5 g/l iron sulfate. Process sequence and parameters were selected based on earlier work AAS results confirm that wool absorbs slightly more metal than cotton. The presence of dye significantly increases the amount of metal absorbed by fabrics irrespective of dye or mordant. The dyed fabrics possessed satisfactory fastness properties. Unmordanted fabrics may find applications as metal filters.

KEYWORDS: Natural dyes: padding: AAS: mordant: metal absorption.

1.INTRODUCTION:

The name *natural dye* applies to all colouring matter derived from natural sources, such as plants, animals and minerals, with inherent variations. The outcome is either a) the textile acquires a unique shade for every batch or b) repeatable shades can be produced with difficulty only by a skilled and knowledgeable dyer. However, similar to the multitude of colours present in nature, a wide variety of colours can be obtained using these dyes. These dyes are classified according to the Colour Index based on structure, origin, application method and colour [1-3]. Although the use of natural dyes has been recorded globally since ancient times [1, 4], their industrial use is minimal since the discovery of the first synthetic dye "mauviene" in 1856 [5].

Consumers have become very conscious about the environment and are prompting manufacturers to act on the same. Several authors [1, 6-8] suggest the use of natural dyes as one avenue for the colouration industry in embracing eco-conservation. Consequently work has been carried out in regards to dye sources, extraction and application methods, dye chemistry and performance of natural dyes [9-16]. A difference in the ideal amount of mordant required for a given dye concentration was identified by the authors [9] prompting the present investigation. The focus is on determining the quantity of metal absorbed from the mordant by the fabric.

1.1 Mordant:

'Mordant' is derived from Latin *mordere* meaning 'to bite' because mordants were believed to eat away the surface and thus facilitate dye absorption [17]. Most natural dyes have low affinity for textiles and require mordants to fix them and hence known as mordant or adjective dyes [10]. Mordants are chemicals that react with fibre and dye to form a complex and thereby fix the dye [2, 17]. According to the metal involved, each complex yields a distinct shade [18-20]. The process of

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applying mordants or mordanting is classified into pre-mordanting,meta-mordanting and post-mordanting [10, 17].

Naturally occurring aluminium, copper, potassium and iron salts, the traditional mordants, are employed even today. Their quality, or purity, affects the richness and durability of the shades obtained [2]. Purer salts and other metals such as tin and chromium were introduced with advancements in chemistry [21]. Health and environmental hazards posed by incorrect handling of some of these salts, chromium salts in particular, have been identified. Hence, the most widely used metal-mordants are aluminium sulfate, potash-aluminium sulfate, tin chloride, copper sulfate and iron sulfate. The exact mechanism involved maximum combining capacity of dyes with metal is still under investigation [2]. This is attributed to complexity of dye molecules and as mentioned earlier, the decline in industrial use of natural dyes [7].

1.2 Atomic absorption spectroscopy (AAS):

AAS is a precise technique for quantifying metals in the parts per million (PPM) range present in a sample. It works on the principle that metals in their elemental form uniquely absorb ultraviolet (UV) light when they are excited by heat. This absorption follows Beer's Law, which states that as concentration goes up, absorbance goes up. Hence a calibration curve for a metal may be constructed by recording the absorbance for a series of known standards. Such a curve may be used to determine metal content of unknown sample by compaing its absorbance [22-25]. Therefore AAS was selected to determine the extent to which cotton and wool fabrics retained metal ions from the mordant in the absence and presence of dye.

2.MATERIALS AND METHODS:

2.1. Fabric:

Ready-for-dyeing mercerised bleached cotton fabric and 100% merino wool fabric was received from Bruck Textiles, and Macquarie Textiles, Australia respectively. Both fabrics were used as received without further chemical treatments. The fabric specifications are given in Table 1.

Table 1 Fabric specifications

Characteristic		Cotton	Wool
Weight (g / m^2)		297	230
Yarn count (Tex)	Warp	42	36
	Weft	81	41
Ends/cm		32	36
Picks/cm		20	24
Weave		3/1 twill	2/1 twill

2.2 Dyes:

Two commercial dyes, Thar (CI Natural brown 3) and Caspian (CI Natural brown 3:3), derived from Acacia catechu and Acacia nilotica respectively, were sourced from Alps Industries, Ghaziabad India. Dye is extracted from heartwood of the first plant, while for the second it is from the bark [2]. All other chemicals were at least of industrial grade.

2.3 Padding:

Padding was carried out on a laboratory-scale two-bowl horizontal squeeze-roller geometry padding mangle manufactured by Werner-Mathis. A Werner-Mathis laboratory-scale steamer was employed for the steaming of samples. An Electrolux TS 560 forced-air-flow convection drying chamber was used for drying.

Thar and Caspian were padded individually on cotton and wool fabrics at 80% wet pick-up. Padding dye liquor was prepared according to the recipe in

Table 2 to obtain 1% shade. Sodium alginate served as an anti-migrant, while potassium sulfate acted as a cationising agent and promoted dye fixation. Freshly prepared liquor was stored for 2–3 hours for sodium alginate to swell and become effective.

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Table 2 Pad liquor (dye) recipe

Constituent	Concentration (g/l)
Caspian or Thar	10
Sodium alginate	1
Potassium sulfate	1

2.4 Mordanting:

Copper sulfate and iron sulfate, two widely used mordants, were padded as post-mordant with above dyes in individual combinations. Undyed and unmordanted fabric was used as reference in order to establish the capacity of fabric to retain metal ions by itself, AAS studies were conducted on cotton and wool fabrics mordanted by Pad → Steam → Dry process and washed at boil. Individual concentrations of 5, 10, 15 and 20 g/l of copper sulfate and 3, 5, 10 and 15 g/l of iron sulfate were evaluated. Fabrics dyed by post-mordanting with 5 g/l iron sulfate or 15 g/l copper sulfate were subjected to AAS to bring out the effect of dye in altering the ability of fabric to retain metal. These concentrations were used for 10 g/l dye liquor based on previous work [9].

2.5 Steaming and washing off:

Steaming of samples was conducted at 100˚C and 100% RH for 10 minutes followed by drying at 65˚C. The dried samples after padding and mordanting were washed off (soaped) with 1 g/l anionic detergent at boil for 20 minutes. This was followed by consecutive rinses in hot and cold water respectively.

2.6 Evaluation:

2.6.1 Shade determination

Instrumental colour evaluation of conditioned dyed samples was done using a Datacolour 600 spectrophotometer with 10° Large Area View observer using D65 illuminant. An average of three measurements of reflectance was recorded.

2.6.2 Fastness properties

Wash fastness was evaluated according to AS 2001.4.15-2006 method using an Atlas launder-o-meter. The colour of wash solution, staining of adjacent multifibre fabric and dyed fabric colour change were evaluated against AATCC grey scales for colour change and staining.

Light fastness was tested as per AS 2001.4.21-2006 method for a period of 48 hours. Wet and dry rubbing fastness was evaluated according to AS 2001.4.3-1995 using a crock-meter. The staining of standard cotton fabric was evaluated using AATCC grey scales for staining.

2.6.3 Atomic absorption spectroscopy (AAS)

A Varian-AA-280-FS AAS was used to quantify the metal content in different fabric samples. An acetylene flame in air was employed to excite the metal atoms. Iron and copper were detected at wavelengths of 248.5 nm and 324.7 nm respectively.

3.OPERATING PROCEDURE:

A fabric sample of approximately 0.2 g is digested in concentrated acid to obtain a clear solution that contains only the metal component. The volume of solution is brought down by boiling and then diluted with distilled water to produce a 2% w/w sample solution of the acid according to recommendations from the manufacturer.

As depicted in Figure 1, the AAS instrument aspirates the test solution, as an atomised spray, into a flame. A beam of UV light of appropriate wavelength is focused through the flame and into a detector. If the metal is present in the sample, it will absorb some of the light. The instrument measures the change in intensity that is converted into absorbance by a computer data acquisition system

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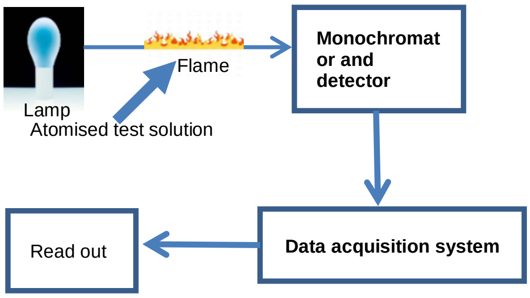

Figure 1 Schematic diagram of AAS

The maximum quantity of metal that may be present in the sample solution prepared as above is calculated taking into consideration the wet pick-up, concentration of metal salt in dye liquor and ratio of atomic mass of metal to molecular weight of the metal salt. Based on the above calculation, calibration solutions of required PPM range of concentrations are prepared by dissolving appropriate salts in distilled water.

Sample solutions were prepared using concentrated nitric acid (70% w/w). Table **3** and Table **4** present the calculations used to calculate maximum mass of metal applied on a 0.2 gram fabric sample at the stipulated mordant concentration, and wet pick-up of 80%. This was the basis for preparing calibration solutions containing 0, 1, 2, 3, 4 and 5 PPM of metal ion (copper or iron). These solutions were analysed using AAS with the detector set at wavelength specified for the metal under consideration. Average of three readings of absorbance was recorded for each sample. Data from calibration samples were plotted as a scatter graph. Equation for trend-line fitted to this graph was used to calculate the amount of metal present in the sample solutions prepared by digestion of fabric. The results were extrapolated to determine the mass of metal retained by unit mass of fabric.

Table 3 Atomic mass of elements present in mordants

Element	Atomic mass
Cu (Copper)	63.55
Fe (Iron)	55.85
H (Hydrogen)	1.01
O (Oxygen)	15.99
S (Sulfur)	**32.07**

Table 4 Calculation to determine maximum mass of metal applied on 0.2 g of fabric

Mordant	Molecular Weight	Metal content (%)	Concentration (g/l)	Mass of metal (mg)*
Copper sulfate ($CuSO_4.5H_2O$)	249.63	25.46	20	0.81
Iron sulfate ($FeSO_4.7H_2O$)	277.95	20.09	15	0.48

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*Maximum mass of metal that may be present on 0.2 gram of fabric padded to 80% wet pick-up at given mordant concentration.

4.RESULTS AND DISCUSSION:

4.1 Shades obtained

The two mordants produced different shades for the same dye (Figure 2 and 3) as mentioned previously [9]. Mordanting with copper sulfate yielded a copper-beige shade while iron sulfate resulted in a yellowish-grey shade for both cotton and wool. When used as a mordant, copper tends to bloom the final colour, while iron dulls it [2]. This effect is evident in the flatter and lower reflectance curve of grey as compared to beige.

The change in colour according to mordant indicates the polygenetic behaviour of some natural dyes [18]. This has been attributed to formation of metal chelates by the tannins in dyes derived from Acacia family [17, 26-29]. Although a simple depiction of this interaction is shown in **Error! Reference source not found.**, the polymeric characteristic of poly-phenolic dyes precludes exact determination of the features of the metal complex [29].

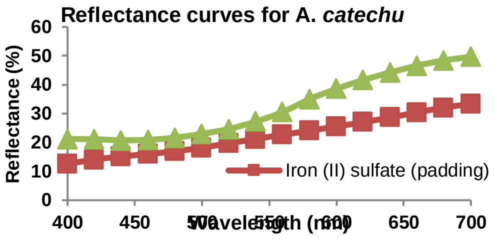

Figure 2 Reflectance curves for A. *catechu* on cotton

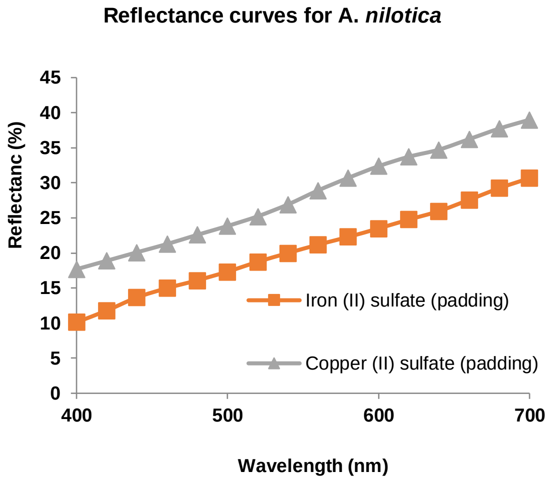

Figure 3 Reflectance curves of A. *nilotica* on cotton

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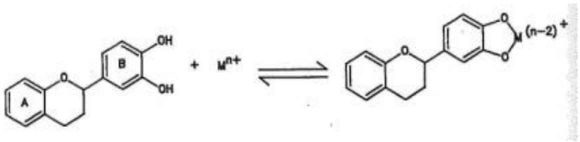

Figure 4 Tannin-metal chelate representation

The calibration graphs and trend-line equations for copper and iron shown in Figure 5 exhibit high degree of correlation consistent with the working principles of AAS. Amount of metal in the fabric was calculated based on the trend-line equations.

Mass of metal padded-on and retained-by fabric samples weighing 10 g each are presented in

Table 5. In considering these results, the following facts should be kept in mind: 1) a 10 g fabric sample padded with 5 g/l iron sulfate picks up only 0.04 grams of the salt, which in turn contains a meagre 0.008 g of iron; and 2) a 10 g fabric sample padded with 15 g/l copper sulfate picks up 0.12 g of salt, translated as 0.03 g of metal. It can be observed that both cotton and wool retained increasing quantities of metal as the corresponding salt concentration was raised in the pad liquor. However, such increases were not directly proportion. In the presence of dye, a significant increase in mass of metal retained was observed for both mordants confirming the formation of a dye-metal-fibre complex.

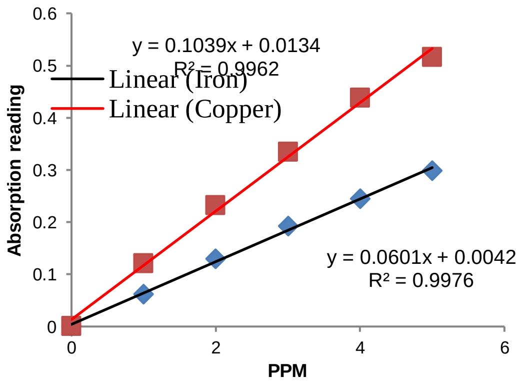

Figure 5 Calibration curve for AAS

Table 5 Metal retained (mg) measured using AAS

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Copper sulfate (g/l)	Metal (mg)				
	On 10 g fabric, 80% wet pick up	***Retained by***			
		Cotton	*Cotton and dye*	*Wool*	*Wool and dye*
5	10.2	0.86		2.49	
10	20.4	1.29		8.87	
15	30.6	3.52	6.49	10.40	28.52
20	40.8	5.88		18.69	
Iron sulfate (g/l)	Metal (mg)				
	On 10 g fabric, 80% wet pick up	*Retained by*			
		Cotton	*Cotton and dye*	*Wool*	*Wool and dye*
3	4.8	2.52		1.02	
5	8.1	5.22	6.12	2.88	6.04
10	16.1	5.78		4.07	
15	24.2	7.57		5.11	

Good fastness to rubbing, washing and light are desirable properties in dyed textiles. As evident from the test results shown in Table 6 all fastness ratings are 3-4 or better.

Table 6 Fastness testing results for pad-dyed cotton

Dye		Thar (A. *catechu*)		Caspian (A. *nilotica*)	
Mordant		$CuSO_4.5H_2O$ (15 g/l)	$FeSO_4.7H_2O$ (5 g/l)	$CuSO_4.5H_2O$ 15 g/l)	$FeSO_4.7H_2O$) (5 g/l)
Washing		3–4	3–4	3–4	3–4
Light fading		4–5	3–4	4–5	3–4
Rubbing test	*Dry*	5	5	5	5
	Wet	5	5	5	5

Both dyes, when mordanted either copper sulfate or iron sulfate, exhibited excellent rubbing fastness. There was no staining of the white fabric under both dry and wet conditions. During washing, the colour did not bleed into the liquor or onto adjacent fabric. However, a colour tone change was observed after washing, leading to a rating of 3–4. This change may be attributed to long exposure

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(30 min) to high temperature (60˚C) during standard washing. A similar temporary change was observed during light fading test. Here, samples regained their original colour after conditioning for 24 hours. It is possible that at elevated temperatures one or more bond angles in the dye-mordant-fabric complex undergo changes, altering the shade. The change is reversible in the absence of excess moisture during light fading but becomes permanent when this restraint is removed during washing. Fading to light at 48 hours of exposure was rated 4–5 against blue wool standards.

The fastness results agree well with Patel et al. [28]. Tannins, the main components of dyes derived from Acacia family, are inherent mordants used to improve fastness properties of other natural dyes. This factor combined with the metallic salts used in this study resulted in strong covalent bonds between cotton and the dye-mordant complex, leading to the robust fastness ratings observed. The results support the findings of Gupta [30], who postulate characteristic of mordants to play an important role for fastness properties of natural dyes than the dyes themselves. Samples treated with copper sulfate showed less significant colour change as opposed to those treated with iron sulfate. This may be due to the more stable structure of copper-dye-fabric complex.

CONCLUSIONS:

The capability of Acacia natural dyes to absorb metal ions has been quantified. Wool absorbs more metal as compared to cotton probably due to bonds present in its bicomponent structure. Further studies may be conducted in investigating the maximum quantity of metal that can be absorbed by a given dye concentration or other dye-metal combinations.

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