



DYEING POTENTIAL OF *CURCUMA LONGA* (TURMERIC) ON CHROME-TANNED LEATHER

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ABSTRACT

In this study, the yellow dye of *Curcuma longa* (turmeric) was investigated for its potential as a natural dye for the colouring of leather. The rhizome of turmeric was sourced from Jaban-Kogo in Kaduna State, Nigeria. The colouring matter of *Curcuma longa*, curcumin, was extracted using batch extraction. The extract was purified by column chromatography and gave a percentage yield of 11.92% and melting point of 182.7°C. It was successfully applied on chrome-tanned leather with the aid of mordants such as aluminium sulphate, ferrous sulphate, stannous chloride and zinc sulphate. The chemical structure of the extract was also modified by using it as a coupling component in azo dye formation with sulphanilic acid. The azo dye was applied similarly on leather as with the extract above. As a result, brown, yellow, orange and green shades were obtained respectively. The dyed leathers showed moderate fastness properties for wet and dry rub tests. The mordanted azo dye had better fastness when compared to the substrate dyed with the mordanted *curcumin*. This work was aimed at helping local tanners produce leathers with reasonably fast dyes from this plant in their locality, and also provide entrepreneurship opportunity for the youths since the modification of curcumin to azo dye was done with low level technology.

Keywords: dyeing, turmeric, chrome-tanned leather, mordants, fastness.

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INTRODUCTION

The use of natural dyes to give colour to our world in art, fashion and design is an ancient one [1]. No matter which culture we examine, people have experimented and explored every conceivable source of colour in their environment. Everything from shellfish to lichens, roots, barks, leaves, berries, fungi and flower stamens have been explored to yield every shade of colour in the rainbow. Dyes are coloured natural or synthetic organic compounds possessing ability of imparting colour to other materials. When applied on these materials, such as textile fibres, a dye is capable of attaching itself to the substrate, and also retains its colour on prolonged exposure to light, water and soap. This property is often referred to as the fastness property of dye [2]. Before the advent of synthetic dyes, natural colouring substances have been used to dye fabric and other materials [3, 4]. Generally, dyes are applied on different types of fibres such as cotton, nylon, jute, wool, leather and other materials to give a characteristic colour.

Unlike fabrics, leather is not a flat material of uniform thickness, but a three dimensional substrate into which dyes can penetrate to a varying extent. In addition, leather is a substrate with two surfaces of different affinity and accessibility for dyes. Leather dyeing is a transition process between tanning and finishing. In leather dyeing, sometimes surface dyeing is required as in the case of shoe upper leathers, and at other times the dyes are required to penetrate to a certain extent or through the entire cross section as in clothing leather and furniture upholstery leather. Thus, on the one hand good covering power is required while on the other hand a certain degree of penetration is desired [5]. Leather is dyed to improve the appearance and appeal of the finished product and also to make the leather adaptable for fashion styling. Proper

dyeing of leather enhances its value as a commodity and also contributes to its general quality. Leather dyeing fixes the dye molecules, not only on the surface of the tanned leather but inside as well [6, 7]. In leather industries, dyestuffs are used to intensify or enhance the aesthetic value of the finished leathers. The dyed baths can be neutralized effectively through the addition of either acid or alkaline and then discarded [8]. Mordanting helps to improve the wash fastness property of the dye. The dye is usually employed for the dyeing of clothing and gloving leathers [9].

Curcuma longa L. (Turmeric) is a rhizomatous perennial plant of the ginger family, Zingiberaceae (Fig. 1-3). It is native to tropical South Asia and needs temperatures between 20°C and 30°C, and a considerable amount of annual rainfall to thrive. Turmeric is cultivated and utilized in 19 states of Nigeria [1]. Of the curcuminoids, Curcumin (Fig. 4) is the most biologically active. Figure 5 illustrates the various derivatives of Curcumin. Because of the curcuminoid content, turmeric makes a good colouring agent [10]. The curcuminoids are natural phenols and are responsible for the yellow colour of the turmeric. Curcumin has a molecular formula of C₂₁H₂₀O₆, and according to the research finding [3, 4, 5], it can exist in at least two tautomeric forms, that is, the keto and the enol forms (Fig. 6). Curcumin is used as spice and as natural food colorant. In addition to its main application as colouring and flavouring agent in food, it has medicinal activity including antioxidant, anti-inflammatory and anti-digestive trouble. It is also used as a biological stain, pH indicator and indicator for boron [6, 7]. Curcumin is also known as potent anti-tumor agent with inducing apoptosis in cancer cells and inhibiting phorbol ester protein kinase activity [8, 9]. Apart from the rhizome's richness in curcuminoid pigments (6%) and essential oils (5%), it also

contains 69.43% carbohydrate, 6.30% protein, 3.50% mineral and other important elements [1]. Its systematic chemical name is (1E, 6E)-1, 7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione. It is called C.I Natural Yellow 3, WHO (World Health Organization) and FAO (Food and Agricultural Organization) committees have approved it as food additive, its colour index number is C.I, 75300, E100 [11].

The present study focused on the dyeing of leather with aqueous extracts of curcumin (turmeric), using post-mordanting method of dyeing. The aim was also to investigate the dyeing behaviour and fastness properties of curcumin and curcumin-azo-dye on leather and comparisons between dyeing with and without mordants were also made.



Fig. 1: *Curcuma longa* plant



Fig. 2: *Curcuma longa* rhizome



Fig. 3: *Curcuma longa* powder

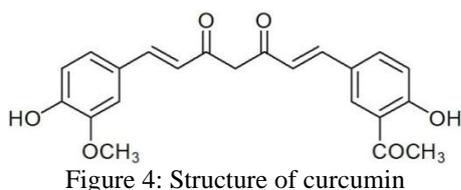


Figure 4: Structure of curcumin

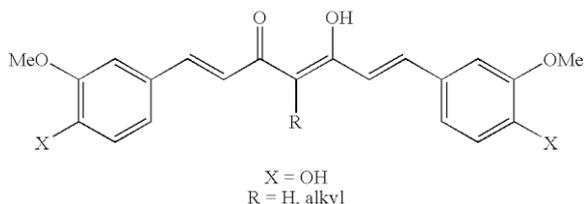


Fig. 5: Structure of curcumin derivatives

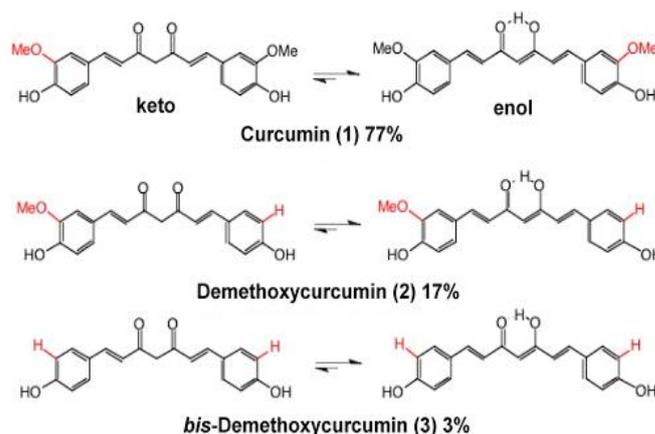


Fig. 6: Isometric forms of curcumin

EXPERIMENTAL

Collection and extraction of sample

The *Curcuma longa* rhizome was collected from Jaban Kogo, in Jaba Local Government Area of Kaduna State, Nigeria. The rhizomes were kept at room temperature to maintain the moisture content of the stock. The fresh rhizomes were pounded to allow for easy extraction. The powdered *Curcuma longa* (50 g) was soaked in ethanol (300 ml), and vigorously stirred for about an hour and filtered. This procedure was repeated two more times on the same sample until the dye appeared to have been completely extracted. The solvent was recovered from the resulting solution by distillation, and the concentrated paste was dried in the oven at 60°C. It was defatted with n-hexane and purified using column chromatography.

Preparation of azo dye

Sulphanilic acid (2.50 g) and sodium carbonate (0.75 g) were dissolved in distilled water (50 ml) and cooled in ice bath. Sodium nitrite (1.80 g), was also dissolved in distilled water (10 ml) and cooled in an ice bath. The sodium sulphanilate was warmed on a water bath and then cooled in an ice bath. The cold solution of sodium nitrite was added to the cold solution of sodium sulphanilate in portions and with constant stirring in an ice bath in a fume cupboard. Cold concentrated hydrochloric acid (10 ml) was diluted in water (10 ml) and added to the sulphanilate solution. Instant blue-black colour on starch iodide paper indicated the presence of free nitrous acid and completion of diazotization. curcumin (0.50 g) was dissolved in distilled water (10 cm³) and made alkaline with 20% NaOH (20 cm³). This was cooled in an ice bath. The sulphanilic diazonium chloride was slowly added to the alkaline solution of the extract in small portions and with constant stirring until all of it was added. After the reaction, the

resulting azo dye was filtered, dried in the oven at 60°C and ground into powder. The melting point was determined using an electro thermal melting point apparatus.

Ultra-violet spectroscopic analysis

The Ultraviolet Spectroscopy of the dye was carried out using a JENWAY 6305 Spectrometer from the Nigerian Institute of Leather and Science Technology (NILEST), Zaria to obtain the wavelength of maximum absorption.

Identification of curcumin by IR spectroscopy

5mg of purified dry sample was placed directly into the infrared beam of IR spectroscopy. As the IR radiation was passing through the sample, the transmitted energy is being measured and a spectrum is generated.

Dyeing of chrome-tanned leather

Dyeing was carried out using the curcumin extract and the azo dye on wet leathers. This was done to determine the intensity and depth of the dyes prepared on leather. The dyeings were carried out as follows: The chrome-tanned leather samples were cut to 10x8 cm, labelled and soaked appropriately for the curcumin and azo dye samples respectively. The samples were each weighed and placed in conical flasks containing 2% dye and 200% water. The leather samples were agitated for about an hour at a temperature of 60°C, after which the dye penetration was checked and ascertained. The leather was fat liquored using 6% fat liquor based on the weight of the individual leather samples. The dye was fixed using 4% formic acid. The fixing was carried out for 30 min after which the dyed leathers were rinsed with clean water, horsed up to drain, dried, staked and toggled.

Mordant dyeing of leather

5% solution of ferrous sulphate, aluminium sulphate, zinc sulphate and stannous chloride were each separately used for mordanting. The leather samples were soaked in the mordant solution for 5 min with shaking. *Curcuma longa* extract (0.2 g) was dissolved in ethanol (2 cm³) and dispersed in water. The mordanted leather was put in the dye solution and agitated for an hour at a temperature of 60°C, and then fat liquored using 6% fat liquor based on the weight of the leather. The curcumin dye was fixed on the leather by adding 4% of formic acid for 20 min. Unfixed dye was then washed off and rinsed [12]. The process was repeated with the azo dye.

Light fastness

This test was carried out according to the official method of analysis by the Society of Leather Technologists and Chemists [12]. A piece of dyed leather of size 3 x 3cm was half covered with a black polythene sheet such that half of the length, 1.5 x 1.5cm was covered, and the remaining half was left uncovered. This was exposed to the daylight for 5

consecutive days between the hours of 9.00 am-3.00 pm (6 hr) after which the change in colour was compared using the Standard grey scale.

Dry and wet rub fastness

The leather samples were rubbed with pieces of standard wool felt under a given pressure for 140 revolutions. The samples were cut and clamped on a Rub Fastness Tester (Machine Model STM 421). The changes in colour of the pelt and of the leather were assessed with the standard grey scale [12].

RESULTS AND DISCUSSION

Batch extraction

The extracts are weighted after drying and weight percentage of Curcuminoid dye was calculated. The percentage yield was found to be 11.92%. The curcuminoid dye is obtained in the form of golden yellow colour by using ethanol. In addition, the melting point of the curcumin extract was 182.7°C while that of the azo dye formed from it was 193°C.

UV spectra

The curcumin dye had its highest absorbance at 430nm, 460nm and 480nm (the yellow- orange range) in the UV-spectra, thus, confirming the golden yellow extract to be curcumin dye. Whereas the azo dye had its λ_{max} at 530nm indicating the introduction of the diazonium component which accounts for the absorption at a further longer wavelength responsible for the deep shades obtained.

Infra-red spectra

The instrument gives a positive identification of the purified material. The infrared spectrum of curcumin and curcumin azo dye are shown in Fig.7 and 8, which is determined by IR spectroscopy. The purified curcumin spectrum is almost same as the spectrum [11]. The dye chromophore was confirmed using the FTIR-8400S spectrophotometer. An absorption shift at 3411.2 cm⁻¹ and 3444.02 cm⁻¹, confirmed the presence of a strong phenolic (-OH) group in the pure dye and the coupled dye respectively. The details of the functional groups present in the curcumin and curcumin azo dye and their respective wave numbers are presented in Table 1.

Colour effects of mordanted *Curcumin* on leather

The Table 2 below showed the various colours obtained as seen by the eye (visualization) when the chrome-tanned leather was dyed with different mordanted curcumin. Table 3 shows the actual colour obtained when dyed with raw curcumin dye and the curcumin azo dye respectively. However, it was observed that slightly deeper hues were obtained as percentage of mordant in the dye used increases from 0.5 to 2% as shown in Table 4.

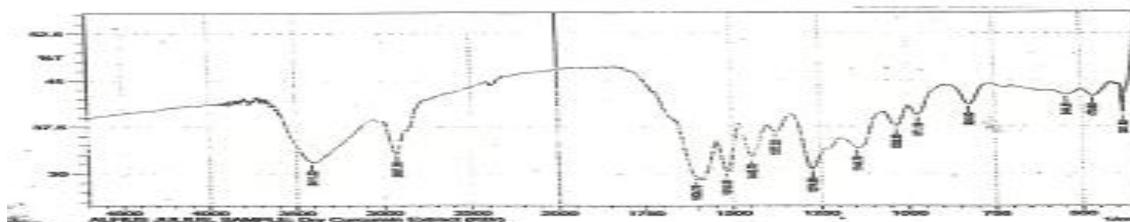


Fig. 7: IR of curcumin



Fig. 8: IR of azo dye

Table 1: Observed functional groups of curcumin and azo dye

Curcumin Dye		Curcumin Azo Dye	
Functional Group	Wave No. (cm ⁻¹)	Functional Group	Wave No. (cm ⁻¹)
OH- stretch (hydrogen bonded)	3411.22	OH-stretch (high conc.)	3444.02
-C-H- stretch	2927.08	Strong tert. -OH	1185.30
-C=O(stretch) unsaturated ketone	1606.76	-N=N-stretch	1633.76
-C=C(stretch) of aromatics	1518.99	-C-O-C stretch	1130.32
-Ar-H, =C-H(bend)	1445.70	C-N stretch	1042.56
Ph-OH (bend)	1377.22	Meta-disubstituted benzene	879.57
Ph -C-O stretch	1274.99	Ortho-disubstituted benzene	833.20
-C-O-C stretch	1144.79	Para-disubstituted benzene	703.06
Ar =C-H (in plane bend)	1033.88		-
aromatic para-disubstitution	824.60		
Ar =C-H (out of plane bend)	971.19		

Table 2: Colour effect of mordants on leather

% of dye Used	Al ₂ (SO ₄) ₃		FeSO ₄		ZnSO ₄		SnCl ₄	
	Curcumin	Azo Dye	Curcumin	Azo Dye	Curcumin	Azo Dye	Curcumin	Azo Dye
0.5%	Yellow	Faded green	brown	light orange	yellow	light brown	light yellow	light brown
1.0%	deeper yellow	Faded green	deep brown	light brown-orange	Yellow shade	deep brown	yellow	Brown
2.0%	dark yellow-orange	deep green	dark brown	dark orange	deep yellow	deeper brown	deep yellow	Green

Table 3: Physical appearance of the dyed leathers without mordant

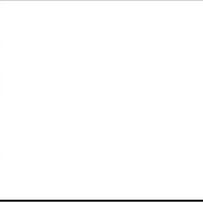
Curcumin dye		Curcumin azo dye	
			

Table 4: Physical appearance of the dyed leathers with mordants

Mordant	Mordanted Curcumin Dye		Mordanted Curcumin azo dye	
	0.5% Mordant	2.0% Mordant	0.5% Mordant	2.0% Mordant
FeSO ₄				
Al ₂ (SO ₄) ₃				
SnCl ₄				
ZnS				

FASTNESS PROPERTIES

Light fastness

The results of the colouring effect on leathers mordanted curcumin (Table 5 and 6) showed a lot of differences on the leathers and the shade of the dye. The unevenness and patches in dyeing, indicated in the mordanted samples was an effect ascribable to ion-effect on the flesh side of the leather, and consequent sticking of the dye to the walls of the container due to coagulation. Uniformity of the colour was more marked on the 0.5% ZnS, 0.5% SnCl₄, 2% Al₂(SO₄)₃ and 2% FeSO₄ mordanted dye sample.

The curcumin on wet blue leather was pale green in colour and quite uniform in shade. The action of curcumin on chrome-tanned leather mordanted with aluminium sulphate produced a prominent yellow shade, with FeSO₄ producing a prominent brown (biscuit/ chocolate) shade. These results of course present an interesting case to contend with, that is, uniform biscuit/brown, orange and yellow colours. The not-so-appealing brown colour must be a consequence of the bluish colour of the chrome powder, and the yellowish curcumin. The results obtained from mordanting the azo dye indicate a movement towards darker shades as evident in the green shade produced with aluminium sulphate.

Table 5: Result of light fastness on unmordanted leather

Sample	Fastness
Curcumin	3
Azo dye	4

Table 6: Results of light fastness Curcumin on mordanted dye leather

Mordant	$Al_2(SO_4)_3$			$FeSO_4$			$SnCl_4$			$ZnSO_4$		
	%	0.5	1%	2%	0.5	1%	2%	0.5%	1%	2%	0.5%	1%
Fastness	4	5	5	5	4	4	4	4	5	4	4	4
Staining	2	2	2	2	3	3	2	3	3	2	3	2

Table 7: Rub fastness on unmordanted leather

Dyed Samples	No. of Revolutions	Dry Rub Fastness		Wet Rub Fastness	
		Fastness Rating	Stain Rating	Fastness Rating	Stain Rating
Curcumin	140	3	3	3	3
Azo dye	140	3	4	3	3

Table 8: Result of rub fastness of curcumin on mordanted leathers

Mordant	Dry Rub Fastness				Wet Rub Fastness			
	Fastness rating		Stain rating		Fastness rating		Stain rating	
	Curcumin	Azo dye	Curcumin	Azo dye	Curcumin	Azo dye	Curcumin	Azo dye
0.5% $FeSO_4$	4	4	3	3	3	4	4	2
1% $FeSO_4$	4	4	2	2	4	5	2	3
2% $FeSO_4$	3	3	3	2	3	5	3	2
0.5% $Al_2(SO_4)_3$	4	4	3	2	4	4	3	3
1% $Al_2(SO_4)_3$	4	4	2	2	4	4	2	3
2% $Al_2(SO_4)_3$	5	5	3	2	5	5	2	2
0.5% $ZnSO_4$	3	3	2	2	3	4	2	3
1% $ZnSO_4$	3	3	2	2	4	5	3	3
0.5% $SnCl_4$	3	3	3	3	3	4	3	2
1% $SnCl_4$	4	4	3	2	4	5	3	3
2% $SnCl_4$	4	4	3	3	4	5	3	3

Rub fastness

Dyeing analysis of physical tests on wet and dry rub fastness of Curcumin dyed leathers are presented in Tables 5a and 5b, and showed that standard fastness test were met in all conditions for wet and dry rub tests. There was an increase in glossy appearance with increased number of revolutions, as well as a smoother feel of the grain. Similarly, there was no obvious colour change on the pelt. However, the dry rub fastness test results on the azo dye indicate that the mordanted azo dye had better fastness when compared to the substrate dyed with the mordanted curcumin. Also, wet rub fastness test results appeared to have better results with the mordanted azo dye.

By and large, natural dyes are mostly eco-friendly, biodegradable, less toxic, and less allergenic as compared to synthetic dyes. However, studies have shown that certain natural dyes may have detectable mutagenic effects e.g., elderberry colour and safflower yellow; others, like carmine, can cause asthma by continuous inhalation, but it can be said that most of the natural dyes are safe and some even have curative effect e.g., curcumin in turmeric has antibacterial [8]

CONCLUSION

This project attempted to explore the dyeing potential of crude extract from *Curcuma longa*, as a dyestuff for chrome-tanned (wet blue) leathers, as well as modifying the structure of curcumin and testing its potential on the same substrate. This study has also enabled the production of yellow shades on leathers which is characteristic of most turmeric, as well as green shades from the azo dye with the help of mordants. Brown and orange colours are other shades produced to meet fashion demands. Perhaps the most significant outcome of this work, was obtaining the dry powdered extract of the curcumin dye as well as the good shades from different mordants. These were very encouraging, though, not conclusive. The dyes had moderate to good rub and light fastness properties on the leathers. Dyeing trials could be carried out using other suitable mordants to ascertain their substantivity and depth penetration.

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