CHARACTERIZATION AND UTILIZATION OF NATURAL DYES FROM *TECTONA GRANDIS* LEAVES AS P^H INDICATOR AND INFLUENCE OF MORDANTS ON FASTNESS PROPERTIES OF COTTON FABRICS

Supported by tetfund
TERTIARY EDUCATION TRUST FUND

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Received: December 14, 2023 Accepted: March 28, 2024

Abstract: Natural dyes extracted from fresh *Tectona grandis* (Teak tree) leaves as one of the Non-Wood Forest Products (NWFPs) using 50 % ethanol as solvents has been utilized for dyeing of cotton fabric with or without mordants. Simultaneous mordanting method using mordants such as alum, $CuSO_4$ and $K_2Cr_2O_7$ of various concentrations (1-2 %) was employed during the dyeing of scoured cotton fabrics and stability of colour on the dyed fabrics were determined in terms of light, wash and rub colour fastness. The dye extract was characterized using ultraviolet-visible (UV- Vis) and Fourier transform infrared (FTIR) spectroscopy. The applicability of the dye extract as P^H indicator in acid-base titration was also studied. UV-Vis absorption spectra indicates maximum wavelength at -- nm and structural characterization by FTIR revealed among other functional groups the presence of C=O, O-H and C=C of aromatic compound. The end points obtained using the natural dye extract from *Tectona grandis* leaves in acid-base titration involving HCl and CH_3COOH as acids and NaOH and NH_4OH as bases are comparable to synthetic indicators (Phenolphthalein and Methyl orange) used. Mordanting was found to improve the dyeing properties of the fabrics and can be utilized in eco-friendly textile dyeing and as replacement for synthetic indicators that are carcinogenic.

Keywords: *Tectona grandis*, natural, dyes, mordants, leaves, textile

Introduction

Several products derived from the forests aside wood or timber-based products have contributed greatly to the economy of developed and underdeveloped nations including Nigeria and are equally attracting more attention in recent years. These categories of products are severally referred to as Non-Wood Forest Products (NWFP), Non-Timber Forest Products (NTFP), Multi - Use Forest Produce (MUFP), Minor Forest Products (MFP) or Special Forest Products (SFP) (Tan *et al.*, 1996). They include all materials of biological origin (plants and animals) that are extracted on an industrial scale except timber (FAO, 2010). These could be leaves, fruits, fungi (mushrooms), roots, barks, essential, oils, fodders, bee wax, natural dyes, fibres and bush meats. They contribute to poverty alleviation through generation of income, provision of food and improve nutrition, medicine and foreign exchange (Chikamai *et al*., 2000) as well as in recreational activities and plays important cultural and spiritual roles (Lovric *et al.*, 2020). Natural colourants and dyestuffs are categorized along with these important products and currently had been in used as raw materials for textiles, food and other related industries. There has been increase in the use of natural dyes in textile applications as a result of the legal environmental standards imposed by many countries in response to several hazards linked with the use of synthetic dyes. Synthetic dyes are considered toxic, allergic, non - degradable, carcinogenic and caused pollution while natural dyes are eco-friendly, safe, easily prepared and has better biodegradability properties and are considered more compatible with the environment (Ali *et al.*, 2009; Onuegbu *et al.*, 2020; Oyeleke *et al.*, 2020).

Natural dyes have many shortcomings in terms of colour fastness to fabrics but their application along with mordants enhances their affinity and provides variety of shades with improved colour fastness (Farooq *et al.*, 2012; Saravanan *et al.*, 2013; Moniruzzaman *et al.*, 2018). Mordants (natural and synthetic) have the ability to open up the fibre structure thereby enhancing the dye-fibre fixation through the formation of co-ordination complex between the mordants and dyes. Synthetic mordants are metallic salts (of iron, copper, tin, potassium etc) while natural mordants includes plants, animals and their wastes that are capable of improving the affinity between the dyes and fabrics leading to increase in dye uptake properties.

There has been immense increase in the focus of researchers and scientists to replace synthetic colourants with natural products as acid-base indicator because of their harmful effect on the user, climate and living organisms. In chemical reactions, indicators are molecules that respond to change in P^H of a solution by change in their colours. They change colour over a range of hydrogen ion concentration which is expressed as P^H ranges of blue, red and colourless (Onuegbu *et al.*, 2020). They are usually weak acids or weal bases, but their conjugate base or acid forms have different colours due to differences in their absorption spectra (Mane *et al.*, 2016).

Titrimetric analysis is a method of analysis where solution of the substance being determined is treated with a solution of a suitable reagent of exactly known concentration which depends on determining the end point of an acid-base reaction when the solution forms salt and water in a neutralization reaction (Nair *et al.*, 2018). Titration can be classified as acid-base, redox, precipitation and complexometric but indicators are majorly and commonly used for acid-base titration. Titrants and titrands in acid-base titration could be strong acid- strong base, weak acid-strong acid, strong acid- weak base and weak acid- weak base.

Nature has blessed Nigeria with much green nature that is dye yielding at this present time when the focus on consumption of green nature and as raw materials for industrial growth has been on the increase. One of such tree plant is Teak tree (*Tectona grandis*). *Tectona grandis* is a tropical hardwood tree species in the family *Verbanaceae*. It is a large, deciduous tree of about 10-20 m tall that occurs in mixed hardwood forests and most widely cultivated high value hardwood in the world. Leaves are opposite, ovate-elliptic to ovate, 30-50 x 15-20 cm. The flowers are small, whitish and bisexual that appeared in large panicles containing up to a few thousand flower buds which open only few at a time during flowering period of 2- 4 weeks (Alabi and Oyeku, 2017).

Aside making use of the timber from the tree, other parts such as the leaves, barks, roots and fruits are always left uncared for. The aim of this work was to determine the performance of the extracted dyes from *Tectona grandis* tree leaves on cotton dyeing and to produce fashionable colours from the dyes using different mordants as well as to evaluate the fastness properties of the dyed fabrics and to unlock the potential of the extracted dyes as P^H indicator.

Materials and Methods

Sample collection and preparation

The leaves of *Tectona grandis* were collected behind Faculty of Science Central Laboratory, Osun State Polytechnic, Iree, Osun state**.** The fresh leaves was removed from the stalk manually and pounded with the laboratory mortar and pestle for ease of the dye extraction. Purified cotton fabrics measured (10 x 10 cm) with an average weight of 1.54 g were scoured by washing them in sodium carbonate solution (0.5 g/l) and non-ionic detergent (2 /l) at 60°C for 30 min. the scoured fabrics were thoroughly washed with distilled water and hung at room temperature in the laboratory to dry. The different mordants such as potassium dichromate, alum and copper sulphate used as mordants were BDH products.

Dye extraction

Dye was extracted from fresh leaves of *Tectona grandis* using 50 % ethanol. 500 g of the pounded leaves was soaked in 50 % ethanol (1000 ml) in a beaker for 3 days at room temperature. The dark red colour obtained was

Results

filtered and the filtrate stored in an air tight container ready for dyeing process and further analysis.

Dyeing process

Simultaneous mordanting process was employed in the dyeing of scoured cotton fabrics following the methods highlighted by Janani, (2013). The cotton fabrics were put in a beaker containing the dye extract and the different concentrations (1-2 %) of the mordants (alum, $CuSO_4$, $K_2Cr_2O_7$ and their mixtures) at the same time for 3 hours over a shaking water bath. The cotton fabrics were removed from the dyeing bath, washed with cold water and air dried at room temperature. The air-dried cottons fabrics were further evaluated for fastness properties.

Fastness properties determination

A wash fastness test was carried out according to the ISO 105: CO6 A2S test in a rotaway machine (SDL ATLAS, UK). Rub fastness (wet and dry) was done by ISO 105: X 12 procedure. The wash and rub fastness properties were determined using ISO grey scales. Light fastness (sun and Xenon arc lamp) was carried out using ISO 105: BO2 method. Colour fastness to light was assessed using the blue scale.

UV Spectroscopy analysis

An aliquot of the dye extract was introduced into a quartz cell (1 cm pathway) and analyzed in UV/Vis spectrophotometer (Jenway UV/Vis). A scan from 300 to 600 nm was performed in order to generate the characteristics absorption spectra of the sample.

Fourier Transform Infrared Spectroscopy analysis

5 mg of the lyophilized dye sample was mixed thoroughly with 200 mg of Potassium bromide and homogenized in an agate mortar. The mixture was then placed in the sample compartment of the Fourier Transform Infrared Spectrophotometer (Shimadzu IR, Affinity, Japan)

Titrimetry analysis using dye extract as P^H Indicator

Titration experiment using young teak leaves extract as pH indicator. The extracts were tested to ascertain their application as pH indicators, Each titration was repeated 3 times to validate the end-point readings for each neutralization titration. Similar titration experiment was repeated using synthetic indicators (methyl orange and phenolphthalein). The end points obtained with the synthetic and extracted dye were documented.

Results and Discussion

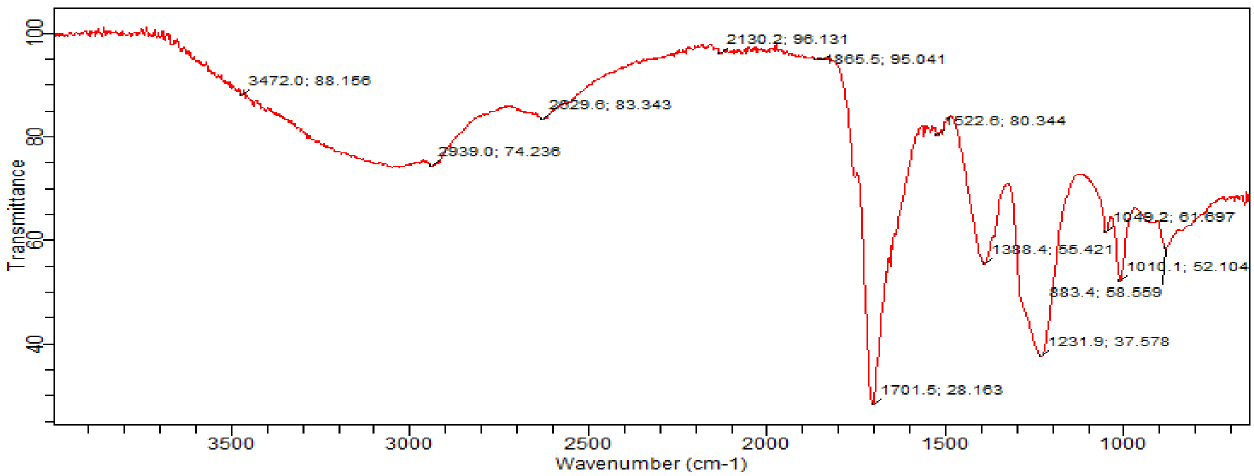

Figure 1: Fourier Transform Infrared (FTIR) of dye extracted from *Tectona grandis* leaves

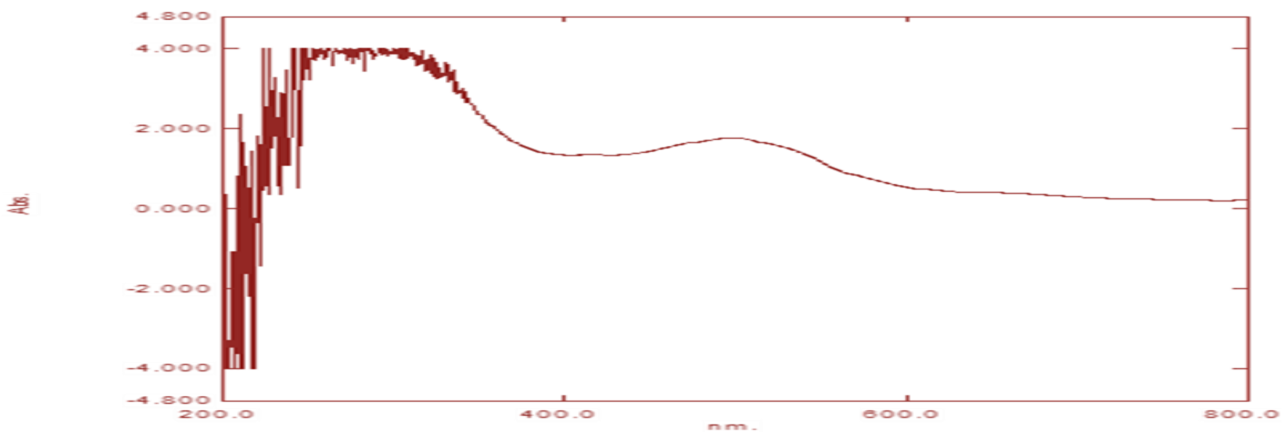

Figure 2: Ultra violet spectroscopy of dye extracted from *Tectona grandis* leaves

Table 1: Fastness properties of dyed cotton fabrics

Mordant	Light		Rub		Wash
	Sun	Artificial	Wet	Dry	
1 % Alum	4	4	3	5	3
1 % $CuSO_4$	4	4	3	5	3
1 % $K_2Cr_2O_7$	5	5	4	5	3
1 % $CuSO_4$+1 % $K_2Cr_20_7$	5	5	4	5	2
2 % Alum	4	4	4	5	3
2 % $CuSO_4$	4	4	3	5	3
2 % $K_2Cr_2O_7$	5	5	4	5	3
2 % $CuSO_4$+2 % $K_2Cr_20_7$	4	4	3	5	2
No Mordant	5	5	3	5	1

Scale:
1- Poor, 2- Moderate, 3- Fairly good, 4- Good, 5-Very good

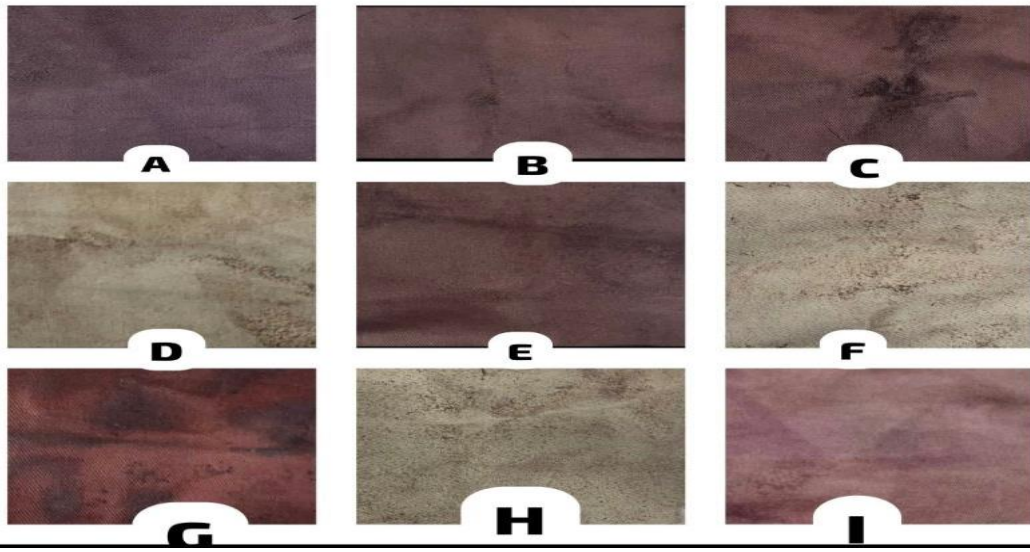

Plate 1: Dyeing properties of the fabrics
KEY
A = 2 % Alum, B = 1 % $CuSO_4$ + 2 % $K_2Cr_2O_7$, C = 2 % $CuSO_4$, D = 2 % $K_2Cr_2O_7$,
E = 1 % $CuSO_4$, F = 2 % $CuSO_4$ + 2 % $K_2Cr_2O_7$, G = No mordant, H = 1 % $K_2Cr_2O_7$,
I = 1 % Alum

Table 2: Results obtained for using extracted dyes as P^H Indicator

Titrant vs Titrand	Indicator	Colour Start – End point	Value (Mean cm^3)
HCl vs NaOH	Methyl Orange	Yellow – Pink	22.50
	Phenolphthalein	Colourless-Pink	20.20
	Dye extract	Blue – Black	25.0
CH_3COOH vs NaOH	Methyl Orange	Pink –Colourless	23.50
	Phenolphthalein	Pink – Colourless	22.00
	Dyes extract	Blue – Black	25.0
HCl vs NH_4OH	Methyl Orange	Yellow –Pink	23.50
	Phenolphthalein	Purple – Colourless	13.00
	Dyes extract	Blue – Pink	24.00

Table 3 Spectra data of FTIR of the dye extract

S/N	Peak Position (cm^{-1})	Functional group	Class
1.	3472.0	O-H stretching	Alcohol
2.	2939.0	C-H stretching	Alkane
3.	2629.6	O-H stretching	Carboxylic Acid
4.	2130.2	N=C=N stretching	Carbodiimide
5.	1865.5	C-H bending	Aromatic Compound
6.	1701.5	C=O stretching	Conjugated Aldehyde
7.	1522.6	N-O stretching	Nitro Compound
8.	1388.4	C-H bending	Aldehyde
9.	1231.9	C=O stretching	Alkyl Aryl Ether

Discussion

The FTIR results from Fig 1 as presented on Table 1 revealed the lists of the important functional groups identified in the alcoholic extract of the *Tectona grandis* leaves. The results of UV-visible of *Tectona grandis* dye extract are revealed on Figure 2. The peak that appeared in the wavelength transition range of 333.50 – 399.90 nm may be attributed to n- π bond in the compound as a result of the presence of non spectral colours and chromophores.

The color fastness results for light (sun and artificial), rubbing (wet and dry) and washing are presented on Table 1. Mordants were found to have beneficial effects on the fastness properties of the dyed fabrics. The light fastness of mordanted and unmordanted cotton fabric gave a value of 4-5. Higher concentration (2 %) of the mixed mordants produced lower values of light fastness (4) relative to lower concentration (1 %) with a grade of 5. $K_2Cr_2O_7$ mordanted fabrics (irrespective of their concentrations) produced a value of 5 while $CuSO_4$ gave a slightly lower value (4). This may be attributed to the fact that $K_2Cr_2O_7$ bind with more dye molecules than $CuSO_4$ and therefore fade less with light.

Dry rubbing with or without mordants was found to be excellent (5) while wet rubbing showed a range of 3-4 (moderate – very good). Since rub fastness is related to the unfixed dyes deposited on the fibre surface (Avinc *et al.,* 2013), dry rubbing was found to be preferable with dye extract from Teak tree leaves as a result of good fixation of the dye to the fabrics. The ability of the unmordanted dyed fabrics to give a grade value of 5 just as the mordanted dyed fabrics pointed to the affinity of the dye from *Tectona grandis* leaves to fix well the cotton fabrics.

The colour fastness to washing was found to be 1-3 (poor - moderate) in mordanted and unmordanted fabrics. The unmordanted and mixture of mordants at various concentrations (1 % and 2 %) showed comparatively lower wash fastness grades of 1 and 2 respectively. All other mordanted dyed fabrics exhibited an improved wash fastness of 3 (moderate).

The end point of titrimetric analysis using methyl orange, phenolphthalein and dye extracts from *T grandis* as indicators were presented on Table 2. It was revealed that dye extracts *from T. grandis* can be a harmless and easily obtainable replacement to synthetic colourants that have been labelled carcinogenic and embedded with other harmful effects (Nair *et al.,* 2018). Reasonable colour change and suitable end points were obtained for each categories of titration carried out using the extracted dyes which is a pointer to the successful utilization of the extracted dyes as indicator in titrimetry analysis.

Conclusion

Natural colorants were successfully extracted from *Tectona grandis* leaves using 50 % ethanol as solvent. The results of the UV-Vis and FTIR analysis suggest the presence of useful functional groups in the extracted dye component. Fastness properties analysis in terms of light, rub and wash were carried out on the dyed cotton fabrics, the results obtained from these analyses showed that the dyed cotton fabrics showed improved fastness properties and therefore can be used to impart colour on fabrics. The extracted dyes also showed comparative values to synthetic colourants in titrimetry analysis. The results obtained herein indicate that the eco-friendly dyes extracted from *Tectona grandis* leaves could be a useful alternative to synthetic dye in textile industry and other colour related processes.

Conflict of interest

None

Acknowledgement

All researchers and authors whose knowledge were used in this research work are acknowledged.

References

Alabi, K. & Oyeku, T. (2017). The chemical constituents extractable from Teak tree (*Tectona grandis* Linn) obtained from Fountain University, Osogbo. *Nig. Jour. Basic & Appl. Sci*. 25(1):73-80

Ali, S., Hussain, T. & Nawaz, R. (2009). Optimization of alkaline extraction of natural dye from Henna leaves and dyeing of cotton by exhaust method. *Jour. Cleaner Prod*. 17(1): 61-66.

Avinc, O., Celik, A., Gedik, G. & Yavas, A. (2013). Natural dye extraction from waste barks of Turkish red pine (*Pinus brutia* Ten) timber and eco-friendly natural dyeing of various textile fibers. *Fibres & Polymers* 14(5): 866-873.

Chikamai, B. N., Mbinu, S. S. & Casadei, E. (2000). Report on the meeting of the network of natural gum and resins in Africa (NGARA), KEFRI.

FAO (2010). Global forest resources assessment. Country report. United repub;lic of Tanzania. FRA 2010/222. Rome, Italy.

Faroog, A., Ali, S., Abbas, N., Zahoor, N. & Ashraf, M.A. (2013). Optimization of extraction and dyeing parameters for natural dyeing of cotton fabric using Marigold (*Tagetes erecta*). *Asian Jour. Chem*. 25(11): 5955.

Janani, L. (2013. Effects of mordanting methods on dye from *Vernnia amygdalina* on cotton fabrics coloration. *Jour. Lang, Tech. & Entrepre. Africa*. 4(2): 17-27.

Lovric, M., Re, R. D., Vidale, E., Prokofieva, I., Wong, J., Pettenella, D., Verkerk, P. J. & Mavasar, R. (2020). Non-wood forest products in Europe – A quantitative overview. *Forest Policy & Economics*, 116 (2020): 102175.

Mane, A. N., Koli, D. S. & Kumbar, V. B. (2016). Use of *Combretum indicum* flower extract as a natural indicator in acid-base titration. *Int. Jour. Institu. Pharm & Life Sci*. 6(3): 316-324.

Moniruzzaman, M., Mondal, M. S. & Hossain, M. N. (2018). The influence of mordant and mordanting techniques on ecofriendly dyeing of cotton fabric by extracted used tea. *Jour. Eng. Sci.* 9(1): 111-117.

Nair, A., Kelkar, A., Kshirsagar, S., Harekar, A., Satardekar, K., Barve, S. & Kakodkar, S. (2018). Extraction of natural dye from waste flowers of Aster (*Aster chinensis*) and studying its potential application as P^H indicator. *Jour. Innov. Pharma & Biol. Sci*. 5(4): 1-4.

Onuegbu, G., Nnorom. O., Okonkwo, S. N. & Ojiako, P. (2020). Acid-base indicator properties of dye from local plant: The rosella calyces (*Hibiscus sabdariffa*). *Jour. Text. Sci. & Eng*. 10(4): 2020.

Oyeleke, G. O., Abdulazeez, I.A., Adebisi, A. A. & Akinbode, S. O. (2020). Extraction of dyes from Sunflower petal and their fourier transform infrared characterization. *Org. Polym. Mater. Res.* 3(2): 1-6.

Saravanan, P., Chandramohan, G., Saivaraj, S. & Deepa, D. (2013). Extraction and application of ecofriendly natural dye obtained from barks of *Odina wodier* L on cotton fabric. *Jour. Nat. Prod. Plant Resour*. 3(2): 80-85.

Tan, L. C., Perez, M. R. Ibach, M. (1996). Survey on non-timber forest product databases. Center for International Forestry Research (CIFOR) Special Publication.