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Efficacy of *guajavarin* as a coupler in the synthesis of azo dyes and its application on chrome tanned leather

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ABSTRACT

Guajavarin was extracted from guava leaf and successfully used as a coupler in the synthesis of some azo dyes with sulphanilic acid, p-phenylenediamine, diphenylamine and p-anisidine to form a coloured azo dyes exhibiting absorption maxima (λ max) at 480, 640,600 and 500nm for dye A, B, C and D respectively. The synthesis azo dyes are stable for more than two hours. The retention factor (RF value) calculated for the dyes are 0.72, 0.76, 0.78,0.88 and 0.85 respectively which indicates that the molecular weight of the dyes decreases in the order of sulphanilic acid > P- anisidine> diphenylamine> P-phenylenediamine respectively. The fastness properties on chrome tanned leather showed very good fastness indicative of a great potential in future application of these dye in colour technology.

KEYWORDS

Guajavarin;
Sulphanilic acid;
Retention factor;
Colour.

INTRODUCTION

Dyes are organic compounds either in nature or synthesized artificially. A dye is a water soluble molecule, which is taken up by the substrate from a state of molecular solution or dispersion. Dyes can also be said to be an organic colored substance which imparts more or less permanent color to other materials. (Adebayo, 2007). In 1868, Graere and Lieberm Ann observed that all organic dyes then known was decolourized on reduction and they suggested that color must be associated with unsaturation. Kekules, via His brilliant intuition regarding the structure of benzene led to a systematic study of the constitution of the aromatic hydrocarbon and their derivatives. In 1870, kekule coupled diazotized aniline with phenol. The simplicity and vertility of the diazotization and coupling reaction resulted in the preparation of large number of azo dyes.

In 1876, Witt extended this view by pointing out that the colour of organic dye is associated with the presence of a group of colors known as chromophore. These chromophores are unsaturated organic compound containing one or more double or triple bonds. Typical example of chromophore are –N=N-, N=O, C=O, C=C,NO_2 etc Witt gave the name chromogenes to compound containing such groups and showed the next major development was Quinoid theory which also advance that quinoid structure are coloured compound and that compounds or molecules containing one or more quinoid structure are coloured compound but did not attempt to explain why.

Lanch. R, Kokrekre and Kuzel. H, developed the first chrome dyed for wool between 1887 and 1890. These chrome dyes are chrome on fiber after dyeing and resulted in a marked increase in fastness properties expecially to light. The present century opened with outstanding discovery Indanthrene Blue by Boln in 1901 a product of alkali fusion of B-aminoanthraquinone. In 1915,a series of metal complex dye were marked. The development of dye capable of forming a covalent bond cellulose was announced in 1956 by I.C.I. These dyes have greatly improved wash fastness properties and established a new class of reactive dyes (Venkataraman, 1952).

According to (Herman et al 1988), azo dyes are by far the largest of dyes. It account for over 60% of the total number of dye structures known to be manufactured. It include the basic, direct, disperse, reactive dyes etc Azo dyes are further classified depending on the number of azo groups in a dye group into mono azo, diazo, triazo, polyazo dyes according to whether they contain one, two, three, four or more azo groups in the dye molecule.

The history of azo dyes goes back over hundred years. First dye named as Mauve was synthesis accidentally by William Henry Perkin in 1856. He commercialized his accidental innovation and then a new process was developed on large scale for the synthesis of that dye which leads to the beginning of a new chemical industry (Zllinger, 1987). Almost 0.1 million dye are registered or in other word s are available in market on commercial lines. Annual production of dyes from all classes is estimated to be about one million tones (Selvam et al 2003). The present paper developed the efficacy of guajavarin as a coupler in the synthesis of azo dyes and there application on chrome tanned leather.

MATERIAL AND METHOD

Materials

Apparatus/Instruments

Sohxlet extractor, Jenway 6305 Spectrophotometer

Reagent

Distilled water, Chrome tanned leather and Analytical reagent chemicals were used.

Experimental method

Sample collection

The sample was collected in Nigeria Institute of Leather and Science Technology and was taken to Herbarium, Biological Science Laboratory, Faculty of Science of Ahmadu Bello University for identification.

Method of sample preparation

The sample was collected and dried at room temperature to reduce moisture content, after which it was dried in the oven at 110^0C for 15min. It was then grinded using mortal and pestle to fine powder sieved, and kept in a cool dry place.

Extraction of *guaijaverin* from guava leaf (*psidium guava*)

The extraction of *guaijaverin* from guava leaf was carried out using soxhlet extraction method. 300g of the sample was weighed and transferred into the thimble chamber of the apparatus using 700ml of methanol.

The soxhlet extraction was carried out based on the solid liquid extraction, a basic type of continuous extraction. The extracted compound was then isolated from the solvent by using calibrated evaporating dish and heating mantle (Vogel, 1961).

Diazotization of sulphanilic acid

(3.5g of 0.02M) of sulphanilic acid was dissolved in 30ml of NaOH. The solution was cooled in an ice bath. A solution of sodium nitrite (50ml of 1m) and 10ml concentration of HCl was added dropwise with continuous stirring for 30min to form the diazonium salt.

Diazotization of P -phenylenediamine

P-Phenylenediamine (2.2g, 0.02M) was dissolved in 30ml concentration HCl. The mixture was cooled 0-5^{o}C in an ice block, cold solution of sodium nitrite (50ml, 1M) was added drop wise with constant stirring for about 30min to form the diazonium salt.

Diazotization of diphenylamine

Diphenylamine (2.2g, 0.02M) was dissolved in 30ml concentration HCl. The mixture was cooled

0-5^{o}C in an ice block, cold solution of sodium nitrite (50ml, 1M) was added drop wise with constant stirring for about 30min to form the diazonium salt.

Diazotization of P-anisidine

P-Anisidine (2.2g, 0.02M) was dissolved in 30ml concentration HCl. The mixture was cooled 0-5^{o}C in an ice block, cold solution of sodium nitrite (50ml, 1M) was added drop wise with constant stirring for about 30min to form the diazonium salt.

Coupling reaction of the synthesized dye

Coupling between *guaijaverin* extract and sulphanilic acid

50ml of *guaijaverin* extract was added drop wise to the diazonium salt of sulphanilic acid still in the ice bath. The mixture was stirred vigorously for an hour and left overnight.

Coupling between guaijaverin extract and P-phenylenediamine

50ml of *guaijaverin* extract was added drop wise to the diazonium salt of p-phenylenediamine still in the ice bath. The mixture was stirred vigorously for an hour and left overnight.

Coupling between *guaijaverin* extract and diphenylamine

50ml of *guaijaverin* extract was added drop wise to the diazonium salt of diphenylamine still in the ice bath. The mixture was stirred vigorously for an hour and left overnight.

Coupling between *guaijaverin* extract and P-anisidine

50ml of *guaijaverin* extract was added drop wise to the diazonium salt of p-anisidine still in the ice bath. The mixture was stirred vigorously for an hour and left overnight.

CHROMATOGRAPHIC ANALYSIS

Column chromatography

This analysis purifies the dye sample for other chromatographic analysis. 5g of each sample were each weighed into 100ml beaker and dissolved with 60ml methanol followed by stirring.

The dissolved sample was added to the column packed with glass wool, silica gel 60-120 mesh (pack size 500g) and the solvent added. The diluents was collected and concentrated in an evaporating dish using heating mantle at 10^{0}C.

Thin layer chromatography

This analysis is to separate the synthesized dyes into its various colour component. The silica gel was prepared by mixing silica with water, it was stirred to a thickness and coated on a glass plate spreader (0.75MM) and air dried for 30min at 50^{0}C.

The dyed sample were spotted on a line of 4cm from the bottom of the glass plate and 2cm apart and dipped into a thin layer chromatographic tank containing a solvent system of methanol. The solvent font was measured together with the solute distance and the retardation factor (Rf) was calculated using:

Rf= distance moved by the solute spote /distance moved by the solvent

ULTRA VIOLET- VISIBLE SPECTROPHOTOMETRIC ANALYSIS

The Jenway 6305 spectrophotometer was used, the cell to be used for the Uv-visible spectroscopy was washed thoroughly with distilled water. Distilled water was used to calibrate the instrument at the wavelength of 400nm. Thereafter, 0.001g of each dye was diluted with 10ml distilled water and 5ml of the diluted dyes was measured and placed in the cell. The absorbance of the dyes was determined within the visible region of 400-750nm and the wavelength of maximum absorption (λ max) of each dye was extrapolated from the graph.

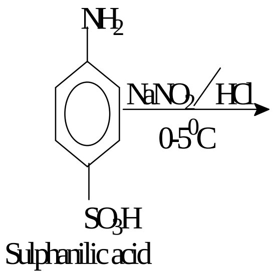
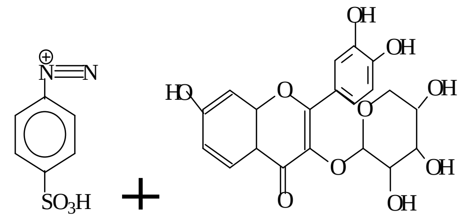
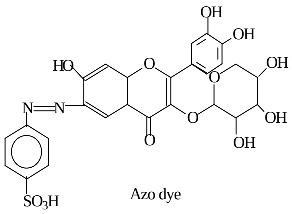
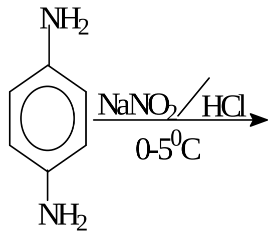
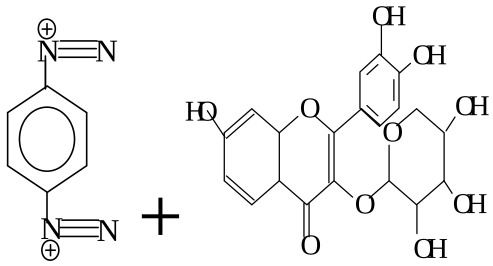
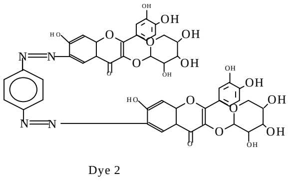
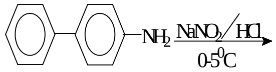
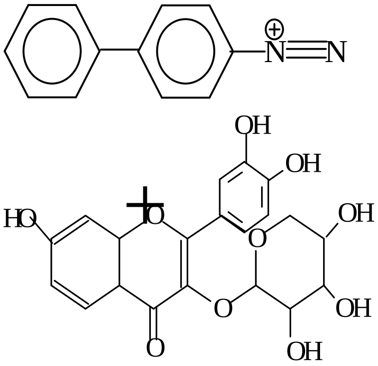
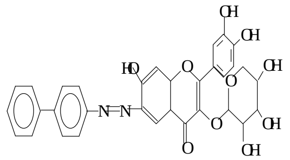
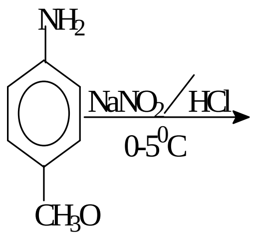
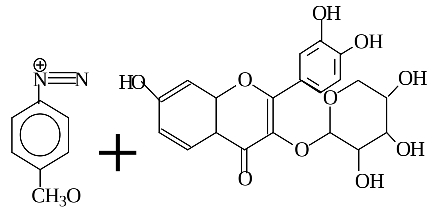
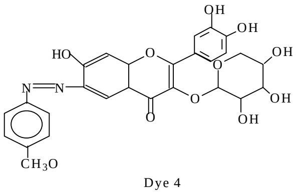
RESULT AND DISCUSSION

Synthesis of dyes

Synthesis of dye A

Dye A was synthesized by the diazotization of sulphanilic acid and then coupling it with *guaijavarin* extract. The reaction involves two steps: First is the diazotization of sulphanilic acid and then

TABLE 1 : Reaction scheme

S/NO	Diazotization Reaction	Coupling Reaction	Dyes
1.			
2.			
3.			
4.			

followed by coupling reactions.

Synthesis of dye B

Dye B was synthesized by the diazotization of P- Phenylenediamine acid and then coupling it with *guaijavarin* extract. The reaction involves two steps: First is the diazotization of p-phenylenediamine and then followed by coupling reactions.

Synthesis of dye C

Dye C was synthesized by the diazotization of diphenylamine and then coupling it with *guaijavarin* extract. The reaction involves two steps: First is the diazotization of p-phenylenediamin and then followed by coupling reactions.

Synthesis of dye D

Dye D was synthesized by the diazotization of p-anisidine and then coupling it with *guaijavarin* extract. The reaction involves two steps: first is the diazotization of P- anisidine and then followed by

TABLE 2 : Characteristic of the synthesized dyes

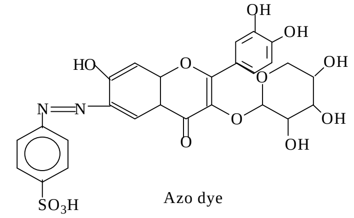
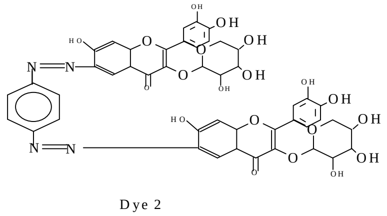
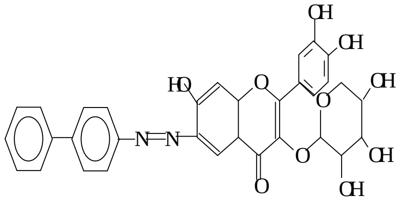
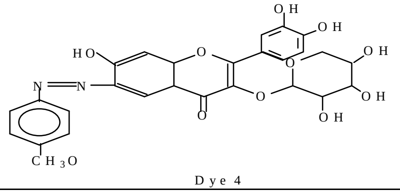
S/NO	Dye structures	Dye names	Melting points (^{0}C)	TLC	RF value	Recrystallization solvent	Appearance
1.	 Azo dye	Dye A	161	Two spot	0.72, 0.76	Water	Maroon
2.	 Dye 2	Dye B	156	One spot	0.78	Water	Orange
3.		Dye C	159	One spot	0.88	Water	Reddish brown
4.	 Dye 4	Dye D	157	One spot	0.85	water	Purple

TABLE 3 : Fastness properties of dyed chrome tanned leather

Dye name	Light fastness	Wash fastness	Acid fastness	Alkaline fastness	Rub fastness
Dye A	4	3	4	4	4
Dye B	4	4	4	3	3
Dye C	3	3	4	4	4
Dye D	4	4	4	3	3

Key: 1 = Poor 2 = Fair 3 = Good; 4 = V – good 5 = Excellent

coupling. The reactions pathway is shown below.

Temperature for the solvent used in the synthesis of the dye varies from 0-5^0 depending upon the stability of the diazonium salt. Diazotization involves the attack of a nitrosonium ion, NO$^+$,on the free aromatic amine. Coupling generally involves an electrophilic attacks by the diazonium ion on a highly nucleophilic centre in the coupling component, a position of high electron density. Coupling takes place at the carbon atom ortho or para to NH$_2$ or OH groups, with para coupling predominating.

Characterization of the synthesized dyes

The table below represents the general characterization of the synthesized dyes comprising of the structures. It also comprises of the melting point, the thin layer chromatographic separation of the dyes and the color appearance of the dye.

The close similarities in the range of the melting point of the synthesized dyes can be accounted for by the backbone symmetry which is *guaijavarin* (100- 200). This shows that the dye melts as the backbone melts.

Thin layer chromatography

The thin layer chromatography was carried out

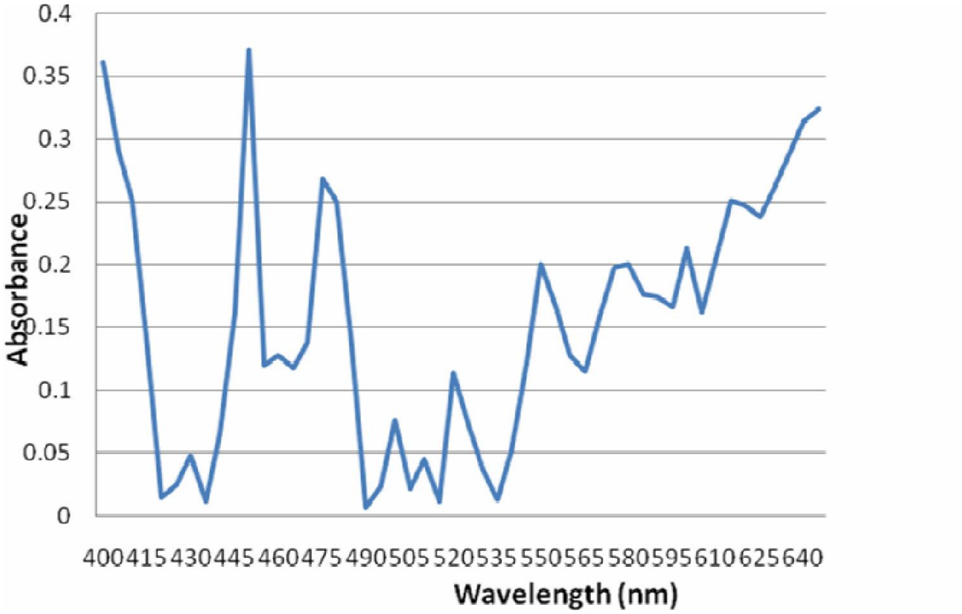


Fig. 1: UV/Visible Spectroscopy of purified methanol extract

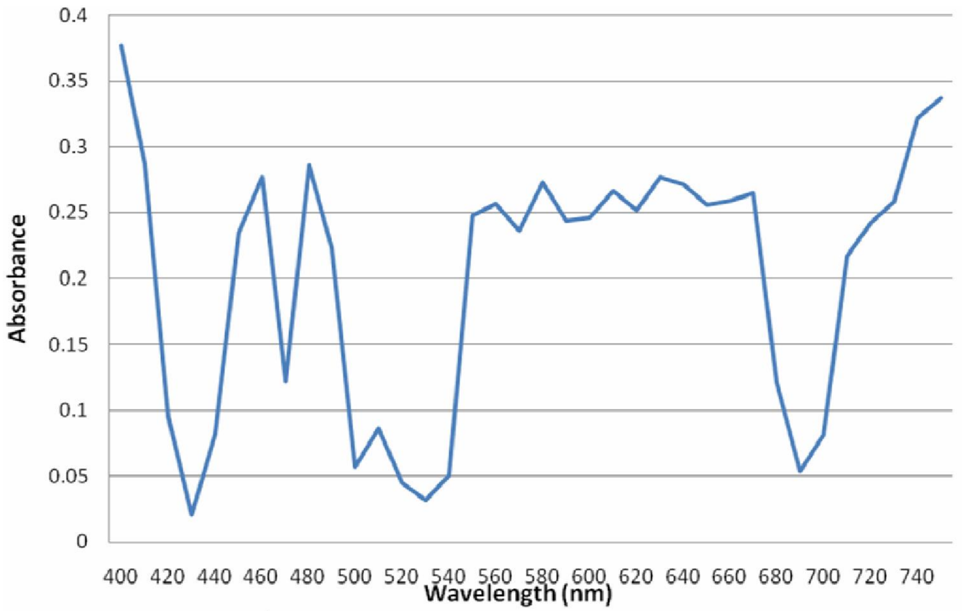


Fig 2: UV/Visible Spectroscopy of Sulphanilic Acid and guajaverin Extract

to analyze the dye synthesized. Some showed one spot indicating that there were no impurities in the dye, while some showed two spot due to the presence of impurities. The dye synthesized from the diazonium salt of p-sulphanilic acid showed two spot for thin layer chromatography (TLC) which makes it to be impure and gives a pink color dye. The other synthesized dye showed one spot for TLC which implies that the dyes are pure with different characteristics color such as yellow colour dye from the diazonium salt of p-phenylenediamine, reddish brown color dye from the diazonium salt of p-anisidine and brown color dye from the diazonium salt of diphenylamine with *guaijavarin* as a coupler respectively as represented in TABLE 1 the heavier the dye, the less the distance moved and the more the adherent to the substrate or the absorbent. The retention factor (RF value) of each dye was calculated using the equation below:

$$\text{RF value} = \frac{\text{Distance moved by dye}}{\text{The dye front}}$$

The retention factor (Rf value) calculated for the

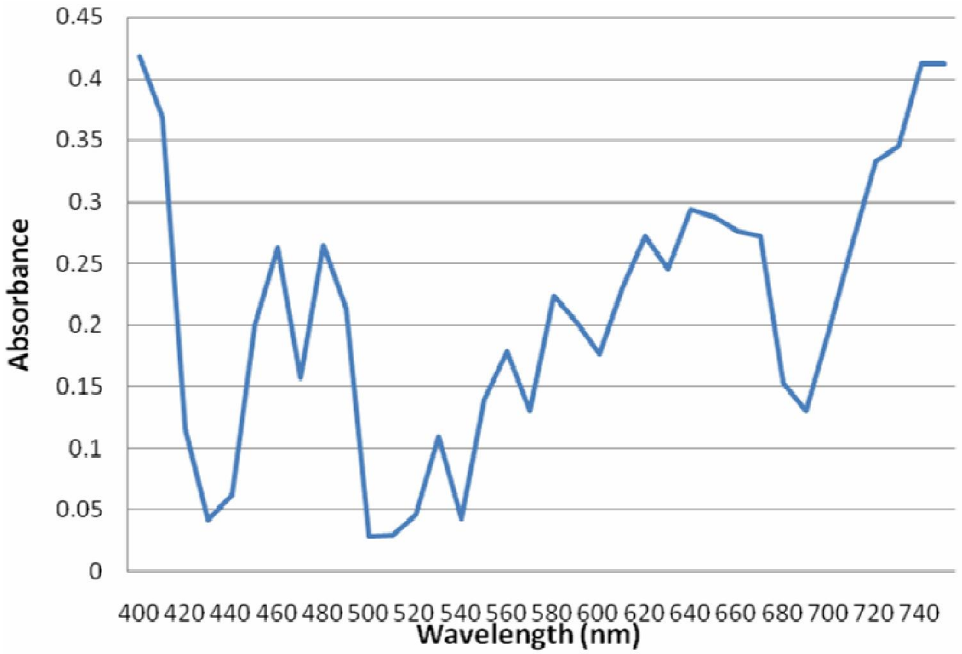


Fig. 3: UV/Visible Spectrum for P-phenylenediamine

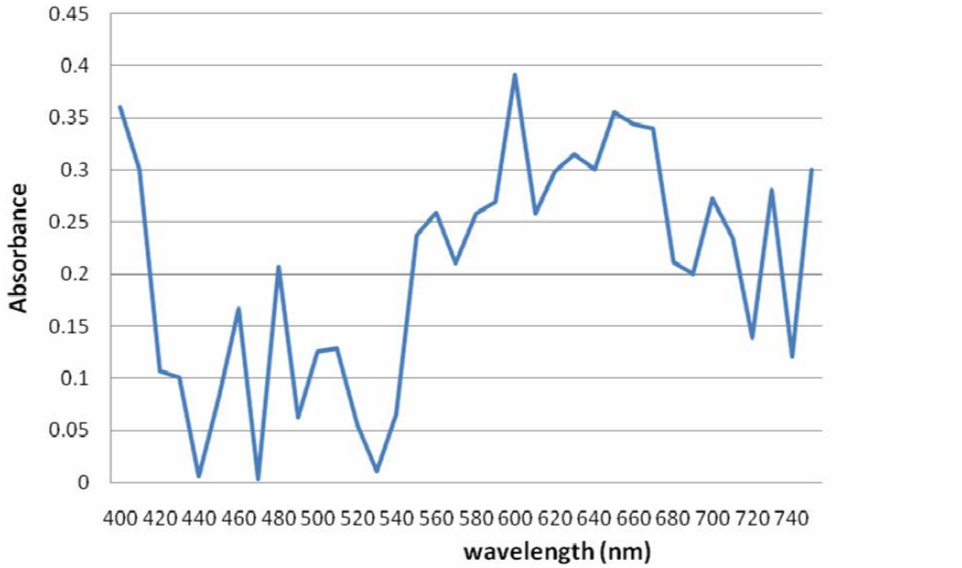


Fig 4: UV/Visible Spectroscopy of Diphenylamine and guajaverin extract

dye synthesized from sulphanilic acid, p-phenylenediamine, diphenylamine and p-anisidine as the diazo component with bisphenol serving as the coupling component with *guaijaverin* serving as the coupling agent are 0.71, 0.75, 0.84, 0.86 and 0.89 respectively which indicate that the molecular weight of the dyes decrease in order of sulphanilic acid > diphenylamine > P- anisidine > P-phenylenediamine respectively.

Fastness properties of the synthesized dyes on chrome tanned leather

The table below gives the results of the fastness properties of dyed leather with the synthesized dyes to external agencies. This comprises of the light fastness, wash fastness, acid fastness, rub fastness and alkaline fastness of the synthesized dyes respectively. The fastness property ranges from good to very good for each dyed leather material indicate by the grey scale 3 and 4 respectively. This can be attributed to photostability and affinity effect of the dyed.

Ultraviolet/visible spectroscopy of synthesized dyes

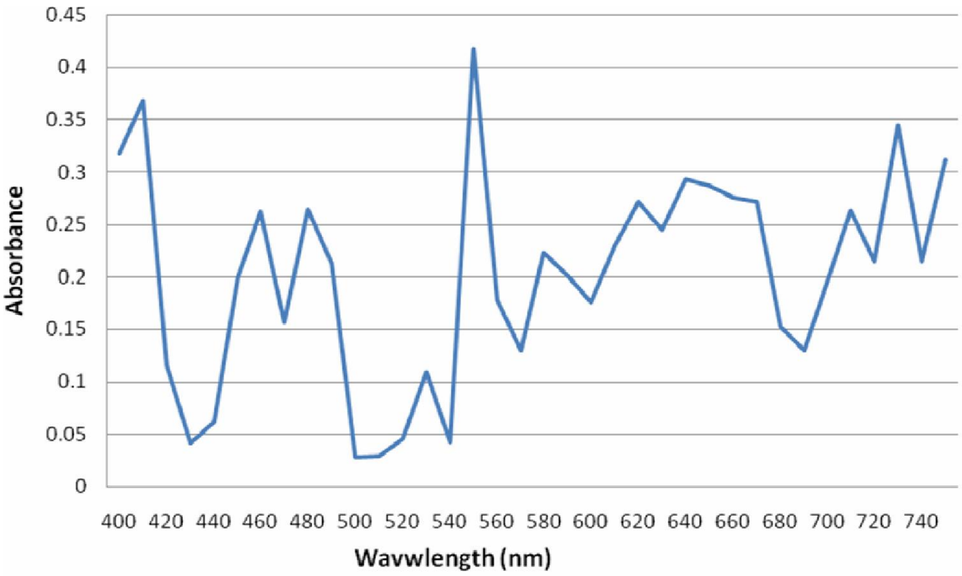


Fig. 4.5: UV/Visible Spectroscopy of P-anisidine and guajaverin extract

The ultra- violet and regions of the spectrum are used to determine the molecule present in the sample. From the result obtained in Figure 1, 2, 3 and 4 respectively, the plot of absorbance against wavelength, shows that the compounds are conjugated and are colored because of their λmax (nm), and their absorption in the visible region above 400.00nm of the electromagnetic spectrum. The result obtained from the Ultraviolet/Visible spectroscopy of the dyes indicates that Dye A absorb at the λmax 480nm, Dye B absorbs at the λmax 640nm, Dye C absorb at the λmax 600nm and Dye D absorbs at the λmax 550nm respectively. The multiplicity of the λmax (nm) indicates that the mixtures of color of closely related compounds may be present in the synthesized dye products, Dudley et al, (1935).

CONCLUSION

Guajaverin was use as a coupler in the synthesis of some azo dyes with different aromatic amines such as sulphanilic acid P-phenylenediamine, diphenylamine and P-anisidine serving as dye azo component. The synthesized dye posses different visible absorption properties that span the visible spectrum. Thus, the wave lengths of maximum absorptions are 480,640, 600 and 550nm respectively for dye 1, 2, 3 and 4. The light, wash, rub, acid and alkaline fastness for the dye on chrome tanned leather ranges from good to very good indicative of the potential of these dyes for the colouration of leather.

Recommendation

Further work should be done on the following areas;

- IR (Infra-red) spectrophotometric characterization of the dye stuff.
- NMR (Nuclear Magnetic Resonance) spectrometric characterization of the dye stuff.
- Mass spectrometry characterization to the dye stuff.
- Application of the dyes on fabric such as wool, cotton, nylon and acrylic fibers.
- Commercialization of these dyes.

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