

# Synthesis and Application of Azo Dyes Derived From the Methanolic Extract of *Cissus Populnea* as the Coupling Component on Nylon 6, 6

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**Abstract:** Three different dyes derived from the methanolic extract of *Cissus populnea* as the coupling component with Sulphanilic acid, 4-aminophenol and 4-chloroaniline was successfully synthesized. The identity of the plant extract and dyes were investigated using spectroscopic analysis such as UV-visible spectrometry and Fourier Transform Infra-red Spectrometry. The dyes absorbed within the visible region of the electromagnetic spectrum DMSO, methanol and acetone but the UV-visible of the dyes in DMSO was more bathochromic with wavelength range of 605-607 nm as compared to that of methanol (498-500 nm) and acetone (397-403 nm). The infra-red spectra of the extract and dyes confirmed the presence of chromophores such as OH, C=O, N-H, -C-H, C=C and N=N in the dyes, which account for the colored nature of the extract and dyes. The dyes gave brown shades on nylon 6, 6 and exhibited good to very good fastness properties on the dyed fabric. For wash fastness, it was between 3 (good) and 4 (very good), while for light fastness it was between 6 (good) and 4 (moderate).

**Keywords:** Azo dyes, Nylon 6, 6, Fastness Properties, Diazotization and coupling.

## I. INTRODUCTION

The art and science of dyes began more than 10,000 years ago. The very first dyes may have been crude components made from plants mixed with water by early uncivilized man for the purpose of tribal rituals, to identify or differentiate class of status group or simply amuse children with colours (Shore, 1990).

Dyes from natural resources especially from plants are increasingly becoming important alternatives to synthetic dyes for use in the textile industry (Samanta *et al.*, 2007). Unlike synthetic dyes which have been found to be toxic and harmful to the environment, natural dyes are biodegradable, non-toxic and generally have higher compatibility with the environment when comparable to synthetic counterparts. The use of non-allergic, non-toxic, eco-friendly and biodegradable natural coupling components in dye synthesis has become a matter of importance. Thus synthetic dyes however produce skin allergy, toxic wastes and other harmfulness to humans and environment and therefore there is need to synthesize dyes that are less toxic, biodegradable and with good colouristic properties by using a natural coupling component (Ozan, 2011).

Some synthetic dyes are toxic to humans and not biodegradable. Therefore, the need to synthesize eco-friendly dyes by incorporating natural couplers from plant origin into the synthetic process in order to reduce the toxicity and harms they cause to humans and to make it biodegradable becomes of paramount importance.

## II. MATERIALS AND METHODS

### 2.1 Materials

Acetone, sodium nitrite, sulphanilic acid, hydrochloric acid, acetone, acetic acid, DMSO, methanol, ethanol, 4-aminophenol, 4-chloroaniline, distilled water, ice block, sodium chloride, textile material (Nylon 6, 6), *Cissus populnea* leaves sample.

### 2.2 Apparatus

Agilent CARY 300 UV-visible spectrophotometer, Agilent CARY 630 FT-IR, Electric Oven, beakers, round bottom flask, 250ml volumetric flasks, Buchner flask, hot plate, steam bath, sample bottles, thermometer, pH meter, heating mantle, magnetic stirrer, electronic balance, Gallenkamp melting point apparatus.

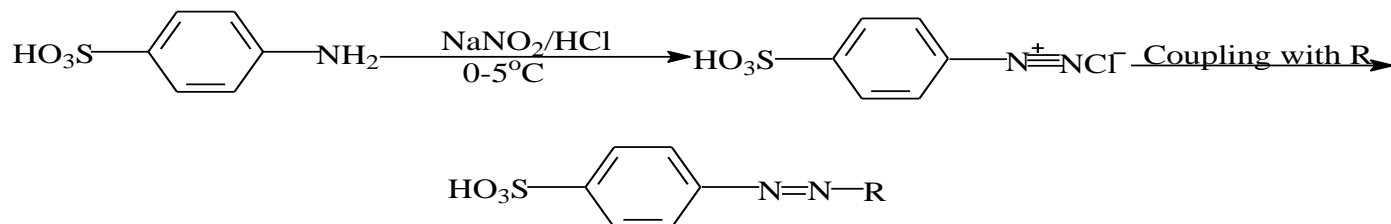
### 2.3 Collection and Preparation of the Plant Sample

The leaves of *Cissus populnea* was harvested from a farm in Olamobora local government area in Kogi state and kept in a clean polythene bag; it was then transported to the Department of Biological Science of Ahmadu Bello University, Zaria for identification. The plant leaf was air dried and grinded into fine powder using mortar and pestle and kept in an air tight container with proper labeling for later use.

### 2.4 Diazotization of the Amines

#### 2.4.1 Diazotization of Sulphanilic Acid

Sulphanilic acid (2.5 g of 0.02 M) was dissolved in 30ml sodium hydroxide. The temperature of the mixture was cooled in ice bath. Cold solution of sodium nitrite (50 ml of 1 M) and concentrated hydrochloric acid (10 ml) was added drop wise with continuous stirring for 30 minutes to form the diazonium salt solution. The reaction scheme is as given below;

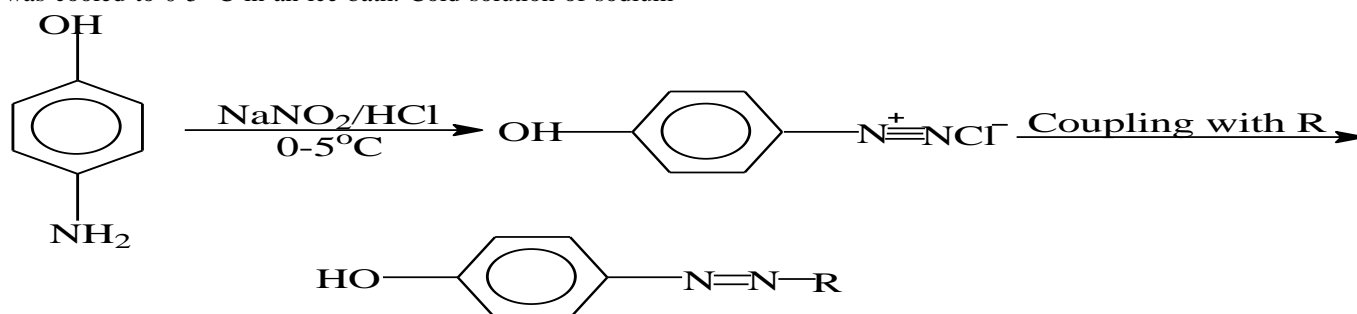


Scheme 2.1: Diazotization and coupling reaction of Sulphanilic acid and plant extract

#### 2.4.2 Diazotization of 4-Aminophenol

4-aminophenol (2.5 g of 0.02 M) was weighed and dissolved in 30 ml sodium hydroxide. The temperature of the mixture was cooled to 0-5 °C in an ice bath. Cold solution of sodium

nitrate (50 ml of 1 M) and dilute hydrochloric acid were added drop wise to the mixture with constant stirring for 30 minutes to form the diazonium salt. The reaction scheme is as given below;

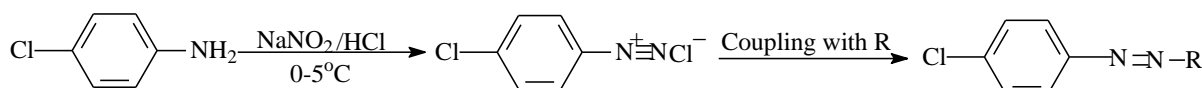


Scheme 2.2: Diazotization and coupling reaction of 4-Aminophenol and plant extract.

#### 2.4.3 Diazotization of 4-chloroaniline

4-chloroaniline (2.5 g of 0.02 M) was weighed and dissolved in 30 ml concentrated hydrochloric acid in a water bath. The temperature of the mixture was cooled to 0-5 °C in an ice

bath. Cold solution of sodium nitrate (50 ml of 1 M) and dilute hydrochloric acid were added drop wise to the mixture with constant stirring for 30 minutes to form the diazonium salt. The reaction scheme is as given below;



Scheme 2.3: Diazotization and coupling reaction of 4-chloroaniline and plant extract.

Where R represent Coupling component (i.e. plant extract) for each reaction scheme.

#### 2.5 Preparation of Coupler

Plant extract (0.5 g) was weighed and dissolved in 20 ml 10 % sodium hydroxide solution at a temperature of 0-5 °C in an ice bath with constant stirring until it was completely dissolved.

#### 2.6 Coupling and Synthesis of Dye

The solution of the coupler was added drop wise to the diazonium salt of sulphanilic acid, 4-aminophenol and 4-chloroaniline within 30 minutes in an ice bath with continuous stirring for another additional 1 hour and left overnight. The solution of the dye sample was then filtered and air dried. The dye was purified using re-crystallization method from ethanol as the solvent.

#### 2.7 Percentage Yield of Dyes and Intermediates

The percentage yield of the synthesized dyes and intermediates were determined using the formula as shown below:

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

#### 2.8 Characterization of the Synthesized Dyes and Plant Extract

##### 2.8.1 Determination of Melting Point

The melting point of the dyes and the plant extract were determined by using Gallenkamp melting point apparatus.

##### 2.8.2 FT-IR Determination

FT-IR spectra of the plant extract and dyes were recorded on Agilent Technologies CARY 630 FT-IR spectrophotometer.

##### 2.8.3 Determination of Visible Absorption Spectra

The visible absorption spectra of the dyes were recorded on a CARY 300 UV-VISIBLE spectrophotometer from dye solutions in DMSO and methanol at a concentration of  $1.5 \times 10^{-5}$  mol/l as described by Yuh and Wei (2006).

## 2.9 Dyeing Procedures

### 2.9.1 Preparation of Dye Bath Liquor

Stock solution (1 %) of each dye was prepared with a liquor ratio of 50:1. 2 % shade on weight of the fabric (o. w. f) and 0.5 g of Nylon 6, 6 was used. The volume required from each stock solution will be calculated based on the formula below (Maradiya, 2010);

$$V = \frac{P \times W}{c}$$

Where:

P = percentage shade

W = weight of fabric

C = percentage concentration of stock solution

### 2.9.2 Dyeing of Substrate (Nylon 6, 6)

The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the dye bath at 40 °C and was allowed to reach the boil within 15 minutes. Dyeing was carried out for one hour at a temperature of 100 °C with constant agitation. At the end of the dyeing process, the dyed substrate was removed, squeezed and rinsed thoroughly under running tap water and allowed to dry at room temperature (Nkeonye, 1987).

## 2.10 Assessment of the Fastness Properties of Dyed Textile Material

### 2.10.1 Wash Fastness Test

The dyed sample was subjected to wash fastness test by the following procedures: The specimen was prepared by cutting the dyed fibre into 5 cm × 2 cm dimensions; it was then made into composites by stitching the tests specimen made of the dyed sample placed in between white cottons of dimension 10cm×4cm. The composite will be agitated in the solution made up of the following (Nkeonye, 1987):

Soap solution 5 g/l

Sodium carbonate 2 g/l

Liquor ratio 50:1

The washing was maintained at 50°C for 45 minutes with continuous agitation. At the end of the washing test, the composite specimen was removed, rinsed in running tap water and the components were separated and dried at room temperature. The change in colour of the dyed sample and the staining of adjacent on dyed cloths were assessed using the appropriate grey scale.

### 2.10.2 Light Fastness Test

The dyed sample was exposed facing due south and inclined at an angle of the horizontal approximately equal to latitude of the place where the exposure is being made. Adequate ventilation of the sample during exposure will be ensured. The partly covered sample was exposed to UV radiation. Exposure

proceeded for 3 days then the samples under test were examined at intervals and the changes in colour of the samples were compared visually with the changes that occur in the standard. The light fastness of the sample is the number of the standard that will show a similar visual contrast between the expose and unexposed part of the sample. The exposure will be terminated when the exposed and unexposed test sample is equivalent to grade 3 on the grey scale (Sakomaet *al.*, 2012).

## III. RESULT

### 3.1 Physical Properties of the Plant Extract and Synthesized Dyes

The physical properties of the plant extract and synthesized dyes are shown in Table below;

Table 3.1: Physical Properties of Plant Extract and Synthesized Dyes

S/N	Sample	Melting Point	%yield	Appearance
1	Plant extract	231.8	20.5	Dark brown
2	Dye 1	240.4	68.8	yellow
3	Dye 2	228.7	56.3	yellow
4	Dye 3	197.2	54.8	yellow

Where: Dye 1 is dye from Sulphanilic acid

Dye 2 is dye from 4-aminophenol

Dye 3 is dye from 4-chloroaniline

### 3.2 Visible Absorption Spectroscopy of Dye

The visible absorption spectra of the dyes were measured in DMSO, methanol and acetone as presented in Table below;

Table 3.2: Visible Absorption Spectroscopy of Dyes

Dye No.	DMSO	Methanol
Dye 1	605.00	498.00
Dye 2	605.00	499.00
Dye 3	607.00	500.00

### 3.3 Infra-Red Spectra of the Plant Extract and Dyes

The FT-IR peaks observed with their corresponding groups for both the plant extract and dyes is as shown in the table below;

Table 3.3: Infra-Red Spectra of the plant extract and dyes

Extract/Dyes	Vibrational frequencies (cm <sup>-1</sup> )
Plant extract	3306.4 (OH Stretch), 2970.7, 2922.2 (C-H Stretch), 1718.3, 1632.6 (C=O Stretch), 1509.6 (C=C Stretch)
Dye 1	3377.0 (N-H- Stretch), 2922.0, 2855 (C-H Stretch), 1707, 1640 (C=O Stretch), 1509.0, 1453.7 (-N=N- Stretch).
Dye 2	3302.4 (OH Stretch), 2926.0, 2855.1 (C-H Stretch), 1699.7, 1628.0, 1602.8 (C=O Stretch), 1509.0 (-N=N- Stretch)
Dye 3	3283.8 (N-H Stretch), 2922.2 (C-H Stretch), 1586.4 (-N=N- Stretch).

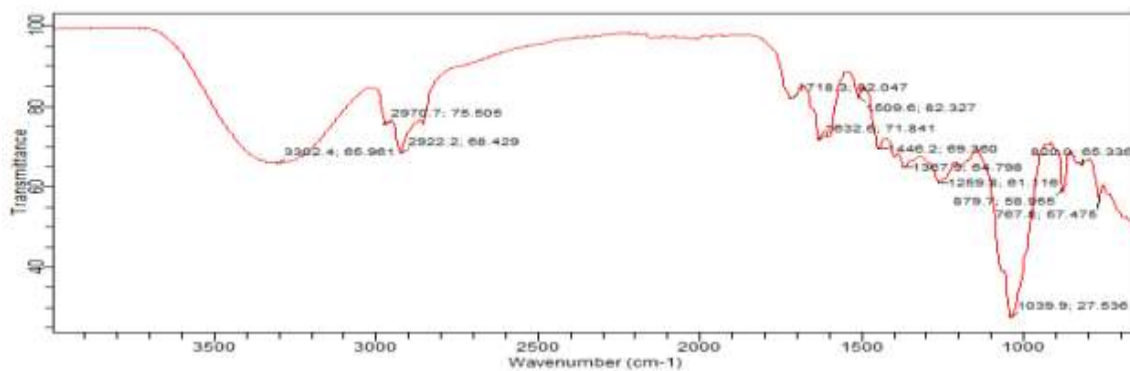


Fig. 3.7: FT-IR Chart of the methanolic extract of *Cissus populnea*

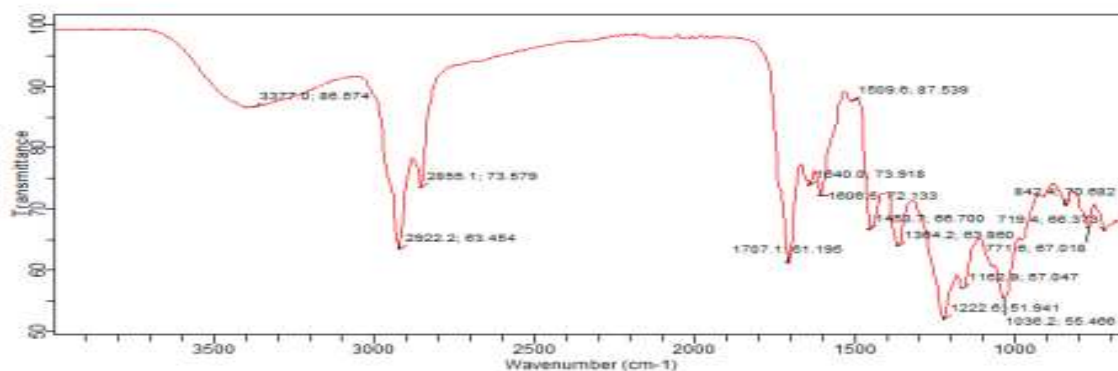


Fig. 3.8: FT-IR Chart of Dye 1

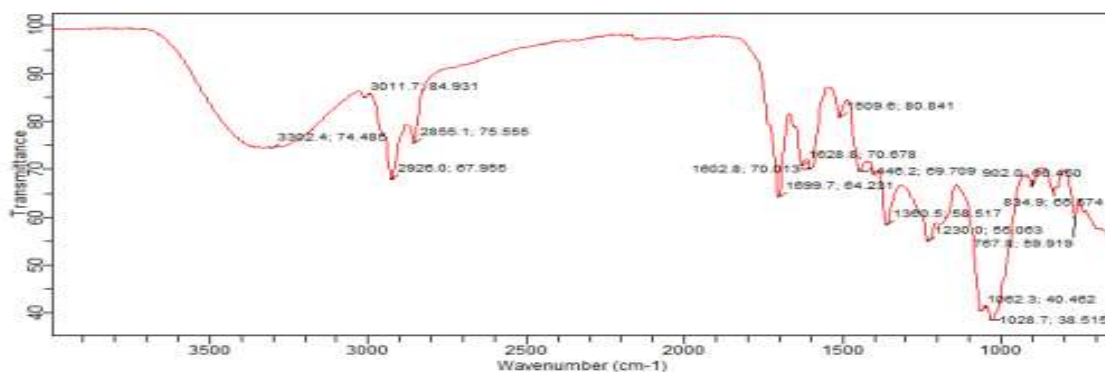


Fig. 3.9: FT-IR Chart of Dye 2

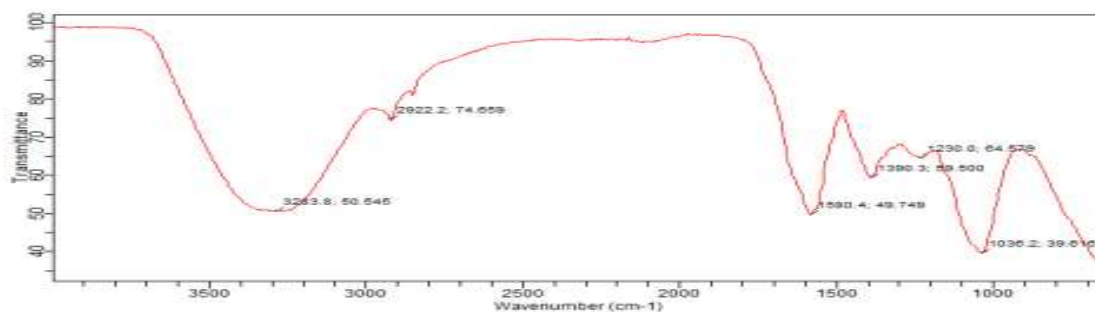


Fig. 3.10: FT-IR Chart of Dye 3

### 3.4 Assessment of Fastness Properties to Washing and Light

The resistance of dyed materials to laundry treatment such as washing is referred to as washing fastness. The washing fastness test is considered very useful since dyed fabrics are subjected to various washing conditions during use. The general procedure recommended by the International Standard Organization, number 3 (ISO 3) for wash fastness and 8-Blue Wool standards for light fastness were adopted and the results are shown in Tables below.

Table 3.4: Wash Fastness of the Synthesized Dyes Using ISO 3 Standards.

Dye Sample	Change in Colour on Nylon 6, 6	Staining of Adjacent Fabric	Colour on Fabric
Dye 1	3	3	Light Yellow
Dye 2	4	3-4	Light Yellow
Dye 3	4	4	Dark Yellow

Change in shade	Staining
5 = Excellent	5 = no staining
4 = Very good	4 = very slight staining
3 = Good	3 = moderate staining
2 = fair	2 = significant staining
1 = poor	1 = deep staining

Table 3.5: Light Fastness of the Dyes on Nylon 6, 6 fabrics using 8-Blue Standard

Dye Samples		Nylon 6, 6	
Dye 1		5	
Dye 2		4	
Dye 3		6	
Fastness grade	Degree of fading	Fastness grade	Degree of fading
8	None	4	Appreciable
7	Very slight	3	Significant
6	Slight	2	Extensive
5	Moderate	1	Very extensive

## IV. DISCUSSION AND CONCLUSION

### 4.1 Discussion

#### 4.1.1 Physical Properties of the Plant Extract and Synthesized Dyes

The melting point, percentage yield and the appearance of the extract and dyes are presented in Table 3.1. The extract was granular and appeared dark brown in colour while the dyes were crystalline in nature with color ranges from light yellow to dark yellow. The percentage yield of the extract was reasonably encouraging (20.5%) when compared with the economic value of the raw material. The average percentage yields for the dyes were more than 50% which is high as compared to that of pure natural dyes.

All the extracted dyestuff exhibited fairly well-defined melting points characteristics of a pure compound as shown in Table 2.1 above ranging from 197.2-240.4°C.

#### 4.1.2 Visible Absorption Spectroscopy of Dye

Table 3.2 shows the  $\lambda_{max}$  (Wavelength of maximum absorption) of the dyes obtained in different solvents. All the dyes showed strong and broad absorption in the visible region, which shows the presence of colour imparting chromophores which are responsible for the hues. Hue is the predominant colour transmitted by an organic compound when the complementary colour contained in the light passing it has been absorbed (Griffith, 1984). The wavelength of the dyes ranges from 605 to 607 nm in DMSO and 498 to 500 nm in methanol, which from literature corresponds to the complementary colours of yellows, green, purple, violet, and blue as recorded by Griffiths, 1984. It can be observed that the UV-visible of the dyes recorded in DMSO has the highest wavelength of maximum absorptions which makes the dyes to be more bathochromic as compared to methanol. This means that the higher the polarity of the solvent, the more the bathochromic shift in the wavelength of maximum absorption (Venkatarama, 1978).

#### 4.1.3 Infra-Red Spectra of the Plant Extract and Dyes

The results of the infra-red analysis carried out on the plant extract and dyes are shown in Table 3.3. The plant extract had peak that appeared at frequency of 3306.4  $\text{cm}^{-1}$  indicating the presence of O-H, H-bonded stretch of the alcohols, phenols compounds. The peak that appeared at frequency of 2970.7 and 2922.2  $\text{cm}^{-1}$  indicated the presence of C-H symmetrical stretch of the alkane compounds. The peak that appeared at frequency of 1718.3 and 1632.6  $\text{cm}^{-1}$  indicated the presence of C=O stretch of aliphatic, beta-unsaturated esters while the peak that appeared at frequency of 1509.6  $\text{cm}^{-1}$  indicated the presence of C=C asymmetric stretch of carbonyl compounds.

The Dye 1 had peak that appeared at frequency of 3377.0  $\text{cm}^{-1}$  which indicated the presence of N-H stretch of the primary, secondary amino, amides. The peak that appeared at frequency of 2922.0 and 2855.0  $\text{cm}^{-1}$  indicated the presence of C-H symmetrical stretch of the alkane compounds. The peaks that appear at frequency of 1707.0 and 1640.0 correspond to C=O stretch of aliphatic, beta-unsaturated esters while the peaks that appeared at frequency range of 1509.0 and 1453.7 indicates the presence of an azo chromophoric group (N=N-).

The dye 2 had peak that appeared at frequency of 3302.4  $\text{cm}^{-1}$  indicating the presence of O-H, H-bonded stretch of the alcohols, phenols compounds. The peak that appeared at frequency 3011.0  $\text{cm}^{-1}$  indicated the presence of C-H stretch of the alkene compounds. The peak that appeared at frequency of 2926.0 and 2855.1  $\text{cm}^{-1}$  indicated the presence of C-H symmetrical stretch of the alkanes. The peak that appeared at frequency of 1699.3, 1628.0 and 1602.8  $\text{cm}^{-1}$  indicated the presence of C=O stretch of aliphatic, beta-unsaturated aldehydes while the peak that appeared at frequency range of 1509.0  $\text{cm}^{-1}$  indicated the presence of -N=N-.

The dye 3 had peak which appeared at frequency of 3283.8  $\text{cm}^{-1}$  which indicates the presence of N-H stretch of the

primary, secondary amino, amides. The peak that appeared at frequency  $2922.2\text{ cm}^{-1}$  indicated the presence of C-H stretch of the alkane compounds while the peak that appeared at frequency of  $1586.4\text{ cm}^{-1}$  indicated the presence of -N=N- of azo chromophores.

#### 4.1.4: Wash Fastness of Dyed Substrates Using ISO 3 Standards.

The wash fastness of the dyed Nylon 6, 6 fabrics is presented in Table 3.4 and the result comprises of the change in color on the fabric and staining of adjacent fabric. These dyes gave deep yellow to light yellow hues with brighter and deeper shades, high tectorial strength and excellent levelness on the fabric. The variation in the shade of the dyed Nylon 6, 6 results from the alteration in the diazo components. Thus from Table 3.4, dyes 2 and 3 exhibited very good fastness to washing on the fabric while acid dye 1 showed fair to good fastness to washing. The remarkable degree of levelness and brightness after washing (grey scale 4) indicate good penetration and excellent affinity of the dyes to the fibres. In addition, the result obtained showed that the dyed nylon fabric with Dye 2 and 3 have very good fastness level (grey scale 4) to washing as compared to the dye 1 (with grey scale 3), which may be due to the presence of solubilising group, which affect solubility and washing ability of the dye-out of the dyed substrate (Lan, *et al.*, 2000; Abrahart, 1977).

#### 4.1.5: Light Fastness of the Dyes on Nylon 6, 6 using 8-Blue Wool Standards.

The light fastness ratings of the dyed nylon 6, 6 are presented Table 3.5 and the results indicate moderate to very good light fastness. However, the light fastness observed for the dyes ranges from 4-6 which could be ascribed to the coupling components used, molecular structure of the dyes, planarity and dye substituents from the diazo components that provided shield from radiant energy on azo chromophores, and which conferred good light fastness properties on the dyed substrate (Sakoma *et al.*, 2012).

## 4.2 Conclusion

An eco-friendly dyes that are biodegradable and less toxic were synthesized using methanolic extract of *Cissus populnea* as the coupling components along with Sulphanilic acid, 4-aminophenol and 4-chloroaniline as the diazo components were synthesized. The dyes were yellow, the melting points ranges from  $197.2 - 240.4\text{ }^{\circ}\text{C}$ . The percentage yield of the plant extract and the synthesized dyes were also calculated. The dyes absorption varies in the level of bathochromicity based on the degree of polarity of the solvents used. From the UV-

visible spectra, the dyes with the DMSO were more bathochromic, followed by methanol to acetone.

The infra-red spectra of the extracts confirmed the presence of chromophores such as C=O, N-H, -C-H, C=C and N=N in the dyes, which account for the colored nature of the extract and dyes. The results obtained showed that the extract is aromatic in nature with groups such as hydroxyl group (OH) in the phenolic group, but the number and the position of the hydroxyl groups present in the extracts could not be established. The dyed nylon 6, 6 showed very good fastness to washing and moderate to good light fastness properties. The remarkable degree of levelness after washing indicates good penetration and affinity of these dyes on nylon 6, 6.

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