



Synthesis, Characterization, Antimicrobial Activity and Dyeing Potential on Leather using Bromamine-Derived Anthraquinone Acid Dyes

¹Ajani Olayinka Oyewale, ²Kasali Ademola Bello, ¹Martha Bamidele Omotola and ^{1*}AbdulRazaq Tukur

¹Department of Chemistry, Ahmadu Bello University Zaria, Kaduna State, Nigeria

²Department of Polymer and Textile Engineering, Ahmadu Bello University Zaria, Kaduna State, Nigeria

*Correspondence Email: abdulrazaqtukur@gmail.com

ABSTRACT

Three different anthraquinone acid dyes were synthesized by condensation of bromamine acid with *p*-acetamido aniline, *p*-aminophenylacetic acid and *p*-benzaldehyde to obtain two blue and one green crystalline solid dyes. The synthesized dyes were fully characterized using UV-Visible, FT-IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques. The results of the antimicrobial screening of the dyes as indicated by the zone of inhibition (ZOI) showed that, all the synthesized dyes have significant activities against the test microbes compared to the standard drugs used, except *Candida albicans* which was resistant against all the synthesized dyes. The result of minimum inhibitory concentration (MIC) showed that, at concentrations of 100µg/ml and 50 µg/ml of dyes I and II, the growth of *Escherichia coli* and *Salmonella typhi* were inhibited, while for dye III, 25 µg/ml was the minimum concentration required to inhibit the growth of *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli*. Furthermore, investigating the minimum bactericidal concentration (MBC) showed that, at a lower concentration of 25 µg/ml of dye III *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* were killed compared to 50 µg/ml of dyes I and II required to completely kill *Bacillus subtilis*, *Salmonella typhi* and *Staphylococcus aureus*. The results for dyeing and fastness properties on leather showed that, the synthesized dyes gave excellent homogeneity of coloration on leather. A remarkable degree of evenness indicates good penetration and affinity of these dyes to fabrics. Thus, the synthesized dyes possess excellent light and washing fastness rating of 6 and 4 hence, gave good dyeing on leather.

Keywords: Anti-microbial, Bathochromic, Bromamine, Dye, Fastness, Spectroscopy

INTRODUCTION

Dyes are complex unsaturated aromatic compounds accomplishing characteristics like colour, intensity, solubility, fastness (Zhang *et al.*, 2018). Dyes are intensely coloured organic compounds used in imparting suitable colours to various substrates such as foods, drugs, cosmetics, papers, plastics, waxes, leathers, textiles, photographs among others (Marini *et al.*, 2018). Acid anthraquinone dyes are one of the most important classes of acid dyes being principally used for green, blue or violet shades having excellent light and wet fastness. One important group of such dyes are those obtained by condensation of bromamine acid with 1, 2, 4-triazole by an Ullmann reaction catalyzed by copper salt. This condensed amine is diazotized and coupled with various coupling components. This group of the acid dyes has important usage valuematerial (Sharma *et al.*, 2016).

Acid dyes have found wide applications in dyeing wool, polyamide fibres and blends of both fibress but they meet very high requirements as regards to their application and fastness. The characteristics chromophore of the anthraquinone

series consists of one or more carbonyl groups in association with a conjugated system (Zollinger, 1991). The more important are acid, direct moderant, vat, solvent and reactive dyes even as pigments. As a class, anthraquinone acid dyes are known for their specific colour and high light fastness characteristics. Anthraquinone acid dyes provide a number of bright fast to light blue and green colours, which are neither available among the azo dyes nor in fact equaled by any other class of dyes. The colour of anthraquinone dyes depends upon substitution among definite lines (Choi *et al.*, 2013, Taman *et al.*, 2019).

In addition to their known use as natural dyes, several biological activities have been described in the literature for these compounds (Malik and Muller 2016), among which are; antitumor (Huang *et al.*, 2007, Chien *et al.*, 2015), anti-inflammatory (Chien *et al.*, 2015, Khan *et al.*, 2011), diuretic (Chien *et al.*, 2015), antiarthritic (Davis *et al.*, 1986), antifungal (Wuthi-udomlert *et al.*, 2010), antibacterial (Fosso *et al.*, 2012), antimalarial (Winter *et al.*, 1996), and antioxidant activities (Dave and Ledwami 2012). In addition, anthraquinones have laxative activity, which is

found mainly in physcion, chrysophanol, aloemodin, and rhein. Physcion is one of the most important representatives with laxative activity. This characteristic is attributed to the presence of hydroxyls at the C-1 and C-8 positions of the anthraquinone ring (Simo-es *et al.*, 2007). These anthraquinones, in addition to catenarin, are the more common isolated from natural sources (Duval *et al.*, 2016, Seigler 2012). This family of compounds has been known for a long time as there are ancient reports of the use of plants containing the anthraquinone alizarin as dye and food for humans and animals in Egypt, Persia, and India (Simo-es *et al.*, 2007).

This study was aimed to synthesize, characterize some anthraquinone acid dyes by the condensation reaction of bromamine acid with *p*-acetamidoaniline, *p*-aminophenylacetic acid and *p*-aminobenzaldehyde. Consequently study their antimicrobial activities as well as dyeing properties on leather.

MATERIALS AND METHODS

General Procedure

All reagents and solvents were purchased from Sigma-Aldrich (Germany) and used as purchased without further purification. Thin-layer chromatography was performed using precoated silica gel 60 (F254) from MERCK (Germany). Spots on the TLC plates were visualized under UV light (254 nm and 366 nm) and by heating with 10 % H₂SO₄ acid in MeOH. The melting point was recorded using a Gallenkamp melting point apparatus. The maximum absorption wave length of synthesized dyes was determined in ethanol using Agilent CARY 300 UV - visible Spectrophotometer in the visible region between 400 – 800 nm using a glass cell of 1cm path length. The molar extinction co-efficient (Molar absorption) of the synthesized dyes was calculated at each dye absorption maximum (λ max) using the relation: $\epsilon = \frac{A}{cl}$, Where ϵ = molar extinction co-efficient (Mol⁻¹ cm⁻¹): A = Absorbance: C = concentration in (mole/litre): and l = path length of cell. The infrared spectra of the solid products were recorded on a Perkin Elmer spectrum 100 FTIR spectrometer using ATR sampling accessory. ¹H and ¹³C-NMR spectra were recorded using Bruker Avance III 400MHz spectrometer at room temperature (400MHz for ¹H and 100MHz for ¹³C), using TMS as reference. Chemical shift values (δ) were reported in parts per million (ppm) relative to TMS and coupling constants are given in Hz. The solvent used for these measurements was deuterated DMSO. Multiplicities are given as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), and multiplet (m). The percentage yield of the dyes was obtained using equation 1 below:

$$\%Yield = \frac{Mass\ of\ product}{Mass\ of\ reactant} \times 100 \quad \text{--- (1)}$$

General Procedure for the Synthesis of Dyes I, II and III

Exactly 100 cm³ of distilled water was added to dissolve the mixture of bromamine acid (0.00465 mol, 1.88 g), *p*-acetamidoaniline (0.00466 mol, 2.21 g), copper (I) chloride (0.00505 mol, 0.5 g) and sodium carbonate (0.113 mol, 12 g) in a round bottom flask and stirred, the mixture was refluxed (80 - 90 °C) with continuous stirring for 3 hours. After cooling, a precipitate was formed which was later filtered under suction, washed with 12.5 cm³ conc. HCl, and dried at 60 °C to afford dye I as a blue crystalline solid (Olagboye *et al.*, 2013). Dye II was synthesized from bromamine acid (0.0047 mol, 1.88 g) and *p*-aminophenylacetic acid (0.00465 mol, 2.21 g) using the same procedure as for dye I to obtain a blue crystalline solid (Olagboye *et al.*, 2013). While dye III was also synthesized from bromamine acid (0.00466 mol, 1.88 g) and *p*-aminobenzaldehyde (0.00466 mol, 2.21 g) using the same procedure as for dye I to obtain a green crystalline solid (Olagboye *et al.*, 2013).

ANTIMICROBIAL SCREENING

Pathogenic Organisms Used

The test compounds were evaluated on *Candida albicans*, *Salmonella typhi*, *Escherichia coli*, *Staphylococcus aureus* and *Bacillus subtilis*. obtained from the Department of Microbiology, Ahmadu Bello University Zaria, Nigeria.

Antimicrobial Susceptibility Test

The cork and bore diffusion method as reported by Karou *et al.* (2006) was used to determine the antimicrobial activities of the test compounds. Pure cultures of the organism were inoculated on to Mueller Hinton Agar (MERCK) and incubated for 24 h at 38 °C for bacteria and 48 h at 34 °C for fungi. About 5 discrete colonies were aseptically transferred using sterile wire loops into tubes containing sterile normal saline (0.85 % NaCl) and were adjusted to a turbidity of 0.5 McFarland Standard. The suspensions were then inoculated on the surface of sterile Mueller-Hinton Agar plates using sterile cotton swabs. A sterile 6 mm diameter cork borer was used to make holes (wells) into the set of inoculated Mueller-Hinton Agar. The wells were filled with different concentration of the test compounds. The plates were then incubated, all the tests were performed in triplicate and the antimicrobial activities were determined as mean diameter of inhibition zone (mm) produced by the test compounds.

Minimum Inhibitory Concentration (MIC)

The MIC was determined for the compounds using micro broth dilution method in accordance with the National Committee for Clinical Laboratory Standard (CLSI, 2019). Serial dilution of the least concentration of the compounds that showed activity was prepared

using test tubes containing 9 ml of double strength nutrient broth (OXOID). The test tubes were inoculated with the suspension of the standardized inoculum and incubated at 38 °C for 24 h. The MICs were recorded as the lowest concentration of the compounds showing no visible growth (turbidity) in the broth.

Minimum Bactericidal and Minimum Fungicidal Concentrations (MBC and MFC)

The MBC and MFC were determined by aseptically inoculating aliquots of culture, from the minimum inhibition concentration (MIC) tubes that showed no growth, on sterile nutrient agar (OXOID) plates incubated at 38 °C for bacteria and 34 °C for fungi for 48 hr. The MBC and MFC were recorded as the lowest concentration of compounds showing no bacterial/fungal growth at all.

Dyeing of leather

A solution of each dye sample (2 % w/v) was prepared with 50 cm³ distilled water and the mixture was heated using a heating mantle at 60 °C. The pH of the dyeing bath was adjusted to 5.5 with 0.1N formic acid. The leather samples were introduced into the bath and run for 1 hour in a mechanical shaker at a controlled speed of 6 r/min, 7 r/min, 6 r/min for dyes I, II and III respectively.

RESULTS AND DISCUSSION

1-amino-4-(acetamidoaniline) anthraquinone-2-sodium sulphate (Dye I)

Blue crystalline solid, 88 % yield, Melting point 400 °C – 505 °C. ¹H-NMR- (600MHz, DMSO – d₆) δ ppm -2.03 (1H,d, J = 10.2, NH), 2.08 (3H,s,CH₃),7.24 (1H,d, J = 12, H-12),7.47 (1H, d, J = 8.3, H-2),7.86(1H, s, H-13), 7.95 (1H, s, H-1), 8.29 (1H, s, H-9),10.09 (2H, s, NH₂),12.08 (1H, s, NH). ¹³C-NMR - (400 MHz, DMSO – d₆) δ ppm - 24.43 (CH₃),109(C-16), 111.18(C-15),120.59 (C-14), 123.04 (C-8), 124.65 (C-6),126.37 (C-5),126.49 (C-4),133.20 (C-3),133.50 (C-12),134.10 (C-2),134.29 (C-1),134.60 (C-13), 136.94 (C-9), 142.17 (C-7), 143.31 (C-11), 144.67 (C-10), 168.60

(C=O), 182.50 (C=O), 183.27 (C=O). UV analysis λ_{max}(EtOH)/nm 228 (ε/dm³mol⁻¹ cm⁻¹ 40 900) - 624. IR (ν cm⁻¹) – 1650 (C=O),1665 (C=O), 1670 (C=O), 3295 (Ar C-H), 3350 (N-H), 3403 (N-H).

1-amino-4-(aminophenylacetic) anthraquinone-2-sodium sulphate (Dye II)

Blue crystalline solid, 86 % yield, Melting point 420 °C - 425 °C. ¹H-NMR - (600MHz, DMSO – d₆) δ ppm - 7.57 (1H, d, J = 18, H-2), 7.86 (1H,d, J = 9.2, H-1),10.14 (2H, s, NH₂),12.08 (1H, s, NH), 12.21 (1H,d, J = 16, COOH). ¹³C-NMR - (400 MHz, DMSO – d₆) δ ppm – 110.00 (C-16), 120.10 (C-15),120.59 (C-14),124.55 (C-8), 126.27 (C-6),126.39 (C-5),133.15 (C-4),133.49 (C -3),134.15 (C-12),134.32 (C-2),134.50 (C-13),134.57 (C-1),136.92 (C-9), 142.27 (C-7), 143.30 (C-11), 144.47 (C-10), 168.61 (COOH), 180.10 (C=O), 181.1 (C=O).UV analysis λ_{max}(EtOH)/nm 228 (ε/dm³ mol⁻¹cm⁻¹ 40 900)- 626. IR (ν cm⁻¹) = 1682 (C=O), 1685 (C=O), 3158 (N-H),3258 (ArC-H), 3423 (OH).

1-amino-4-(aminobenzaldehyde) anthraquinone-2-sodium sulphate(Dye III)

Green crystalline solid,60 % yield, Melting point 410 °C– 413°C. ¹H-NMR - (600MHz, DMSO – d₆) δ ppm – 6.67 (1H, d, J = 8.6, H-19), 6.68 (1H, s, H-18), 7.05 (1H, d, J = 12, H-11), 7.72 (1H, s, H-12), 7.73 (1H, s, H-20), 7.85 (1H, s, H-5), 7.88 (1H, d, J = 10.5, H-6), 7.90 (1H, s, H-4), 10.14 (2H, s, NH₂), 12.01 (1H,d, J = 14,CHO),12.08 (1H, s, NH). ¹³C-NMR - (400 MHz, DMSO – d₆) δ ppm – 112.25 (C-7), 116.00 (C-8), 118.20 (C-19), 119.00 (C-18), 121.89 (C-11), 124.93 (C-12), 126.02 (C-3), 126.03 (C-4), 131.00 (C-20), 131.02 (C-21), 131.03 (C-22), 133.00 (C-2), 133.60 (C-1), 133.80 (C-5), 134.00 (C-6), 138.60 (C-14), 146.00 (C-13), 181.20 (C=O), 182.32 (C=O), 190.21 (CHO). UV analysis λ_{max}(log ε) - 740. IR (νcm⁻¹) - 1386 (Ar C-N),1319(Ar C-N), 1670 (C=O), 2903 (ArC=H), 3753 (N-H).

Table 1: Characteristic Properties of the Synthesized Dyes.

Dye/Colour	Melting Point (°C)	Molecular Weight (g/mol)	Wavelength in Ethanol (nm)	Molar extinction co-efficient in (DMF) X 10 ⁴ (L/mol cm ⁻¹)
I (Blue)	400- 405	400- 405	624	5.727
II (Blue)	420- 425	420- 425	626	5.672
III (Green)	410- 413	410- 413	740	6.227

Table 2: Antimicrobial activity showing the diameter of the zone of inhibition (ZOI) (mm) at varying concentrations ($\mu\text{g/ml}$)

Test Organisms	Dye I				Sp		Fl		Dye II				Sp		Fl		Dye III				Sp		Fl	
	100	50	25	12.5	100	100	100	50	25	12.5	100	100	100	50	25	12.5	100	100	100	50	25	12.5	100	100
<i>S. aureus</i>	17	14	12	0	30	0	14	12	0	0	30	0	19	15	13	0	32	0						
<i>B. Subtilis</i>	21	18	14	0	32	0	22	19	12	0	32	0	24	17	14	12	33	0						
<i>E. Coli</i>	12	14	9	0	33	0	14	12	10	0	32	0	17	14	12	0	34	0						
<i>S. typhi</i>	13	14	10	0	34	0	13	11	0	0	33	0	18	16	0	0	35	0						
<i>C. albicans</i>	0	0	0	0	0	32	0	0	0	0	0	33	0	0	0	0	0	32						

Key: Sp = Sparfloxacin, Fl = Fluconazole, mm = millimeter

Table 3: Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal and Fungicidal Concentrations

Test Organisms	MIC ($\mu\text{g/ml}$)			MBC/MFC ($\mu\text{g/ml}$)		
	Dye I	Dye II	Dye III	Dye I	Dye II	Dye III
<i>S. aureus</i>	50	50	25	100	100	50
<i>B. Subtilis</i>	25	25	25	50	50	50
<i>E. Coli</i>	100	100	25	0	0	50
<i>S. typhi</i>	100	100	50	0	0	25
<i>C. albicans</i>	ND	ND	ND	ND	ND	ND

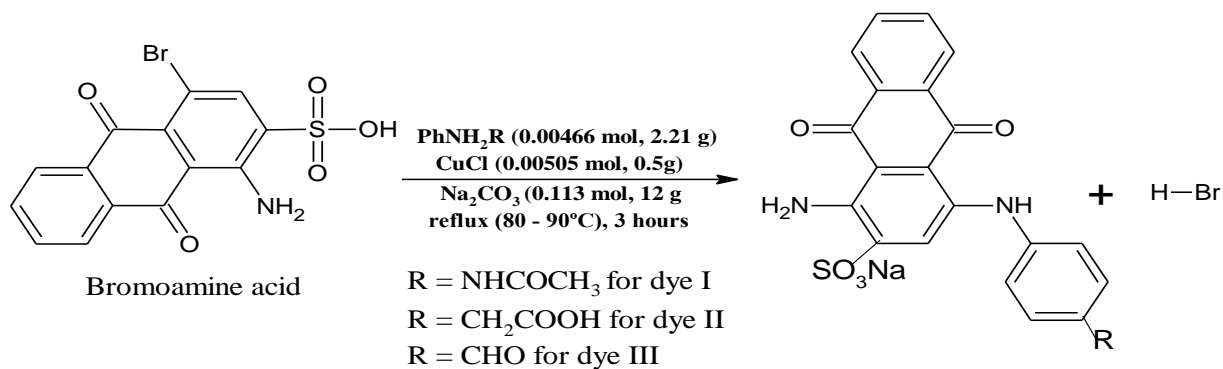
Key: ND = Not determined

Table 4: Results of Dying Fastness Properties

Type of fastness	Dye I	Dye II	Dye III	Bromamine
16 Revolution	5	5	5	4
32 Revolution	5	5	4	4
64 Revolution	5	4	4	3
128 Revolution	4	4	4	3
256 Revolution	4	4	4	3
512 Revolution	4	4	4	3
Light Fastness	5	5	5	3
Wash fastness	4	4	4	2

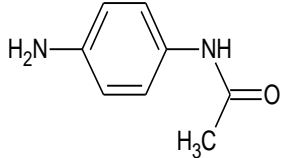
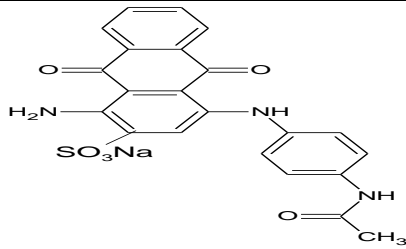
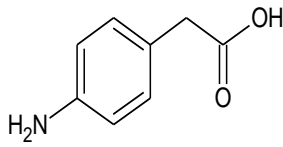
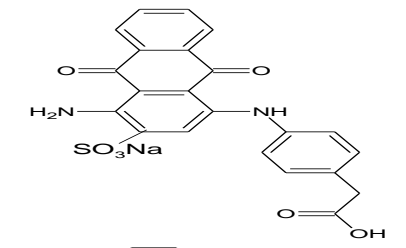
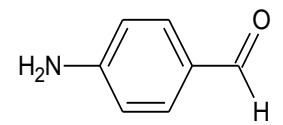
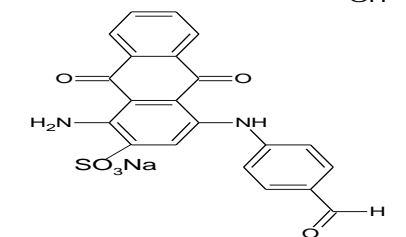
Light: Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7

Wash and Rubbing: Poor-1, Slight-2, Moderate-3, Fair-4, Good-5, Very good-6 and Excellent-7



SCHEME 1: Preparation of Dyes I, II & III

Table 5: The Synthesized Compounds and their Percentage yield (%)

Dyes	Amine(s)	Product(s)	Percentage yield (%)
I			88
II			86
III			60

Chemistry

The synthetic approach involved a nucleophilic substitution reaction, where bromine atom was displaced from bromamine acid and the hydrogen of the amine reacted with the bromine to produce desired products and gave out hydrogen bromide gas. The maximum wavelength (λ_{\max}) (Figures 1, 2 and 3) for absorption of the

synthesized dyes I, II and III were found to be 624 nm, 626 nm and 740 nm respectively signifying that the hue of the dyes was bathochromically shifted. For instance, Dye III ($\lambda_{\max} = 740$) is more bathochromically shifted than dye I and II. Due to its highest wavelength, which is the characteristic of its highly conjugated structure.

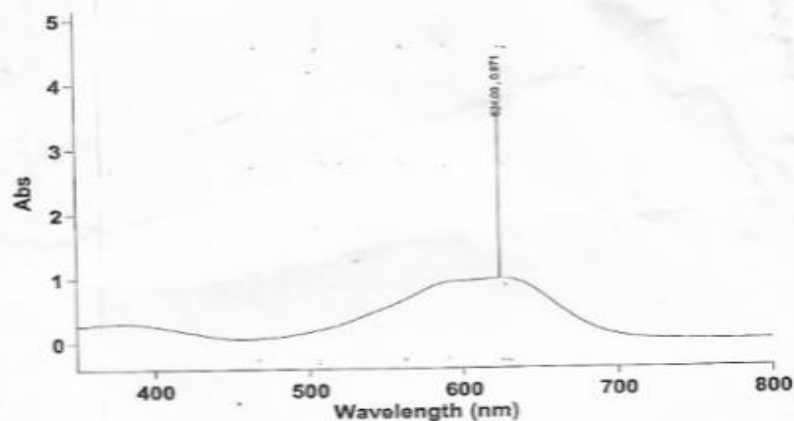


Figure 1: UV spectrum of DYE I

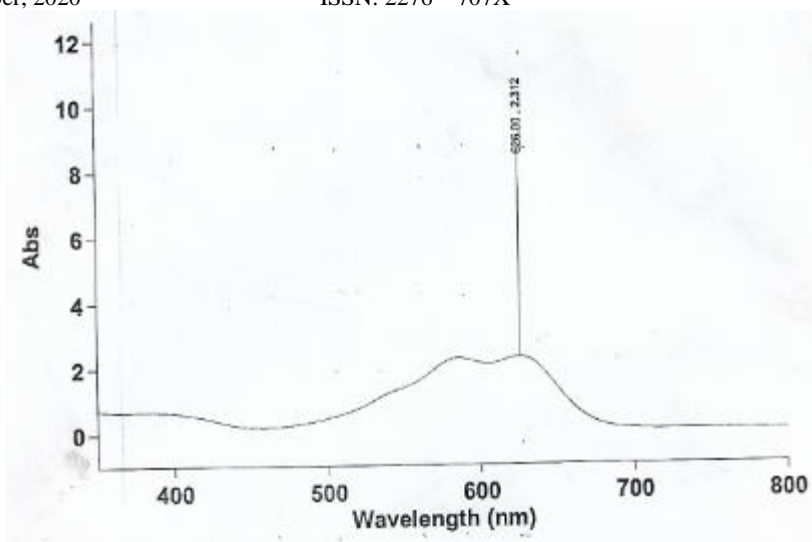


Figure 2: UV spectrum of DYE II

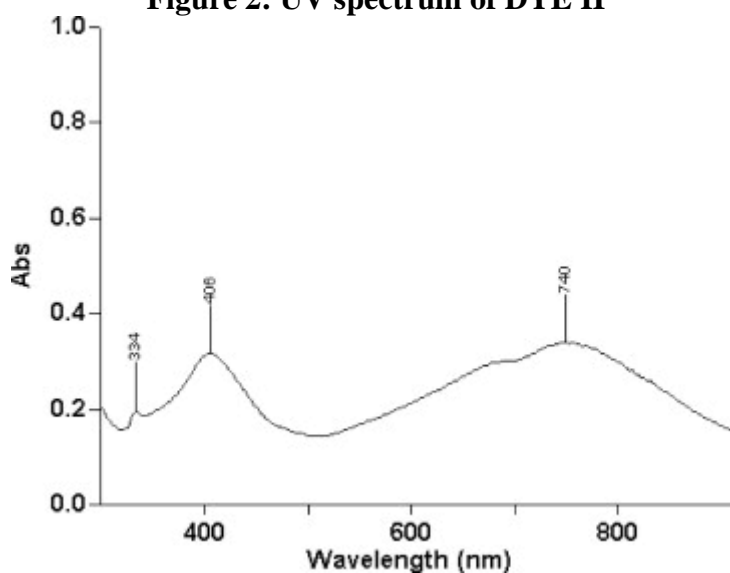


Figure 3: UV spectrum of DYE III

The infrared spectra of dyes I, II and III (Figures 4, 5 and 6) showed that bands at 3421cm^{-1} is indicative of the O-H stretching. While the carbonyl C=O stretching vibration bands were observed at 1682cm^{-1} and 1666cm^{-1} . The band at

$1200\text{cm}^{-1} - 1386\text{cm}^{-1}$ indicated secondary C-N stretching vibration formed after condensation of bromamine with the amino groups.

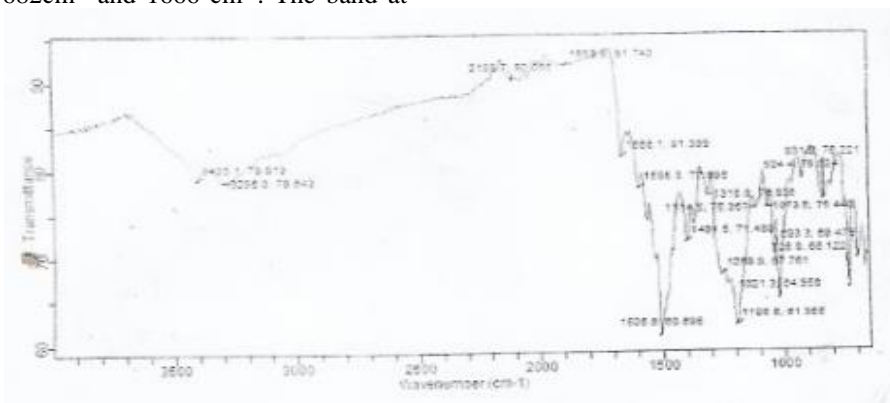


Figure 4: FTIR spectrum of DYE I

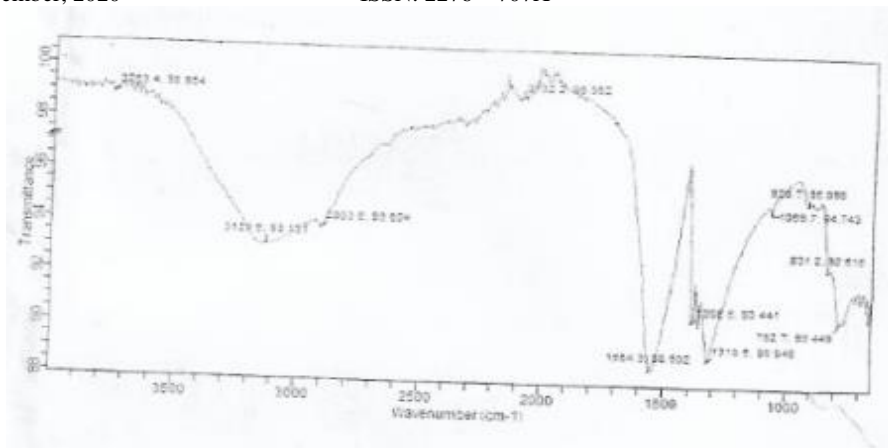


Figure 5: FTIR spectrum of DYE II

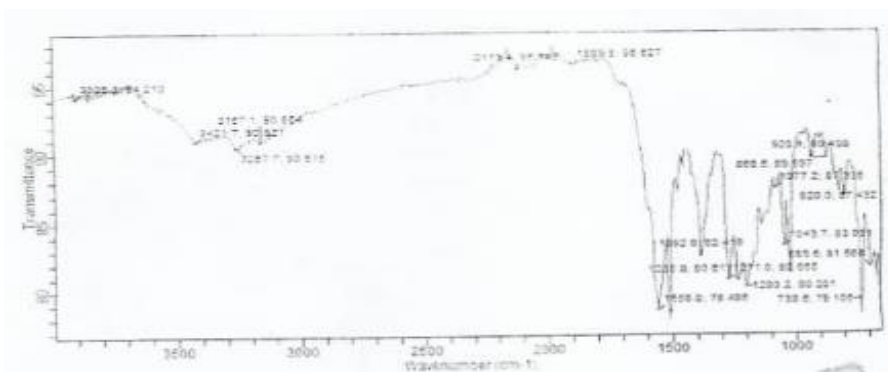


Figure 6: FTIR spectrum of DYE III

The bands between 3257 cm^{-1} and 3403 cm^{-1} are attributed to the stretching absorption of aromatic N-H group. The data obtained from the UV-Vis and FTIR analyses is in agreement with the data reported by Lavinia *et al.* (2007) and Navin and Ashok (2009). Due to the presence of conjugated double bonds, anthraquinones absorb wavelengths in the visible spectrum and in the ultraviolet (UV) region, having, for example, maximum absorptions (λ_{max}) between $430 - 554\text{ nm}$, and characteristic of anthraquinone chromophores. The infrared (IR) spectra of these types of compounds present intense bands between 1630 cm^{-1} and 1700 cm^{-1} characteristic of the chelated carbonyl group of quinones. These absorptions differ from the carbonyl group of ketones, esters, and carboxylic acids, whose absorptions are usually reported above 1700 cm^{-1} (Gaspar Diaz-Mun *et al.*, 2018). Since the synthesis

involved substitution reaction, the $-\text{NH}_2$ group would have displaced bromine present in bromamine to form a new secondary N-H bond.

The ^{13}C -NMR spectrum of dye I (Figure 7) showed 22 recognizable carbon atoms, indicating 9 methine carbons, 1 methyl carbon and 12 quaternary carbons, including carboxylic carbons. Also, the ^{13}C -NMR spectrum of dye II (Figure 8), indicated 22 carbon atoms, in which, 9 are methine carbons, 1 methylene and 12 quaternary carbons. Whereas the ^{13}C -NMR spectrum of dye III (Figure 9) showed the presence of 21 different carbon atoms, indicating 9 methine carbons and 12 quaternary carbons, including the carboxylic carbons. It has been found that the Carbon-Nitrogen bond resonated at 147.17 ppm and 147.27 ppm . According to (Gaspar Diaz-Mun *et al.*, 2018).

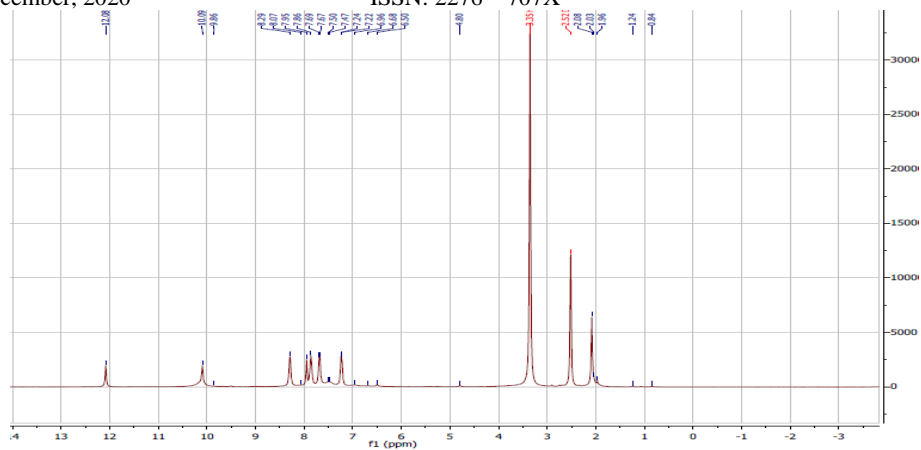


Figure 10: ¹H NMR spectrum of DYE I

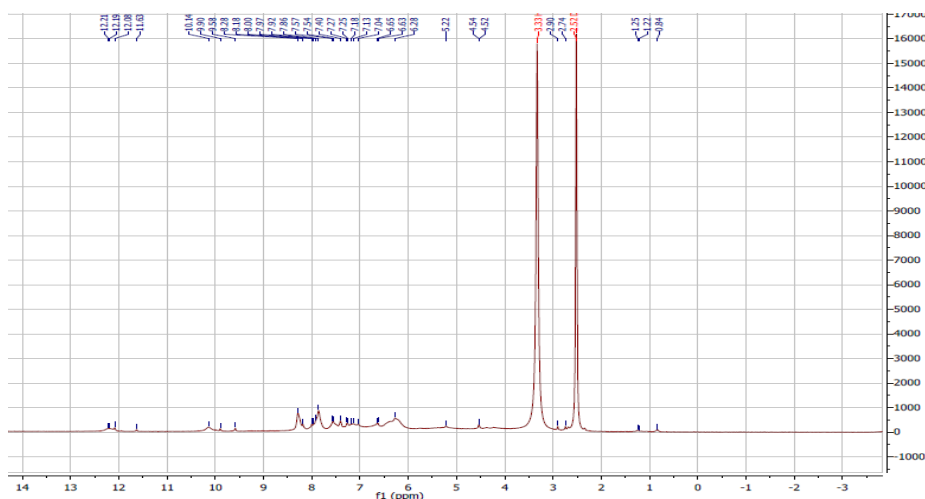


Figure 11: ¹H NMR spectrum of DYE II

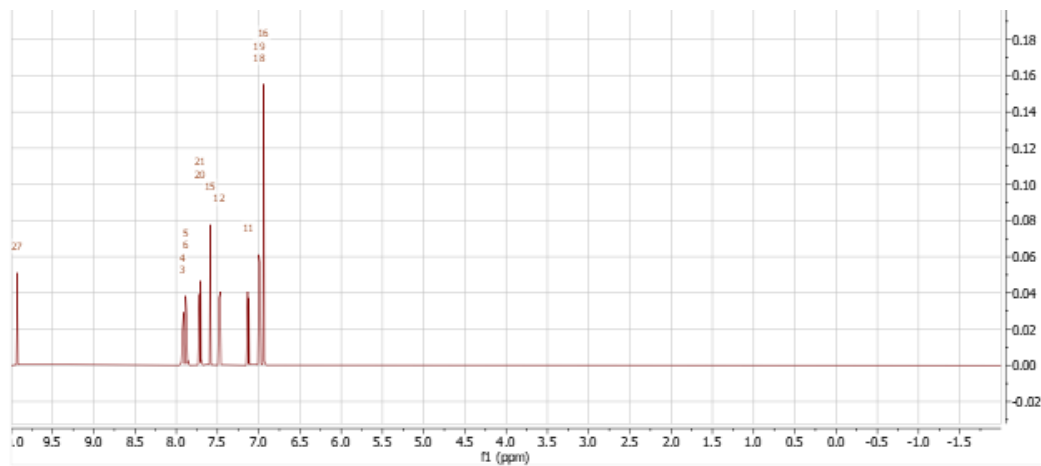


Figure 11: ¹H NMR spectrum of DYE III

The microbial sensitivities against the synthesized dyes are contained in Table 2, it was observed that, the test compounds had significant zones of inhibitions against all tested organisms as compared to the standard drug. At concentration of 100 µg/ml, dye III showed highest zone of

inhibition of 24 mm against *Bacillus subtilis*, followed by dye II with 22 mm against *Bacillus subtilis*, while the least zone of inhibition of 9 mm was exhibited by dye I against *Escherichia coli* at the concentration of 25 µg/ml. Hence, the result of the anti-microbial screening showed that all the

synthesized dyes possessed reasonable activities against the test microbes, with the exception of *Candida albicans* which was resistant to all synthesized dyes.

Minimum Inhibitory Concentration (MIC)

The result of (MIC) as shown in Table 3, revealed that at 100 µg/ml, 50 µg/ml and 25 µg/ml *Candida albicans* was completely resistant against all the synthesised dyes. Dyes I and II inhibited the growth of *Escherichia coli* and *Salmonella typhi* at concentrations of 100 µg/ml and 50 µg/ml, while *Staphylococcus aureus* and *Bacillus subtilis* were inhibited at 25 µg/ml respectively. For dye III, 25 µg/ml was the minimum concentration required to inhibit the growth of *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli*, while the growth of *Salmonella typhi* was inhibited at concentration of 50µg/ml.

Minimum Bactericidal Concentration (MBC)

As indicated in Table 3, dyes I and II were able to kill *Bacillus subtilis*, *Salmonella typhi* and *Staphylococcus aureus* at the concentration of 50 µg/ml. while, for dye III, *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* were killed at 25 µg/ml.

Dyeing Fastness Properties leather

As shown in Table 4, dyeing on leather of the synthesized dyes produced blue shade for dyes I and II and green shade with dye III. In general, leather dyed with the anthraquinone acid dye exhibited better fastness properties. For instance rub fastness for leather was 4 (very good) for dyes I, II and III. Light fastness rating is 5 (excellent) for dyes I, II and 5 for dye III. While the wash fastness rating is 4 (very good) for dyes I, II and III, This can be attributed to increase in affinity and hydrogen bonding (Oyewale *et al.*, 2003) and electrostatic interaction of charged sulphonate molecule.

CONCLUSION

The different test compounds were successfully synthesized and their structures were confirmed using UV-Vis, FTIR and NMR spectroscopic techniques. The difference in the colour of newly synthesized dyes depends upon the substituents present and/or the position of substituents on the ring. Generally, Dye III showed better antimicrobial activity compared to dyes I and II, although dyes I and II showed a remarkable activity against the test microbes. All the synthesized dyes gave excellent homogeneity of coloration on leather. A remarkable degree of evenness indicates good penetration and affinity of these dyes to the fabrics. Therefore, these dyes can be viable commercially, since the reactants for the new dyes are readily available.

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