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Synthesis and Characterization of Some New Azo-imine Dyes and their Applications

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Abstract

Some new azo-imine dyes have been synthesized via the diazotization of sulphanilic acid and its coupling reaction with salicylaldehyde giving a starting material 4-((3-formyl-4-hydroxyphenyl)diazenyl)benzenesulfonic acid. The later reacted with different substituted anilines to give the target azo-imine dyes [4-((3-((4-substitutedphenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid] which were confirmed by using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra. The synthesized dyes are used for dyeing performance on acetate, cotton, nylon, wool, acrylic and polyester fibers, along with the effect of mordant on dyeing process. All the synthesized dyes gave moderate to excellent fastness properties on each fiber. The effect of cationic and anionic surfactants on the wash fastness has been studied.

Introduction

The sulphanilic acid is one of the most important compounds that can be used for the preparation of different azo dyes and their derivatives due to the presence of diazotizing amino group and the good binding sulphonyl group. Most of the synthetic dyes are useful for dyeing fabrics and textiles. Noticeably the most important kind of dyes are the azo dyes and some compounds that derived from it are imine compounds, to understand why some compounds have intense colors and how these compounds can interact with natural and synthetic fibers we must know the chemical structure and the chromophoric system for both dyes and the textiles [1].The introducing imine system to the synthetic dyes will increase the coordination with metal ions, and the coordination complex can be applied as improvement factors in dye techniques. The metal ions have been used as mordent in dyeing techniques. The principle of complication and mordent has the same idea in coordination applications [2,3].

Many imine compounds and complexes have been synthesized and studied due to their interesting and important properties, such as biological activity, catalytic activity in hydrogenation of olefins, transfer of an amino group, photochromic properties and complication ability towards some toxic metals [4].

Our aim in this study is to synthesize and to test directly stain ability of a variety of fibers that have been woven into a piece of Multi-fiber fabric or introduce the imine system to see the improvement in dyeing techniques.The process of attachment of the dye molecule to the fiber is one of adsorptions. It involves direct bonding, by ionic forces, hydrogen bonds, covalent linkages and “Van der Waal” forces. The presence of certain functional groups like HSO_3,NO_2, Cl, and NH_2 in suitable positions in the dye molecule causes its coordination, these are best sites for engagement rather than azo , and azomethine groups [5].

Experimental

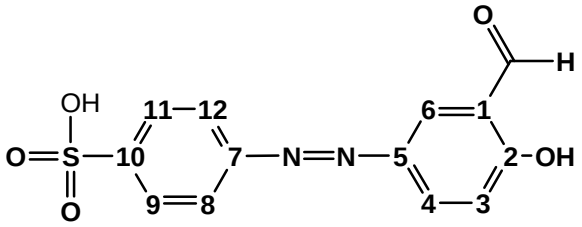
Melting points were determined using an Electrothermal melting point apparatus, IR spectra were recorded on a IR Affinity-1 Spectrophotometer, using KBr disc. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker (400MHz) with TMS as internal reference.

A. Synthesis of 4-((3-formyl-4-hydroxyphenyl)diazenyl)benzenesulfonic acid. (1)

The preparation of the starting material (1) was carried out successfully according to the literature procedures [6].The yellow azo-dye collected on a Buchner funnel, washed several time with water, dried and recrystallized from the acetic acid giving yellow crystals of compound(1): m.p.>300 ^{o}C, yield (96 %). IR(cm^{-1}): 3468(OH), 2742& 2872(CHO), 1660(C=O), 1577, 1288(C-O).

^{1}H-NMR(ppm) : 7.20 (d, 1H, Ar-H-C_3); 7.78-8.03 (m, 4H, Ar-H-$C_{4,6,9,11}$+1H of Ar-SO_3H); 8.10 (d, 2H, Ar-H-$C_{8,12}$); 8.20 (s, 1H, Ar-H-C_6); 10.37 (s, 1H, aldehydic proton); 11.55 (b , 1H , OH).

^{13}C-NMR: 115.05:C_3, 118.52:C_6, 119.25:$C_{8,12}$, 120.55:$C_{9,11}$, 123.33:C_1, 126.4:C_4, 141.47:C_5, 147.08:C_{10}, 148.18:C_7, 159.98:C_2, 187.31:C=O.



Starting material (1)

B. Synthesis of azo-imine: 4-((3-((4-sbstitutedphenylimino)methyl)-4-hydroxyphenyl) diazenyl)benzenesulfonic acid (2a-e) [7].

A mixture of compound(1) (0.91gm, 0.003mol),and substituted anilines(0.004mol) in ethanol (40ml) without catalyst (acid), was stirred under reflux for (1-2) hr. until all starting materials had reacted , the cooled mixture was solidified and filtered off , dried and recrystallized from acetic acid to give (red- orange – yellow) colored products.

4-3-3-methylphenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid (2a):

$C_{20}H_{17}N_3O_4S$, Yield: 80%,Time: 1.5hrs., m.p>300; IR(cm^{-1}): 3468(OH), 1622(C=N); **^{1}H-NMR(ppm)**: 2.38 (s, 3H, Ar-CH_3); 7.17-8.31 (m, 11H Ar-H + 1H Ar-SO_3H); 9.17 (s, 1H , of an imine); 13.98 (b , 1H , OH); **^{13}C-NMR:**23.66:Ar-CH_3-C_{19},117.62:C_3, 118.91:C_{18}, 119.31:$C_{14,}$ 121.43:$C_{1,}$ 121.57:C_6, 126.35:$C_{8,12}$, 126.66:C_4, 127.13:C_{16}, 127.43:$C_{9,11}$, 128.09:C_{17}, 138.48:C_{15}, 141.31:C_5, 144.36:C_{13}, 149.72:C_{10}, 151.33:C_7, 160.73:C=N, 163.53:C_2.

4-3-4-chloro-4-methylphenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid (2b):

$C_{20}H_{16}ClN_3O_4S$, Yield: 87%, Time: 1.5hrs., m.p>300; IR(cm^{-1}): 3441(OH), 1620(C=N); **^{1}H-NMR(ppm)**: 2.20 (s, 3H, Ar-CH_3); 7.15-8.30 (m, 10H Ar-H + 1H Ar-SO_3H); 9.15 (s , 1H , of an imine); 13.52 (b , 1H , OH); **^{13}C-NMR:** 19.22:Ar-CH_3-C_{19},117.93:C_3, 119.34:$C_{18,}$ 121.48:$C_{1,}$ 121.81:$C_{14,}$ 121.9:C_6, 126.73:$C_{8,12}$, 127.55:C_4, 127.67:$C_{9,11}$, 131.9:C_{17}, 133.96:C_{16}, 134.35:C_{15}, 144.55:C_5, 146.75:C_{13}, 150.28:C_{10}, 151.64:C_7, 163.29:C=N, 163.40:C_2.

4-3-4-ethoxyphenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid (2c):

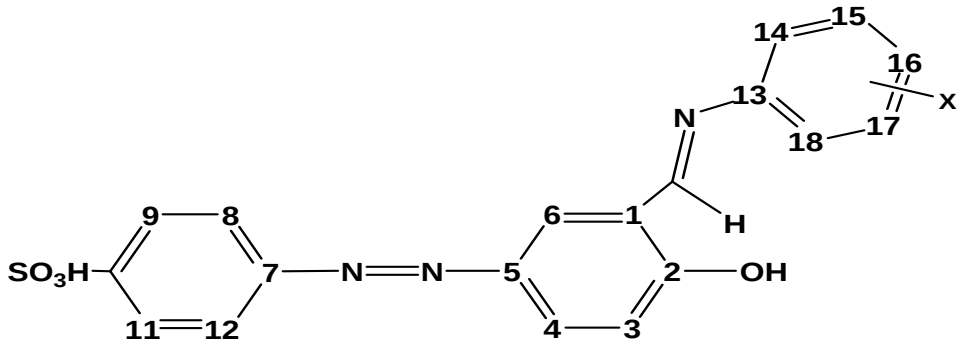
$C_{21}H_{19}N_3O_5S$, Yield: 77%, Time: 1.75 hrs., m.p>300; IR(cm^{-1}): 3464(OH), 1622(C=N); **^{1}H-NMR(ppm)**: 1.33 (t, 3H CH_3 of Ar-OCH_2CH_3); 4.06 (q, 2H CH_2 of Ar-OCH_2CH_3); 7.02-8.21 (m, 11H Ar-H + 1H Ar-SO_3H); 9.14 (s , 1H , of an imine); 14.18 (b, 1H , OH); **^{13}C-NMR:** 14.01**:**CH_3, of Ar-OCH_2CH_3,62.781**:**CH_2, of Ar-OCH_2CH_3, 114.6**:**$C_{15,17}$, 117.33**:**C_3, 118.71**:**$C_{14,18,}$ 121.15**:**$C_{1,}$ 122.17**:**C_6, 126.112**:**$C_{8,12}$, 126.28**:**C_4, 127.10**:**$C_{9,11}$, 139.09**:**C_5, 146.75:C_{13}, 150.28**:**C_{10}, 151.64**:**C_7, 157.52**:**C_{16}, 159.89**:**C=N, 163.26**:**C_2.

4-3-4-acetylphenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid (2d):

$C_{21}H_{17}N_3O_5S$, Yield: 91%, Time: 1.25 hrs., m.p>300; IR(cm^{-1}): 3448(OH), 1676(C=O), 1624(C=N); **^{1}H-NMR(ppm)**:2.61 (s, 3H CH_3 of Ar-$COCH_3$); 7.17-8.36 (m, 11H Ar-H + 1H Ar-SO_3H); 9.17 (s , 1H , of an imine); 13.38 (b , 1H , OH); **^{13}C-NMR:** 26.73**:**CH_3, of $COCH_3$,118.05**:**C_3, 119.34**:**$C_{14,18,}$ 121.66**:**$C_{1,}$ 121.91**:**C_6, 126.72**:**$C_{8,12}$, 126.74**:**C_4, 129.77**:**$C_{9,11}$, 130.53**:**$C_{15,17}$, 135.23**:**C_{16}, 144.91**:**C_5, 150.47**:**C_{10}, 151.60**:**C_7, 153.60**:**C_{13}, 163.36**:**C=N, 163.53**:**C_2, 198.76:C=O.

4-3-4-N-acetylaminophenylimino)methyl)-4-hydroxyphenyl)diazenyl)benzenesulfonic acid (2e):

$C_{21}H_{18}N_4O_5S$, Yield: 85%, Time: 1.5 hrs., m.p>300; IR(cm^{-1}): 3462(OH), 3290(NH), 1662(C=O), 1622(C=N); **^{1}H-NMR(ppm)**: 2.08 (s, 3H CH_3 of Ar-$NHCOCH_3$); 7.14-8.31 (m, 11H Ar-H + 1H Ar-SO_3H); 9.16 (s , 1H , of an imine); 10.12 (s, 1H NH); 13.95 (b , 1H , OH); **^{13}C-NMR:** 23.60**:**CH_3, of $NHCOCH_3$,117.55**:**C_3, 118.89**:**$C_{14,18,}$ 119.28**:**$C_{15,17}$, 121.33**:**$C_{1,}$ 121.52**:**C_6, 126.29**:**$C_{8,12}$, 126.67**:**C_4, 127.28**:**$C_{9,11}$, 138.42**:**C_{16}, 141.35**:**C_5, 144.36**:**C_{13}, 149.95**:**C_{10}, 151.24**:**C_7, 160.75**:**C=N, 163.42**:**C_2, 167.96**:**C=O.



2 (a-e)

Compounds (2a-e)

Dyeing applications

A. *Mordants*

Some dyes and pigments, requiring a mordant to fix to the fabric, prevent the color from either fading with exposure to light or washing out. These compounds bind the dyes to the fabric by forming a chemical bridge. Mordant can also determine how the dye reacts to the fiber, resulting in several colors. The chemical names of some mordants are the metal salts such as, ammonium aluminiumsulfate, Potassium aluminiumsulfate, Potassium dichromate, tannic acid, Copper (II) sulfate, Iron (II) sulfate etc. Mordant can be pre-mordant, one-bath method or post mordant, in many cases mordants may not be necessary, and the dyes can color synthetic fibers directly. Simple salts such as sodium chloride and sodium sulfate can be used in the dyeing bath to increase the concentration of dye molecules on the textile [8].

B. *Dyeing a multi-fiber strip*

The dyeing procedure involve preparation of three types of dyeing bath for dyeing a multi-fiber strip (using multi-fiber strip is relatively inexpensive and will reduce the number of experiments to set up to investigate dyeing effectiveness) as shown in plate (1). The SDC multifiber test fabric is made up of six different fibers: each is a band of about 1.5 cm. Cellulose acetate (cellulose di-or triacetate); bleached cotton; nylon 6.6; polyester (Terylene); acrylic (Courtelle); and wool (polyimide) as shown in plate(1).

Dyeing procedure

Case I: Dyeing without salt and mordant

The dye 1gm was dissolved in 200 mL of distilled water,5 mL of 1 M sodium hydroxide was added with stirring. The solution heated to near boiling on a hot plate for 30 minutes making sure the strip is immersed throughout. The strips removed by tweezers, allowed it to cool, and rinse it with tap water. The dyed fiber dried with a paper towel.

Case II: Dyeing with salt and without mordant

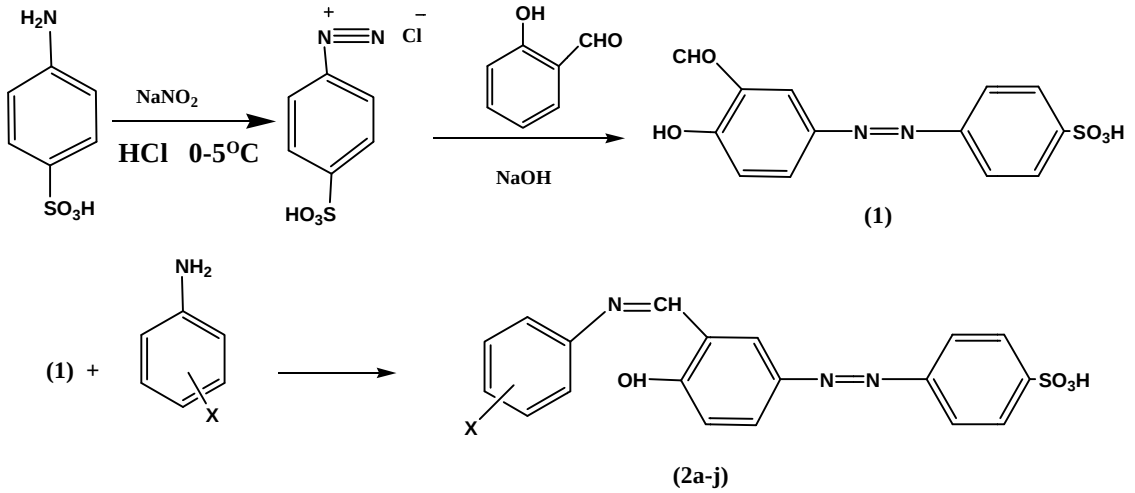
1g of the dye and 0.5 gm of sodium chloride dissolved in 200 mL of distilled water. 5 mL of 1 M sodium hydroxide was added and worked out as in case I.

Case III: Dyeing with mordant and without salt

1g of the dye and 0.5 gm of alum mordant dissolved in 200 ml of distilled water. Added 5 mL of 1 M sodium hydroxide and with stirring and the procedure worked out as caseI and II.

Results and Discussion

The present study involves synthesis, characterization and dyeing applications of some new azo-imine derivatives on multi-fiber strips in three types of dyeing baths. The synthetic pathway of the starting material azo-benzaldehyde (1) and azo-imines (2a-e) are outlined in Scheme 1. The structures of the newly synthesized compounds were confirmed on the bases of their IR, ^{1}H-NMR and ^{13}C-NMR spectral data**.** The IR spectrum of the synthesized starting material 4-((3-formyl-4-hydroxyphenyl) diazenyl)benzenesulfonic acid (1) shows a broad band at 3468, two characteristic peaks at 2742 & 2872 and a strong band at 1660 cm^{-1} belongs to (OH) str, the Fermi resonance of aldehydic C-H proton, and carbonyl group stretching vibrations respectively [9]. The ^{1}H-NMR spectrum observed two singlet signals at 11.55 and 10.37ppm due to hydroxyl and aldehydic C-H proton respectively along with aromatic protons at 7.2-8.2ppm and eleven signals in ^{13}C-NMR spectrum for eleven types of carbons confirms the expected structure [10,11]. Also the structure of the synthesized azo-imine dyes were elucidated through the disappearance of carbonyl of the starting material and showing a new peaks of imine system in IR at 1620cm^{-1} , ^{1}H-NMR at 9.1 and ^{13}C-NMR spectral at 160ppm[12], as shown in Figures (1,2 &3).



X= 3-CH_3, 3-Cl-4-CH_3, 4-OCH_2CH_3, 4-$COCH_3$,4-$NHCOCH_3$
Scheme (1)

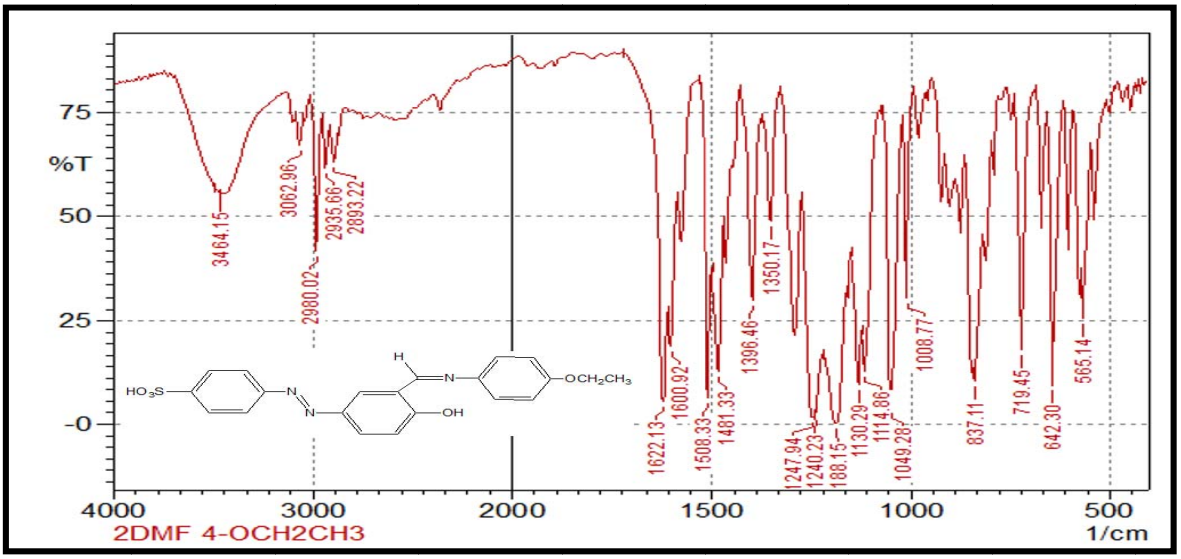


Figure (1): IR spectrum of compound (2c)

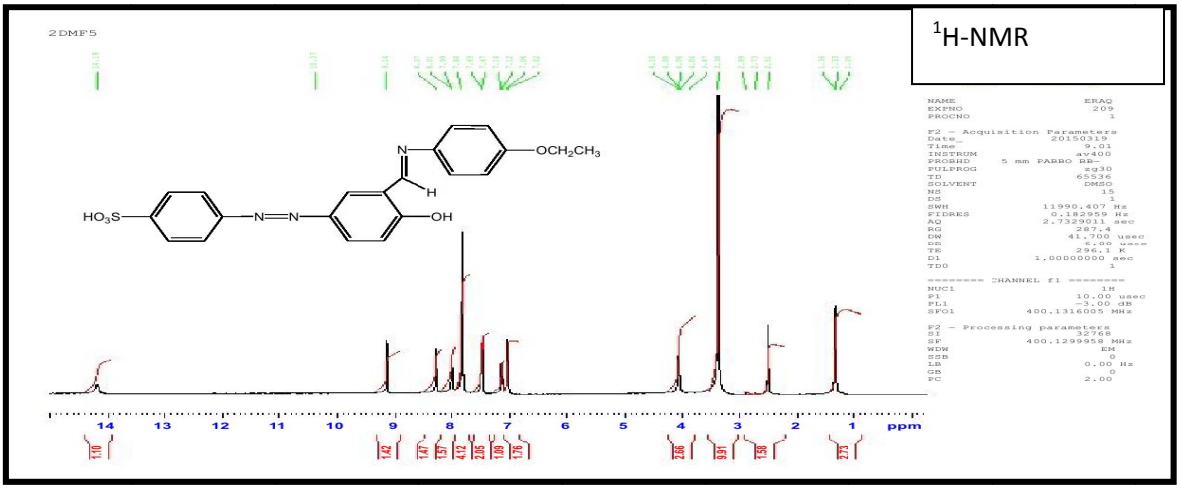


Figure (2):^{1}H-NMR of compound (2c).

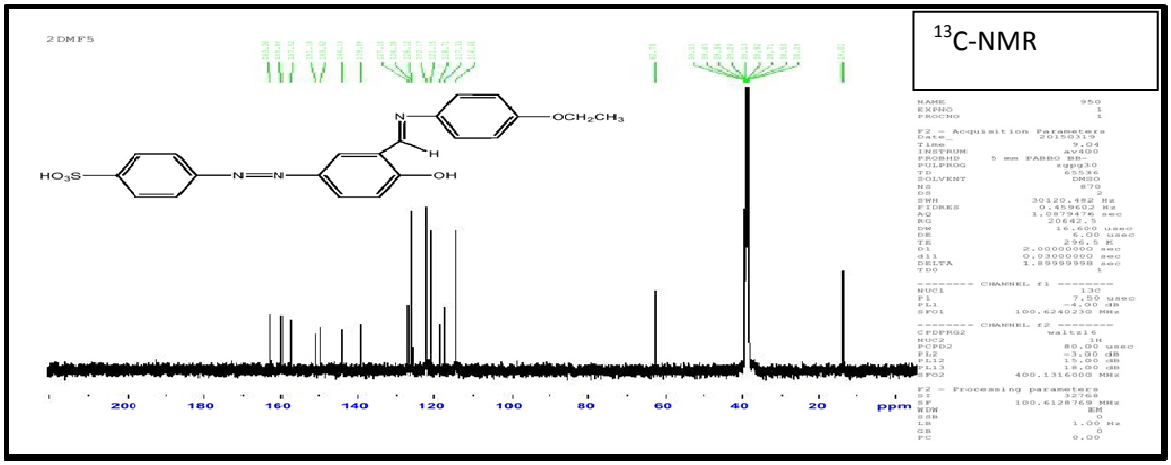


Figure (3):^{13}C-NMR of compound (2c).

Dyeing properties of azo - imine dyes

All the dyes (2a-e) were applied on acetate, nylon, and wool fabrics but they didn't applied on cotton, polyester and acrylic fabrics Dyeing process was carried out at *pH* 5 - 8 and it was adjusted with 1 M sodium hydroxide.

The dyeing results with azo - imines compounds are summarized in Table (1) Cases I, II, III.

The variation in color hues of the dyed fabric which results from the modification in the coupling components was studied. All the dyes gave a wide range of colors change from light yellow to dark orange with good levelness, brightness and depth on the fabrics. The change in the shades of the dye fabric was caused by the nature and position of the substituent present on the diazotized-imines.

Fastness properties

All the data of fastness properties of light, and wash are shown in Table (1). The fastness properties of light were assessed in accordance with BS: 1006-1378, and the wash fastness test in accordance with IS: 765-1979 [13,14]. The light fastness was tested using Xenon Arc Test with a Window Glass Filter and the results were compared to with two outdoor exposure sun light change in color of the dyed samples in the normal way visually by giving grade marks 1-5 (1=poor, 5= excellent). The results of light fastness was good to excellent for nylon and wool ,but moderate for acetate .Samples in case II, and case III became darker after exposer to natural sunlight, and the results shown in plates (2,3)

Wash and rubbing fastness was fair to moderate for nylon, and wool, but it's bad with acetate.

A noticeable smoothness after washing was observed. This may be due to the good penetration and the attractive force of the dye molecule with the structure of the fabrics [15]. The results are shown in plates (4, 5).

Conclusion

The azo-imine dyes are good for dying acetate, nylon, and wool fabrics but they didn't applied on cotton, polyester and acrylic fabrics, the strips in cases II&III shows stronger color than in case I this due to the presence of an electrolyte and mordant in the dyeing process, which enhance the application of dyes on the multi-fiber strips by induce the formation of bonding.

The light and wash fastness of all dyed textile samples treated with NaCl and Alum as mordant have bright and shiny color, and they showed fair to good fastness to light, and washing fastness.

The test samples shows that addition of NaCl salt increases the solubilization of dyes in a solution of an ionic surfactant, and the dyes with polar substituents can interact by inter-molecular interactions with the polar

head of the surfactant, these interactions increase solubilization efficiency of the dyes, i.e., cationic surfactants interact with anionic dye and the cationic dyes interact with oppositely charged surfactant.

Plate (1): Dyeing a multi-fiber strip in cases I, II, and III

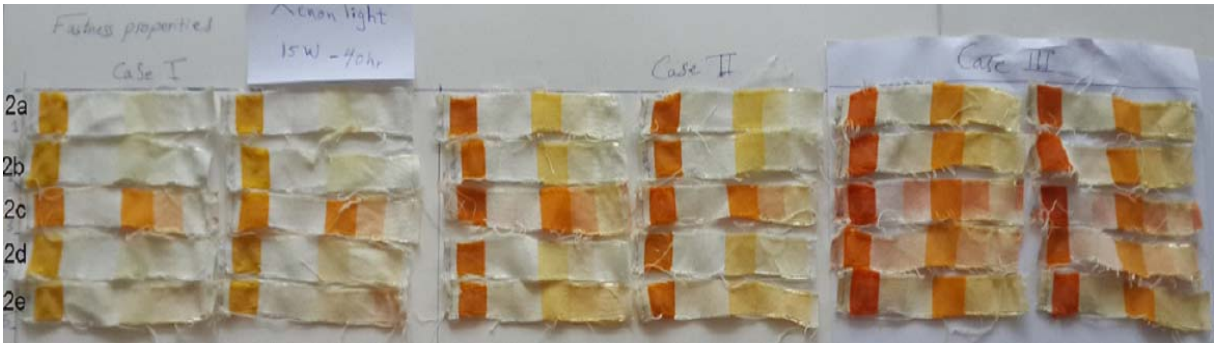


Plate (2): Light fastness was tested using Xenon Arc Test

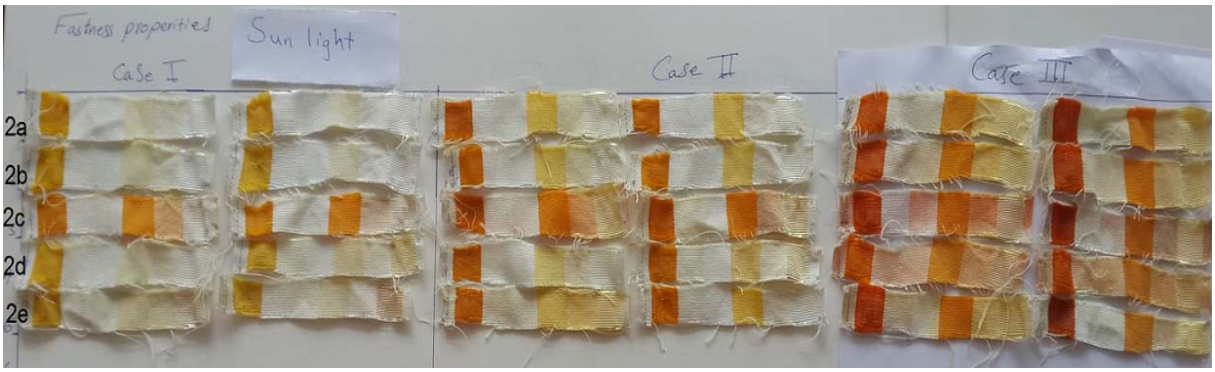


Plate (3): Light fastness outdoor exposure to sun light

Plate (4): Wash and rubbing fastness of dyes in an anionic surfactant solution

Plate (5): Wash and rubbing fastness of dyes in a cationic surfactant solution

Table (1): Dyeing colors and fastness properties (F.P) of a multi-fiber strip in three cases (I, II, III), for the synthesized azo-imines (2a-e).

Table .1: Case I: Dyes without salt & mordant

Ent	**pH**	**F.P**	**Acetate**	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**
2a	7		White	Light beige	Pale yellow	White	White	Turmeric
		A	5	5	5	5	5	5
		B	5	4/5	5	5	5	5
		C	3	1	5	1	1	2
		D	3	1	5	1	1	2
2b	7	F.P	White	Light beige	Pale yellow	White	White	Turmeric
		A	5	5	5	5	5	5
		B	5	3	5	5	5	4/5
		C	3	1	3/4	1	1	2
		D	3	1	3/4	1	1	2
2c	7	**F.P**	Tan white	Peach	Imitation gold	White	White	Chrome yellow
		A	5	5	5	5	5	4/5
		B	5	3	5	5	5	4/5
		C	2	1	3	1	1	2
		D	2	1	3/4	1	1	2/3
2d	7	F.P	White	Light beige	Pale yellow	White	White	Turmeric yellow
		A	4	5	4	5	5	5
		B	2	5	3	5	3/4	5
		C	2	1	5	1	1	2/3
		D	2	1	5	1	1	2/3

2e	8	F.P	Tan cream	beige	Pale yellow	White	White	Turmeric yellow
		A	4	5	5	5	5	4/5
		B	3	3	4/5	5	5	5
		C	2/3	1	3/4	1	1	2
		D	2/3	1	3/4	1	1	2

A: Xenon light 15W-40 hr.; **B:** Sun light 40 hr. **C:** Washing with anionic surfactant 65c°- 30min; **D:** Washing with cationic surfactant 65c°-30min

***Light & Wash fastness:** (Grading: 1- poor, 2- fair, 3- good, 4- very good, 5- excellent).

Table .1:Case II: Dyes +salt & without mordant

Ent	**pH**	**F.P**	**Acetate**	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**
2a	7		White	White	beige	Lemon yellow	White	White
		A	5	5	5	5	5	5
		B	5	3/4	5	5	5	5
		C	3	1	4	1	1	2/3
		D	3	1	4/5	1	1	2/3
2b	7	F.P	White	White	beige	Lemon yellow	White	White
		A	5	5	5	5	5	5
		B	5	3	5	5	5	5
		C	3	1	4	1	1	2/3
		D	3	1	4/5	1	1	3
2c	7	**F.P**	Tan white	Ecru yellow	Peach	Imitation gold	White	White
		A	5	5	5	5	5	5
		B	5	4	5	4	4	5
		C	2/3	1	3	1	1	2
		D	2/3	1	3/4	1	1	2/3
2d	7	F.P	White	White	Tan white	Lemon yellow	White	White
		A	5	5	4	5	5	5
		B	2	3	4/5	5	4	5
		C	2	1	4/5	1	1	2/3
		D	2	1	4/5	1	1	2/3
2e	8	F.P	Ecru	Beige yellow	Yellow	Tan white	Tan white	Chrome yellow
		A	5	5	5	5	5	5
		B	1/2	1	2/3	4	4	4/5
		C	1	1	3/4	1	1	2
		D	1	1	3/4	1	1	2/3

Table .1: Case III: Dyes +mordant & without salt

Ent	**pH**	**F.P**	**Acetate**	**Cotton**	**Nylon**	**Polyester**	**Acrylic**	**Wool**
2a	7		Beige yellow	Beige yellow	Imitation gold	White	Tan white	Rust orange
		A	5	5	5	5	5	5
		B	5	4/5	4/5	5	5	4/5
		C	3/4	1	3	1	1	3
		D	3/4	1	4	1	1	3/4
2b	7	F.P	Beige yellow	Lemon yellow	Imitation gold	Tan white	White	Rust orange
		A	5	5	5	5	5	5
		B	5	4	5	5	5	5
		C	3/4	1	3/4	1	1	2/3
		D	3/4	1	4	1	1	3/4
2c	7	**F.P**	Tan cream	Peach	Orange	Peach	Cream	Rust red
		A	5	5	5	5	5	5
		B	5	4	5	4	5	5
		C	2/3	1	3	1	1	2
		D	2/3	1	3/4	1	1	2/3
2d	7	F.P	Tan cream	Ecru	Imitation gold	Ecru	Ecru	Chrome yellow
		A	5	5	5	5	5	5
		B	5	5	5	5	5	5
		C	2/3	1	3	1	1	2/3
		D	3	1	3/4	1	1	3
2e	8	F.P	Pale yellow	Beige yellow	Imitation gold	beige	beige	Rust orange
		A	5	5	5	5	5	5
		B	5	3/4	3/4	5	4/5	4/5
		C	2/3	1	4	1	1	2
		D	3	1	4/5	1	1	3

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