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Synthesis and Characterization of Some Azo Dyes Derived from 4-Aminoacetophenone, 1, 4 Phenylene Diamine and Studying its Dyeing Performance and Antibacterial Activity

Noor Sabah Al-Obaidi*, Omar D. Abdul Sattar, Fayhaa Fadhil Hadi, Anfal S. Ali and Buraq Th. Zaki

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Abstract

New azo and diazo dye was synthesized by coupling reaction of dizonium salt of P-amino acetophenone, P-phenylene diamine with phenolic derived. The products were characterized by FTIR and ^{1}H NMR; they were identical to literature. A_1, A_2, A_4, A_5, B_2 and B_3 were used dyes in dying process which were applied on wool, cotton and sawdust. We note that there are variations in the hues of the dyed fabrics which is resulted from the modifications in the coupling components. All the dyes gave color changes from light yellow to dark red with good levelness, brightness and depth on the fabrics. The antibacterial activities of the compound were studied and evaluated using gram positive and negative gram stains; A_5 and B_4 were positive against *S. aureas*, B_1 and B_4 were positive against *Pseudomonas*, and A_1, A_4, and B_4 were positive against *E. coli*. The purity of the dye was checked by thin layer chromatography (TLC), and also the melting point of the purified dyes was measured.

Keywords: Azo dyes, Dyeing performance, Antibacterial Activity.

Introduction

Presently, thousands of synthetic dyes are obtainable in the market (Hanadi, et al., 2018). Azo dyes constitute one of the largest and most varied groups of synthetic organic dyes in use today. The history of dyeing could be divided into two great periods, the "pre-aniline," extending to 1856 and the "post-aniline" period (Xu, H. & Zeng, 2010). Among them organic chromophores including azo compounds are widely utilized as pigments in many commercial products. Azo dyes attain the widest range of application by having easily tunable structure and simple application procedure (Ratna PBS Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation., 2012). The importance of azo-dyes is due to its economy, versatility, relative ease of production and good dying performance, and sequential anaerobic–aerobic treatment of azo dyes (decolourisation and amine degradability) (Patel et al., 2007). Synthetic dyes have been extensively used in numerous industrial processes and the target of dying process is color durability as well as resistance to physical and chemical degradation (Santhanalakshmi & Komalavalli, 2012). Furthermore, azo dyes have been investigated widely due to their excellent thermal and optical features with interesting applications in optical recording medium, toner, ink-jet printing, and oil-soluble light fast dyes (Arunkumar et al., 2005). They are usually strongly colored compounds which can be intensely yellow, red, orange, blue or even green, based on the exact structure of the molecule. As a result of their color, azo compounds have been tremendously important as dyes and also as pigments for a long time (Otutu JO Synthesis and application of azo dyes derived from 2-amino-1, 3, 4-thiadiazole-2-thiol on polyester fibre, 2013) In fact, about half of the dyes in industrial application today are azo dyes, which are mostly prepared from diazonium salts (Adegoke et al., 2008). Azo dyes contain at least one nitrogen-nitrogen double bond (N=N), however many different structures are possible (Kirkan and Gup, 2008). Anti-microbial agents play a major role in maintaining good health (Ahamed & Lakshmi, 2018). Some azo dyes have been found to have antimicrobial properties due to the presence of active functional groups, this biological activity of some azo dyes has increased their usage in textile, foods, and pharmaceutical industries. They have this vital ability to inhibit microorganisms which cause degradation of textile materials, degradation of food materials, skin diseases produced from bacteria which live inside clothing and textile fabrics and other ailments that affect human health (Balcerzak et al., 2014). Azo compounds are a class of chemical compounds that are continuously receiving attention in scientific research (Diler et al., 2016).

Noor Sabah Al-Obaidi*, Omar D. Abdul Sattar, Anfal S. Ali, Buraq Th. Zaki

Department of Chemistry, College of Science, University of Diyala, Iraq.

Fayhaa Fadhil Hadi
Ministry of Education, the General Directorate of Education of Diyala, Al-Zahra`a Preparatory School for Girls, Diyala, Iraq

Experimental:

Preparation of azo compounds series (A) (Noor Sabah Al-Obaidi et al., 2018)

- *Preparing diazonium salt*

2 ml Conc. HCl with 10 ml distilled water were dissolved in 0.54 g – 0.004 mol of p-Amino acetophenone at 0-5 ˚C. In the second flask solution was prepared by dissolving 0.200 g of sodium nitrite in 5 ml of distilled water at 0-5 °C; then the first solution was added to the second solution as batches at 0-5 °C.

- *Coupling Reaction*

In 5 ml of 35% NaOH 0.360 g – 0.004 mol of phenol was dissolved at 0-5 °C and then diazonium salt was added with stirrer at 0-5 °C to obtained yellow precipitate. Finally the precipitate was collected and the yield was calculated.

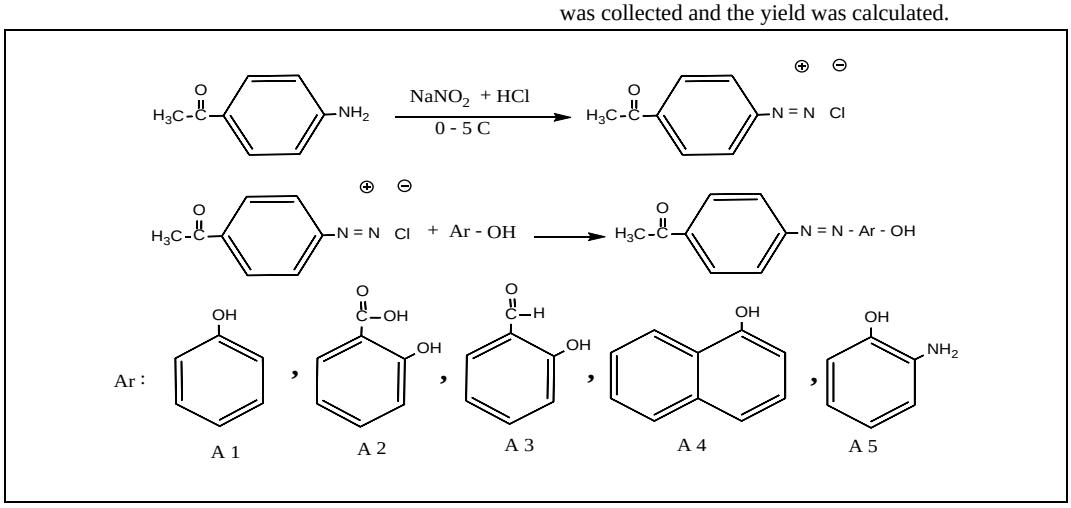


Fig. 1: the preparation of azo compound series A.

Preparation of diazo compounds series (B)

All of diazo compounds series (B) were prepared by a similar method above, but by using di amines with similar phenolic derived compounds above.

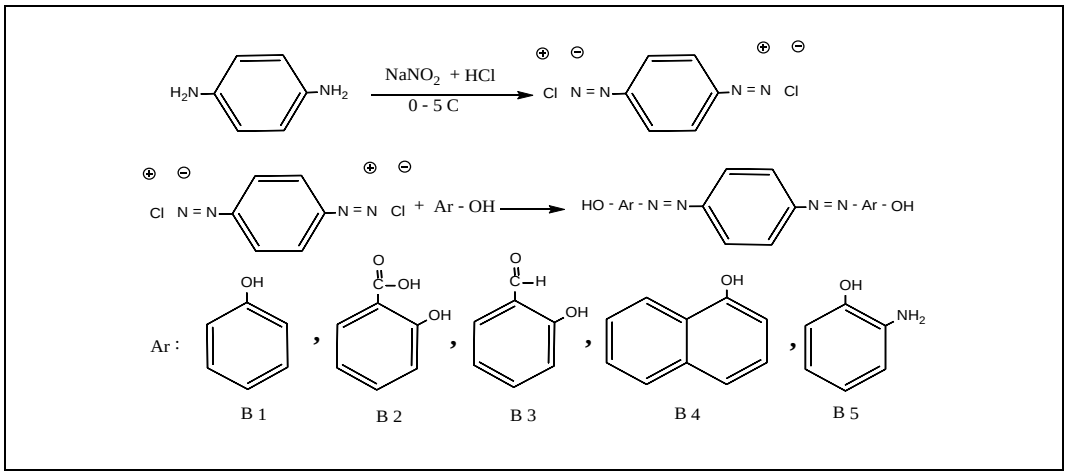


Fig. 2: the preparation azo compounds series (B)

Dyeing process

The dyeing process requires, among other things, the selection of dyes used for this process, as well as the identification of the materials to be dyed (fibers, yarns or textiles). The dyeing process requires the dye to be transferred from the dissolved solution to the dye to be dyed:

- *Preparing the materials to be dyed:*

It includes the cleaning process to remove impurities and dust, especially if the fibers to be dyed are natural by washing with distilled water and drying from moisture.

- *Preparation of dyeing solution:*

It involves taking 1 gm of dye and dissolving it in 15 ml of ethanol with continuous stirring to prepare a homogeneous solution and color in the dye used.

- *Completion:*

The fibers to be dyed were placed in the solution above, so that the tissue was completely immersed for 30 minutes, then removed from the solution and left to dry completely. To study the dyed fabrics and determine the stability of these dyes, we washed them once with water and soap again. The changes in the fabric color were noted.

Results and Discussion:

Spectroscopic studying

- *Spectroscopic studying by IR spectrum*

The infrared spectrum of A_1 showed absorption bands at 3151.6 cm^{-1} attributed to stretching vibration of υ (O – H) group, the band appeared at 3012.7 cm^{-1} was attributed to stretching vibration of υ (C – H aromatic), the band appeared at 2961.5 and 2815.2 cm^{-1} were attributed to stretching vibration of υ (C – H aliphatic), the band appeared at 1665.3 cm^{-1} was attributed to stretching vibration of υ (C = O) group, the band appeared at 1584.8 cm^{-1} was attributed to stretching vibration of υ (C = C) group, the band appeared at 1467.8 cm^{-1} was attributed to stretching vibration of υ (- N = N -) group, the band appeared at 1361.7 cm^{-1} was attributed to bending vibration of υ (C – H aliphatic) group, the band appeared at 1219.1 and 1281.3 cm^{-1} were attributed to stretching vibration of υ (C – N) group, and the band appeared at 1138.7 cm^{-1} was attributed to stretching vibration of υ (C – O) group. The IR spectrum showed disappearance of absorption bands υ (NH_2) of amine which were used as reactants substance, and bands of the synthesized compounds at the below tables (1) and (2).

Table 1- Vibration bands of synthesized compounds series (A)

Comp. No.	υ $(cm)^{-1}$, IR							
	O - H	**C-H aromatic**	**C-H Aliphatic**	**C = O**	**C=C aromatic**	**-N=N-**	**C - O**	**C - N**
A_1	3151.6	3012.7	2961.5 2815.2	1665.3	1584.8	1467.8	1138.7	1219.1 1281.3
A_2	3239.4	3012.7	2866.4	1665.3	1614.	1445.9	1157	1244.7 1299.6
A_3	3415	3056.5	2866.4	1676.2	1573.8	1475.1	1157	1274
A_4	3415	3056.5	2910.3	1669	1592.1	1482.4 1544.6		1270.3
A_5	3348.3	3147.2		1668.8	1627.2	1471.2		1218.1 1277

Table 2- Vibration bands of synthesized compounds series (B)

Comp. No.	υ $(cm)^{-1}$, IR						
	O - H	**C-H aromatic**	**C = O**	**C=C aromatic**	**-N=N-**	C - O	C - N
B_1	3445.3	3064	1682.7	1585.6	1505.9	1096.8	1235.5 1270.1
B_2	3232	3005.3	1665.3	1614	1445.9 1482.4	1153.3	1208.2 1299.6
B_3	3195.5	3071.2	1672.6	1577.5	1508	1096.6	
B_4	3202.8	3071.2	1636	1584.8	1438.5	1061.9	
B_5	3305.2	3071.2	1610.4	1504.4		1138.7	1226.4

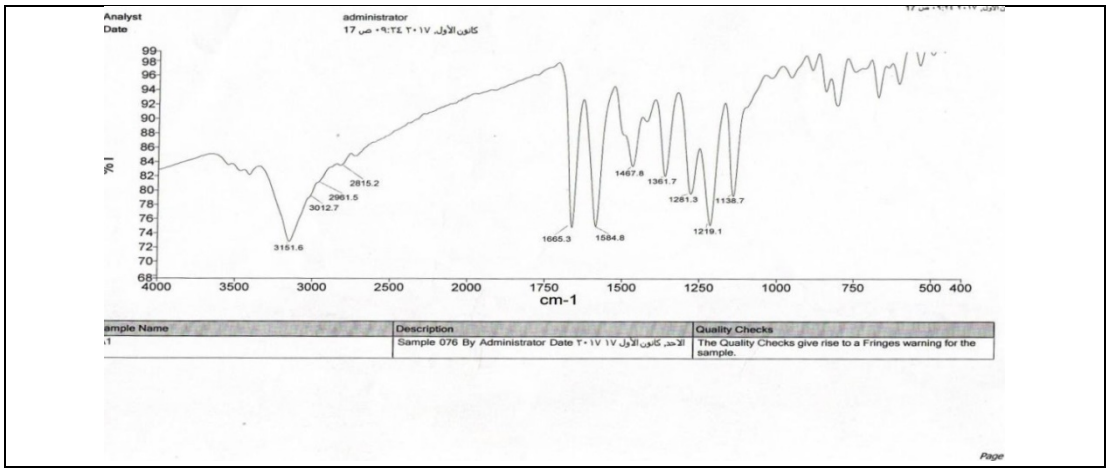


Fig. 3: Infrared spectrum of A_1

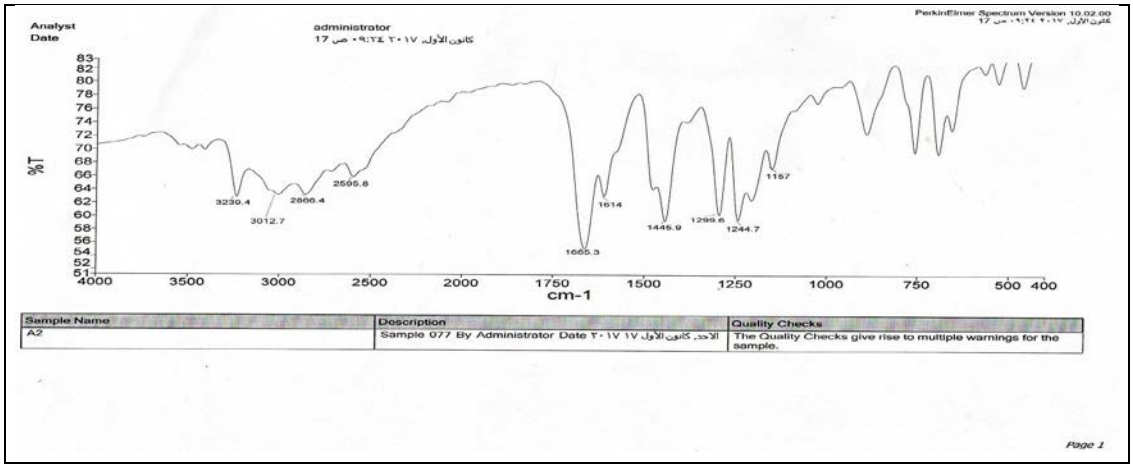


Fig. 4: Infrared spectrum of A2

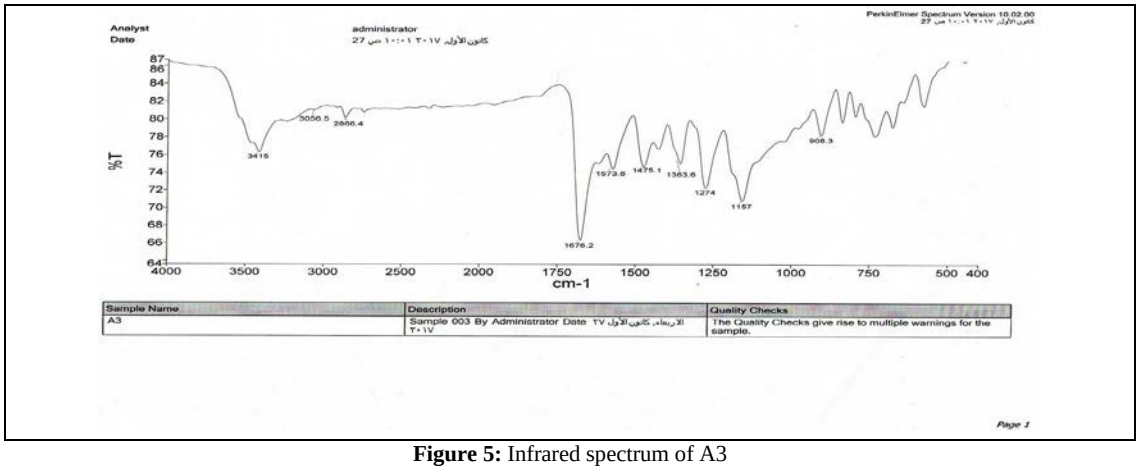


Figure 5: Infrared spectrum of A3

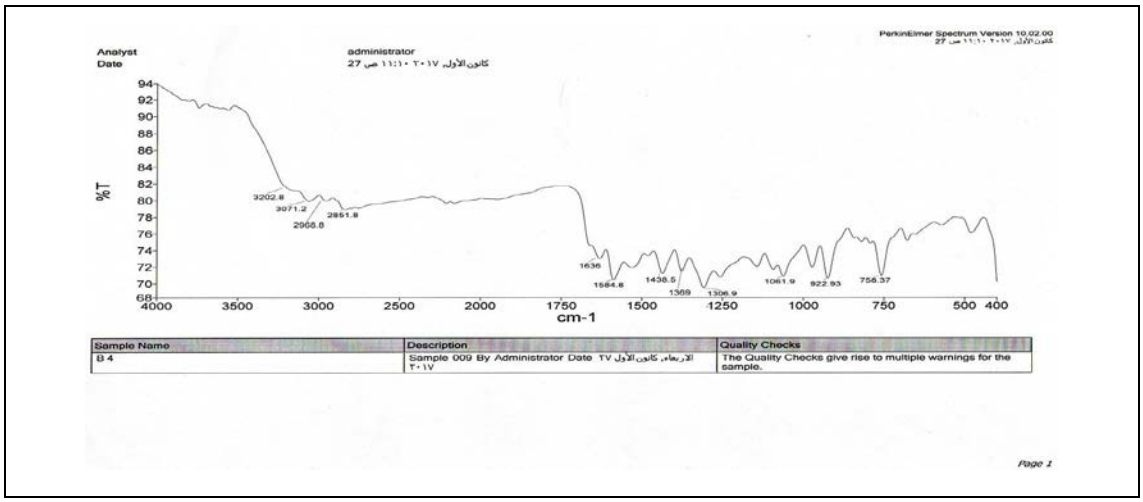


Figure 6: Infrared spectrum of B4

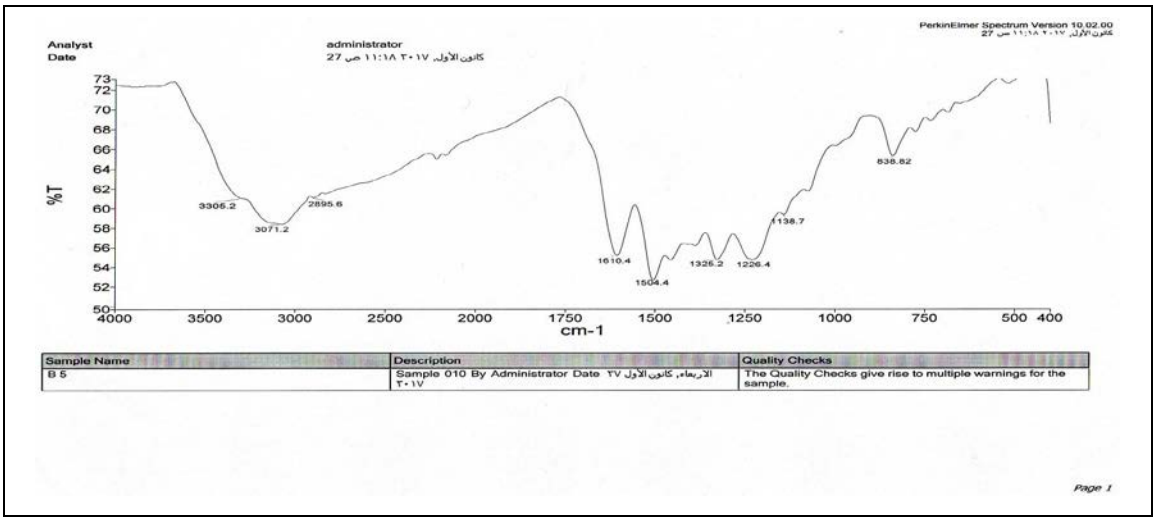


Fig. 7: Infrared spectrum of B5

Spectroscopic studying by ^{1}H NMR spectrum

In ^{1}H NMR spectrum (Figure 8), (DMSO-d6, TMS) δ ppm = 2.81 ppm (s, 3H, CH_3), 6.77 ppm (d, 2H, CH), 7.73 ppm (d, 2H, CH), 8.31 ppm (d, 2H, CH), 8.87 ppm (d, 2H, CH), 9.80 ppm (s, H, O-H).

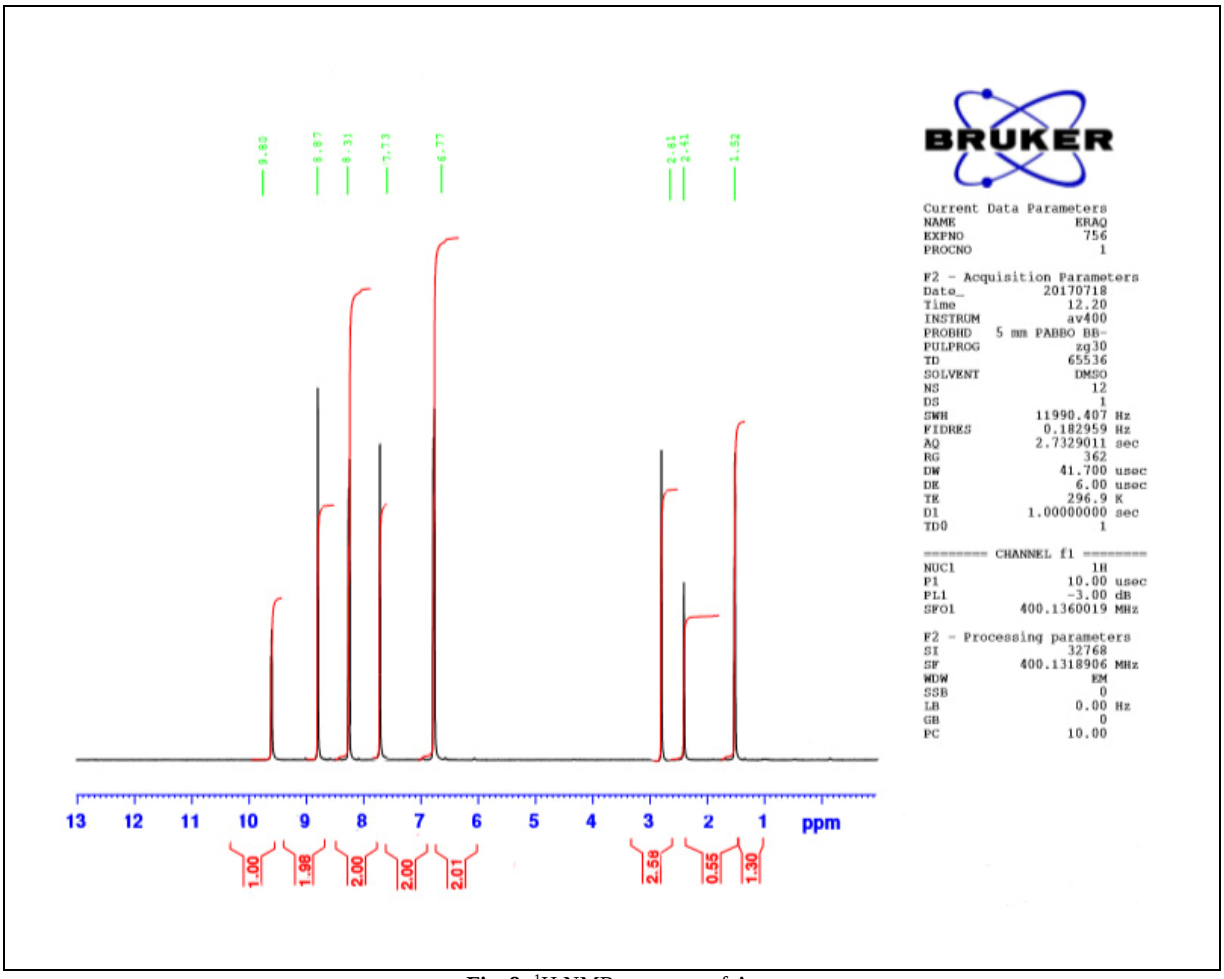
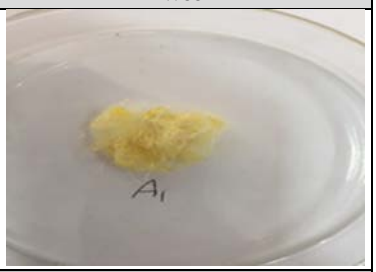


Fig. 8: ^{1}H NMR spectrum of A_1

Studying dyeing process

Dyes (A_1, A_2, A_4, A_5, B_1, B_2 and B_3) were applied on sawdust, cotton, and wool. We note that there is a variation in the hues of the dyed fabric which is resulted from the modification in the coupling components. All the dyes gave a wide range of color change from light yellow to dark red with good levelness, brightness and depth on the fabrics **(**Zollinger, 2003). The changes in the shades of the dyed fabric was caused by the nature and position of the substituent present on the diazotized compound. The dyeing compounds showed fair to good fastness to washing fastness. A noticeable smoothness after washing was observed; this may be due to the good penetration and the attraction of the dye molecule to the structure of the fabrics **(**Hawaiz et al., 2016**).** Below are figures showing cotton, wool and sawdust after dyeing with prepared pigments and after washing with water (Figures 8-14).

	After dyeing process		
	Sawdust	cotton	Wool
A1			
	After washing with water		

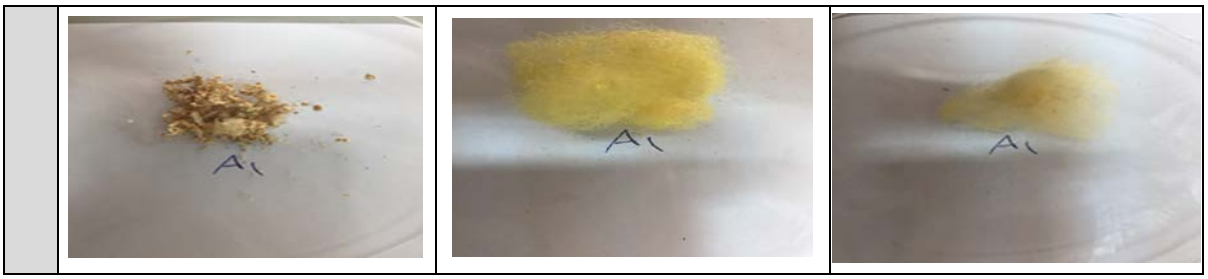


Fig. 9: Dyeing process of A_1

	After dyeing process		
	Sawdust	cotton	Wool
A_2			
	After washing with water		
			

Fig. 10: Dyeing process of A_2

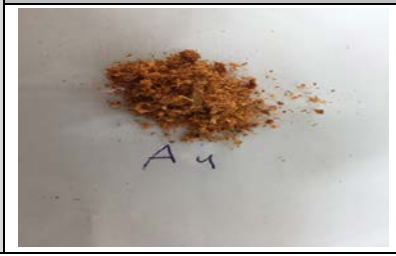
	After dyeing process		
	Sawdust	cotton	Wool
A_4			
	After washing with water		
			

Fig. 11: Dyeing process of A_4

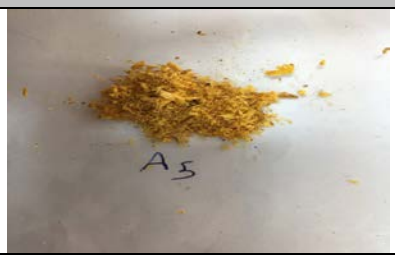
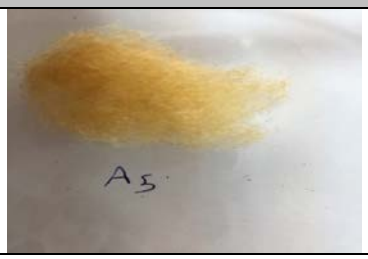
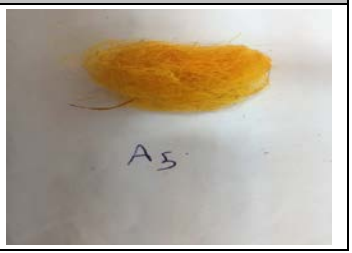
	After dyeing process		
	Sawdust	cotton	Wool
A_5			
	After washing with water		
			

Fig. 12: Dyeing process of A_5

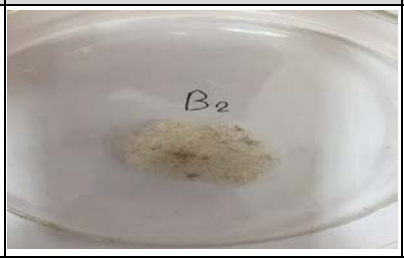
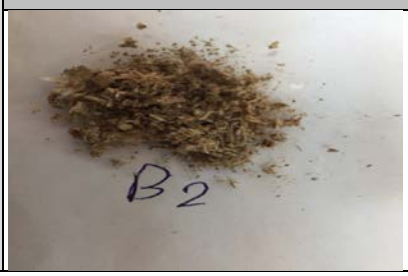
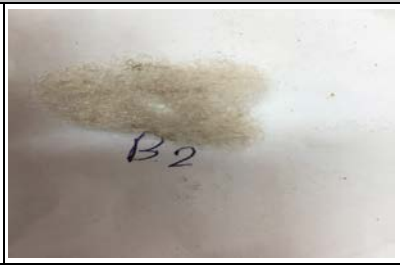
	After dyeing process		
	Sawdust	cotton	Wool
B_2			
	After washing with water		
			

Fig. 13: Dyeing process of B_2

	After dyeing process		
B_3	Sawdust	cotton	Wool

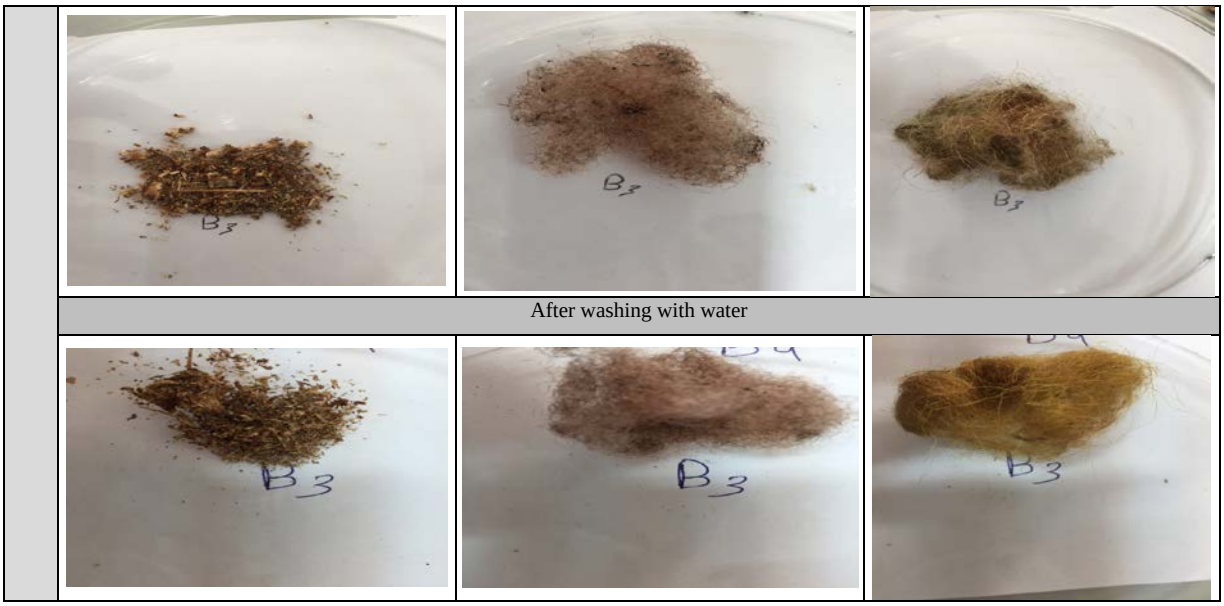


Fig. 14: Dyeing process of B_3

Studying antibacterial activity

Antibacterial activities for the compound under test were determined by disk agar diffusion method. The samples that we tasted were dissolved in DMF (this solvent has no inhibition activity). The inhibition activity of the compound was studied and evaluated using gram positive and negative gram stains; A_5 and B_4 were positive against *S. aureas*, B_1 and B_4 were positive against *Pseudomonas*, and A_1, A_4, and B_4 were positive against *E. coli*. The activity of any chemical compounds against microorganism is a complex combination of some factors which decrease the work of derivatives, involved with connect to hydrogen bond out of (O-H, C=O) with center of the bacteria constituent, produced interferences to bacteria process The antibacterial activity of synthesized compounds was Shown in Tab. 3.

Table 3- The antibacterial activity of synthesized compounds

Compound No.	S.aureas	Pseudomonas	E.coli
A1	-	-	+
A2	-	-	-
A3	-	-	-
A4	-	-	+
A5	+	-	-
B1	-	+	-
B2	-	-	-
B3	-	-	-
B4	+	+	+
B5	-	-	-

Conclusions

In this research inhibition activities of some azo and diazo dyes were studied against *S. aureus*, *Pseudomonas* and *E. coli*. In addition to their dyeing process, the dyeing compounds showed fair to good fastness to washing and noticeable smoothness after washing.

References

Adegoke OA, Idowu OS, Olaniyi AA. Synthesis and spectroscopic characterization of 4-carboxyl-2,6- (2008).

Ahamed, S.T. & Lakshmi, T.2018. Antibacterial Activity of Taxifolin Isolated from Acacia Catechu Leaf Extract An in Vitro Study.International Journal of Pharmaceutical Research & Allied Sciences. 7(4):133-137.

Arunkumar E. Forbes CC. Smith BD Improving the Properties of Organic Dyes by Molecular Encapsulation. Eur. J. Org. Chem. 4051–4059. DOI: 10.1002/ejoc.200500372 (2005).

Balcerzak ES,Konieczkowska J, SiwyM, Sobolewska A,Wojtowicz M, Wiacek M Comparative studies of polyimides with covalently bonded azo-dyes with their supramolecular analoges: thermooptical and photoinduced properties. Opt Mater 36:892–902(2014).

Diler D.Kurda, Darya J. Raheem, Mohammed K. Samad,." Synthesis, Characterization and dying performance studies of some azo dyes derived from m-phenylenediamine".ZJPAS. J.28(6): 841-851(2016).

Hanadi, K.I. Muneer, A. AL-Da'amy, E. T. 2018. Effective Adsorption of Azure B Dye from Aqueous Solution UsingSnail Shell Powder. J Biochem Tech. 9(3): 39-44.

Hawaiz, F. E., Raheem, D. J. & Samad, M. K., Synthesis and Characterization of Some New Azoimine Dyes and their Applications (2016).

Kirkan, B. and Gup, R. Synthesis of New Azo Dyes and Copper (II) Complexes Derived from Barbituric Acid and 4-Aminobenzoylhydrazone. Turk. J. Chem. 32, 9-17(2008).

Noor Sabah Al-Obaidi, Hanaa Kaain Salih, Ahmed N.Abd, Preparation and Characterization Some Monomers and Polymers Derived from Azo-Schiff Base Compounds and Studying Liquid Crystalline Properties, Electrical Conductivity and Dielectric Constant J. Diyala Journal for pure sciences Vol: 14 No:2 (2018) .

Otutu JO Synthesis and application of azo dyes derived from 2-amino-1, 3,4-thiadiazole-2-thiol on polyester fibre. IJRRAS 15: 292–296 (2013).

PATEL, R., PATEL, N. & PATEL, K. Synthesis and Properties of Acid Dyes Derived from 4, 4'-Methylene bis (2, 5-dichloro aniline). Asian Journal of Chemistry, 19, 149 (2007).

Ratna PBS Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. Int J Environ Sci 3:940–955 (2012).

Santhanalakshmi J, Komalavalli R Nano TiO2 assisted degradation of textile dyes in H2O2 aqueous solution: kinetic studies with pH and mass effects. Chem Sci Trans 1:522–529 (2012).

Xu, H. & Zeng, X. "Synthesis of diaryl-azo derivatives as potential antifungal agents". Bioorg. Med. Chem. Lett., 20, 4193-4195(2010).

Zollinger, H. Color chemistry: syntheses, properties, and applications of organic dyes and pigments, John Wiley & Sons. (2003).