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Preparation and Characterization of Some New Compounds of Azo Dyes Derived from 4-amino Antipyrine, the Study of Some Physical Applications, and Evaluation of Their Biological Activity

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Abstract:

In this research, new azo dyes were prepared from the reaction of 4-amino Antipyrine with nitrous acid by the sublimation method. Uv-vis., FT-IR, ^{1}H-NMR, ^{13}C-NMR, (S.E.M.). The electrical conductivity and biological activity of some prepared compounds and two types of pathogenic bacteria were studied, of them were Gram-positive (G+), and were Gram-negative(G-). These include (*Staphylococcus aureus*, *Klebsiellia pneumonia*,) and the Acker Muller-Hinton culture medium. (Molar Huntin Agar) Aqueous solutions of the two compounds [S1, S3] with concentrations (0.01,0.001,0.0001) mg/mL were also prepared using dimethyl sulfoxide (DMSO) as solvent. The sensitivity test of bacterial isolates used in the study was conducted by diffusion method, and the antibiotic Ampicillin were used as a control sample. The electrical conductivity and industrial stability of some prepared compounds were also studied.

Keywords: 4-amino Antipyrine*, Azo Dyes, Staphylococcus Aureus, Klebsiellia.*

تحضير وتوصيف بعض المركبات الجديدة من أصباغ Azo المشتقة من -4 امينو انتيبايرين ودراسة بعض التطبيقات الفيزيائية وتقييم فعاليتها البيولوجية

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مستخلص

في هذا البحث تم تحضير أصباغ آزو جديدة من تفاعل 4-أمينو أنتيبايرين مع حمض النيتروز بطريقة التسامي.وتم تشخيصها بطيف الأشعة فوق البنفسجية ، FT-IR ، 1H-NMR ، 13C-NMR ، (S.E.M.). وتمت دراسة الموصلية الكهربائية والنشاط البيولوجي لبعض المركبات المحضرة ونوعين من البكتيريا الممرضة أحدهما موجب الجرام (G +) وسالب الجرام (G-). وتشمل هذه (Staphylococcus aureus ، والالتهاب الرئوي Klebsiellia ،) ووسط الزراعي Acker Muller-Hinton. (Molar Huntin Agar) تم أيضًا تحضير المحاليل المائية للمركبين [S1 ، S3] بتركيزات (0.01،0.001،0.0001) مجم / مل باستخدام ثنائي ميثيل سلفوكسيد (DMSO) كمذيب. تم إجراء اختبار الحساسية للعزلات البكتيرية المستخدمة في الدراسة بطريقة الانتشار ، واستخدم المضاد الحيوي الامبيسيلين كعينة تحكم. كما تم دراسة التوصيل الكهربائي والاستقرار الحراري لبعض المركبات المحضرة.

الكلمات المفتاحية: 4- امينو انتيبايرين ، اصباغ الازو ، المكورات العنقودية الذهبية ، الكليبسيلا الرئوية.

1. Introduction:

Over the previous years and until the middle of the nineteenth century, the colored materials were natural sources such as organic and inorganic dyes, and organic dyes are aromatic and have an ancient history in dyeing, as they were used in textile dyeing and supplied from a vegetable source [1]. The industrially prepared azo dyes are of the largest varieties, as they can bind to the substance to be dyed and give it distinctive colors [2]. Some of the azo dyes are unaffected by light, oxygen, washing, or acids and bases [3]. Azo dyes are named because they contain the azo group [4]. The azo group consists of two nitrogen atoms linked by a double bond (-N=N-). It has SP^2 hybridization, bonded with aromatic or aliphatic carbon atoms [5]. Azo dyes may contain one azo group called mono azo dyes, or they may be dichotomous may have more than two azo groups called triple azo dyes [6]. According to the IUPAC system, goose dyes are defined as diamide derivatives HN=NH [7], containing two aryl groups and being the most stable, while the -N=N- group is called the Azo group [8]. There is also another classification based on the method of applying these dyes on an industrial scale. The dyes are grouped as dispersed, acidic, basic, or reactive [9]. The main factors that show colors are the presence of unsaturated groups in the molecule, and just as the axochromic groups are essential in increasing the intensity of the color, they give the dye molecule acidic or essential qualities as it expands its ability to contact the substance to be dyed [10]. It is an organic compound whose formula is $C_{11}H_{13}N_3O$ derived from pyrazolone, and the synonyms for its name are metapyrazone, 4-aminophenazone, which is derived from pyrazolone and has a lactam ring consisting of five functional groups in the pyrazolone molecule and a free amino group. Analgesic, antipyretic, and antipharyngeal inflammatory [11,12], and 4-AAP is used in the field of analytical chemistry, as mineral chelates are widely used such as corrosion inhibition, antioxidants, and anthelmintic activity, as well as its chelating properties. 4-AAP has the ability to form a wide variety of mineral complexes with all types of transition metals [13], and 4-AAP is also used as a primary and basic material in the preparation of mono and binary azo dyes because

of its biological importance and importance in many fields, especially in the preparation of organic compounds and supporting metal complexes [14], and 4-AAP possesses antibacterial and antifungal biological properties, analgesic, sedative, antipyretic and anti-inflammatory, as well as It is an anti-rheumatic drug for the peripheral nervous system EC. From an industrial point of view, 4-AAP has been used as an inhibitor of corrosion of steel and zinc in a solution of sulfuric acid and nitric acid. It has also been used as an electrophilic reagent for the determination of ferric iron in water, industrial effluents and soil samples. It was also used in the preparation of a large number of azo dyes for tissues, estimation from abroad, 4-AAP was used in the estimation of pesticide residues in the estimation of cost and aromatic amines, and 4-AAP was used in the estimation of aromatic compounds and substances, and 4-AAP was used in some pharmaceuticals in some compounds [15] .

2. Experimental:

2.1. Chemicals used: All chemicals used in this work were purchased from BDH, Aldrich

and Fluka companies and were used without further purification.

2.2. Devices used: The melting points were measured using Electrothermal Melting Apparatus 9300. The FT-IR spectra were captured using a Shimadzu FT-IR 8400S spectrophotometer with a (4000-400) cm^{-1} by KBr disc. DMSO-d_6 as solvents were used to capture ^{1}H-NMR and ^{13}C-NMR spectra on Bruker instruments running at (400) MHZ.

2.3. Preparation of azo dyes (S1-S5)

2.3.1. Preparation of the compound (S1) [16,17]:

In a round flask (100 mL) (0.01 mol) sodium nitrite was dissolved in (25 mL) distilled water in an ice bath (0-5) 0°C. To (0.01 mol) of hydrochloric acid, and in a flask of (100 ml) capacity, (0.01 mol) 4-aminoantipyrine was dissolved in (25 ml) of distilled water, then (0.01 mol) of 4-chlorobenzaldehyde was added from the separation funnel, the contents of the beaker were added to sodium nitrite drop by drop while maintaining the temperature. As the distillation continues, the color of the solution changes from transparent to purple. After the distillation was completed, the stirring was continued for an entire hour without

heating. Then the residue was filtered and dried .

2.3.2. Preparation of the compound (S5) [18,19]

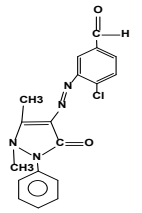
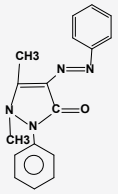
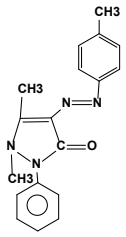
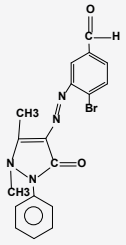
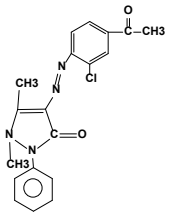
In a round flask (100 mL) (0.01 mol) sodium nitrite was dissolved in (25 mL) distilled water in an ice bath (0-5) 0°C. To (0.01 mol) of hydrochloric acid, and in a flask of (100 ml) capacity, (0.01 mol) 4-aminoantipyrine was dissolved in (25 ml) of distilled water, then (0.01 mol) Chloroacetophenone was added from the separation funnel, the contents of the beaker were added to sodium nitrite drop by drop while maintaining the temperature. As the distillation continues, the color of the solution changes from transparent to Orange. After the distillation was completed, the stirring was continued for an entire hour without heating. Then the residue was filtered and dried .

The rest of the chemical compounds [S2,S3,S4] were prepared in the same way.

Table (1) shows some physical properties of azo dyes.

Comp. No.	Molecular Formula	Color	M.P ^{o}C	Yield %
S1	$C_{18}H_{16}ClN_4O_2$	purple	210-212.	89
S2	$C_{17}H_{18}N_4O$	purple	175-177	91
S3	$C_{18}H_{20}N_4O$	Dark Red	166-168	83
S4	$C_{18}H_{17}BrN_4O_2$	Brown	104-106	88
S5	$C_{19}H_{19}ClN_4O_2$	Brown	191-193	84

Table (2): Shows the prepared azo compounds

.Comp. NO	Structure & Name
S1	 (*E*)-4-chloro-3-((2-(cyclohexa-1,5-dien-1-yl)-1,5-dimethyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)benzaldehyde
S2	 (*E*)-2-(cyclohexa-1,5-dien-1-yl)-1,5-dimethyl-4-(phenyldiazenyl)-1,2-dihydro-3*H*-pyrazol-3-one
S3	 (*E*)-2-(cyclohexa-1,5-dien-1-yl)-1,5-dimethyl-4-(*P*-tolyldiazenyl)-1,2-dihydro-3*H*-pyrazol-3-one
S4	 (*E*)-4-bromo-3-((2-(cyclohexa-1,5-dien-1-yl)-1,5-dimethyl-3-oxo-2,3-dihydro-1*H*-pyrazol-4-yl)diazenyl)benzaldehyde
S5	 (*E*)-4-((4-acetyl-2-chlorophenyl)diazenyl)-2-(cyclohexa-1,5-dien-1-yl)-1,5-dimethyl-1,2-dihydro-3*H*-pyrazol-3-one

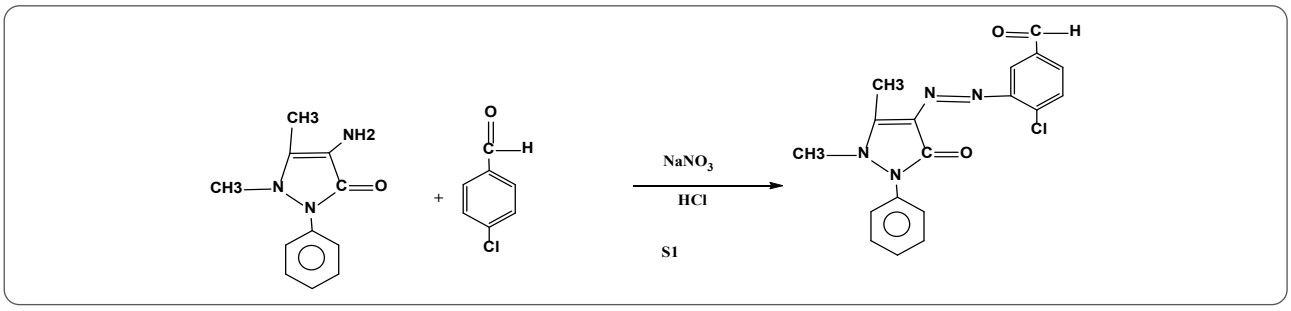
2.4. Study of biological activity [20, 21]:

This Study was used on two types of pathogenic bacteria, of which are gram-positive, are gram-negative, and they are: *Staphylococcus aureus* and, *Klebsiellia pneumonia*, are essential in the medical field because of their resistance to antibiotics. These bacteria were taken from the laboratories of the College of Education for Pure Sciences, Department of Bio-Sciences, and a

Mueller-Hinton-Agar culture medium was used. Molar Huntin Agar) is used to measure the biological activity of antibiotics and chemicals for medical uses and is used to measure and determine the minimum inhibitor (MIC). Aqueous solutions of the two compounds [S1, S3] were also prepared. At concentrations of (0.01, 0.001, 0.0001 , mg/mL) and using a solvent dimethyl sulfoxide (DMSO), a sensitivity test was performed for the bacterial isolates that were used in Study by diffusion method in the nutrient medium of Mueller-Hinton agar, which is a transparent nutrient medium with a dark yellow color. in the sensitivity test of microorganisms towards antibiotics because it contains an animal infusion extracted from casein and starch.

3. Results and Discussion:

The azo dyes were prepared from the reaction of one mole of) 4-aminoantipyrine with one mole of nitrous acid and 4-chlorobenzaldehyde .



3.1. Spectroscopic interpretation (U.V-vis., FT-IR .,^{1}H-NMR, ^{13}C-NMR, Mass)

The reaction of the compounds [S1-S5] was confirmed by diagnosing the prepared azo dyes by measurements of ultraviolet (Uv-vis.), infrared (FT-IR), proton nuclear magnetic resonance (^{1}H-NMR), and carbon nuclear magnetic resonance (^{13}C-NMR) spectrum

When studying the ultraviolet (U.V-vis.) spectrum of the prepared azo dyes,[S1] shown in figure (1), we notice the appearance of an absorption band of greater intensity and lower wavelength due to the electronic transitions π→π * and caused by (C=C) bonds, which Pathochromia displacement appears in the prepared azo dyes within a range of (280) nm, as well as a beam of greater wavelength and lower intensity, which is attributed to the electronic transitions n→π*, which are caused by the electron pairs. There is no participation in the oxygen and nitrogen atoms. These bands appear

pathochromically shifted in the prepared compounds due to oxo groups and succession within the range (380-325) nm [22].

When studying the infrared (FT-IR) spectrum of azo dyes [S1], shown in figure (2), it was noticed that the stretching band of the amine group (NH_2) disappeared in the prepared compounds with the appearance of several bands within the range Absorption bands within the range (1698 cm -1) bel

ong to the group (C = O) imide, a band at the range (1647 cm -1) belong to the group (N = N), and a band at the range (3141 cm -1) (1590-1570 cm -1) belong to (C = C) olivine . As for the (C-N) group, curvature beams appeared in the areas (1207) cm^{-1} and group curvature beams. (C-O) appeared in areas (1132) cm^{-1}, and as shown in table (2), these bundles were close to what is found in the literature [23].

Table (3): Results of the ultraviolet (nm) and infrared spectra of azo dyes

Comp. No.	UV,λmax (nm), DMSO	νCH alkene νC=C aromatic ν CH aliphatic	νC=O amide	ν(C=C) olefinic νC=C aromatic δ (C-H) aliphatic	ν(N=N)	ν (C-N) ν (C-O)	δ (C-H) aromatic monosubstituted of plane
S1	289	3141	1698	1647 1590, 1482	1570	1207 1167	766-827
S2	283	3186,3157 3043,2966,2869	1708	1614, 1583 1483,1456	1515	1282 1251	844,808
S3	287	3201 3031, 2935	1702	1602,1548,1508 1398,1367	1508	1288 1107	640,707, 748
S4	236	3253 3043, 2927	1691	1593,1521 1448,1406,1380	1521	1282 1224	748
S5	288	3208 3042	1713	1652,1633, 1485,1456	1558	1219 1176	769

When performing the ^{1}H-NMR of the compound [S1], shown in figure (4), we note the protons of the benzene ring appeared as two overlapping beams in the range (7.5-7.4) ppm, The spectrum showed signals at the site (5.39-5.84) belonging to the protons of the pentagonal ring. as well as the emergence of protons of alkyl groups in the position of (3.6-3.4) ppm, and a signal appeared at (2.6-1.2) ppm belonging to the protons of the solvent (DMSO- d_6).

When studying the ^{13}C-NMR spectrum for the compound [S1] shown in

figure (5), The signal at (160) ppm belongs to the carbonyl of the five-ring, and the signal at (160) ppm belongs to the carbon of the five-ring linked to the methyl group, and multiple signals appeared at (134-124) ppm belonging to the carbons of the aromatic ring, and the signal at (95) ppm refers to the carbon of the five-ring linked to the azo group, and the sign at(40) ppm belongs to the carbon (CH3) attached to the nitrogen of the five-ring, with the appearance of a signal between (10-37) ppm belonging to the carbon of the aliphatic group [24].

3.2. SEM analysis of the scanning electron microscope:

The technique (SEM) is used to take an image of the surfaces of materials, as it is a focused beam of high-energy electrons to generate a variety of signals on the surface of solid samples, where the different signals emanating from the sample reveal information about the sample, including the external shape and crystal structure, whether it is nanomaterials or not, and a two-dimensional image is created that displays the differences in these properties, and conventional areas whose width ranges from about 1cm to 5μm can be imaged in scanning mode. (with a resolution potential of 50 to 100 nm, magnification ranges from 20X to about 30,000X) Also capable of performing analyzes of the locations of selected points on the sample, this approach is particularly important for SEM and crystal structure. The SEM analysis of the compound[S1] showed that (500nm) was used for the cross-sectional area and the magnification power (MAG: 70.0KX), where the peak of the radii of the compound particles was (70.10nm), which is shown in the Gaussian curve. shown in figure (6),. [25,26].

3.3. Dyeing operations:

One of the essential applications of dyes is their use as dyes with better specifications than the specifications of ordinary dyes. The dye is the colored substance that can give its color to another sense, provided that it meets several conditions, namely, that it has a particular ability to the body to be dyed, to be Intense color and stable qualities against the influence of chemical and natural factors such as fastness to light and washing. Azo dyes [S50, S55] were used in the dyeing process, where an appropriate amount of azo dye was dissolved in a suitable solvent. The resulting solutions were used

to dye equal weight pieces of cotton, wool, cloth, and brocade, where iron was used to fix the dye. When washed with water, it showed apparent stability and had good strength against soap and washing powder shown in figure (7,8), [27, 28].

3.5. Biological activity of some prepared compounds:

The study of the biological activity of the compounds prepared with certain concentrations showed that most of these compounds have antagonistic activity against the types of bacteria studied, compared to the antibiotic Ceftriaxone, Ampicillin (Cefixime, which are a broad-spectrum antibiotic with an antibacterial activity). It has both positive and negative bacterias , and it also has a large inhibitory diameter as it gives a high selectivity when studying the sensitivity of bacteria to the prepared compounds, and since this antibiotic is used to treat many infections and diseases such as urinary tract infections, especially those

Test	*Staph aureus*	*Klebsiellia pneumoniae*

that occur as a result of Infection with colon bacteria and Staphylococcus aureus bacteria, as well as simple cystitis in females caused by coliform bacteria, and prostatitis caused by colon bacteria in addition to infections of the lower respiratory tract, sinusitis, arthritis and bones. It is also used to treat diarrhea caused by colon bacteria and is also effective in treating typhoid. Therefore, two compounds of the compounds prepared in this research [S1, S5] were studied on different types of chromium-positive and negative bacteria, which recorded a global antagonistic activity against the bacteria studied, and compared with the mentioned antibiotics, it is possible to use these compounds As a treatment for the same infections and pathological conditions above, after investigating the biological path of these compounds, their side effects, and the amount of their accumulation in animal tissues. different compounds (0.01,0.001,0.0001, mg/ml), where the diameter of the inhibition ranges between (0 mm minimum diameter of inhibition to 13 mm maximum diameter of inhibition measured) and the table below It shows the inhibitory activity of some of the prepared compounds, and the figures show that the value of the inhibition varies according to the compound, and this is due to the low baseline and because of the presence of resonance shown in figure (9), [29].

Table (4): The inhibitory activity of the two compounds [S1, S5] in the growth of a number of positive and negative bacteria (the diameter of inhibition measured in mm)

Test	Staph aureus			Klebsiellia pneumoniae		
	0.01	0.001	0.0001	0.01	0.001	0.0001
S1	10	9	-	10	9	-
S2	5	6	4	13	10	-
S3	8	-	-	7	-	-
S4	9	8	9	8	12	-
S5	8	7	6	-	-	-

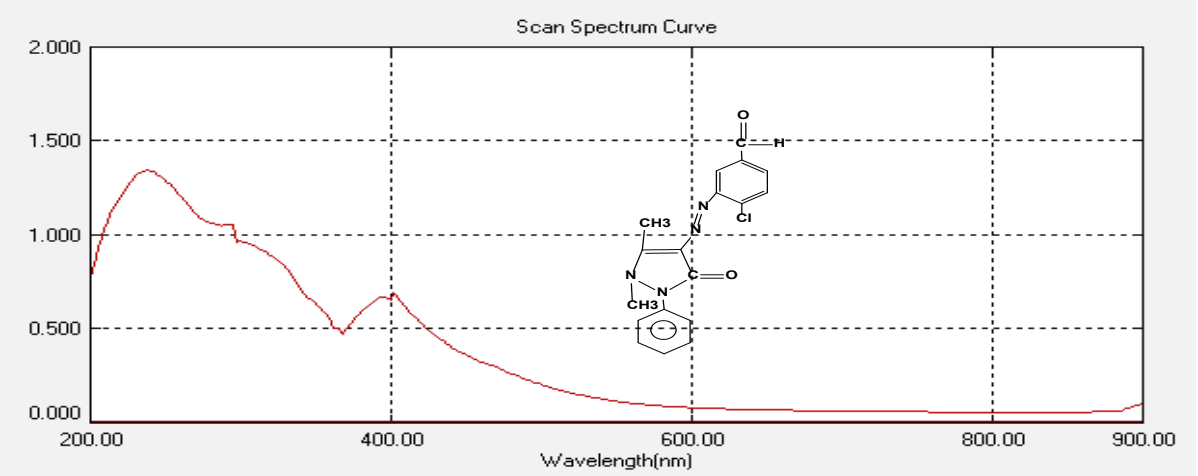


Figure 1: UV spectrum of S1

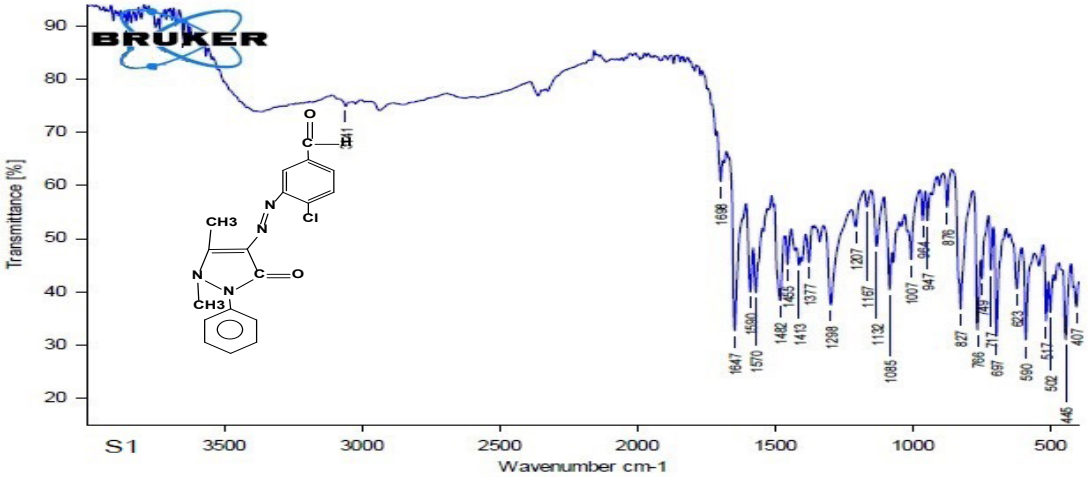


Figure 2: FTIR spectrum of S1

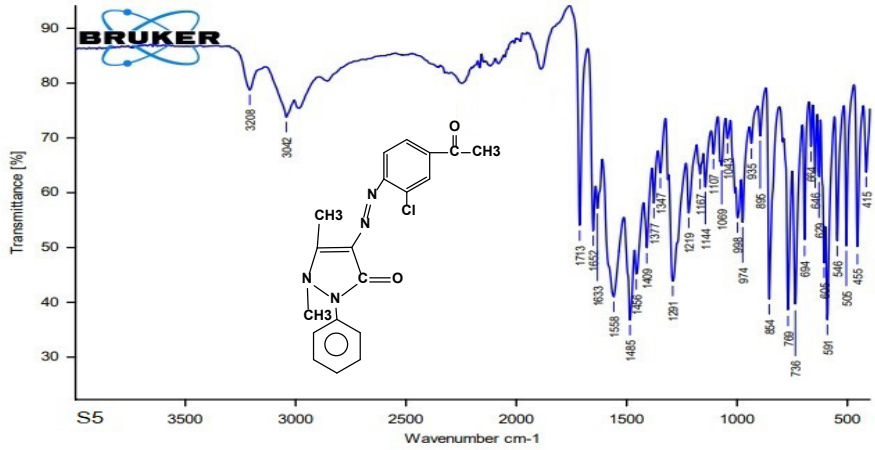


Figure 3: FTIR spectrum of S5

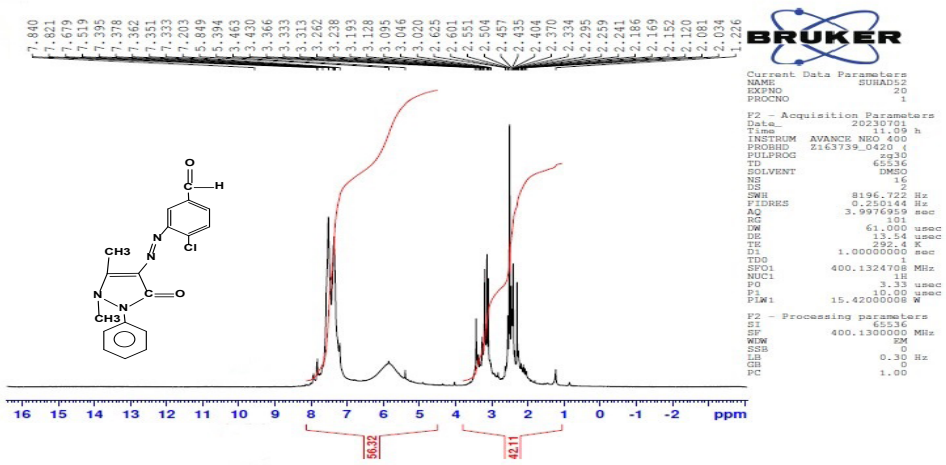


Figure 4: ^{1}H-NMR spectrum of S1

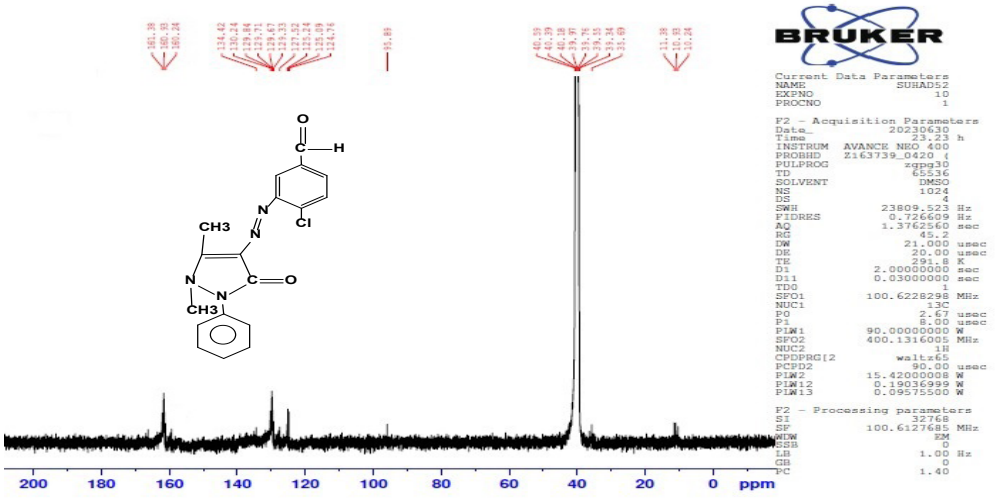
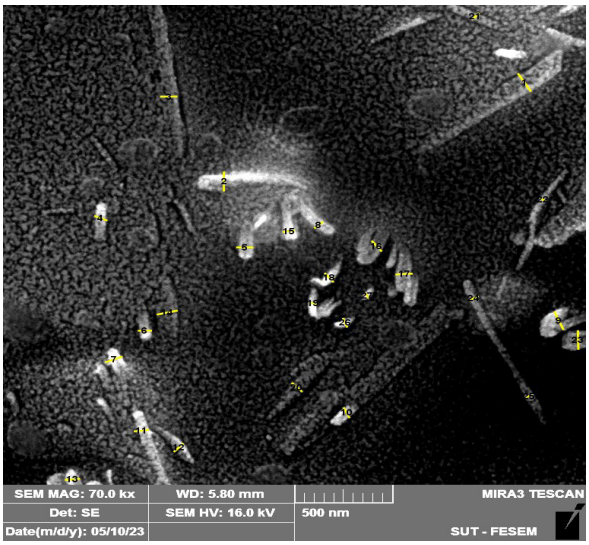
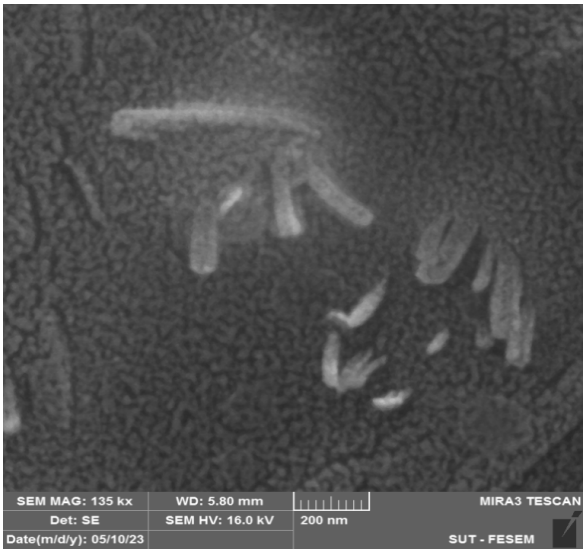
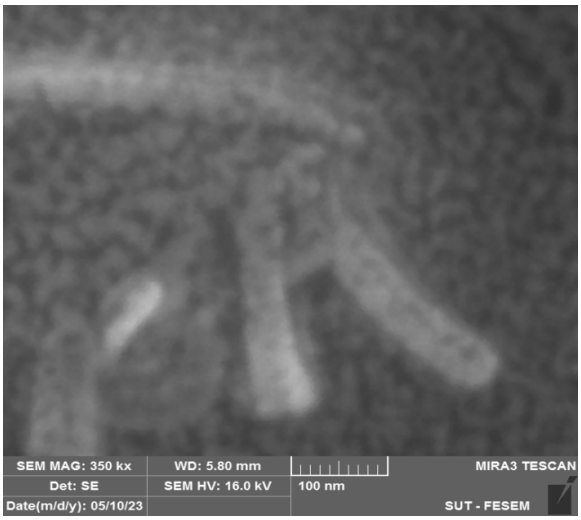


Figure 5: ^{13}C-NMR spectrum of S1







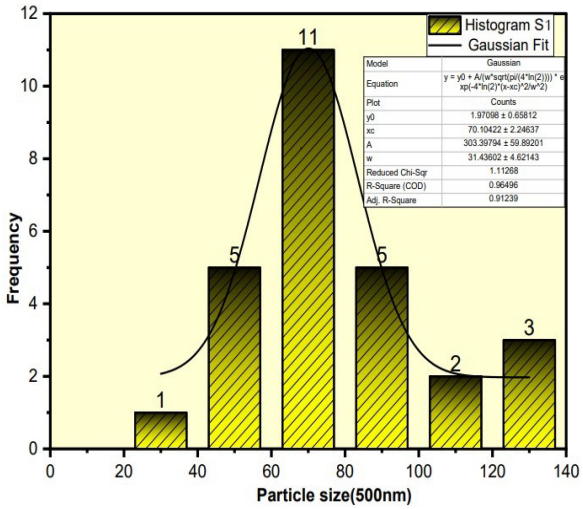


Figure 6: SEM of S1

Figure 7: Dyeing process for compound [S1] before and after washing with water

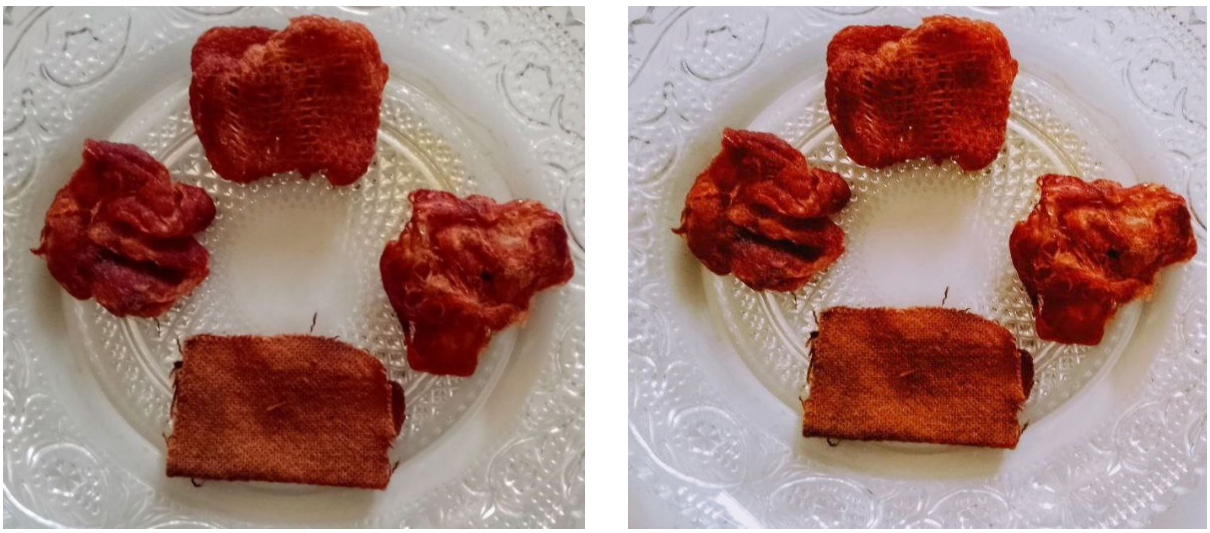


Figure 8: Dyeing process for compound [S5] before and after washing with water

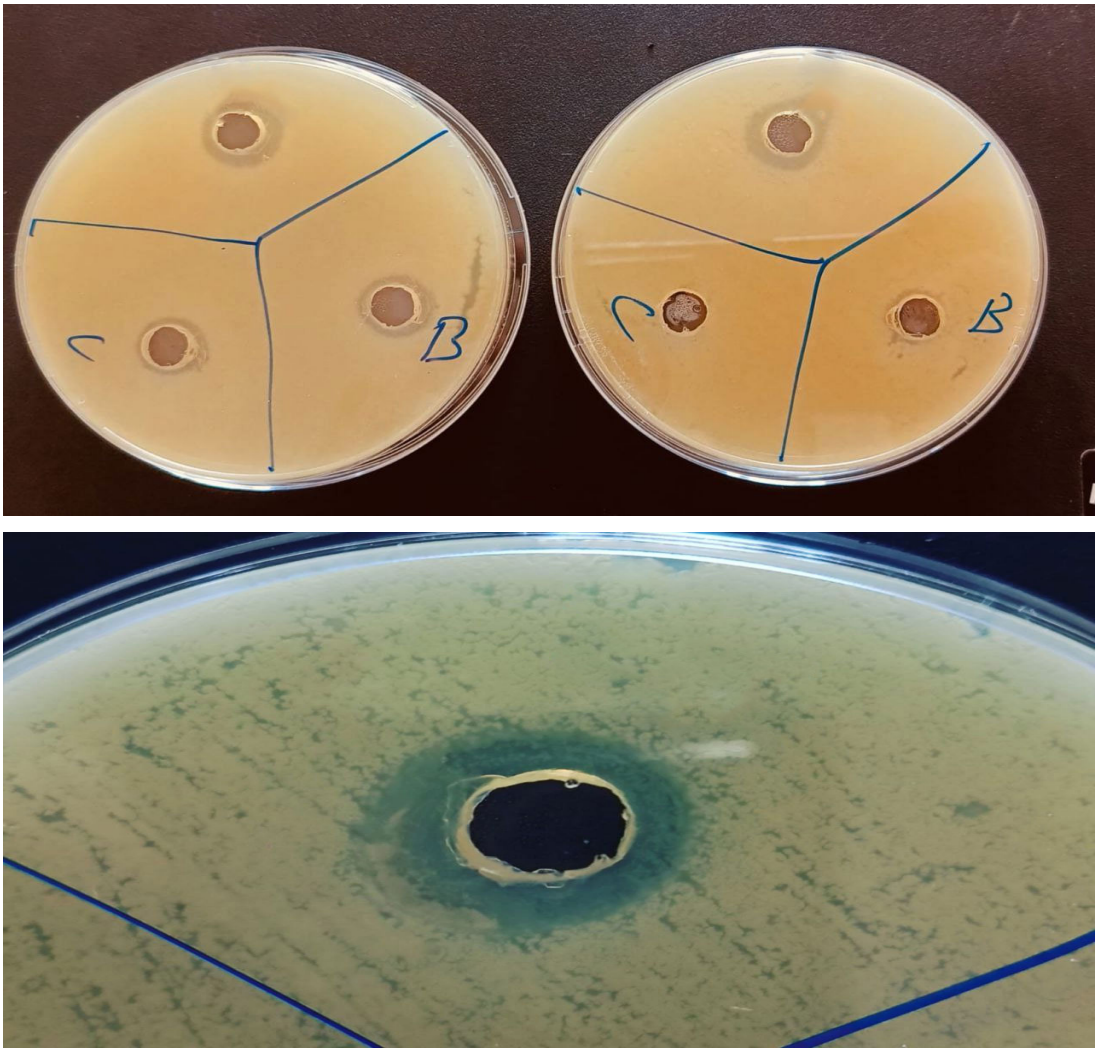


Figure 9: Compound S1,S5 inhibits the growth of all used bacteria

4. Conclusions:

Physical and spectroscopic measurements confirmed the accuracy and validity of the prepared compounds. Therefore, the methods used in the preparation were good, successful and low cost. Through SEM analysis, the surface of the prepared compounds appeared as if they were rocky layers interspersed with deep trenches. The values of the precise analysis of the elements for the prepared compounds were identical or close to the calculated percentage. The vehicles were shown to have good electrical conductivity. The prepared compounds also showed good efficacy against the bacteria used in the study. The prepared azo dyes also showed good industrial stability of their dyes, as it was noticed that the dyes were not removed by washing and maintained their stability.

Reference

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