RESEARCH ARTICLE

Synthesis, Characterization and polymerization of 1Hpyrazolo[1,2-b] phthalazine-5,10-dione derivatives Using CuO nanoparticle Oxide from Natural Source as Catalyst

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ABSTRACT

Copper Oxide (CuO) nanoparticles (NPs) of 17-22 nm size have been synthesized from Syzygium aromaticum (Eugenia caryophyllus). The resulting Nanoparticles (NP) have been described by fourier transform infrared spectroscopy (FTIR) spectroscopy, X-ray diffraction and Transmission electron microscopy. The CuO NPs was used as a nano catalyst for synthesis and polymerization of 1Hpyrazolo[1,2-b]phthalazine-5,10-dione derivatives by a three-component coupling reaction between aldehydes, 5,5-diethyl-2,3-dihydrophthalazine-1,4(5H,8H)-dione and malononitrile. They have good catalytic activity with outstanding yields. Significant features of Copper Oxide nanoparticles (CuO NP) as a catalyst. Reaction time, higher yields, simple chemical separation, catalytic economic efficiency, quick process and no harmful by-products. Using spectroscopic methods (FTIR, 1H-NMR spectral), new derivatives of synthesized compounds were verified, and physicochemical experiments were examined. The action of these compounds was then tested as a possible antibacterial against various forms of pathogenic bacterial isolates and too as acute toxicity.

Keywords: Copper Oxide Nanoparticles, Polymerization, catalyst, FTIR, 1H-NMR.

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INTRODUCTION

Nanoparticles (NP) have gained a lot of notice as effective catalysts in a lot of organic reactions because of the high surface-to-volume rate and coordination constituent that have a higher number of active sites per unit area relative to heterogeneous counter locates.[1] In the current research, we have researched CuO Nanoparticles as a catalyst, because of the low emissions and simple working conditions, organic transformations in solvent-free conditions using a heterogeneous catalyst have taken on of great importance.[2–5] In recent years, due to its low cost, abundant resources, non-toxicity, and ease of preparation with various nanoscale dimensional shapes, we have selected CuO NPs as a promising candidate among the various metal oxides NPs in the current sample. Electrochemical batteries,[6] gas sensors,[7] photovoltaics, thermoelectric structures,[8] nanofluids and photocatalysis are commonly used in CuO NPs.[9–10] Methods such as thermoelectric, electrochemical precipitation, solid-state reaction and sol-gel for the manufacture of CuO nanomaterials are varied.[11–14] Despite that, there are some disadvantages to methods mentioned above for the synthesis of CuO NPs, such as time-consuming, expensive, contaminating, and poor yields. Microwave processing (MW) is favoured over traditional synthesis to overcome all the challenges. The synthesis of 17-22 nm CuO NPs requires just 4 minutes. In terms of energy as well as time, this approach is economical. To investigate different methodologies for the synthesis of organic compounds.[15-16] Transition metal nanoparticles and their role as catalysts in organic reactions.[17–20] We now report the synthesis of 1Hpyrazolo]1,2-b[phthalazine-5,10-dione derivatives using CuO NPs as a heterogeneous catalyst.

EXPERIMENTAL

Chemical

Reagents were collected and used without purification from industrial manufacturers. In open capillary tubes, melting points were determined using the Thermo system FP800 Mettler central processor supplied with the FP81 MBC cell devices (Stuart Research, Redhill, UK) and were not corrected. Using FTIR Shimadzu (Japan), infrared spectra were produced and recorded as KBr disks in the range of (400-4000 cm-1). Chemical change values in δ (ppm) relative to the residual solvent peak are recorded; coupling constants (J) in Hertz (Hz) are reported experimental. 1H-NMR Spectra using

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DMSO-d6 as solvent and tetra methyl silane as internal normal reference were registered on a 400MHz Bruker instrument. The antimicrobial analysis was performed at the University of Baghdad, College of Science for Women, Department of Biology.

The Synthesis of Nanoparticles of CuO[21]

A 5 g fine ground plant powder was collected in a boiling water bath with 100 mL of Milli Q water Filtered for 30 minutes with Whatman no. 1 filter paper. A 10 mL The aliquot was titrated with 100 ml of aqueous plant extract of a 5 mM CuSO45H2O For the reduction of CuO NPs over 2 hours at 50 C. To isolate agglomerated, broad-sized particles and plant admixtures, the collected mixture was centrifuged at 10,000 RPM for 15 minutes. X-ray diffraction (XRD). The morphology was controlled by an electron scanning microscope (SEM). Chemical properties of the FTIR have been examined.

The synthesis of 1Hpyrazolo[1,2-b]phthalazine-5,10-dione derivatives:[C1,C2][22]

Mixture of the malononitrile (0.066 gm,.0.01 mol), different aldehyde]4-(dimethylamino) benzaldehyde, propionaldehyde (0.01mol)[, 5,5-diethyl-2,3-dihydrophthalazine-1,4(5H,8H)-dione (0.220gm,0.01 mol), and nano-CuO (10% mol) They're put in a mortar. It then heated the reaction mixture to (80-100 C) completion of there action as tracked by TLC, the achievement was accomplished. The mixture for the reaction was then cooled, washed with ethanol (2 × 3 mL) and vacuum-evaporated to provide the product C1and C2.

Preparation of 3-(3-carboxyacrylamido)-1-methyl-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carboxylic acid:]C3,C4[[23].

A mixture of C1, C2 (.0.001 mmol) was added to2drops H_2SO_4/ H+ then add (0.196 gm.0.001 mmol) Maleic anhydride dissolve the mixture with 10 ml of DMF and heated the mixture with constant stirring 60–70ºC for 3h until all the materials were fused completion of there action was achieved as monitored by TLC. evaporated under vacuum to give the product C3 and C4.

Synthesis of Polymer:[C5,C6][23]

Amount of (0.01 mol) of C3 , C4 in (5 mL) of DMF and (2.0 gm, 0.01 mol)of acrylic acid, the mixture was introduced in polymerization bottle, , the mixture was reflux at 60-70C0, for 30 minutes was added (0.1 gm, 0.0003 mol)of APS The mixture of reflux was at 70°C, for 30 minuts. The solvent was vacuum evaporated; the substance was obtained, washed with ether and dried in a 50C0 vacuum ovenwith (77%) the new compounds as given below C5 and (89%) the new compounds as given below C6.

RESULTS AND DISCUSSION

Characterization of Nanoparticles of Copper Oxide[25]

Illustrates the pattern of CuO Nanoparticles XRD. The crystal of a monoclinic frame CuO (C2/c space group, JCPDS card # 45-0937) also indexes all CuO Nanoparticles peaks. There were No peaks typical of any inclusions observed, Indicating the good quality CuO Nanoparticles were prepared. The size of the crystal was determined using the XRD process. Using the Shearer equation, the crystal size was calculated from the XRD pattern, where the form factor is the CuO Ka radiation X-ray wavelength (1.54 Å), The diffraction angle of Bragg and the FWHM of the resulting peak of diffraction. It was noticed that the crystal scale corresponding to the highest point measured in XRD was 23.42 nm. The occurrence In the XRD trends and sharp structural peaks of below 100 nm crystal size suggests the nanocrystalline structure of the CuO Nanoparticles. Figures 1 and 2 display the normal SEM and TEM photos of CuO NP. The mean diameter of the CuO

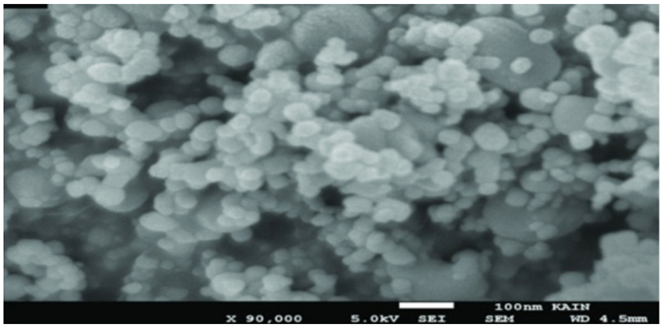


Figure 1: SEM analysis of CuO NPs

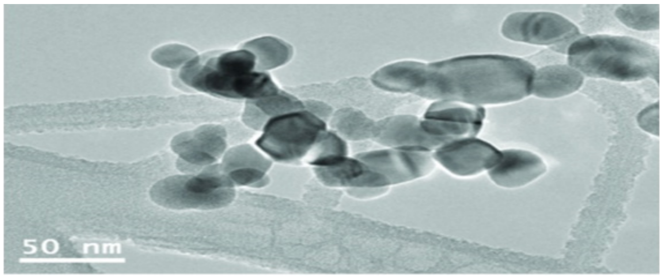
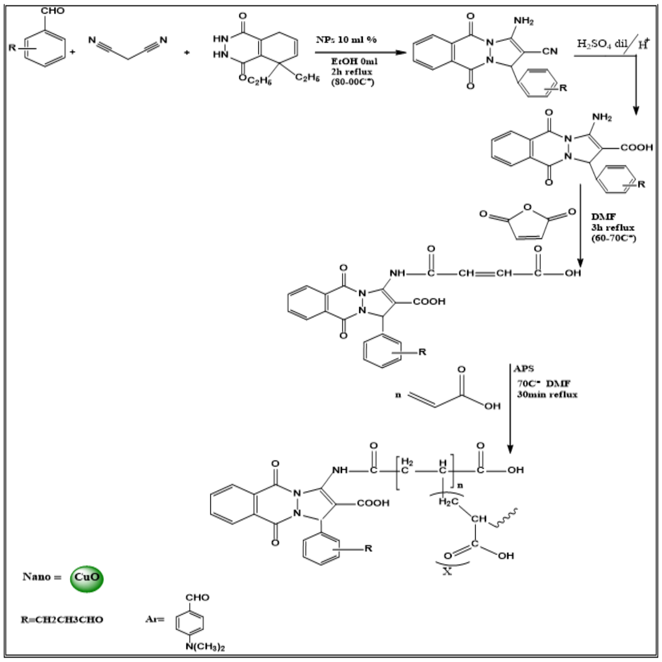


Figure 2: SEM analysis of CuO NPs



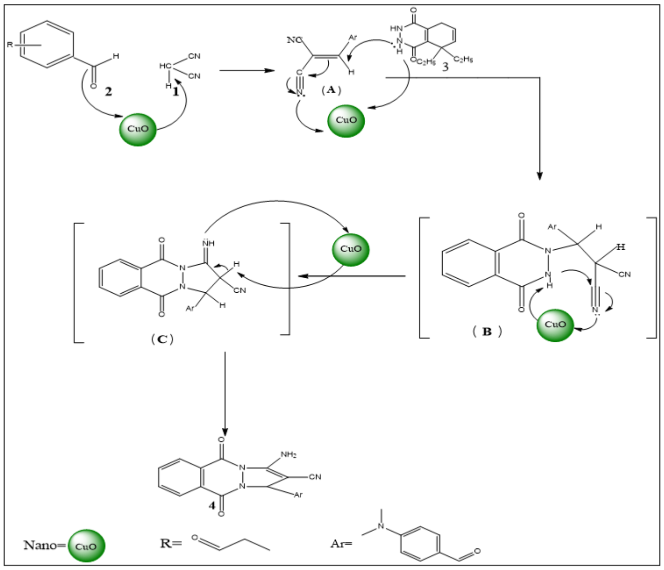
Scheme 1 of reaction

Nanoparticles was determined from a calculation of more than 100 pa. The mean TEM size of the CuO Nanoparticles was approximately 23.17 nm, which is confirmed by the XRD findings. The spectrum of the EDS CuO NPs. The findings of the EDS reveal that No other main impurities are found in the prepared CuO Nanoparticles. A crystalline nature was also demonstrated by high-resolution TEM CuO NP**.**

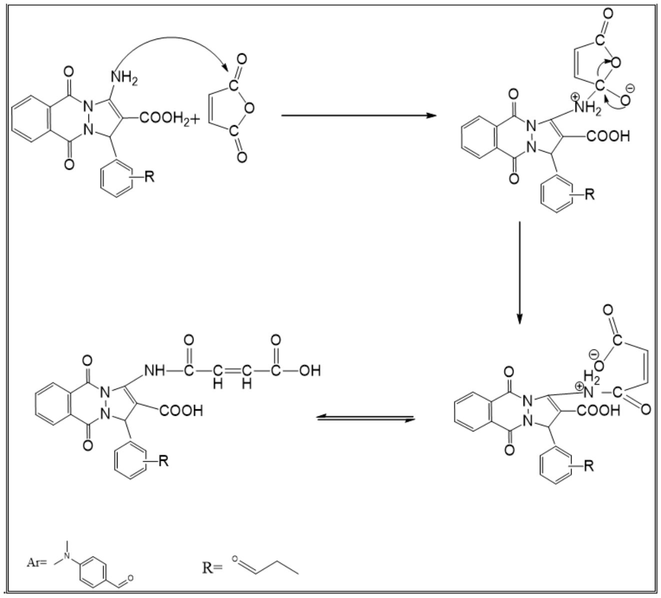
The General Reaction is Summary in Scheme

Compound [C1] was prepared by reacting malononitrile with 4-(dimethyl amino) benzaldehyde, 5,5-diethyl-2,3-dihydrophthalazine-1,4(5H,8H)-dione, in the presence of nano-CuO (10 mol %) The structure of compound [C1] was diagnosed by FTIR spectrum showed disappearance of stretching vibration of (NH2) group υ (3491.16,3444.87) cm^{-1}, vibration of υ (C=N) which appeared υ (2210) cm^{-1}. And several other bands are described in Table 2.

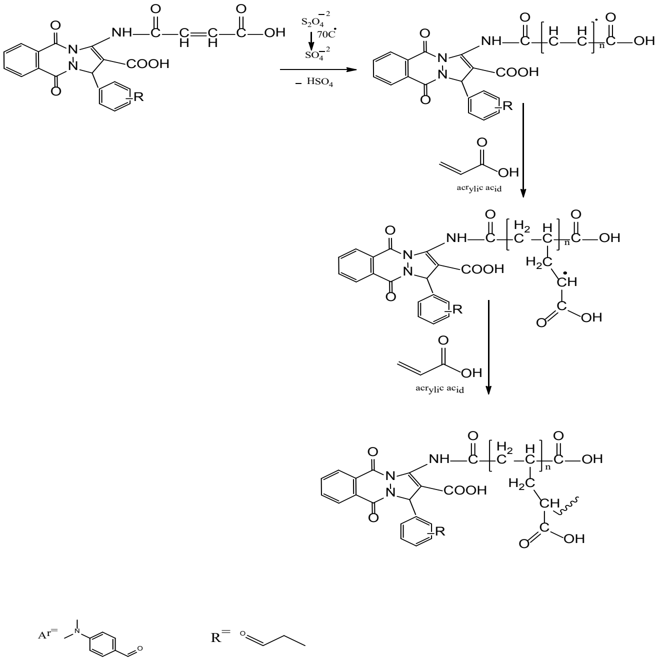
Compound [C2] was prepared by reacting malononitrile with Propionaldehyde, 5,5-diethyl-2,3-dihydrophthalazine-1,4(5H,8H)-dione, in the presence of nano-CuO (10 mol %) The structure of compound [C2] was diagnosed by FT-IR spectrum showed disappearance of stretching vibration of (NH2) group υ (3433.29,3379.29)cm^{-1} and vibration of υ (C=N)



Scheme 1: The mechanism steps for the synthesis of heterocyclic compounds



Scheme 2: The mechanism step of the synthesis of ring opening of maleic anhydride by amino group of NH$_2$



Scheme 3: The mechanism step of the synthesis of Polymer

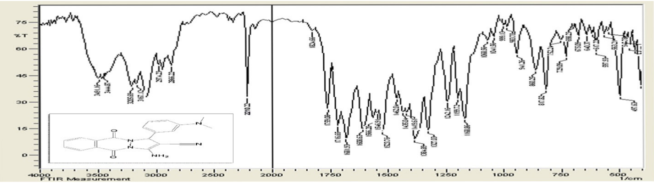


Figure 3: The FT-IR spectrum of compound [C1]

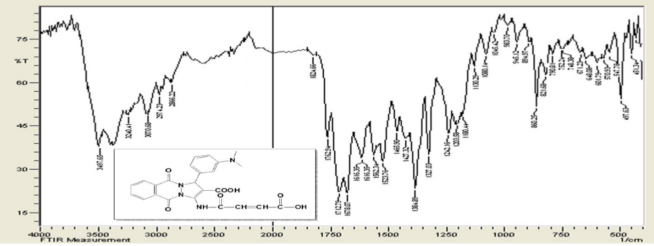


Figure 4: The FT-IR spectrum of compound [C3]

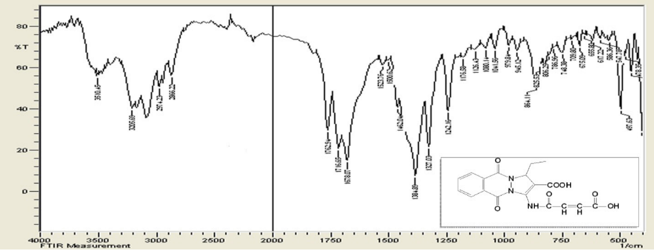


Figure 5: The FT-IR spectrum of compound [C4]

Physical and Spectroscopic Data

Table 1: Physical Properties of the compounds prepared (C1-C6).

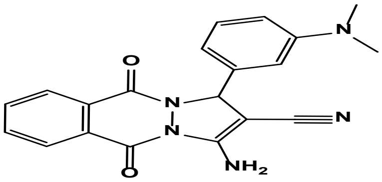
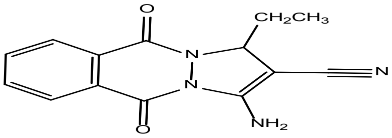
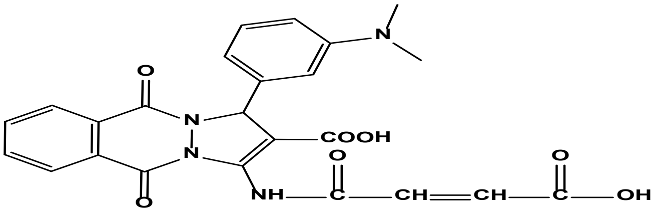
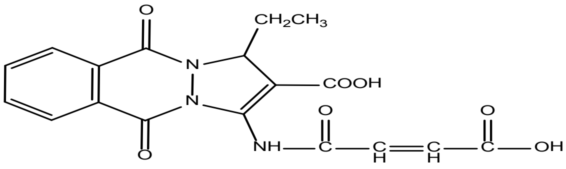
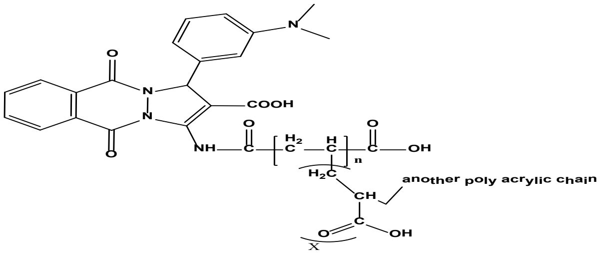
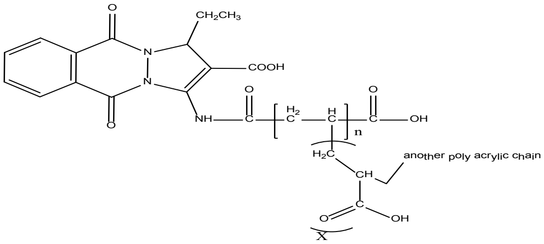
Comp	*Structure formula*	*Yield%*	*Color*	*M.P*
C1	 3¯amino¯1¯(3¯(dimethylamino)phenyl)¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazine¯2¯carbonitrile	88	Brown	122- 124°C
C2	 3¯amino¯1¯ethyl¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazine¯2¯carbonitrile	79	Light green	166-168
C3	 3¯(3¯carboxyacrylamido)¯1¯(3¯(dimethylamino)phenyl)¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazine¯2¯carboxylic acid	75	Yellowish brown	176-178
C4	 3¯(3¯carboxyacrylamido)¯1¯ethyl¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazine¯2¯carboxylic acid	85	Light yellow	160-162
C5	 2¯(2¯((2¯carboxy¯1¯(3¯(dimethylamino)phenyl)¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazin¯3¯yl)amino)¯2¯oxoethyl)pentanedioic acid	77	Dark brown	240-242
C6	 2¯(2¯((2¯carboxy¯1¯ethyl¯5,10¯dioxo¯5,10¯dihydro¯1*H*¯pyrazolo[1,2¯*b*]phthalazin¯3¯yl)amino)¯2¯oxoethyl)pentanedioic acid	89	light Brown	232-234

Table 2: The FTIR Spectrum of Compounds (C1-C6)

comp	*v (OH)*	*v (NH_2)*	*v (NH)*	*v (C≡N)*	*v (C -H) aromatic*	*v (C-H) aliphatic*	*v (C=O)*	*v (C =C)*	*v (N=O)*
C1	/	3491.16 3444.87	/	2210.42	3167.12	2974.23	1759.08	1608.63	1523.76
C2	/	3433.29 3379.29	/	2206.57	3170.69	2978.09	1762.94	1617.99	/
C3	3495.01	/	3371.57	/	3070.68	2684.91	1762.94	1616.35	1562.76
C4	3510.45	/	3244.27	/	3059.10	2966.22	1762	1635.64	/
C5	3500	/	3200	/	3100	2900-2800	1760	1640	1546.91
C6	3450	/	3250	/	3110	2980-2880	1768	1630	/

Table 3: Antibacterial behavior of the compounds being prepared (C_1-C_6) Demonstrates the anti-bacterial activity of the compounds against the four different types of positive and negative bacteria, the Cram stain outside the body of the organism on the culture media.

Compounds No.	*Staphylococcus aureus*	*Bacillus subtilis*	*Escherichia coil*	*Pseudomonas aeruginosa*
3	14	10	10	14
4	18	12	13	0
5	17	14	12	8
6	18	22	14	8
DMSO	0	0	0	0

Table 4: The 1H-NMR spectrum of compounds (C1-C6)

Compounds	*^{1}H-NMR parameters δ (ppm)*
C_1	2.63(s,3H,2CH_3), 4.30(s,2H,NH_2), 7.50-8.35(m,8H,Ar-H)
C_2	0.94(t,H,CH_3), 1.60(q,H,CH_2), 4(s,H,CH), 4.35(s,H,NH_2), 7.85(m,4H,Ar-H)
C_3	3.09(s,3H,CH3), 5.56(s,H,CH), 6.57-7.66(m8H,Ar-H),7.46(2H, CH=CH), 7.93(s,H,CO-NHamide), 11.34 (s,H,OH)
C_4	0.90(t,H,CH3), 1.57(q,H,CH2), 4.27(s,H,CH), 7.85(m,4H,Ar-H) 6.96(2H, CH=CH),7.97(s,H,CO-NHamide)11.25 (s, 1H, OH).
C_5	1.75(m,2H,CH2)2.35(m,H,CH) 3.15(s,3H,CH3), 6.68-7.88(m8H,Ar-H), , 7.90(s,H,CO-NHamide), 11.56 (s,H,OH)
C_6	1.70(m,2H,CH2)2.33(m,H,CH) 0.94(t,H,CH3), 1.66(q,H,CH2), 4.25(s,H,CH), 7.80(m,4H,Ar-H) 7.93(s,H,CO-NHamide)11.14 (s, 1H, OH).

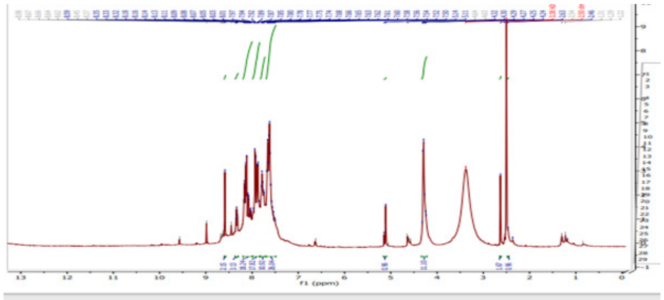


Figure 6: 1H-NMR spectroscopy of the compound [C1]

which appeared at υ(2206.57) cm^{-1}. and a number of other bands are described in Table 2.

Compounds [C3] were prepared of one mmole of compound [C1] with one mmole of Maleic anhydride in the case of DMF as a solvent and stirring of the mixture for 3 hours. compound (C3) have been characterized by FTIR. These spectra showed absorption (OH) acid at (3497.65) cm^{-1} and appearance of bands to ν(NH) at (3240.41) cm^{-1}. ν(C-H) aromatic at (3070.68) cm^{-1}, ν(C-H) aliphatic at (2974.23) cm^{-1}, ν(N=O) at (1523.76) cm-^{1} , ν(C=C) aromatic at (1465.90) cm^{-1}.

Compounds [C4] were prepared of one mmole of compound [C2] with one mmole of Maleic anhydride in the case of DMF as a solvent and stirring of the mixture for 3 hours. compound

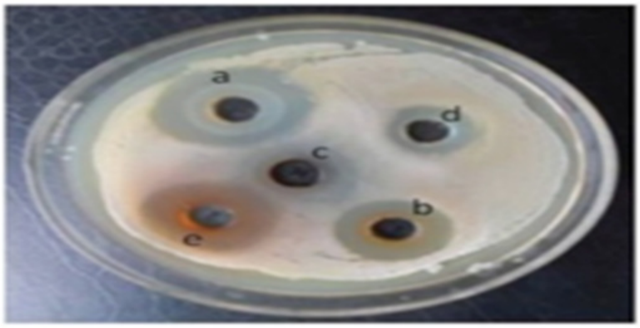


Figure 7: Its high efficacy, especially on gram-positive bacteria (Baslas), for intermediate and final compounds.

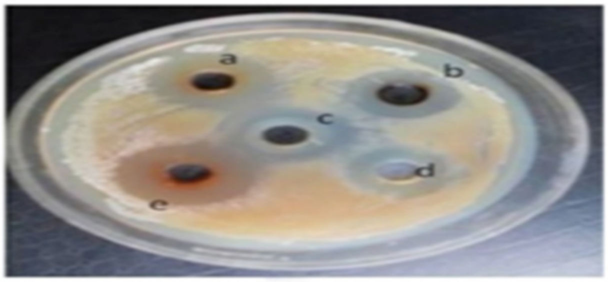


Figure 8: Its high efficacy, especially on gram-positive bacteria (Staphylococcus Iris), for intermediate and final compounds.

(C4) have been characterized by FTIR. These spectra showed disappearance of bands due to NH2 symmetric and asymmetric and appearance of bands due to υ (OH)acid at (3510.45) cm^{-1}. ν(NH) at (3205.69) cm^{-1}, ν(C-H) aromatic at (2974.23) cm^{-1}, ν(C-H) aliphatic at (2866.22) cm^{-1}, ν(C=C) aromatic at (1462.04) cm^{-1}

Compound [C5] A polymer compound was prepared from the reaction of the compound [C3] with acrylic acid and adding APS in the case of DMF as a solvent and stirring the mixture for 30minuts at 70c [C5] showed absorption band (3500) cm^{-1} belong to υ (OH) and appearance the (NH) of the at (3200) cm^{-1} also υ (CH aromatic) at (3100) cm^{-1}. Other absorptions compounds are found in the Table 2.

Compound [C6] A polymer compound was prepared from the reaction of the compound C4 with acrylic acid and adding APS in the case of DMF as a solvent and stirring the mixture for 3 hours at 70c [C6] showed absorption band (3450) cm^{-1} belong to υ (OH) and appearance the (NH) of the at (3250) cm^{-1} also υ (CH aromatic) at (3110) cm^{-1}. Other absorptions compounds are found in the Table 2.

CONCLUSION

This research is complete synthesis and Identification of the novel (FTIR and 1H-NMR). a number of nanoparticles were prepared from locally available natural botanical sources inexpensively and high-product to be used as a catalyst in preparing industrially important1Hpyrazolo[1,2-b]phthalazine-5,10-dione derivatives. These compounds contain a number of active groups that can be polymerized and enter into a number of industrially important reactions and a very high product.

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