Global Journal of Pure and Applied Chemistry Research
Vol.7, No.1, pp.1-12, February 2019
Published by European Centre for Research Training and Development UK (www.eajournals.org)

# SYNTHESIS AND CHARACTERIZATION OF NEW OXIME-FORMALDHYDE POLYMER AND THEIR BIOLOGICAL ACTIVITIES

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**ABSTRACT:** *Synthesis polymer by condensation of 4- hydroxyl benzaldehyde oxime (HBO) formaldehyde (F) and p-amino ,p-nitro,p-hydroxy substituted acetophenones (A) at different conditions. The polymers were characteristic by FT-IR and CHN data and thermo gravimetric analysis, studied the geometrical optimization of this polymer by PM3 method and, the antibacterial and antifungal activities of polymers were also screened on various bacteria.*

**KEYWORDS: Synthesis, New Oxime-Formaldhyde Polymer, Biological Activities**

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## INTRODUCTION

Solid polymer materials undergo both physical and chemical changes when heat is applied ; this will usually result in undesirable changes to the properties of the material,the ability to modify polymers to has allowed the packaging industry to produce better and stronger materials (1,2).

Many polymer invasion by fungi ,bacteria and other organism is manifested by loss mechanical properties ,surface degradation discoloration ,staining and other deterioration(3,4).Resorcinol-acetophenone copolymer was prepared (5) by using triflouroacetic acid as catalyst having some antimicrobial activity .Similarly ,2,4-dihydroxybezaldehyde oxime-formaldehyde polymers were synthesized (6)in the presence of oxalic acid as a catalyst .

Recently ,some new copolymer resins were synthesized (7) by condensing the oxime of benzyl -2 ,4-dihydroxyphenyl ketone with formaldehyde and a number of comonomers such as acetophenones /benzoic acids .some related work in this field has been carried by Rahngdale et al.(8,9)They reported the synthesis and chelation ion exanchge properties of 2,4dihydroxyacetophenone –biuret –formaldehyde terpolymer resins(10). I synthesized some copolymers of 4-hydroxy benzaldehyde oxime ,formaldehyde and nitro,amino,hydroxyl substituted acetophenones(11,12) .These terpolymers have shown excellent antifungal activities as well as good thermal stability(13) .

## EXPERIMENTAL

### Materials

p-Hydroxy benzaladehyde manufacture by Fluka supplements ,formaldehyde manufacture by BDH hydroxylamine hydrochloride manufacture by RDH ,p-hydroxy acetophenone manufacture by Fluka , p-nitroacetophenone manufacture by BDH ,p-amino acetophenone manufacture by RDH. .

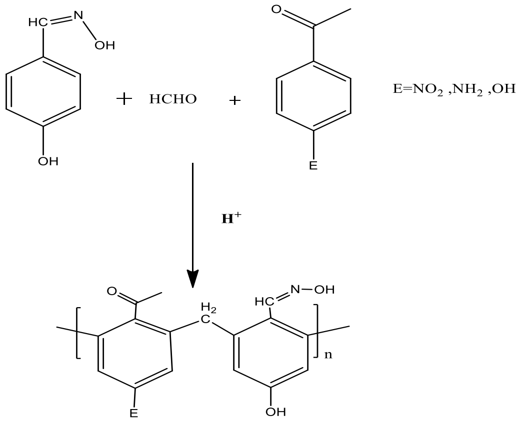
## Method

### Monomer Synthesis

5.0g of hydroxylamine hydrochloride was dissolved in 10.0ml of water in a conical flask and solution of 3.0 g of NaOH (in10 ml water )was added to it .The solution was cooled and 6.0g of 4-hydroxybenzaldehyde was slowly added to the solution .the flask was then cooled oxime .The crystals were filtered melting point 60°C.

### Polymer Syntheses

A mixture of 4-hydroxybenzaldehyde oxime (0.01mol) ,condensing reagent formaldehyde (0.05 mol) and the co-monomer (0.01mol) was taken in a round bottom flask .2ml of 6M HCl was added slowly to the reaction mixture and the contents were refluxed to 100-120°C for 8hour for p-nitro co-monomer and for 1 hour for p-amino co-monomer and for 10 hour for p-hydroxy co-monomer .After completion of the reaction ,the mixture was poured in ice cold water and then washed with hot water to remove unreacted reactants .



Oxime -Polymer

**Table 1: Recored code and name of polymer**

| Code | Synthesized polymer |
|---|---|
| Polymer-1 | p-Hydroxybenzaldehyde oxime –formaldehyde –p-nitroacetophenone |
| Polymer-2 | p-Hydroxybenzaldehyde oxime –formaldehyde –p-aminoacetophenone |
| Polymer-3 | p-Hydroxybenzaldehyde oxime –formaldehyde –p-hydroxyacetophenone |

### Characterization

FT-IR spectra of the polymer samples were recorded by 8400 Shimadzu instrument system 2000(4000-400cm$^{-1}$)spectrometer ,using KBr pellet.CHN done by CE-440 ELEMENTAL ANLYZER .

A plot between weight loss and temperature was recorded by thermogravimetric analysis (TGA) using TGA Q50V20.13Build 39 USA. Initially the sample (of about 4mg )was placed under nitrogen atmosphere (flow rate 20 ml/min)and then the gas was changed to oxygen (flow rate 30ml/min) and heating continued up 800°C with heating rate 20 °C per min. Precision of temperature measurement was ∓ 1.5 °C.

## RESULT AND DISSECTION

### Spectral Analysis

The structure of polymer 1-3 were characterized on the bases of FT-IR spectra and CHN recorded .The spectra are shown in Figure 1to 3(FT-IR)and Table 2(CHN ).

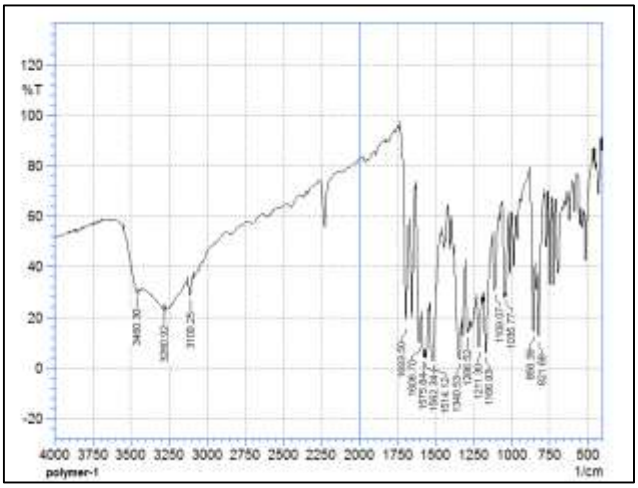


Figure 1:FT-IR spectrum of polymer-1

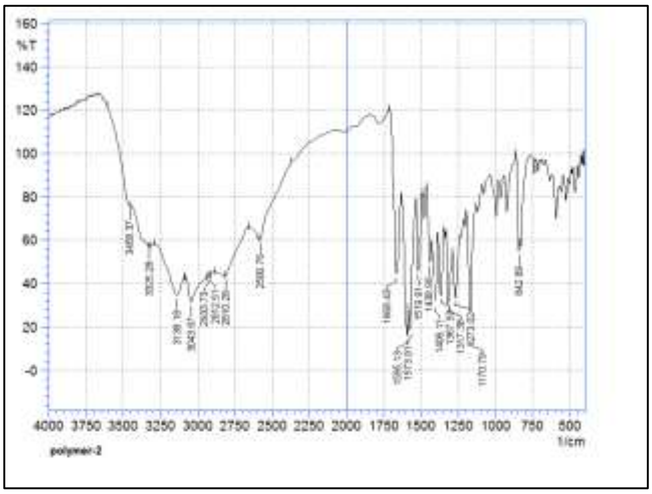


Figure 2:FT-IR spectrum of polymer-2

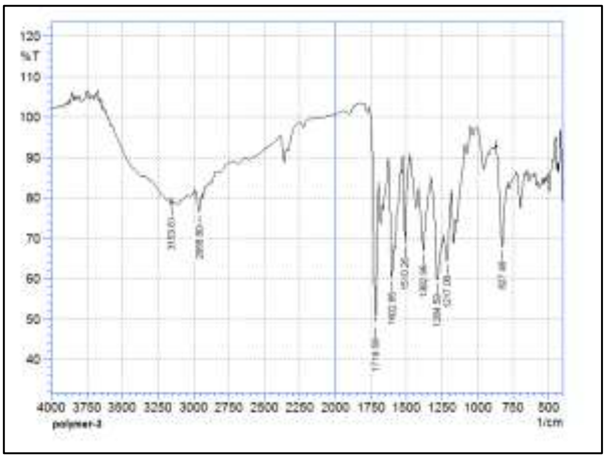


**Figure 3: FT-IR spectrum of polymer-3**

It is clear from the spectra that IR bands at 1382.96-1340.53 $cm^{-1}$ indicates the presence of bridged $–CH_2-$ group in the synthesized polymer.

From CHN indicates the theoretical calculate of element analysis identical with practically product that in Table 2.

**Table :2 recorded theoretical and practically of CHN**

| Code | Theoretical calculate | | | Practically calculate | | |
|---|---|---|---|---|---|---|
| Element | C | H | N | C | H | N |
| Polymer-1 | 59.09 | 5.30 | 10.60 | 60.09 | 4.26 | 10.43 |
| Polymer-2 | 63 | 6.07 | 11.33 | 62.90 | 5.9 | 11.04 |
| Polymer-3 | 62.90 | 6.065 | 5.64 | 62.29 | 5.65 | 5.44 |

## Solubility and Malting point

Solubility characteristics of the polymers were observed by using solvent with different solubility parameter and it was found that polymer insoluble in ethanol ,benzene ,toluene but soluble in acetone and DMSO.

Melting point were determination on a GallenKamp-maelting point apparatus and uncorrected, Table 3 melting point data .

**Table 3 melting point data**

| Code | m.p$^{o}$C |
|---|---|
| Polymer-1 | 162$^{o}$C |
| Polymer-2 | 84$^{o}$C |
| Polymer-3 | Viscose |

## Thermal Analysis

Through curves thermal gravimetric analysis data provide information regarding the thermal stability of a polymer .The thermo grams were obtaind by heating resin sample in air at 20$^{o}$C

/min. the result of percentage weight loss suffered from 100°C to 600°C are furnished in Figure .4 (polymer-1).This polymer sample his disintegration two beams the first at 123°C ,and the second at 344 °C the first rapid stage transition of may be due to loss of $H_2O$ .The second may be due to bond rupture and vitalization of low molecular weight fragment during decomposition similar patterns of TGA were also found for polymer-2 and polymer-3.

**Table 4: thermal gravimetric analysis data**

| Code | Decomposition temp. °C | | Char % at 600 °C | T 50% weight. Loss °C |
|---|---|---|---|---|
| | $Top_1$ | $Top_2$ | | |
| Polymer-1 | 123 | 344 | 27% | 350 |
| Polymer-2 | 181 | 388 | 42% | 460 |
| Polymer-3 | 278 | 347 | 40% | 475 |

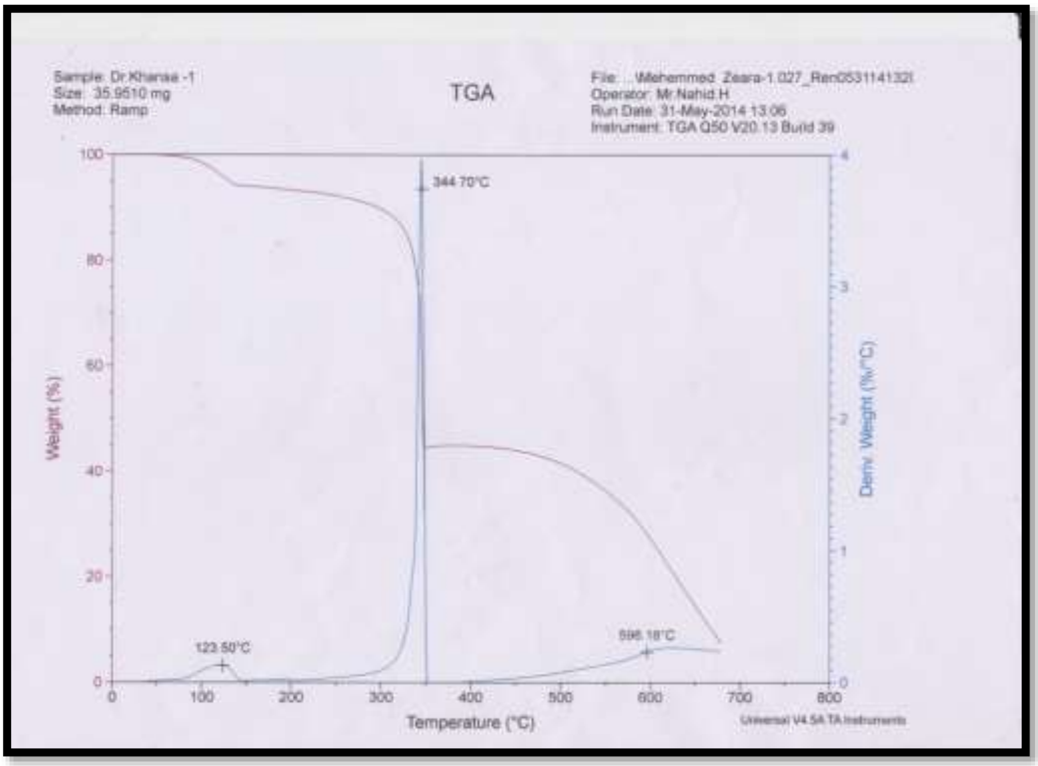


Figure 4: thermogravimatric analysis curve for polymer -1

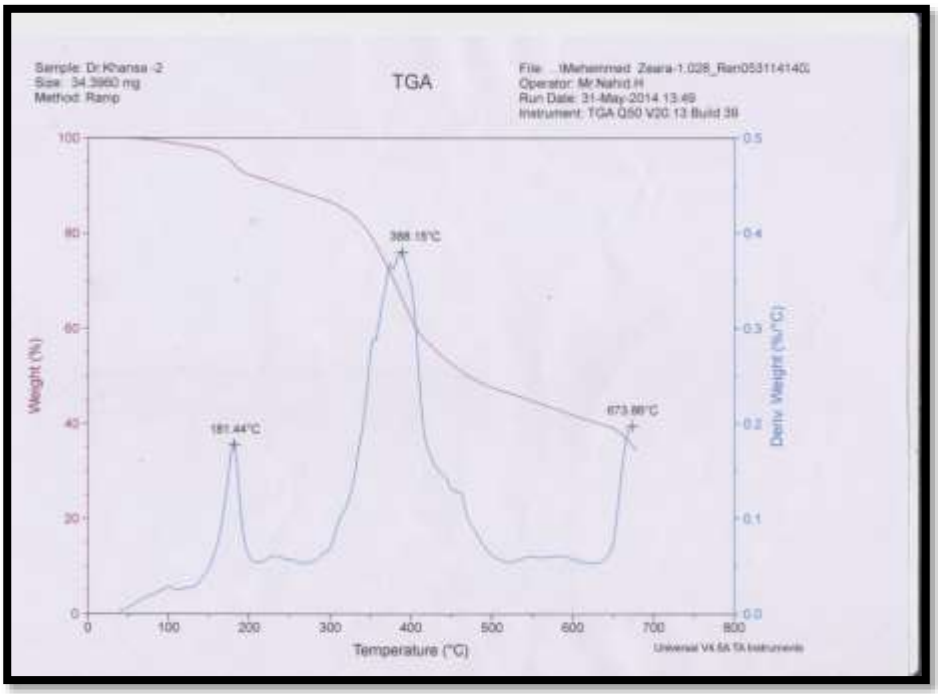


Figure 5:thermogravimatric analysis curve for polymer -2

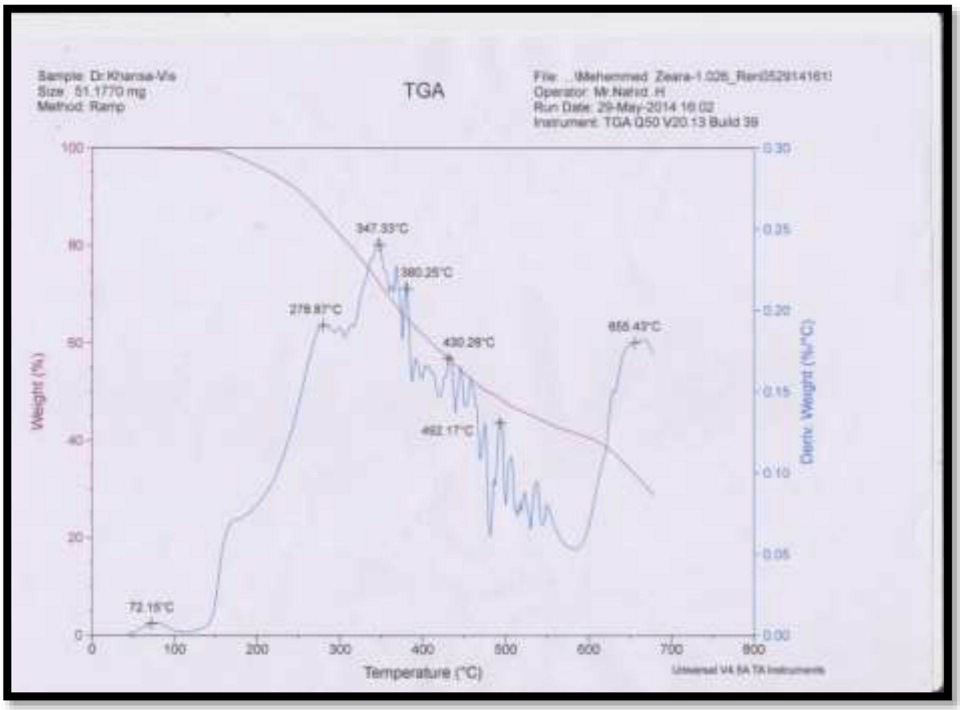


Figure 6:thermogravimatric analysis curve for polymer -3

## Geometrical optimization by PM3 method

From the geometrical optimization models of the polymer can be calculated by the semi empirical method was used to calculate useful parameters such as total energy heat of formation, Isolated Atomic Energy, Binding Energy and Total Energy.we show that energy increases with increases the acidic group in oxime compound .

**Table 4: Geometrical optimization data**

| Code | Total Energy kcal/mol | Binding Energy kcal/mol | Isolated Atomic Energy kcal/mol | Heat of formation kcal/mol |
|---|---|---|---|---|
| Polymer-1 | -89922.5029483 | -4028.5799083 | -85893.9230400 | -41.1169083 |
| Polymer-2 | -77160.3986027 | -4008.5543807 | -73151.8442220 | -36.0053807 |
| Polymer-3 | -79833.3616176 | -3945.2144406 | -75888.1471770 | -78.2084406 |

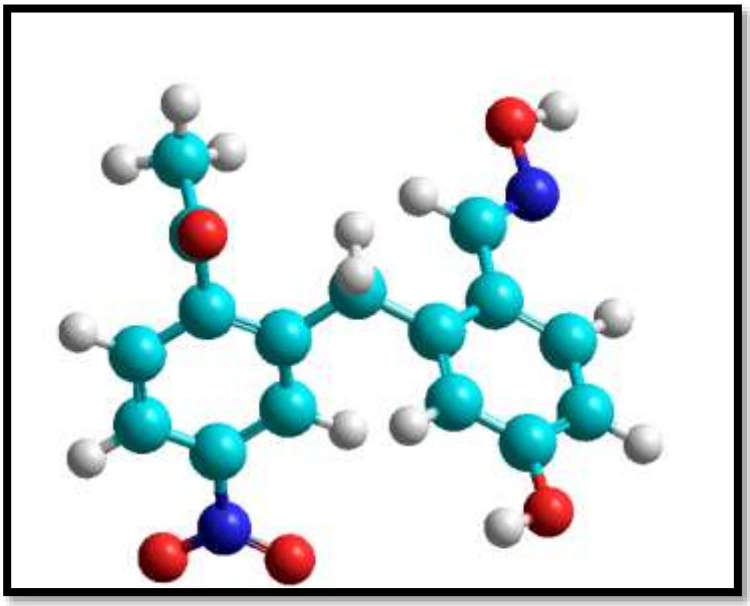


**Figure:7 geometrical optimization of polymer -1**

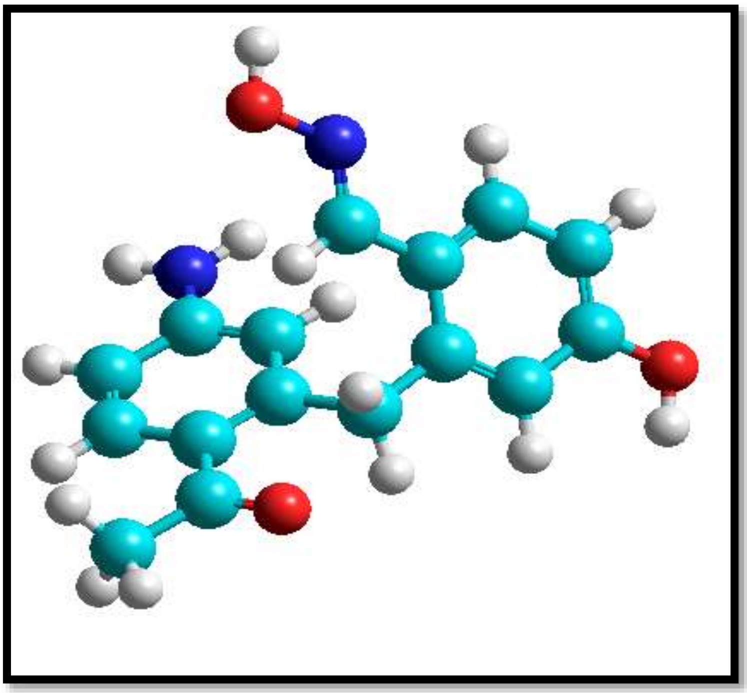


**Figure:8 geometrical optimization of polymer -2**

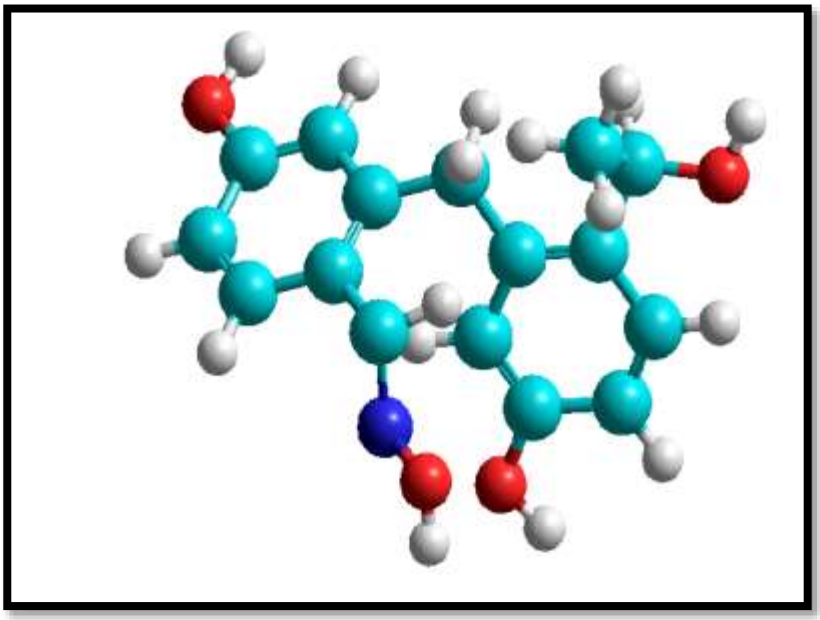


**Figure:9 geometrical optimization of polymer -3**

## BILOGICAL ACTIVITY

### Antibacterial activities

The antibacterial activity test was down by agar diffusion method by waiting 2gm of the compound adding it to 20ml of DMSO then 50 ML were taken from this mixture by microcyringe and was put in holes made by cork poorer in petri dishes which contained the pathogenic bacteria.

The pathogenic bacteria petri dish prepared 0.1 ml of nutrient broth which inoculated with *Staphylococcus aurous* which is gram positive and *Aeromionas hydrophila* which is gram negative separately ,the broth was spreaded by L-shape spreader. The petri dishes were incubated at 37 $^oC$ for 15 minutes then incubated with bacterial broth and incubated over night at 37 $^oC$ then the results were recorded.

### Antifungal Activities

The polymers used were selected by previous antimicrobial activity screening using diffusion method against at least one of the two bacterial strains used during the testing. For the diffusion method well-variant, the solvent used was dimethyl lsulfoxide (DMSO) and for the remaining methodologies, suitable solvents were used for the dissolution of the polymer.

The antifungal activity of polymers was assessed against two fungi species: *Candida albicans and Aspergillus niger*(7).

Overnight cultures were used. After 24 h of incubation, fungal suspension (inoculum) was diluted with sterile physiological solution, for the diffusion test, to $10^8$ CFU/mL (turbidity = McFarland barium sulfate standard 0.5).

The fungal inoculums was uniformly spread using sterile cotton swab on a sterile Petri dish MH agar. 50 µL from 1mg/mL concentration of chemical products were added to each well (7 mm diameter holes cut in the agar gel, 20 mm apart from one another). The plates were incubated for 24 h at 36°C ± 1°C, under aerobic conditions. After incubation, confluent fungal growth was observed. Inhibition of the bacterial growth was measured in mm.

Polymers have been tested for their antibacterial activity against *Aeromionas hydrophila* and *Staphylococcus aurous* zone and inhibiton and activity with respect to standard antibacterial drug (ciprofloxacin) ,and antifungal activity were observed against *Candida albicans and Aspergillus niger* were measured (Table 4 and 5).

**Table 5: Ralative antibacterial activity of different resins**

| Code | Compound | Zone of inhibition (mm)activity index | |
|---|---|---|---|
| | | *Staphylococcus aurous* | *Aeromionas hydrophila* |
| 1 | Polymer-1 | Zero | 10 |
| 2 | Polymer-2 | 35 | Zero |
| 3 | Polymer-3 | Zero | Zero |
| 4 | Ciprofloxacin (standard ) | 25 | Zero |

**Figure10: inhibition zone of *Aeromionas hydrophila***

**Figure11: inhibition zone of *Staphylococcus aurous***

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**Table 6: Relative antifungal activity of different polymers**

| S. no. | Compound | Zone of inhibition (mm)activity index | |
|---|---|---|---|
| | | *Aspergillus niger* | *Candida albicans* |
| 1 | Polymer-1 | Zero | 20 |
| 2 | Polymer-2 | Zero | Zero |
| 3 | Polymer-3 | Zero | 12 |

**Figure12: inhibition zone of *Candida albicans***

**Figure13: Inhibition zone of *Aspergillus niger***

From biological activity show good activity against some bacteria and some fungi among the polymer.

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