

## 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:** Oxime-Formaldhyde, Biological Activities, Synthesis Polymer

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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<sup>(1,2)</sup>.

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

Recently ,some new copolymer resins were synthesized<sup>(7)</sup> 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.<sup>(8,9)</sup>They reported the synthesis and chelation ion exachge properties of 2,4dihydroxyacetophenone –biuret –formaldehyde terpolymer resins<sup>(10)</sup>. I synthesized some copolymers of 4-hydroxy benzaldehyde oxime ,formaldehyde and nitro,amino,hydroxyl substituted acetophenones<sup>(11,12)</sup> .These terpolymers have shown excellent antifungal activities as well as good thermal stability<sup>(13)</sup> .

### 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.

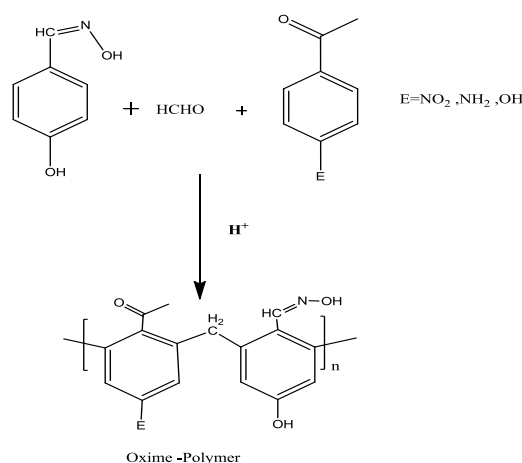
## METHOD

### 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 (in 10 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 to form 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 8 hours for p-nitro co-monomer and for 1 hour for p-amino co-monomer and for 10 hours 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.



**Table 1: Recorded 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

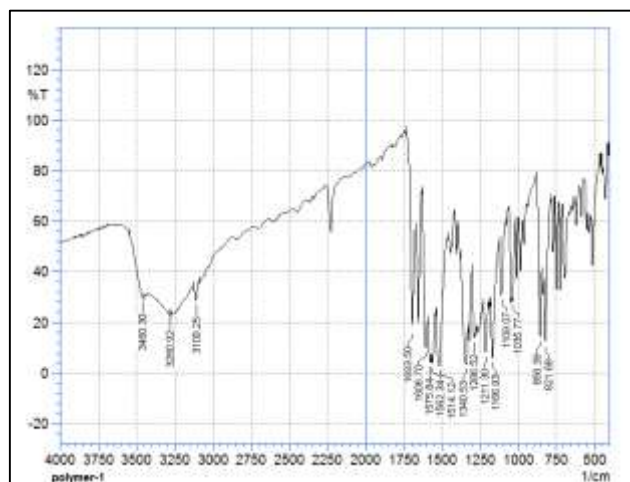
FT-IR spectra of the polymer samples were recorded by 8400 Shimadzu instrument system 2000(4000-400cm<sup>-1</sup>) spectrometer, using KBr pellet. CHN done by CE-440 ELEMENTAL ANALYZER.

A plot between weight loss and temperature was recorded by thermogravimetric analysis (TGA) using TGA Q50V20.13 Build 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  $\pm 1.5$  °C.

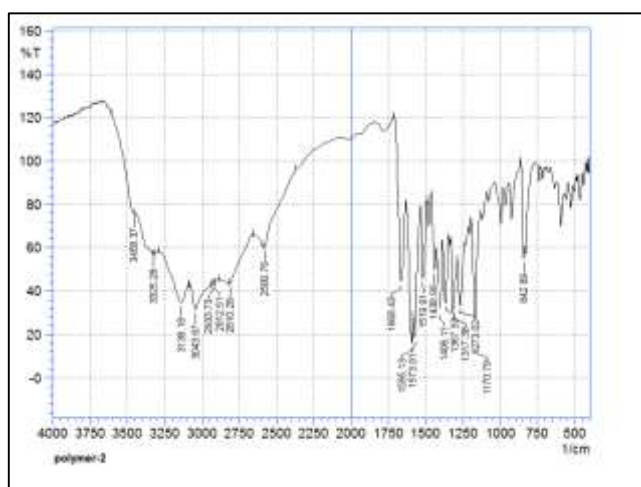
## RESULT AND DISSECTION

### Spectral Analysis

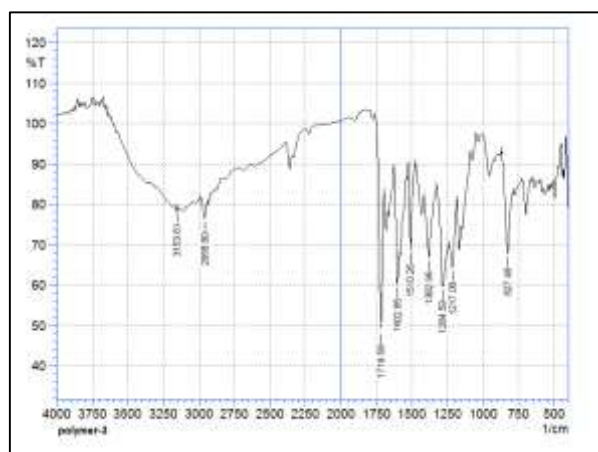
The structure of polymer 1-3 were characterized on the bases of FT-IR spectra and CHN recorded. The spectra are shown in Figure 1 to 3 (FT-IR) and Table 2 (CHN).



**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  $1382.96\text{--}1340.53\text{ cm}^{-1}$  indicates the presence of bridged  $\text{--CH}_2\text{--}$  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°C
Polymer-1	162°C
Polymer-2	84°C
Polymer-3	Viscose

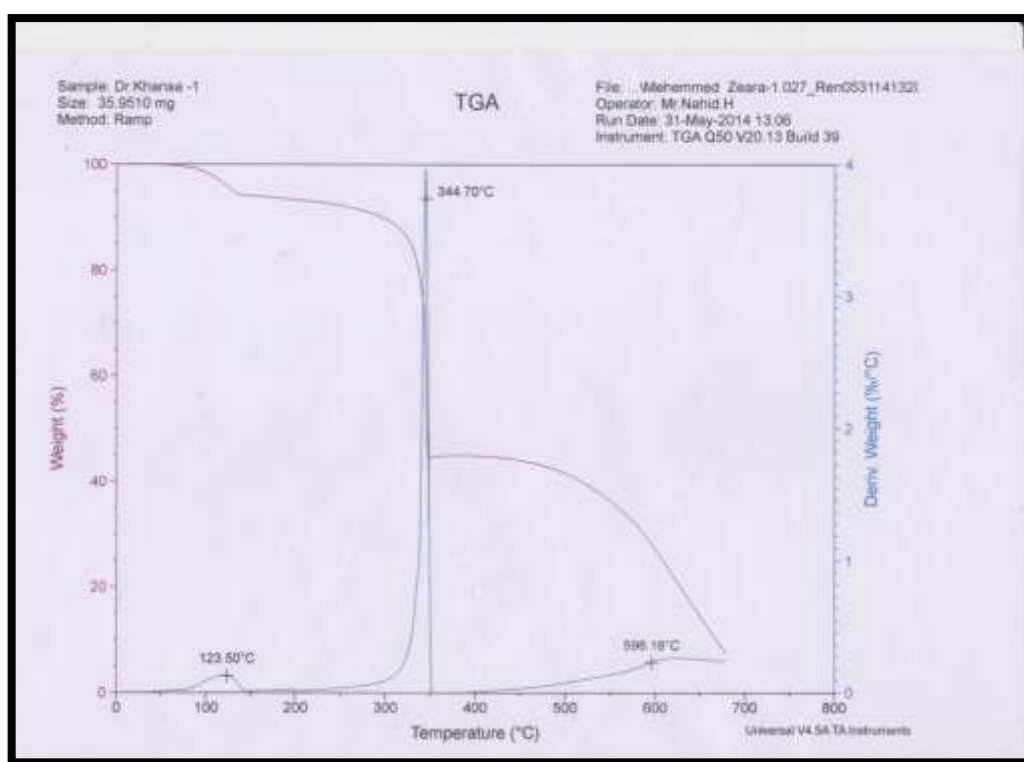
### Thermal analysis

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

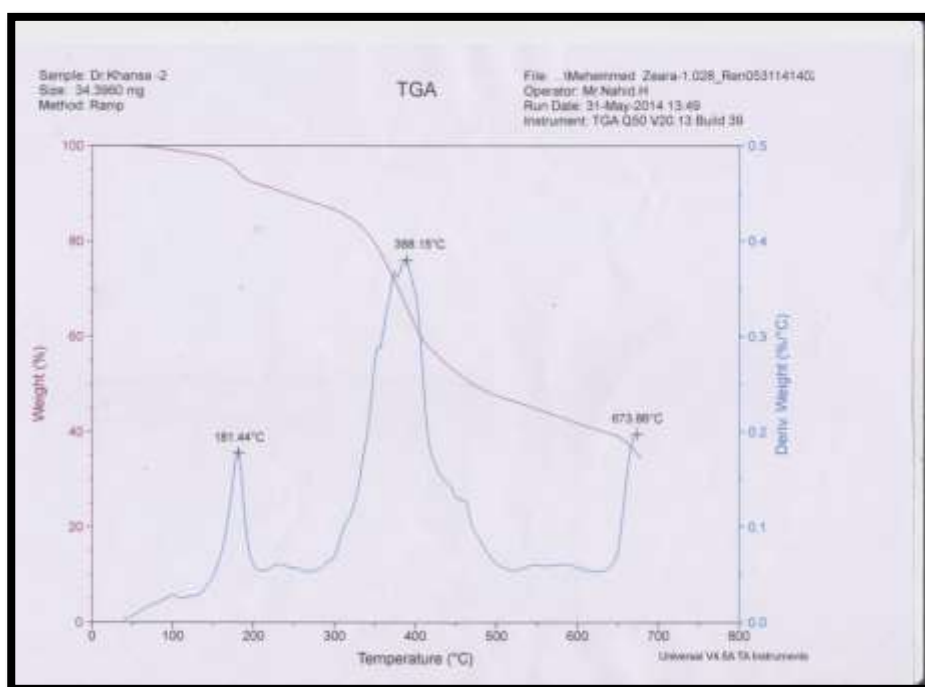
/min. the result of percentage weight loss suffered from 100°C to 600°C are furnished in Figure .4 (polymer-1). This polymer sample has disintegration two beams the first at 123°C, and the second at 344 °C the first rapid stage transition of may be due to loss of H<sub>2</sub>O. The second may be due 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**

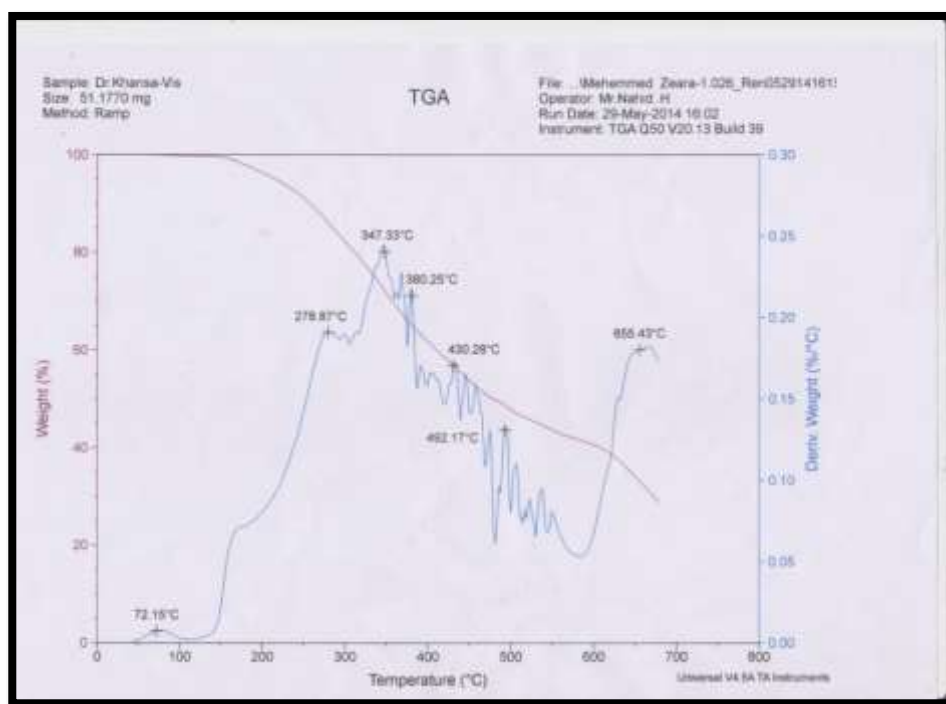
Code	Decomposition temp. °C		Char % at 600 °C	T 50% weight. Loss °C
	Top <sub>1</sub>	Top <sub>2</sub>		
Polymer-1	123	344	27%	350
Polymer-2	181	388	42%	460
Polymer-3	278	347	40%	475



**Figure 4: thermogravimetric analysis curve for polymer -1**



**Figure 5:thermogravimetric analysis curve for polymer -2**



**Figure 6:thermogravimetric analysis curve for polymer -3**

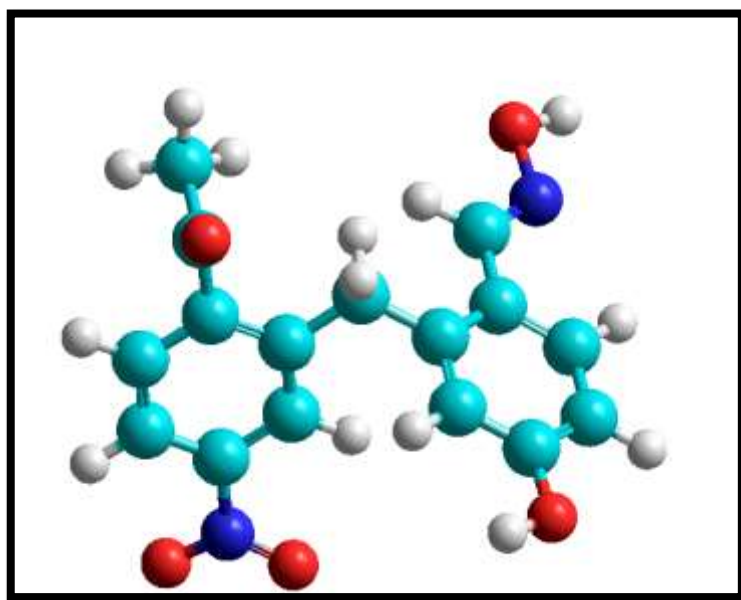
### Geometrical optimization by PM3 method 3.4

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

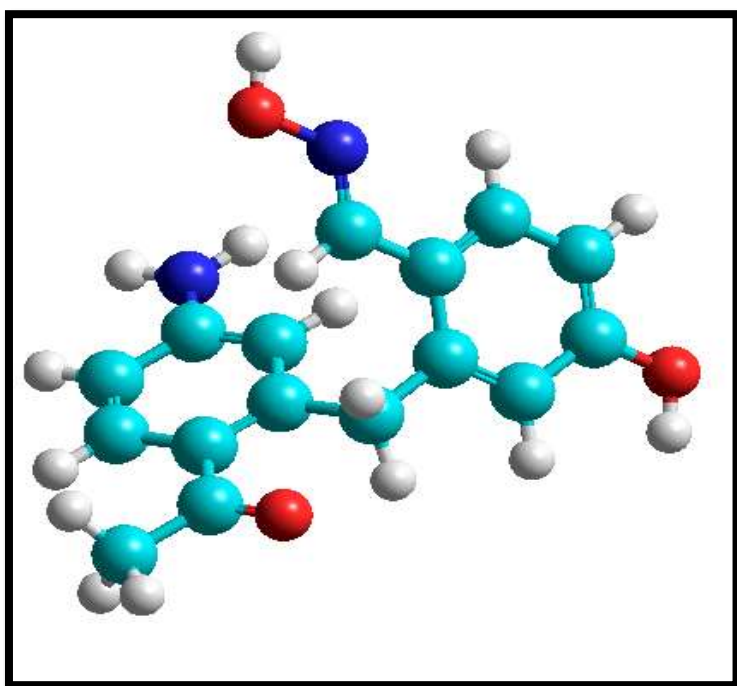
formation, Isolated Atomic Energy, Binding Energy and Total Energy. we show that energy increases with increases the acidic group in oxime compound.

**Table 4: Geometrical optimization data**

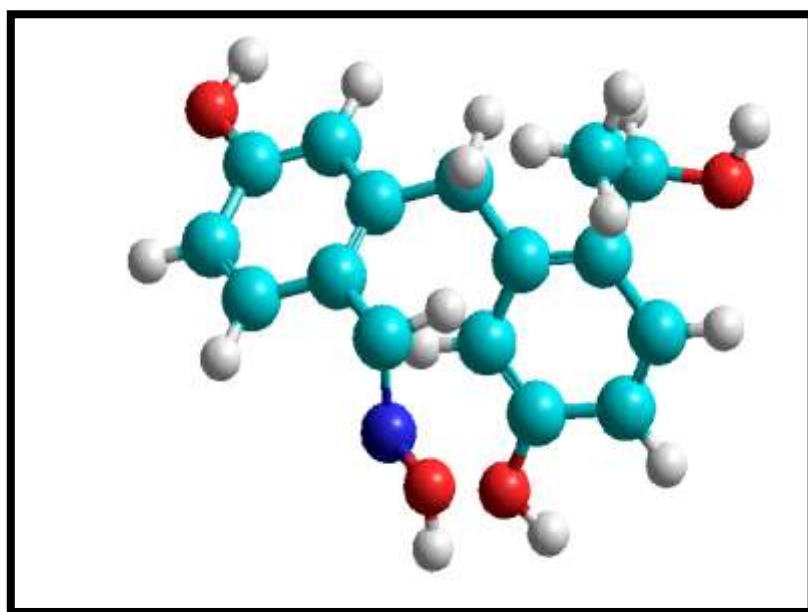
Code	Total Energy kcal/mol	Binding Energy kcal/mol	Isolated Atomic Energy kcal/mol	Heat of formation kcal/mol
Polymer-1	-89922.5029483	-4028.5799083	-85893.9230400	-41.1169083
Polymer-2	-77160.3986027	-4008.5543807	-73151.8442220	-36.0053807
Polymer-3	-79833.3616176	-3945.2144406	-75888.1471770	-78.2084406



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



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



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



## BIOLOGICAL ACTIVITY

### Antibacterial activities

The antibacterial activity test was done 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 microcylinder and was put in holes made by cork borer in petri dishes which contained the pathogenic bacteria.

The pathogenic bacteria petri dish prepared 0.1 ml of nutrient broth which inoculated with *Staphylococcus aureus* which is gram positive and *Aeromonas hydrophila* which is gram negative separately, the broth was spreaded by L-shape spreader. The petri dishes were incubated at 37 °C for 15 minutes then incubated with bacterial broth and incubated over night at 37 °C 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 sulfoxide (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*<sup>(7)</sup>.

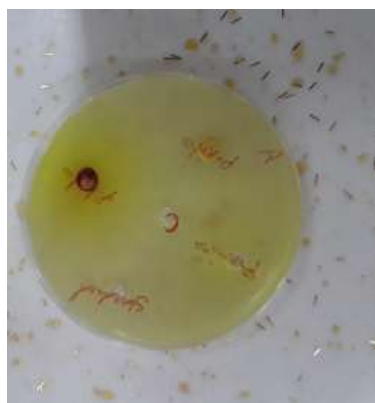
Overnight cultures were used. After 24 h of incubation, fungal suspension (inoculum) was diluted with sterile physiological solution, for the diffusion test, to 10<sup>8</sup> CFU/mL (turbidity = McFarland barium sulfate standard 0.5).

The fungal inoculum 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.

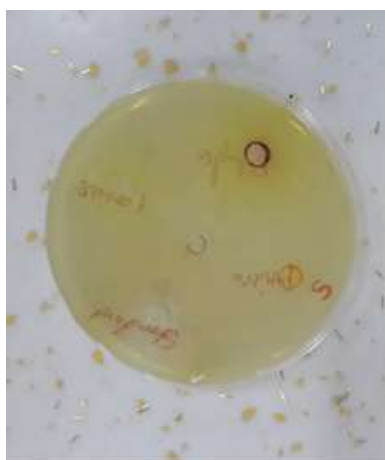
Polymers have been tested for their antibacterial activity against *Aeromonas hydrophila* and *Staphylococcus aureus* zone and inhibition and activity with respect to standard antibacterial drug (ciprofloxacin), and antifungal activity were observed against *Candida albicans* and *Aspergillus niger*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

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

Code	Compound	Zone of inhibition (mm)activity index	
		<i>Staphylococcus aureus</i>	<i>Aeromonas hydrophila</i>
1	Polymer-1	Zero	10
2	Polymer-2	35	Zero
3	Polymer-3	Zero	Zero
4	Ciprofloxacin (standard)	25	Zero



**Figure10: inhibition zone of *Aeromonas hydrophila***



**Figure11: inhibition zone of *Staphylococcus aureus***

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

S. no.	Compound	Zone of inhibition (mm)activity index	
		<i>Aspergillus niger</i>	<i>Candida albicans</i>
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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