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Synthesis, Characterization, Thermal Analysis and Ion Exchange Studies of Newly Synthesized 4-Hydroxybenzophenone-Gaunidine-Formaldehyde (4-Hbpgf-I) Copolymer Resin

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Abstract: *A novel polymer is obtained by condensation of 4-Hydroxybenzophenone, Gaunidine and Formaldehyde in 1:1:2 molar ratio in the presence of acetic acid as a catalyst. The newly synthesized terpolymerhave been characterized by different spectral technique like UV-visible, FTIR, NMR and XRD. The surface analysis of this copolymer was determined by Scanning electron microscopy(SEM). The average molecular weight was determined with the help of non-aqueous conductometric titration. Thermal studies of copolymerwascarried out to determine their mode of decomposition, the activation energy (Ea), order of reaction (n), frequency factor (Z), entropy change (ΔS), free energy change (ΔF), and apparent entropy change (S*). For calculating thermal stability and activation energy of this resin two method have been used these are the Freeman-Carroll and Sharp-Wentworth. Ion exchange studies for Cu2+, Ni2+, Co2+, Zn2+ and Pb2+ ions from strong chelate with the anions of the chloride, perchlorate and sulphates ions electrolytes hence the ion uptake of 4-HBPGF-I copolymer under the influence of chloride, perchlorate and sulphates ions is found lower for all the metal ions. The metal ion Ni2+ and Cu2+, ions required maximum 6 hours for the establishment of equilibrium where as Pb2+, Co2+ and Zn2+ ions required 5hours for the establishment of equilibrium. On the basis of experimental results, it is revealed thatthe rate of metal-ion uptake followed the order of Pb2+> Co2+> Zn 2+> Ni2+>Cu2+.*

Keywords: *Synthesis, Condensation, characterization,Surface analysis, Thermal Analysis, ion exchange.*

I. INTRODUCTION

Nowadays, industrial effluents contain a significant amount of carcinogenic heavy metals, which pose serious risks to human health. Exposure to these metal ions can lead to severe health issues such as nausea, cancer, brain tumors, and other disorders. Therefore, it is essential to develop effective methods for removing heavy metal ions from contaminated water sources. Common techniques used for this purpose include ion exchange, precipitation, and ultrafiltration [1,2].

Different metal ions exhibit varying selectivity toward different polymers, and these interactions are generally reversible in nature. The selectivity and uptake rate depend on the type of functional groups present in the polymer matrix. Previous studies reported by Khobragade and co-workers have investigated the interaction between heavy metal ions and chelating ion-exchange resins containing phthalic acid and thiosemicarbazide [3].

Thermal degradation analysis of polymers provides insight into their stability over a range of temperatures. It has been observed that different functional groups decompose at different temperatures, indicating the overall thermal stability characteristics of the polymer.

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II. MATERIALS AND METHODS

2.1 All the materials and chemicals (Qualigens chemicals) were used as received with analytical grade.4-Hydroxybenzophenone, Guanine, formaldehyde

Synthesis of 4-Hydroxybenzophenone- Gaunidine - Formaldehyde terpolymer in Mole Ratio.(1:1:2)

A mixture of 4-hydroxybenzophenone (1.98 g, 0.1 mol), guanidine (0.9553 g, 0.1 mol), and formaldehyde (7.5 mL, 0.2 mol) was used as monomers in a clean round-bottom flask fitted with a mechanical stirrer and a reflux condenser. The reaction was carried out in 200 mL of 2 M acetic acid as the reaction medium, maintaining a molar ratio of 1:1:2. The resulting homogeneous solution was refluxed in an oil bath at 124 ± 2 °C with continuous stirring for 6 hours. After completion of the reaction, the mixture was allowed to cool and then poured into crushed ice with vigorous stirring to precipitate the product. The obtained material was purified by neutralization using 8% aqueous NaOH followed by treatment with 1:1 HCl/water under ice-cold conditions to remove impurities. This reprecipitation process was repeated three times to ensure purity.

Subsequently, the terpolymer was thoroughly washed with warm water, methanol, and ether, and then filtered. The filtered product was dried in an oven at 75 °C for 24 hours. The dried resin was finely powdered and sieved to obtain a uniform particle size. The overall yield of the terpolymer was approximately 81%.

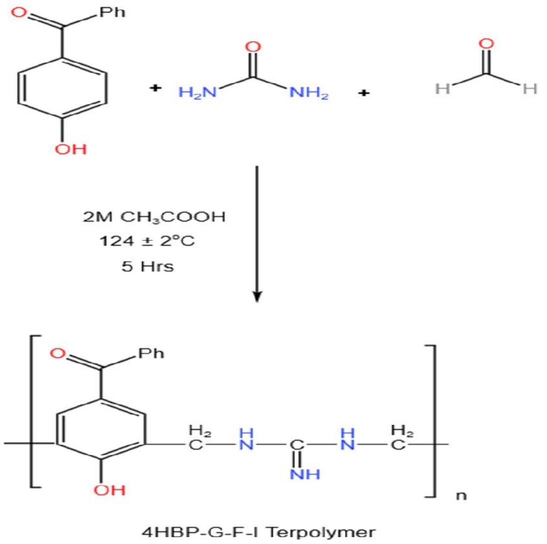

Fig.1. Synthesis of 4HBP-G-F-I Copolymer Resin

III. SPECTRAL AND PHYSICOCHEMICAL ANALYSIS

All analytical and spectral characterizations of the newly synthesized copolymer were performed at the STIC Analysis Centre, Kochi.

3.1. Electronic spectra

The UV-VIS technique is not the common technique as compare to IR and NMR. UV-Visible is the technique that can measure the quantity of analyte depends on the amount of light received by analyte. The UV-VIS measure the span of wavelength between 200 nm to 800 nm. This technique is used for structure determination of organic and inorganic molecule. When the interaction between chromophore and radiation of incident light leads to formation of transition of electron from ground state to higher energy state and the spectra is derived.

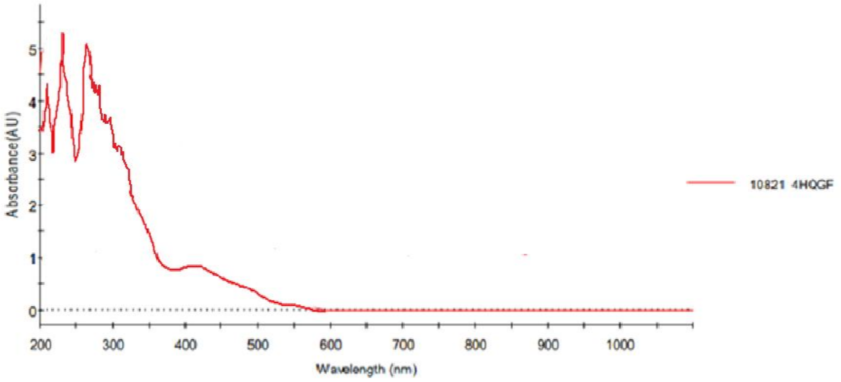

Fig 2. UV-Visible spectra of 4HBP-G-F-I

The UV–Visible spectra of 4HB-G-F I are recorded in N,N dimethyl formamide in 190 to 700 nm range at Sophisticated Test and Instrumentation Centre is an Institution Sponsored Jointly by Kerala State Council for Science Technology and Environment(KSCSTE) and Cochin University of Science and Technology[4].The UV-VIS spectra 4HB-G-F I show a (λ_{max}) at 240nm. At 240 nm there is $\pi \rightarrow \pi^*$ due to the presence of benzophenone group in polymer also it shows a $n \rightarrow \pi^*$ due to the presence of guanidine group. The UV-VIS study of 4HB-G-F terpolymer show a good deal.

3.2. FTIR Spectral analysis

FTIR spectra of 4-HBGF-I copolymer is presented in Fig. 4 and its observed and expected frequency are explained in table 1.

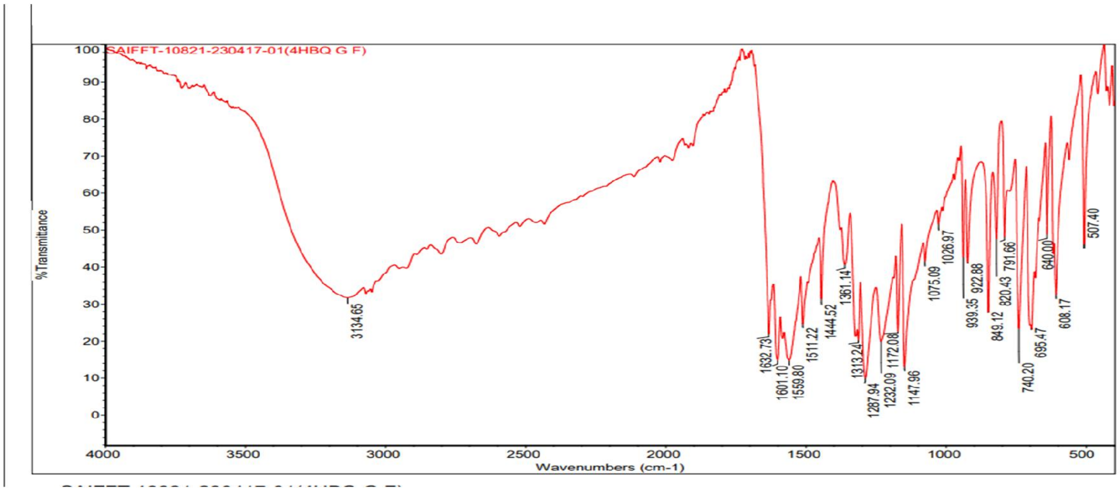

Fig 3. IR spectrum of 4HBP-G-F-I terpolymer

Table 1. Infrared spectral data 4HBP-G-F-I terpolymer resin

INFRARED SPECTRAL DATA 4-HBP-G-F-I TERPOLYMER		
Assignment	**Observed bond frequency in (cn^{-1})**	**Expected band frequency (cm^{-1})**
Phenolic OH group	3134	3700-3100
Aryl c=c	1601	1650-1550
N-H stretch in -NH-	3470	3500-3700
Carbonyl group	1632	1870-1650
C-H Stretching in ring	849	<900

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Methylene C-H bond	2960	2850-3300
C-H bond in methyl	2865	2880-2860
C=N at bridge	1559	1690-1640
C-H Stretching in ring	849	<900
C-H bond in methyl	2865	2880-2860
N-H stretch in -NH-	3470	3500-3700

3.3. Nuclear magnetic resonance spectra

The NMR (H^1) spectra for 4-HBGF-I copolymer was recorded to substantiate the linkages of the proposed structure. ^{1}H-NMR studied using Bruker Avance-II FT-NMR Spectrometer in DMSO-d_6 solvent at SAIF Analysis, Kochi, Kerla.

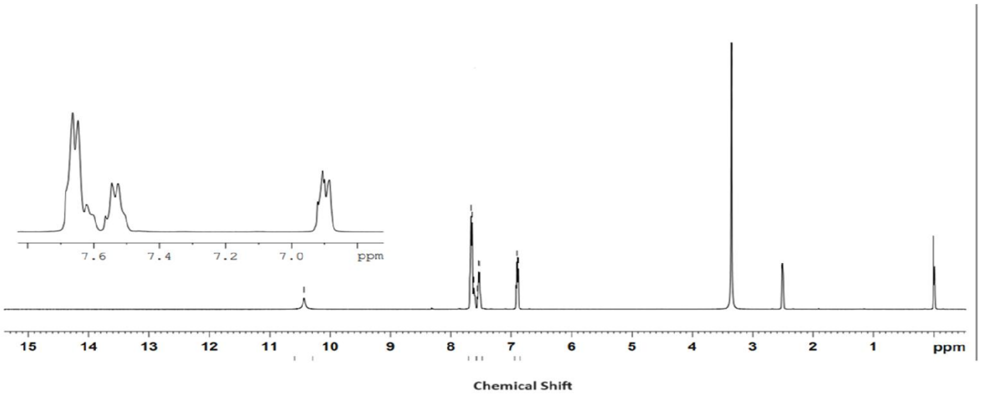

Fig 4. Nuclear magnetic resonance spectra of 4HBP-G-F-I terpolymer

In the spectrum of copolymer, the resonance signal appeared in the range at 10.25 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates easily the intramolecular hydrogen cling of -OH group. The signals in the region 7.68 (δ) ppm are attributed to protons of –NH ground present in the ligand structure and the signals appeared in the range of 4.67 ppm are assigned to methylene protons of Ar-CH2-N half. The weak multiplate signals (unsymmetrical pattern) in the region of 8.97 (δ) ppm may be attributed to aromatic proton (Ar-H)[13].

The signals appeared in the region of 8.23 ppm is assigned to aromatic protons and the signal appeared in the region of 3.86 ppm is attributed to methylene bridges. The signal appeared for –NH bridge is 6.56 in the spectrum[14-17].

4.1. Scanning Electron Microscopy (SEM):

The 4HBP-G-F I resin are study widely with the help of SEM and its magnified images show a presence of deep pits on the surface and it also show a presence of fringes on the surface of polymer this shows a intermediate nature between crystallinity and amorphous. The resin have more amorphous nature as it have deep pits [8].

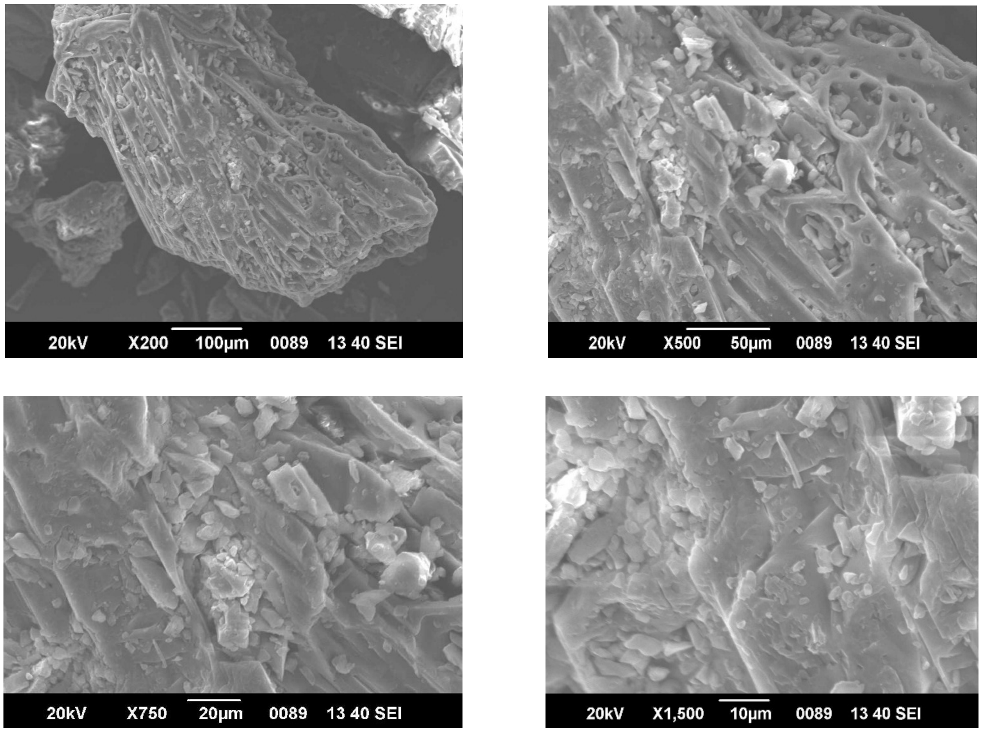

Fig 5. Scanning electron microscopy of 4HB-G-F I terpolymer resin

4.2. Elemental Analysis :-

Table 3. Elemental Analysis Data of 4HB-G-F Terpolymer Resins.

Terpolymer Resins	C (%)		H (%)		N (%)		O (%)		Empirical formula of repeating unit	Empirical formula weight
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.		
4HBGF-I	68.70	68.23	5.45	5.33	14.20	14.92	11.98	11.3	$C_{16}H_{15}O_2N_3$	281.38

4.3. XRD

X- ray diffraction is common technique which is mainly used for the structure determination and its internal composition. The angle of diffraction helps to determine spacing of atomic plane which help in structure determination and crystallinity. This technique use the Bragg's equation[10].XRD study show a polymer 4HBP-G-F I terpolymer are highly crystalline in nature.

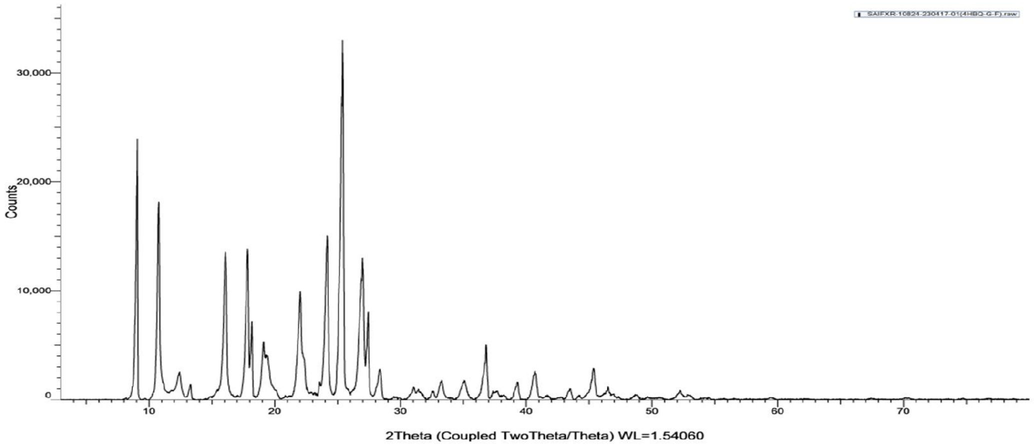

Fig 6.XRD of 4HBP-G-F-I terpolymer

V. THERMAL ANALYSIS

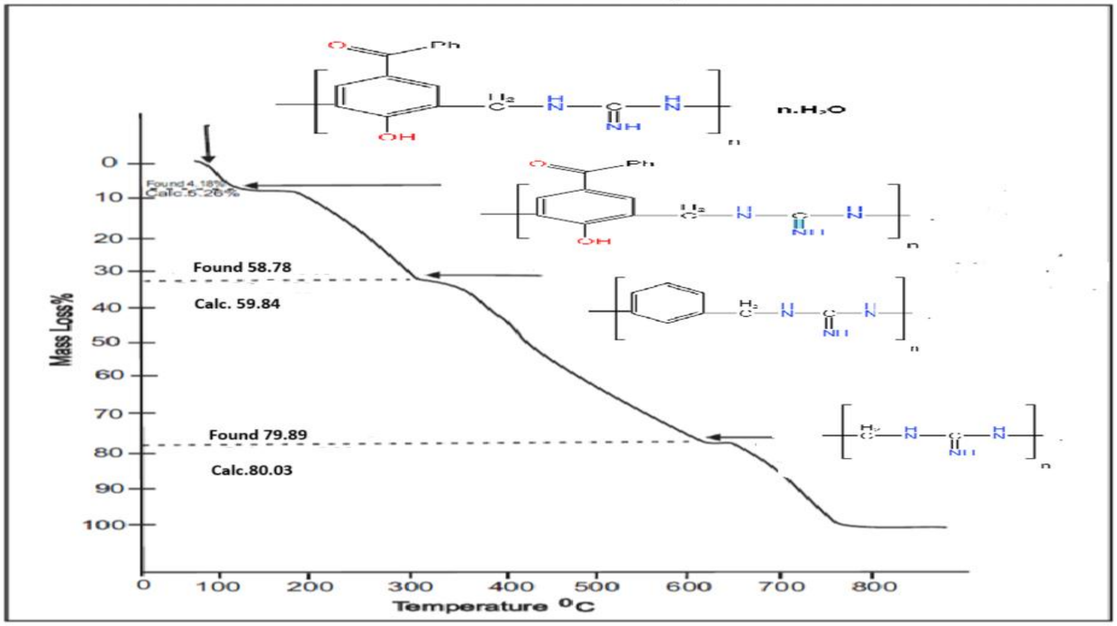

Fig 7. Thermogram of 4HBP-G-F-I terpolymer

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).

Determination of Kinetic PARAMETERS:

In the present work Freeman-Carroll and Sharp-Wentworth methods have been used to determine the kinetic parameters of the copolymer resins with the help of non-isothermal pattern of copolymer resins.

Evaluation of Kinetic Parameters by Freeman and Carroll Method from TG Data:

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(i) **Entropy Change**:

Intercept = $[\log KR/h\phi E] + \Delta S / 2.303\,R$

Where, $K = 1.3806 \times 10^{-16}$ erg/deg/mole, $R = 1.987$ Cal/deg/mole

$h = 6.625 \times 10^{-27}$ erg sec. $\phi = 0.166$

(ii) **Free Energy Change:**

$\Delta F = \Delta H - T\Delta S$

(iii) **Frequency Factor:**

$B_{2/3} = \mathrm{Log}\ ZEa / \phi R$

$B_{2/3} = \log 3 + \log [\ 1 - 3\sqrt{1-\alpha}\ ] - \log P\ (x)$

(iv) **Apparent Entropy Change:**

$S^* = 2.303 \log Zh / KT^*$

Evaluation of Kinetic Parameters by Freeman Carroll Method

Table 5. Thermogravimetric Analysis of 4HBP-G-F-I Terpolymer

Copolymer Resin	**Temperature Range**	**Stage of Decomposition**	**Species Degardation**	**% weight loss**	
				Found	**Calculated**
4-HBP-G-F-I	40-170 ºC	------	Loss of -H2O	5.87	6.37
4-HBP-G-F-I	170-320ºC	First	Loss of -OH and –COPh group	27.31	28.68
4-HBP-G-F-I	320-540 ºc	Second	Removal of aromatic Nucleus and methylene bridge	58.78	59.84
4-HBP-G-F-I	540 - 680 ºc	Third	Removal of Gaunidine moiety	79.89	80.03

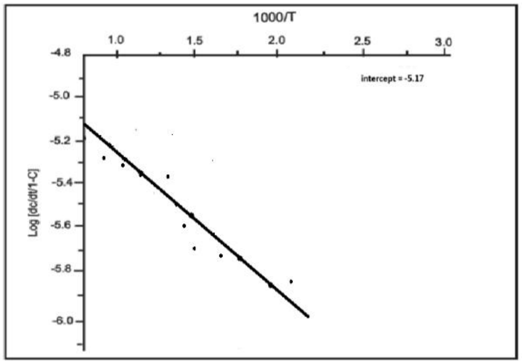

Fig.8: Sharp–Wentworth Plots

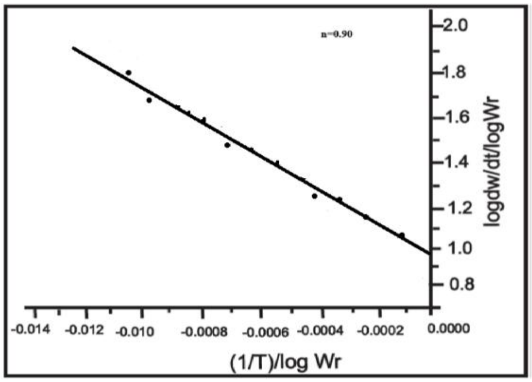

Fig 9: Freeman-Carroll Plot of 4HBP-G-F-I of 4HBP-G-F-I

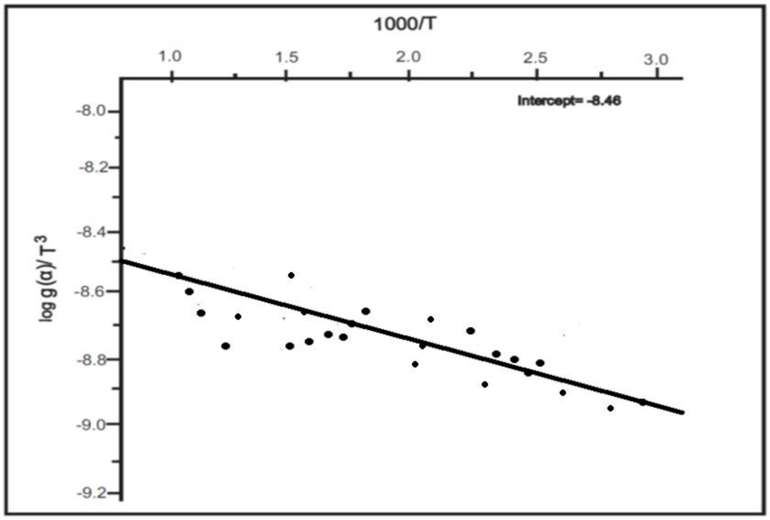

Fig 10. Thermal Activation Energy Plot of 4HBP-G-F-I Terpolymer

Table. 6. Results of Thermogravimetric Analysis of 4HBP-G-F-I Terpolymer

Copolymer	Half Decomposition Temp. (T)	Activation Energy Ea (KJ)/mol	
		SW	FC
4HBP-G-F-I	260	8.29	9.12

Table 7. Kinetic And Thermodynamic Parameters of 4HBP-G-F-I Copolymer

Copolymer	Entropy change ΔS(J)	Free energy ΔF (KJ)	Frequency Z (S^{-1})	Apparent entropy (S*)	Order reaction
4HBP-G-F-I	-169.84	114.28	1586	-23.56	0.90

VI. ION-EXCHANGE PROPERTIES

The ion-exchange behavior of the synthesized copolymer resin was systematically investigated to evaluate its efficiency for the removal of toxic heavy metal ions from aqueous media. The study encompassed the determination of key physicochemical parameters, including the distribution coefficient (Kd), the influence of pH on metal ion uptake, selectivity toward competing metal ions, adsorption capacity, and regeneration performance of the resin. These parameters are critical for assessing the adsorption efficiency, selectivity profile, and reusability of the copolymer, thereby establishing its potential applicability in advanced water treatment and purification systems [19, 20].

6.1. Determination of Distribution Coefficient (Kd)

The distribution coefficient (Kd) is an important parameter used to evaluate the affinity of a resin toward different metal ions [21-22]. It represents the amount of metal ions adsorbed by the resin per unit amount of metal ions remaining in the solution at equilibrium. The distribution coefficient is calculated using the following expression:

Distribution Coefficient (Kd) = $\frac{Ci-Cf}{Cf} \times \frac{v}{w}$ ------ (1)

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Where:
Ci = Initial concentration of metal ion (mg/L)
Cf = Final concentration of metal ion after equilibrium (mg/L)
V = Volume of the solution (mL)
W = Weight of dry resin (g)

A solution containing metal ions of known concentration was equilibrated with a measured quantity of 4HBP-G-F-I copolymer resin. After equilibrium was attained, the concentration of metal ions remaining in the solution was determined using suitable analytical techniques such as UV-Visible spectrophotometry.

The results show that the synthesized copolymer resin has a strong affinity for various heavy metal ions. Among them, Pb(II) exhibited the highest Kd value, indicating a stronger interaction between the functional groups of the resin and the metal ion.

Calculation for Cu(II)
Initial concentration, Ci = 100 mg/L
Final concentration, Cf = 21 mg/L
Volume of solution, V =50 mL
Weight of 4HBP-G-F-I resin, W = 1g

Table 8: Distribution coefficient (Kd) values for different metal ions

Metal Ion	**Kd (mL/g)**
Cu^{2+}	**188**
NI^{2+}	**168**
Zn^{2+}	**154**
Pb^{2+}	**208**
Cd^{2+}	**142**

A higher Kd value means the resin has a stronger ability to adsorb the metal ion. Here, Kd = 208 indicates good adsorption of the Pb(II) metal ion onto the resin than the other given metal ion.

6.2. Effect of pH on Metal Ion Adsorption

Solution pH is a key factor in the adsorption of metal ions because it affects the ionization state of polymer functional groups as well as the form of metal ions present. The influence of pH on adsorption was investigated by equilibrating the resin with metal ion solutions at different pH levels [21-22].

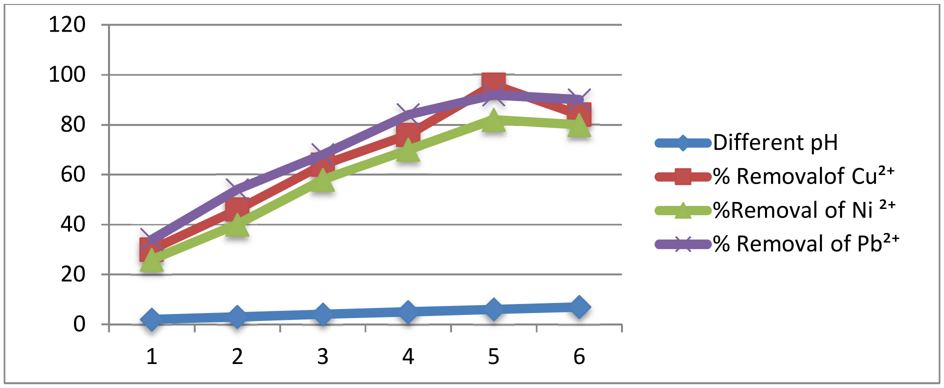

Fig. 11: Effect of pH on metal ion adsorption

Adsorption efficiency improves with rising pH as hydrogen ions compete less with metal ions for the binding sites on the polymer resin. The optimum adsorption is observed near pH 6, after which precipitation of metal ions can occur [23].

6.3. Metal Ion Selectivity

The selectivity of the copolymer resin for various metal ions was assessed using a mixed metal ion solution, and the order of selectivity was established based on the Kd values obtained. The selectivity sequence was $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$.

This behavior can be attributed to coordination interactions between the metal ions and functional groups such as –OH, –COOH, and $-CONH_2$ in the copolymer, where ions with greater affinity for these donor sites show higher adsorption[23-24].

6.4. Adsorption Capacity of the Copolymer Resin

A known amount of copolymer resin was brought into equilibrium with metal ion solutions of known concentration to evaluate its adsorption capacity.

The capacity was calculated using the equation given below.

$$\text{Adsorption Capacity (qe)} = \frac{(Ci-Ce)V}{W} \qquad \text{-----------------(2)}$$

Where:

qe = adsorption capacity (mg/g)
Ci = initial metal ion concentration (mg/L)
Ce = equilibrium concentration (mg/L)
V = volume of solution (L)
W = weight of resin (g)

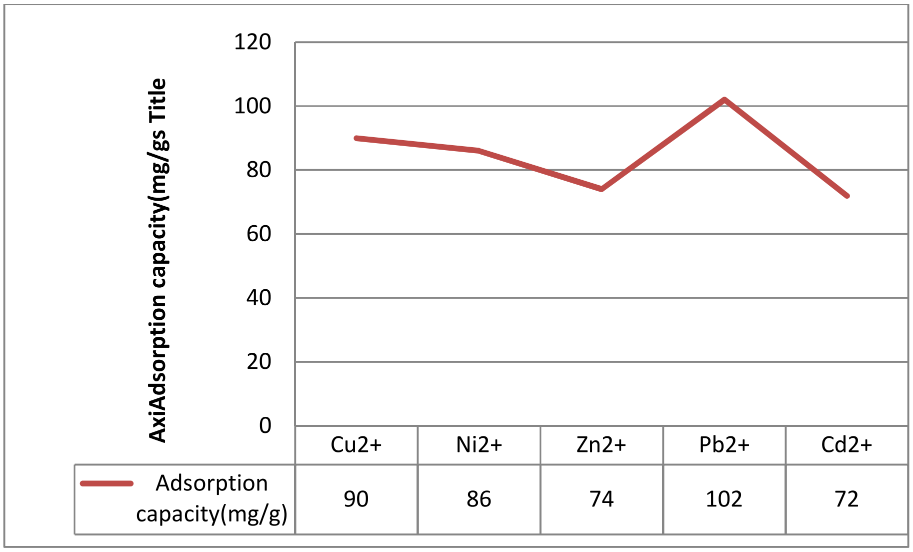

Fig. 12: Adsorption capacity of the copolymer resin

The findings demonstrate that the prepared copolymer resin has a strong ability to adsorb heavy metal ions, especially Pb(II) and Cu(II). This is due to the multifunctional groups in the polymer, which enable binding via chelation and ion exchange[25-27].

VII. CONCLUSION

The terpolymer was synthesized via polycondensation of 4-hydroxybenzophenone, guanidine, and formaldehyde using acetic acid as a catalyst. Its structure was confirmed through FTIR, ^1H NMR, XRD, and UV–Visible spectral analyses, while SEM was employed for surface morphology studies. The molecular weight of the 4HBP-G-F-I terpolymer was determined by non-aqueous conductometric titration. TGA analysis indicated thermal degradation behavior with increasing temperature, revealing high thermal stability of the polymer. Ion-exchange studies demonstrated good adsorption capacity and selectivity toward metal ions in aqueous media, with adsorption strongly influenced by pH and exhibiting favorable distribution coefficients. Additionally, the resin showed good regeneration capability, suggesting its reusability. Overall, the study confirms that the 4HBP-G-F-I terpolymer acts as an eco-friendly cation-exchange resin suitable for the removal of heavy metal ions from wastewater, industrial effluents, and for water purification and desalination applications.

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