

SYNTHESIS, CHARACTERIZATION AND ITS APPLICATIONS: NOVEL 4-HBAGF-I COPOLYMER AND ITS COMPOSITE

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E-mail: wbgurnule@yahoo.co.in**Abstract**

A new technique has been developed for the purification of industrial wastewater by synthesizing an innovative Gaunidine based terpolymer composite gaining a considerable attention in the wastewater treatment community. In the present research work the terpolymer resin was synthesized involving 4-Hydroxybenzaldehyde and Gaunidine with formaldehyde and the novel composite was prepared using terpolymer and activated charcoal for the recovery of toxic and heavy metals from aqueous solutions. The structure and properties of the terpolymer and terpolymer activated charcoal composite were observed by various characterization techniques such as elemental analysis, FTIR, UV–Visible, XRD and SEM. Batch separation technique has been used in the ion-exchange process for the removal of heavy selected divalent metal ions like Cu^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} by terpolymer and its composite. The investigation was carried out over a range of concentrations, different electrolytes, a wide pH range, and varying flow rates. The selectivity order for metal ion removal by the terpolymer was $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$, whereas for the composite it was $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$. The variation in selectivity order may be attributed to differences in particle size, high porosity, large surface area, and the intrinsic properties of both the material and the metal ions. The ion-exchange behaviour of the terpolymer and its composite was further evaluated.

The thermal degradation behavior of the terpolymer and its composite was also examined using thermogravimetric analysis (TGA). The kinetic and thermodynamic parameters were calculated by applying the Freeman–Carroll (FC) and Sharp–Wentworth (SW) methods. The decomposition of the terpolymer followed first-order kinetics, whereas the composite exhibited a higher-order reaction. The calculated activation energy, frequency factor, and entropy change values indicate that both the terpolymer and its composite possess good thermal stability.

1. Introduction

The environment has been severely contaminated by toxic heavy metals such as lead, cadmium, mercury, chromium, and cobalt. These hazardous metals pose serious threats to ecosystems, affecting agriculture, animals, and human health. They are released from various industries including textile, rubber, leather, paper, cosmetics, plastics, food processing, pulp industries and pharmaceuticals discharge substantial amounts of wastewater containing inorganic salts, metal ions, pesticides, and synthetic dyes [1]. Effluents from these sectors

significantly increase the concentration of heavy metals—particularly cadmium, lead, cobalt, and mercury—in soil and aquatic systems, leading to severe health risks and diseases, including skin, lung, liver cancers and mutagenic effects in humans[2, 3].

Currently, the global challenge is the removal and recovery of toxic metals from wastewater and industrial effluents. Several conventional treatment methods such as chemical precipitation, biological treatment, electrochemical processes, coagulation, membrane filtration, flocculation, and ion-exchange techniques have been employed for this purpose. Among these approaches, adsorption—especially the ion-exchange method—is considered highly effective due to its high adsorption capacity and reusability [4].

In the modern scenario, many researchers have focused on the removal of heavy metal ions through the ion-exchange process using different terpolymers. Recently, new efforts have been made to develop various terpolymer composites for the elimination of heavy metals. Chitosan is considered one of the most effective biosorbents for the removal of toxic heavy metal ions because it contains a large number of amino and hydroxyl ($-OH$) functional groups. The adsorption properties of chitosan toward heavy metals are attributed to its high hydrophilicity, which arises from the abundant hydroxyl groups present in the glucose units, as well as the flexible nature of its polymeric chain[5] .

Terpolymeric resins were synthesized by the condensation technique using 8-hydroxyquinoline-5-sulphonic acid and guanidine with formaldehyde, as well as phthalic acid/formaldehyde/thiosemicarbazide, in the presence of an acid catalyst to investigate their ion-exchange behavior toward selective metal ions, as reported by J. V. Khobragade and W. B. Gurnule [6,7]. Several researchers have also described the removal of hazardous metal ions through the ion-exchange method using urea- and thiourea-based chelating terpolymers prepared with formaldehyde, which contain a variety of active chelating functional groups [8,9].

Generally, urea-containing terpolymers possess carbonyl ($>C=O$) groups that significantly influence their ability to selectively bind metal ions such as Fe^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , and Pb^{2+} [10]. Furthermore, terpolymers synthesized from semicarbazide or melamine with formaldehyde have been reported to exhibit superior chelating and ion-exchange properties toward certain metal ions over a range of pH values, electrolyte concentrations, and contact times [11–13].

The aim of the present investigation was to synthesize a novel terpolymer through a solution condensation technique involving 4-hydroxybenzaldehyde and guanidine with formaldehyde as monomers, abbreviated as 4-HBAGF terpolymer. A new composite material was prepared by incorporating activated charcoal, which consists of elemental carbon arranged in irregular graphite layers, with the 4-HBAGF terpolymer. The synthesized adsorbents were characterized using elemental analysis, spectral techniques, and scanning electron microscopy (SEM). Furthermore, the adsorbents were evaluated for ion-exchange studies using a batch separation method by examining the effects of concentration, electrolyte, contact time, and pH.

2. Material and Method

The 4-hydroxybenzophenone (98%) monomer was obtained from Sigma-Aldrich. Activated charcoal and formaldehyde (37%) were purchased from Alfa Aesar. Metal ion solutions (Cd^{2+} , Co^{2+} , Pb^{2+} , and Hg^{2+}) were prepared using their respective nitrate and chloride salts. Ethylenediaminetetraacetic acid (EDTA), N,N-dimethylformamide, dimethyl sulfoxide, and acetone were procured from Merck and were used without any further purification. Double-distilled water was employed throughout all experimental procedures.

2.1. Synthesis of 4-Hydroxybenzaldehyde- Gaunidine – Formaldehyde(4-HBAGF-I) terpolymer

A homogeneous mixture of 4-hydroxybenzaldehyde (1.22 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 1:1:2 molar ratio. The reaction was carried out in a clean round-bottom flask fitted with a mechanical stirrer and a reflux condenser, using 2 M acetic acid (200 mL) as the reaction medium. The mixture was refluxed in an oil bath at $124 \pm 2^\circ\text{C}$ 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. The resulting product was neutralized sequentially with 8% aqueous NaOH and 1:1 HCl/water under ice-cold conditions to remove impurities from the terpolymer. This reprecipitation process was repeated three times to ensure purity. The purified terpolymer was then thoroughly washed with warm water, followed by methanol and ether, and subsequently filtered. The filtered product was dried in an oven at 75°C for 24 hours. The dried resin was finely powdered and sieved through a mesh screen to obtain uniform particle size. The overall yield of the terpolymer was approximately 84%.

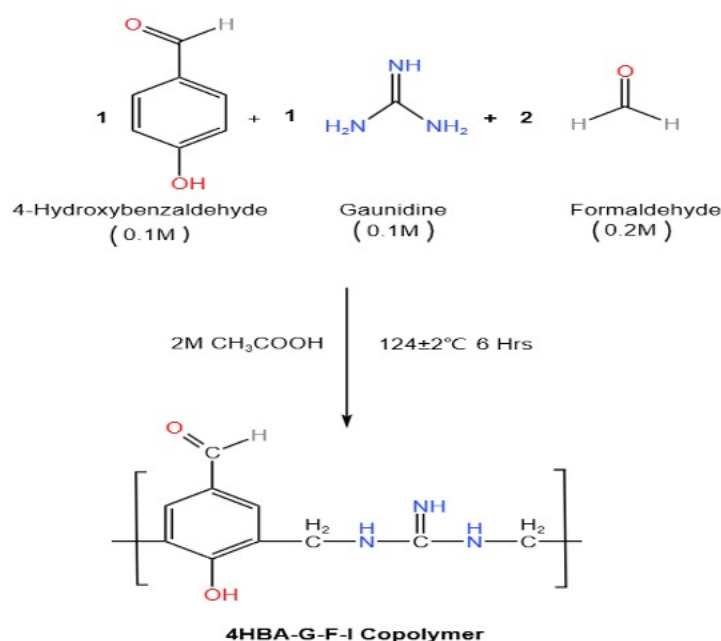


Fig.1. Synthesis of 4HBAGF-I Copolymer Resin

2.2.Preparation of 4-Hydroxybenzaldehyde- Gaunidine – Formaldehyde(4-HBAGF-C-I) Activated charcoal Composite

A novel copolymer/activated charcoal composite was synthesized by blending 4-HBAGF-I copolymer (1.0 g) with activated charcoal (2.0 g) in a 1:2 weight ratio. The activated charcoal was added to a solution of 4-HBAGF-I copolymer dissolved in 25 mL of DMSO in a 100 mL beaker. The mixture was subjected to ultrasonication for 3 hours, followed by continuous stirring at room temperature for 24 hours to ensure proper interaction between the components. Upon completion of the process, a black-colored 4-HBAGF-I composite was obtained. The composite was separated, thoroughly washed with ethanol and acetone to eliminate residual impurities, filtered, and subsequently dried in an oven at 70 °C for 24 hours.

3. Result and Discussion

Elemental analysis

The molecular formula of the 4-HBAGF-I terpolymer has been determined by elemental analysis and found to be $C_{10}H_{11}N_3O_2$. The elements present in the terpolymer was confirmed by the calculated and experimental values. The percentage of carbon is 58.12 (58.54), hydrogen is 5.01 (5.36) nitrogen is 15.88 (15.60) and oxygen is 20.11 (20.47) and Empirical formula weight 205.1.

UV-Visible Spectra

Ultraviolet and visible spectroscopy which is mainly work on the absorption of light of different frequency which gives information of molecule that how much of conjugation and multiple bonds is present in the molecule. UV-Visible spectra of copolymer and its composite with activated charcoal is recorded in DMSO solvent at room temperature. 4-HBAGF-I newly synthesized copolymer shows a two characteristic bands in between 265-288 nm and 358-386 nm. The band appeared in between 265-288 nm are less intense band because of $\pi \rightarrow \pi^*$ transition which is allowed transition. The presence of 4-Hydroxybenzaldehyde ring leads to allowed $\pi \rightarrow \pi^*$ transition. The band in between 358-386 which is more intense in nature because of $n \rightarrow \pi^*$ transition. This presence of $n \rightarrow \pi^*$ is due to guanidine auxochrome group. Hence the $\pi \rightarrow \pi^*$ transition represents the presence aromatic moiety and $n \rightarrow \pi^*$ transition is due to guanidine group. The UV-Vis spectrum of 4-HBAGF-I composite shows two absorption band from 240-265 nm and 334-350 nm as shown in Fig.2. and 3. From the given data it is clear that the composite absorption is decreased compared to the copolymer[14].

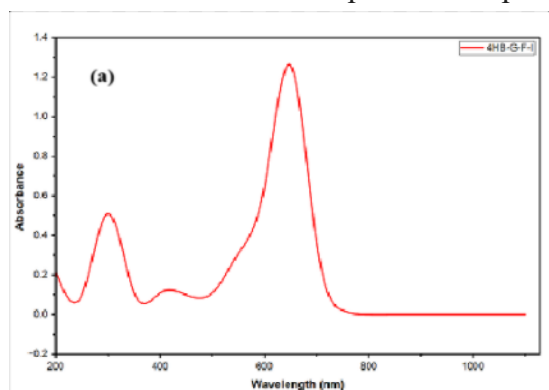


Fig. 2. UV-Visible spectra of 4HBAGF-I composite

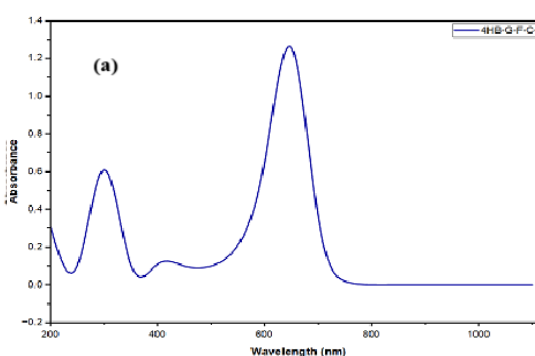


Fig. 3. UV-Visible spectra of 4HBAGFC-I composite

FTIR spectral analysis

The synthesized terpolymer and its composite having many functional groups were confirmed by FTIR spectroscopy which was depicted in Fig. 3.

The stretching of O-H bond is shown at 3116.89cm^{-1} . The band which is present at 1645 cm^{-1} is due to aryl C=C stretching. The carbonyl group of formaldehyde shows a stretching band at 1633cm^{-1} . There is a presence of a band at 2960 cm^{-1} is due to the presence of methylene N-H bond. The C=N bond at bridge shows a band at 1558 cm^{-1} . The polymer have a methylene bridge shows a band at 2867cm^{-1} also there is a benzene nucleus which also have a C-H bond shows a stretching frequency at 848 cm^{-1} . The 4HB-G-F copolymer have a N-H stretch of guanidine nuclei have a stretching band at 3478 cm^{-1} .

The FTIR spectra of composite of newly synthesized copolymer 4HB-G-F from activated charcoal is shown in the Fig. 3.14. It is observed from fig.3.14. the spectrum of composite totally differs from composite [15]. The symmetric and asymmetric vibration of N-H band of composite to be appeared at 2802 cm^{-1} . Furthermore O-H bond stretching of O-H phenolic group occur at 3116.59 cm^{-1} . The aryl C=C stretching vibration band appeared at 1634 cm^{-1} . The band is appeared at 1648 cm^{-1} is due to symmetrical vibration of carbonyl group (C=O) of aldehydic functional group. The methylene C-H bond shows a band at 2986 cm^{-1} in FTIR spectrum. The stretching band of C=N bridge of guanidine nucleus is at 1589 cm^{-1} . The band which is appear at 883 cm^{-1} is due to the C-H stretching in the ring. Also the spectrum shows a presence of vibration stretching frequency at 2896 cm^{-1} is due to C-H bond in methyl.

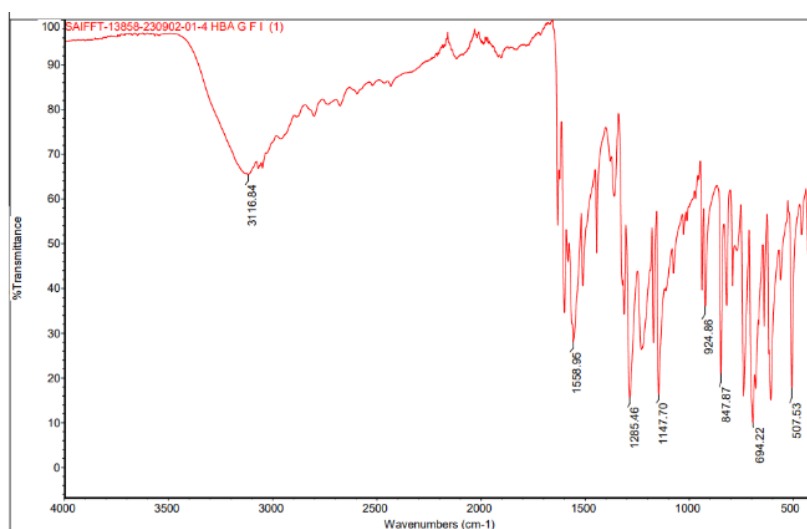


Fig.4. IR spectrum of 4HBAGF-I terpolymer

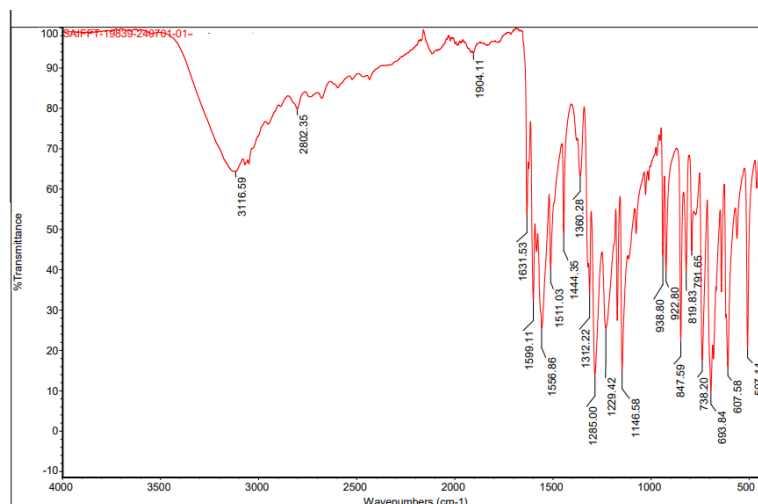


Fig.5. IR spectrum of 4HBAGFC-I composite

¹H NMR Spectroscopy

The proton NMR spectrum of 4HBAGF-I copolymer recorded in DMSO solvent which is shown in Fig. 6 shows. A singlet peak is occur at 3.41 is due to presence of methylene proton of Ar-CH₂-NH linkage. The NMR spectra of 4HBA-G-F shows a presence of multiplate at 7.56 (δ) ppm is due to O-H bond attached to benzene ring. In the spectra a sharp singlet is present at 6.8 (δ) ppm is due C-H bond in aromatic ring[16].

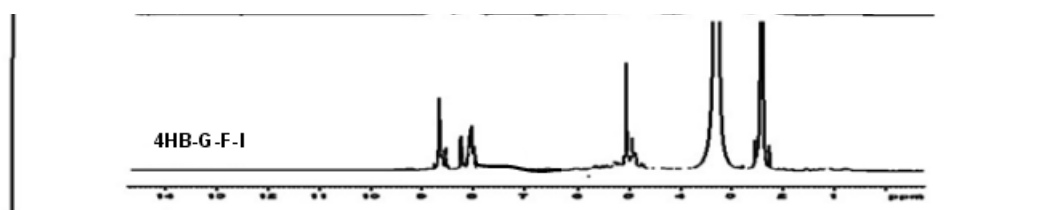


Fig.6. ¹H NMR Spectra of 4HBAGF-I Copolymer

XRD

In an XRD pattern, sharp and high-intensity peaks are characteristic of a crystalline phase, whereas low-intensity and broadened peaks suggest the presence of an amorphous structure. Figures 7 and 8 illustrate the XRD patterns of 4HBAGF-I and 4HBAGFC-I, respectively. Both materials exhibit distinct sharp peaks along with noticeable peak broadening, confirming the coexistence of crystalline and amorphous regions. However, the composite (4HBAGFC-I) displays relatively broader peaks compared to the terpolymer, indicating a higher degree of amorphous character. This increased amorphous nature in the composite is generally associated with greater porosity, which can enhance its adsorption capacity[17-18].

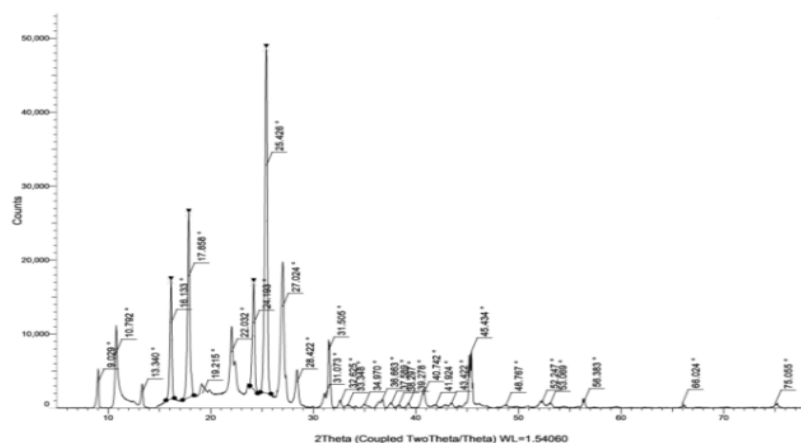


Fig. 7. X-ray diffraction of 4HBAGF-I

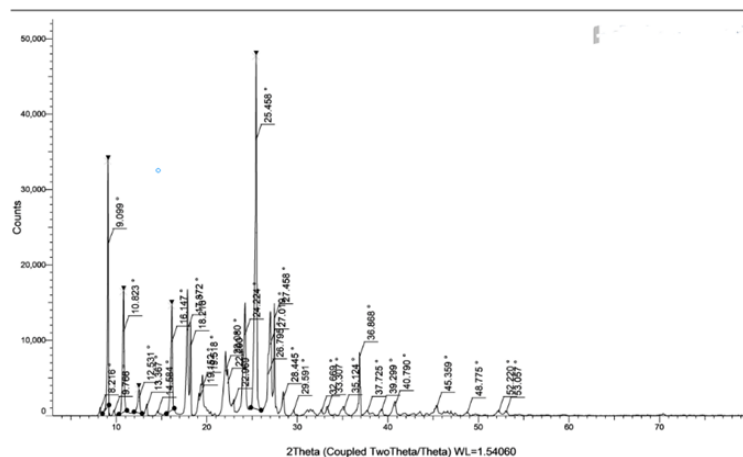


Fig. 8. X-ray diffraction of 4HBAGFC-I composite

Surface Analysis

The surface morphology of 4HBAGF-I copolymer and its activated charcoal composite was examined using scanning electron microscopy (SEM), as shown in Figs. 9 and 10. The SEM images of the copolymer reveal a closely packed, porous structure with deep pits and irregular granular features, indicating the presence of active sites and a semi-crystalline nature. The observed fringes suggest a transition between crystalline and amorphous phases, as the crystalline structure of the monomer transforms into a more amorphous form during polymerization. Some cracks and voids may be attributed to trapped air.

In contrast, the composite exhibits a higher number of distinct pores and active sites compared to the copolymer. The increased surface area and cavity formation confirm the strong incorporation of activated charcoal into the copolymer matrix, resulting in enhanced surface characteristics suitable for adsorption[19-21].

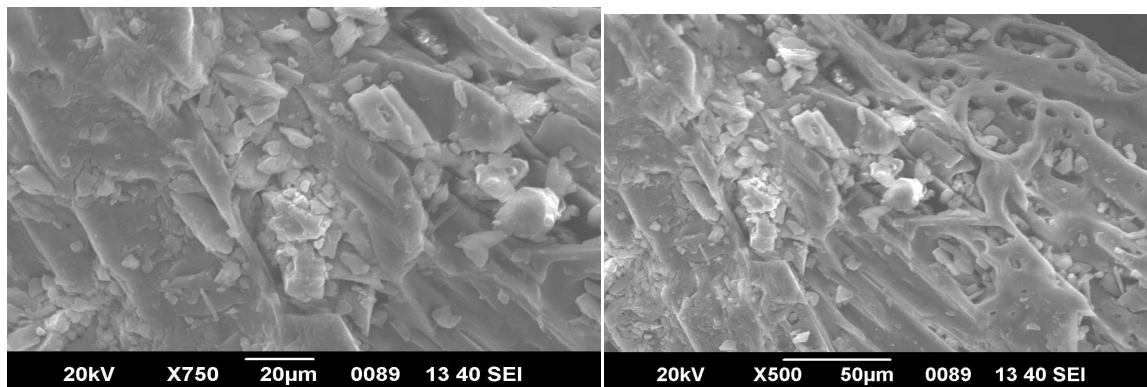


Fig.9. SEM Images of 4HBAGF-I Copolymer

Fig. 10. SEM Images of

4HBAGFC-I Composite

4. Ion Exchange study

The chelation ion-exchange property of the 4HBAGF-I terpolymer resin and 4HBAGFC-I composite was determined by batch equilibrium method for six metal ions *viz.* Cu^{2+} , Fe^{3+} , Zn^{2+} , Co^{2+} and Pb^{2+} . The ion-exchange study was carried out with the following experimental variations such as various electrolytes with different concentrations, pH of the medium and different time intervals.

4.1. Determination of Metal Uptake in the Presence of Various Electrolyte

The influence of Cl^- , NO_3^- and ClO_4^- at various concentrations on the equilibrium state of the metal-polymer interaction at constant pH values have been examined. The amount of metal ions taken up by a given amount of terpolymer and its composite depends on the nature and concentrations of the electrolyte present in the solution.

Generally as the electrolyte concentration increases, the ionization decreases, the number of anionic ligands present in the electrolytes decreases in the solution which form the complex with fewer amounts of metal ions and therefore more ions are available for adsorption process. Hence, the variable metal ions uptake capacity of 4HBAGF-I terpolymer resin may be due to the strong and weak complex formation between electrolyte ligands and the metal ions. If electrolyte ligand – metal ion complex is weaker than the polymer-metal ion complex, the polymer can break easily the electrolyte ligand – metal complex which generate more number of free metal ions which easily form complex with the terpolymer and hence uptake of metal ion increases. Further, if electrolyte ligand – metal ion complex is stronger than the polymer – metal ion chelates, more number of metal ions will try to form strong complex with the electrolyte ligand which decreases the metal uptake capacity lower by the terpolymer. In the presence of Cl^- , NO_3^- and ClO_4^- ions, the amount of uptake of all the metal ions under study increases with increasing concentration of the electrolytes.

chloride and nitrate ions, the uptake of Fe(III), Cu(II) and Ni(II) ions increases in terpolymer and the uptake of Fe(III), Cu(II) and Ni(II) ions decreases in composite with increasing concentration of the electrolytes [22-25].

Moreover, the uptake of Zn(II), Pb(II) and Co(II) ions increases in terpolymer whereas the uptake of Zn(II), Pb(II) and Co(II) ions decreases in composite with the decreasing concentration of the chloride, nitrate and perchlorate. This may be explained on the basis of the stability constants of the complexes with those metal ions. The stability of the

complexes depends on the charge of the metal ions and nature of the electrolyte ligands. The ligands NO_3^- , Cl^- and ClO_4^- may form weak complex with Fe^{3+} , Cu^{2+} and Ni^{2+} metal ions may increase the metal uptake capacity of the terpolymer at lower pH values. While the ligands NO_3^- , Cl^- and ClO_4^- may form strong complex with Zn^{2+} , Co^{2+} and Pb^{2+} at higher pH. As the concentration of these ligands increases the complex formation is favoured and hence the metal uptake capacity of the terpolymer decreases.

At lower pH and higher concentration, the metal ion uptake by 4HBAGF-I terpolymer follows the order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Fe}^{3+}$, while at higher pH and lower concentration it is $\text{Zn}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+}$. For the 4HBAGFC-I composite, the order at lower pH is $\text{Fe}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ and at higher pH is $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$. The uptake of Pb^{2+} by the terpolymer is very low due to its larger hydrated ionic size but is comparatively higher in the composite.

4.2. Evaluation of the Rate of Metal-Ion Uptake

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments were carried out, in which the metal ion taken up by the terpolymer resin was estimated from the time to room temperature (300 K) in the presence of 25 ml of a solution of NaNO_3 . It was assumed that under the given conditions, the state of equilibrium was established within 24 h. The rate of metal-ion uptake was expressed as the percentage of the amount of metal ion taken up after a certain time related to that in the state of equilibrium [26-27].

The results of metal ion uptake in different time intervals used to find out the shortest period of metal ion uptake capacity by the terpolymer and its composite. When the shaking time increases, the polymer gets more time for adsorption, hence the uptake of metal ion by the terpolymer also increases. The rate refers to the simply change in the concentration of the metal ions in the aqueous solution which is in contact with the terpolymer. Among the metal ions Fe^{3+} , Cu^{2+} and Ni^{2+} require about 5 h for the establishment of the equilibrium, Zn^{2+} , Co^{2+} require 6 h and Pb^{2+} ion requires 7 h to reach the state of equilibrium. The experimental results revealed that the rate of metal-ion uptake followed the order of $\text{Fe(III)} \approx \text{Cu(II)} \approx \text{Ni(II)} > \text{Co(II)} \approx \text{Zn(II)} > \text{Pb(II)}$ for 4HBAGF-I while in its composite Pb^{2+} ion requires 5 h and Fe^{3+} , Cu^{2+} and Ni^{2+} require more than 5 h therefore composite followed order $\text{Pb(II)} > \text{Co(II)} \approx \text{Zn(II)} > \text{Fe(III)} \approx \text{Cu(II)} \approx \text{Ni(II)}$

The rate of metal uptake may depend upon hydrated radii of metal ions. The observation indicates that the time required for the rate of metal ion uptake depends on the nature and the ionic size of the metal ions and porosity of terpolymer and its composite.[28,31].

4.3. Evaluation of the Distribution of Metal Ions at Different pH :

The distribution of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} ions between the polymer and aqueous phases was studied at 300 K in NaNO_3 solution up to pH 6.5 to avoid metal ion hydrolysis. The remaining metal ions in the aqueous phase were measured to calculate the amount adsorbed by the resin. The results show that metal ion uptake increases with increasing pH, and equilibrium was reached within 24 h at 25 °C.

For Fe^{3+} ion, the highest working pH is 4, and the results indicate that the terpolymer resin shows more selective uptake of Fe^{3+} compared to other metal ions at this pH. However, when compared with its composite, the distribution behavior of metal ions changes due to the

presence of activated charcoal, which provides additional adsorption sites and improves the overall adsorption efficiency. The difference in distribution ratios for various metal ions may be attributed to the stability of the metal–ligand complexes formed during adsorption. In the case of the terpolymer, the order of metal ion distribution is $\text{Fe(III)} > \text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Co(II)} > \text{Pb(II)}$, whereas the composite shows comparatively enhanced uptake for some ions due to increased surface area and additional active sites. Metals like Zn^{2+} and Cu^{2+} form more stable complexes with certain organic ligands (like those in the terpolymer), whereas heavier ions like Pb^{2+} have a stronger electrostatic attraction to the modified surfaces of composites. Terpolymer ($\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$): Favors smaller transition metals. These ions have smaller ionic radii, allowing them to penetrate the tighter, less porous structure of a pure polymer more easily. Composite ($\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$): Favors larger, heavier metals. Adding a secondary material (like activated charcoal) creates a more open, highly porous structure with a larger surface area. This allows bulky ions like Lead (Pb^{2+}) and Cadmium (Cd^{2+}) to access active binding sites that were previously restricted [32,33].

5. THERMAL STUDIES

Thermal stability of the 4HBAGF-I terpolymer and its 4HBAGFC-I composite has been analyzed by the thermogravimetric analysis (TGA). Sharp wenworth and freeman carroll method have been used for determining activation energy. Following equation are used to determine kinetics parameters[29-30].

Kinetics of Thermal Degradation

Formulas for Calculating Kinetic Parameters

(i) Entropy Change (ΔS)

The intercept can be expressed as:

$$\text{Intercept} = \log (KR/h \phi E) + \Delta S/2.303R$$

where:

- $K = 1.380 \times 10^{-16} \text{ erg/deg/mole-}$
- $R = 1.987 \text{ cal/deg/mole (or } 8.314 \text{ J/K/mol)}$
- $h = 6.625 \times 10^{-27} \text{ erg sec}$
- $U = 0.166$
- ΔS = change in entropy
- E = activation energy derived from the graph.

(ii) Free Energy Change (ΔF)

The free energy change can be calculated using the formula:

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

where:

- ΔH = enthalpy change (activation energy)
- T = temperature in Kelvin

(iii) Frequency Factor (Z)

The frequency factor can be derived from:

$$B_{2/3} = \log ZE_a/R\Phi$$

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

where:

- Z = frequency factor
- $\log p(x)$ = calculated using Doyle's table related to activation energy
- α = degree of transformation, defined as $\alpha = w/W_c$.

(iv) Apparent Entropy (S^*)

The apparent entropy can be calculated as:

$$S^* = 2.303 R \log (Zh/RT)$$

where:

- Z = Frequency factor
- T^* = half decomposition temperature.

Table 1: Results of thermogravimetric analysis of 4HBAGF-I Copolymer and 4HBAGFC-I composite

Copolymer	Half Decomposition Temp $T^*(K)$	Activation Energy (KJ/mol)	
		F.C.	S.W.
4HBAGF-I	620	4.87	5.26
4HBAGFC-I	640	5.45	6.24

Sharp–Wentworth and Freeman–Carroll Method

The expressions to calculate the kinetic and thermodynamic parameters are presented in Table 1 and the results in Table 2.

Table 2: Kinetic and Thermodynamic Parameters of 4HBAGF-I Copolymer 4HBAGFC-I composite

Copolymer Ligands	Entropy Change $\Delta S(J)$	Free Energy Change ΔF (KJ)	Frequency factor Z (S^{-1})	Apparent Entropy Change (S^*)	Order reaction
4HBAGF-I	-146.32	78.40	530.42	-33.3865	0.9
4HBAGFC-I	-130.45	84.20	545.32	-33.4003	1.35

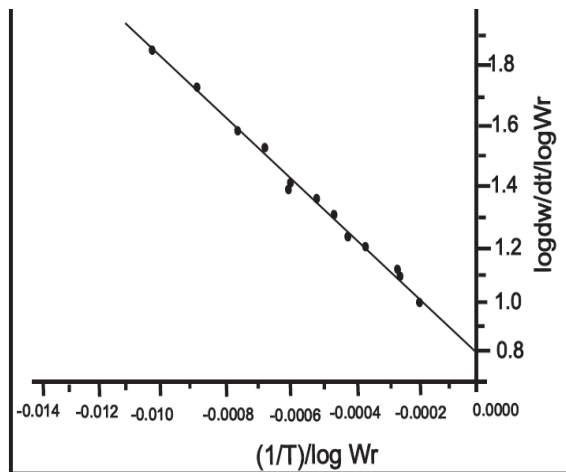
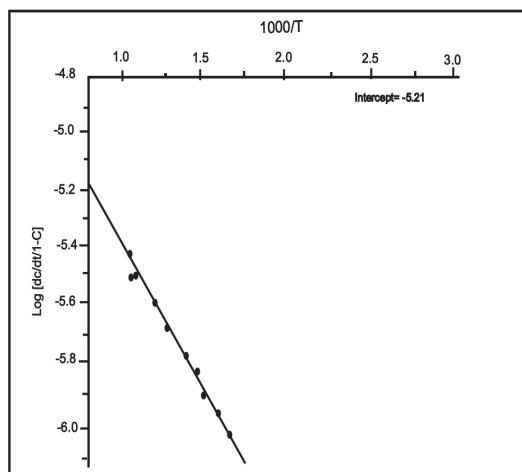


Fig.9: Sharp–Wentworth plot of 4HBAGF-I **Fig.10: Freeman-Carroll Plot of 4HBAGF-I**

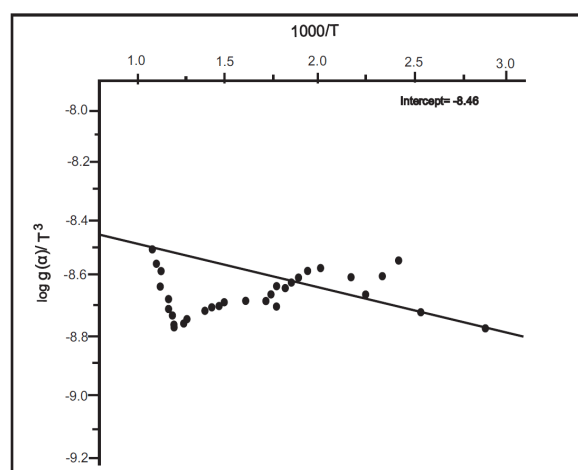


Fig.11. Activation Energy (E_a) By Freeman-Carroll Plot of 4HBAGF-I Copolymer

The terpolymer follows first-order kinetics due to adsorption on uniform functional groups, whereas the composite exhibits higher-order behaviour because the presence of activated charcoal provides multiple heterogeneous adsorption sites and mechanisms.

Conclusion

From the present investigation, a novel 4HBAGF-I copolymer and its composite were successfully synthesized and characterized using various spectral and physicochemical techniques. The results of metal ion recovery indicate that the composite exhibits higher metal ion recovery efficiency compared to the 4HBAGF-I copolymer. This improvement may be attributed to the increased surface area, deeper pores/pits, and the presence of active functional groups in the composite structure. The synthesized adsorbents also demonstrated good reusability for metal ion removal.

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Reference

1. Gurnule WB, Patle DB (2012) Preparation, characterization and chelating ion-exchange properties of terpolymer resins derived from *o*-aminophenol, urea and formaldehyde. *Elixir Appl Chem* 50:10338–10345
2. Rahangdale, S.S. and Gurnule, W.B., 2011. Antimicrobial activity and thermal properties of copolymer resin derived from 2, 2'-dihydroxybiphenyl, dithiooxamide and formaldehyde.
3. Mandavgade, S.K. and Gurnule, W.B., 2022. Synthesis and chelate ion exchange properties of copolymer resin: 8-hydroxyquinoline-5-sulphonic acid-catechol-formaldehyde. *Materials Today: Proceedings*, 60, pp.1814-1818.
4. Rahangdale, S.S., Das, N.C., Vajpai, K.S. and Gurnule, W.B., 2020. Synthesis, Characterization And Thermal Degradation Study Of Copolymer Resin-Ii: Resulting From 2-Hydroxy, 4-Methoxybenzophenone, 1, 5-Diaminonaphthalene And Formaldehyde. *IJBAT*, 8(1), pp.194-204.
5. Asma Sharkawy ^a, Maria Filomena Barreiro ^b, Alirio E. Rodrigues ^a Chitosan-based Pickering emulsions and their applications: A review, *carbohydrate polymer*, vol.250, 15 december 2020,116885
6. Wasudeo b. Gurnule, Yashpal rathod, A. D. Belsare, N.C. das, Thermal degradation and antibacterial study of transition metal complexes derived from novel terpolymer ligand, *Materialtoday:proceeding*, Volume 29, Part 4, 2020, 1044-1049
7. Jyotsana Khobragade¹, W. B. Gurnule², Mudrika Ahamad, removal of toxic metal ions using ion-binding copolymer resin by batch equilibrium technique, *IJARSE* volume 11, 2022, ISSN-2319-8354
8. Damini Shedmake¹, Jyotsna V. Khobragade² and W. B. Gurnule³, synthesis, characterization and antimicrobial activity of copolymer metal complexes and their thermal studies, , *IJBAT*, Issue (XI) Vol (II) May 2023 : 67-79
9. Rahul Thengane¹, Jyotsna V. Khobragade² and W. B. Gurnule³, ion exchange properties of copolymer resin derived from phthalic acid, thiosemicarbazide and formaldehyde, *IJBAT*, Issue (XI) Vol (II) May 2023 : 256-266 .
10. Damini Surendra Shedmake¹, Jyotsna V. Khobragade^{2*}, W. B. Gurnule^{3*} synthesis, characterization and physicochemical studies of terpolymer resin satf-i derived from sulphanilic acid, thiourea and formaldehyde, *Futuristic Trends in Chemical, Material Sciences & Nano Technology* e-ISBN: 978-93-5747-640-9 IIP Series, Volume 3, Book 18, Chapter 33
11. Damini Surendra Shedmake¹, Jyotsna V. Khobragade^{2*}, W. B. Gurnule³ , Chelation Ion-Exchange Studies of Acrylamide and Furfural Copolymer Resin , *Journal of Survey in Fisheries Sciences* 10(3) 269-276 2023

12. Khobragade Jyotsana , Synthesis and characterization of copolymer resin derived from pthallic acid and semicarbazide with formaldehyde Int. Res. J. of Science & Engineering, 2020; Special Issue A7: 89-95 SJIF Impact Factor 6.68 ISSN: 2322-0015,.
13. Jyotsana V. Khobragade¹, Dhanashri M. Borikar² and W. B. Gurnule^{3*}, Sorption Investigation on the Removal of Metal Ions from Aqueous Solutions using Copolymer Resin ,Alochana Chakra Journal ISSN NO:2231-3990.
14. Gurnule WB, Charulata MS, Mudrika A (2013), Synthesis, characterization, morphology, thermal, electrical and chelation ion-exchange properties of a copolymer resin. J Environ Res Develop 7:1183–1192.
15. Bhatt RR, Shah BA, Shah AV (2012), Uptake of heavy metal ions by chelating ion-exchange resin derived from *p*-hydroxybenzoic acid-formaldehyde-resorcinol: synthesis, characterization and sorption dynamics. Malaysian J Anal Sci 16:117–133
16. Gurnule, W.B., Khobragade, J. and Ahamed, M., 2014. Thermal degradation studies of high performance copolymer resin derived from 8-hydroxyquinoline 5 sulphonic acid, semicarbazide and formaldehyde. *Der Pharma Chem*, 6, pp.334-342.
17. Jyotsana Khobragade., Mudrika Ahamed, M.A. and Gurnule, W.B., 2014. Removal of cations using ion-binding copolymer involving 8-hydroxyquinoline 5-sulphonic acid and semicarbazide with formaldehyde by batch equilibrium technique.
18. Gurnule, W.B., Khobragade, J. and Ahamed, M., 2015. Synthesis, Spectral, Morphology and Thermal Degradation Kinetics Studies of Copolymer. *Chem. Sci. Rev. Lett*, 3(12), pp.1329-1340.
19. Khobragade, J. and Gurnule, W.B., 2017. Removal of Toxic Metal Ions Using Ion-Binding Copolymer Resin by Batch Equilibrium Technique. *Int J Res Biosci Agric Technol*, 7, pp.519-26.
20. Khobragade, J., Ahamed, M. and Gurnule, W.B., 2014. Synthesis and characterization of copolymer resin derived from pthallic acid and melamine.
21. Gurnule, W.B., 2012. Sorption Investigation on the Removal of Metal Ions from aqueous solution using Chelating copolymer resin. *International Journal of Environment and Resource*, 1(1), pp.16-25.
22. Khobragade, J. and Gurnule, W.B., 2017. Removal of Toxic Metal Ions Using Ion-Binding Copolymer Resin by Batch Equilibrium Technique. *Int J Res Biosci Agric Technol*, 7, pp.519-26.
23. Gurnule WB, Charulata MS, Mudrika A (2013) Synthesis, characterization, morphology, thermal, electrical and chelation ion-exchange properties of a copolymer resin. J Environ Res Develop 7:1183–1192
24. Azarudeen RS, Burkanudeen AR (2012) Synthesis, spectral, morphology, thermal degradation kinetics and antibacterial studies of terpolymer metal complexes. J Inorg Organomet Polym 22:791–806
25. Gurnule, W.B., Gupta, P.G., Gupta, R.H., Rathod, Y.U. and Singh, N.B., 2023, December. Thermal degradation studies of 2-amino 6-nitrobenzothiazole-oxamide-formaldehyde copolymer and its composites. In *IOP Conference Series: Earth and Environmental Science* (Vol. 1281, No. 1, p. 012026).

26. Gurnule, W.B., Rahangdale, P.K., Paliwal, L.J. and Kharat, R.B., 2003. Chelation ion-exchange properties of copolymer resin derived from 4-hydroxyacetophenone, oxamide, and formaldehyde. *Journal of applied polymer science*, 89(3), pp.787-790.
27. Alexandratos, S.D., 2021. Trends in ion exchange: Analysis of the literature. *Reactive and Functional Polymers*, 169, p.105066.
28. Vinodh, R., Padmavathi, R. and Sangeetha, D., 2011. Separation of heavy metals from water samples using anion exchange polymers by adsorption process. *Desalination*, 267(2-3), pp.267-276.
29. Azarudeen, R.S. and Burkanudeen, A.R., 2012. Synthesis, spectral, morphology, thermal degradation kinetics and antibacterial studies of terpolymer metal complexes. *Journal of Inorganic and Organometallic Polymers and Materials*, 22(4), pp.791-806.
30. Gupta, P.G., Gupta, R.H., Gurnule, W.B., Rao, S.N. and Rathod, Y.U., 2023. Synthesis, Characterization, and Photoluminescence Properties of 2-amino 6-nitrobenzothiazole-Melamine-Formaldehyde Copolymer-Charcoal Composite. *Indian Journal of Engineering & Materials Sciences*, 30(6).
31. Wang, J., Zhou, Q. and Zeng, W., 2019. Competitive adsorption of SF₆ decompositions on Ni-doped ZnO (100) surface: Computational and experimental study. *Applied Surface Science*, 479, pp.185-197.
32. Valle, H., Sánchez, J. and Rivas, B.L., 2015. Poly (N-vinylpyrrolidone-co-2-acrylamido -2 -methylpropanesulfonate sodium): Synthesis, characterization, and its potential application for the removal of metal ions from aqueous solution. *Journal of Applied Polymer Science*, 132(2).
33. Tiebao Wang, Tiebao Wang, Leyao Wang Lichen Zhao, Xin Wang, Fabrication and Mechanical Properties of Porous Fe Skeleton-Reinforced Mg-Zn-Ca-Sr Bulk Metallic Glass Composites, *J. Compos. Sci.* 2026, 10(2), 110; <https://doi.org/10.3390/jcs10020110>