

EFFICIENT REMOVAL OF TOXIC HEAVY METAL IONS FROM AQUEOUS SOLUTIONS USING A NOVEL CHELATING COPOLYMER RESIN

Akshay A. Akare¹, Jyoti N. Thakre², Jyotsna Khobragade³, W. B. Gurnule^{4*} and D. M. Chafle¹

¹Department of Chemistry Taywade College, Mahadula, Koradi, Nagpur- 441111 India

²Department of Engineering, Sciences and humanities, St. Vincent Pallotti College of Engineering & Technology, Nagpur-441108, India

³Department of Chemistry, Gurunank College of Science, Ballarpur-442701, India

^{4*}Department of Chemistry Kamla Nehru Mahavidyalaya, Nagpur- 440024 India

E-mail: akshayakare10@gmail.com, wbgurnule@gmail.com, jdr2105@gmail.com, jyotit2772@gmail.com, dmchafle@gmail.com

Abstract

A new chelating ion-exchange copolymer was prepared using the polycondensation of 2,4-dihydroxybenzoic acid, acrylamide and formaldehyde in a 1: 1: 2 proportion. The copolymer produced was widely characterized by UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (¹H NMR), carbon-13 nuclear magnetic resonance (¹³C NMR), scanning electron microscopy (SEM), X-ray (XRD), elemental analysis, and gel permeation chromatography (GPC) of the molecular weight. The identification of the successful formation of the copolymer and the presence of functional groups that were able to coordinate with metal ions was proven by the spectral and analytical findings. The ion-exchange ability of the synthesized copolymer was tested against the removal of Fe³⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ni²⁺, and Pb²⁺ ions in aqueous solutions using the batch equilibrium technique. The influence of the concentration of the electrolytes and the pH and the contact time on the adsorption of metal ions was systematically studied. The findings showed that the copolymer had a high adsorption capacity and selectivity to the toxic metal ions especially Pb²⁺ and Cd²⁺, because of the presence of hydroxyl and amino functional group, which formed stable chelate complexes. The resulting copolymer was found to have a high potential of being an effective and reusable ion-exchange material in the removal of dangerous metal ions in the polluted water systems.

Keywords: Copolymer, Spectral characterization, Chelating ion-exchange resin, Batch equilibrium method, Heavy metal removal.

1. Introduction

Polymer science has quickly developed, attracting worldwide consideration due to the flexible applications of polymer materials. Copolymers, specifically, are flexible mixtures significant in a great many applications, including glues, high-temperature materials, fire safe filaments, coatings, semiconductors, impetuses, and particle trade pitches. Their multi-layered nature makes copolymers central focuses in state-of-the-art research, driving progressions in materials science across assorted businesses [1-4]. Copolymers and their polychelates exhibit great

protection from changes in temperature, making critical commitments to the progression of polymeric materials [5].

Gurnule and partners inspected the corruption of a copolymer under heat delivered by formaldehyde, 2-hydroxy-4-methoxybenzophenone, and 1, 5- diaminonaphthalene [6]. Utilizing monomers including formaldehyde, 2, 4- dihydroxybenzoic corrosive, and phenylhydrazine (0.1 mol) in a 3:1:5 proportion, the copolymer was made utilizing mass polymerization. A corrosive impetus was available during the polymerization cycle. The subsequent copolymer's intensity solidness was then surveyed and recorded [7-9].

Utilizing 4-hydroxybenzophenone and melamine with formaldehyde, a particle trade saps was made. It was portrayed utilizing essential investigation and other spectroscopic procedures, and its chelating properties with Ni^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Pb^{2+} metal particles were inspected. Phthallic corrosive, melamine, and formaldehyde copolymer were utilized to make the copolymeric chelating particle trade sap, which was a then distinguished utilizing FT-IR and ^1H NMR spectrum [10]. The combined copolymer's capacity to retain metal particles has been tried involving the clump equilibration strategy for different metal particles at different focuses. Solid anion trade hypercrosslinked poly (HEMA-co EGDMA-co-VBC) and solid anion trade poly (Styrene-co-EGDMA-co-VBC) were thought about [11]. Copolymer sap produced using subbed resorcinol, biuret, and formaldehyde has been the subject of combination, antibacterial, and particle trade examinations [12]. Salicylic corrosive and diaminobenzoic corrosive were joined with formaldehyde to make copolymer sap, and the chelating particle trade properties were examined utilizing the group harmony technique. Selectivity for Fe^{3+} , Cu^{2+} , and Ni^{2+} particles was viewed as higher in the tar than for Zn^{2+} , Co^{2+} , and Pb^{2+} particles [13]. Within the sight of a corrosive impetus, copolymer gum is made by buildup of salicylic corrosive, semi- carbazide, and formaldehyde. Its particle trade qualities for Co^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , and Pb^{2+} particles are analyzed [14-15]. Das concentrated on the arrangement of copolymers with formaldehyde, 1,5- diaminonaphthalene, and 2-hydroxy-4-methoxybenzophenone [16]. Besides, a copolymer made of 2-hydroxy-4-methoxyacetophenone, guanidine hydrochloride, and formaldehyde was blended and portrayed by Bisen and partners [17]. Copolymers' reasonable warm soundness and variety in assembling materials make them valuable in various applications, including bundling, glues, coatings, electrical sensors [18], and semiconductors [19]. Furthermore, they have been examined for use as impetuses, particle exchangers, activators, and thermally stable materials [20-21]. By creating plastic items like toys, cups, and car parts, polymers have changed both industry and day to day existence. Specialists are right now exploring breakdown strategies, regardless of the way that polymers for the most part oppose disintegration [22-23].

Although much has been done on the same, the design of new copolymer resins with enhanced adsorption capacity, selectivity and stability is an area of research being looked into. As such, the production of efficient copolymers with appropriate chelating groups is an efficient system to developing efficient ion-exchange material to remove heavy metals.

A new copolymer resin has been synthesized by condensation polymerization and its properties evaluated in the current research by applying different analytical and spectroscopic

methods (elemental analysis, gel permeation chromatography (GPC), UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FT-IR), ^1H NMR, ^{13}C NMR, scanning electron microscopy (SEM), and X-ray diffraction (XRD) to identify its characteristics. Also, ion-exchange behavior of the synthesized copolymer was studied and determination of its effectiveness of the copolymer in removing the toxic heavy metal ions in the aqueous solutions was done. The obtained findings of this study can be used to create effective polymer-based adsorbents to clean the environment and drinking water.

2. Materials and Methods

2.1 Materials

All the chemicals employed in the current study were of an analytical reagent (AR) grade and were used without further purification. 2, 4-dihydroxybenzoic acid, acryl amide and formaldehyde solution (37%) were bought in standard chemical suppliers and utilized as received. Purification and experimental work were done using the solvents, which included ethanol, methanol, and distilled water.

The ion-exchange study mentioned above used metal ion solutions prepared as Cu(II), Ni(II), Zn(II), Pb(II), Cd(II) with their corresponding nitrate or sulfate salts using double distilled water. Glassware utilized in the experiments was washed using the dilute nitric acid and rinsed using the distilled water.

2.2 Synthesis of 2,4-DBAF Copolymer Resin

The synthesis of the copolymer resin, 2,4-Dihydroxybenzoic Acid 2,4-DBAF-Acrylamide-Formaldehyde (2,4-DBAF) was done using a condensation polymerization technique. In a typical synthesis procedure, 2,4-dihydroxybenzoic acid and acrylamide were taken in a round-bottom flask in a suitable molar ratio and dissolved in an appropriate solvent medium. To this mixture, an aqueous solution of formaldehyde (37%) was added slowly under constant stirring. A few drops of acid catalyst (such as hydrochloric acid) (2M) were added to promote the condensation reaction. The mixture was heated to 122°C in an oil bath and stirred in a continuous manner and allowed to take place over a period of approximately 5 hours. The reaction saw condensation polymerization of the monomers to form a three-dimensional network of copolymer by the use of the methylene bridges that were created using formaldehyde.

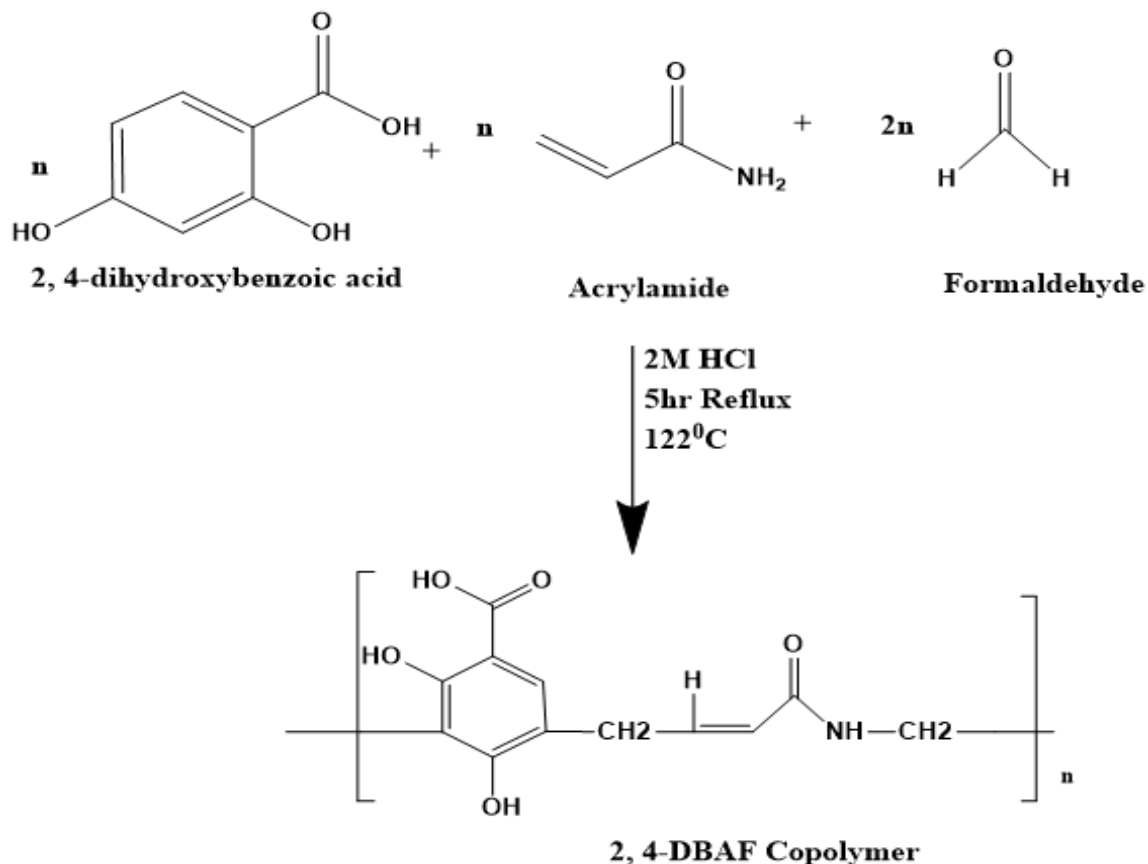


Figure 1: Synthesis of 2, 4-DBAF polymer

Once the reaction was done the viscous polymer mass that was obtained was left to cool to room temperature. This gave a solid copolymer resin which was washed repeatedly with hot distilled water and ethanol to eliminate remaining unreacted monomers and impurities. The clean copolymer was then dried in a vacuum oven with temperature of 607°C in 24 hours. The dried polymer was crushed, ground and sieved to get the same size of particles ready to use in further characterization studies and ion exchange studies.

3. Characterization of the Synthesized Copolymer

The synthesized copolymer resin was characterized using several analytical and spectroscopic techniques to determine its structural, morphological, and physicochemical properties. Some of the characterization techniques used were elemental, gel permeation chromatography (GPC), UV-Visible, Fourier transform infrared (FTIR), proton nuclear magnetic resonance (^1H NMR), carbon-13 nuclear magnetic resonance (^{13}C NMR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). These methods can give valuable data regarding the molecular composition, functional groups, surface morphology, and crystalline structure of the polymer [24].

3.1 Elemental Analysis

To establish the composition of the carbon (C), hydrogen (H) and nitrogen (N) composition of the synthesized copolymer resin in percentage. The theoretically calculated values were

observed to be in good accord with the experimental values which complicated the successful formation of the copolymer structure. Nitrogen in the polymer structure validates the presence of acryamide units into the polymer backbone with the oxygen-based functional groups being formed by condensing 2, 4-dihydroxybenzoic acid and formaldehyde. Elemental analysis thus presents good support to the successful production of the copolymer resin [25].

Table 1: Elemental Analysis of 2, 4-DBAF Copolymer

Polymer	Measured and Theoretical Carbon Percentage	Measured and Theoretical Hydrogen Percentage	Measured and Theoretical Nitrogen Percentage	Empirical Formula of Polymer Subunit	Molecular Weight of Repeat Unit
2, 4-DBAF	52.60 (53.83)	3.11 (4.18)	6.42 (8.37)	C ₁₅ H ₁₄ N ₂ O ₅	334.35

3.2 Molecular Weight Determination by Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) was used to calculate the molecular weight distribution of the produced copolymer. The analysis of the GPC revealed the determination of number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the synthesized copolymer. The GPC analysis revealed that the synthesized copolymer has an intermediate distribution of molecular weight, which is typical of condensation polymerization reactions. Polydispersity index (PDI) gives data concerning uniformity of the polymer chains. A smaller PDI goes to show the evenness of the polymer chains as the polymerization process takes place [26].

Table 2: Molecular Weight Determination of 2, 4-DBAF Copolymer by Gel Permeation Chromatography (GPC)

Polymer	Mass of Empirical Unit (g)	Number-Average Molecular Weight (M _n)
2, 4-DBAF	312	3235

3.3 UV–Visible Spectroscopy

The electronic transitions of the synthesized copolymer were studied by UV- Visible spectroscopy. The UV–Visible spectrum of the copolymer had absorption bands at the region of 245-265 nm and 368-377 nm which can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ rings and carbonyl groups in the structure of the polymer. The peaks of the absorption in the UV spectrum verify the existence of conjugated aromatic systems and functional groups in the copolymer matrix. These functional groups are responsible for interaction with metal ions during ion-exchange processes [27].

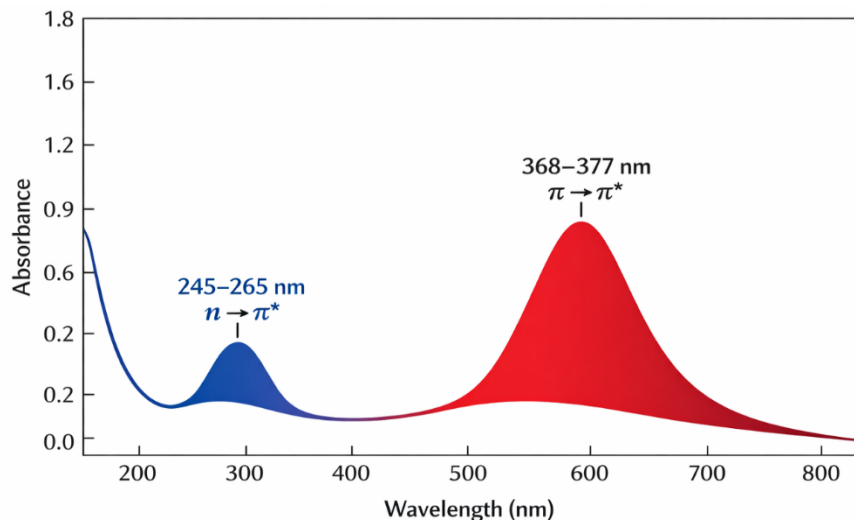


Fig. 2. Ultraviolet–Visible Absorption Spectrum of 2, 4-DBAF Copolymer

3.4 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups in the synthesized copolymer were determined by FT-IR spectroscopy. The FT-IR spectrum of the copolymer had many typical absorption bands which are related to the various functional groups. The common FT-IR absorption bands in the copolymer include: The occurrence of these characteristic peaks is a sure indication that hydroxyl, amide and aromatic functional groups in the polymer structure have been incorporated. These functional groups are active sites that are used in binding metal ions during the adsorption or ion-exchange processes [28].

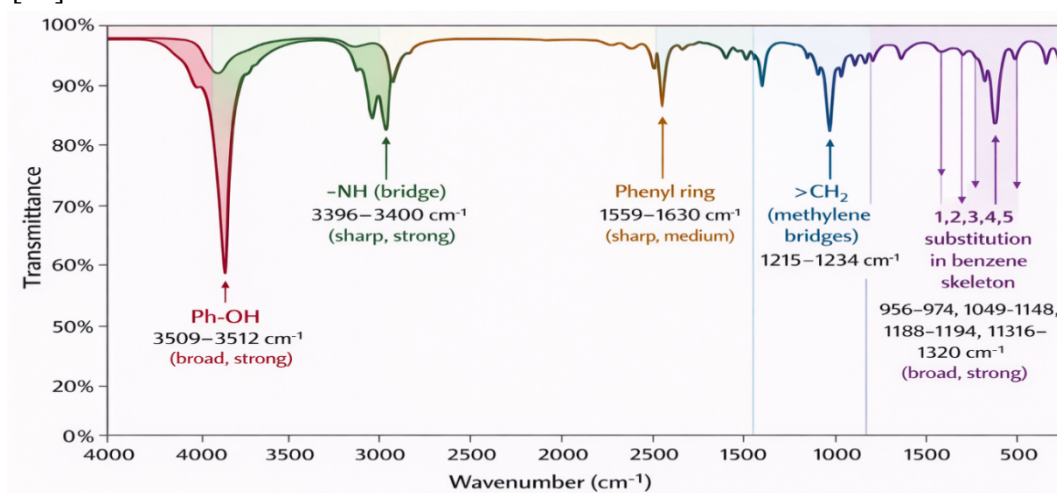


Fig. 3: FTIR Spectroscopic Characterization of 2, 4-DBAF Copolymer

3.5 ¹H Nuclear Magnetic Resonance (¹H NMR)

The ^1H NMR spectrum of the copolymer that is synthesized gives details on the presence of the hydrogen atoms in the various chemical environments of the polymer structure. Typical signals observed in the ^1H NMR spectrum include, These signals confirm the formation of methylene bridges between monomer units and aromatic and amide functional groups in the polymer structure [29]. The methyl protons of the Ph-CO-CH_2 group are accredited with a medium-intensity singlet at δ 2.5–3.0 ppm. The amino proton of the -C-NH-CS- unit appears as a triplet in the δ 7.35–7.41 ppm range. A strong signal between δ 4.96 and 4.98 ppm corresponds to methylene ($\text{-CH}_2\text{-}$) protons in the polymer backbone. Weak, unresolved signals from δ 6.5 to 8.5 ppm reflect aromatic protons of substituted benzene rings. Additionally, a faint signal between δ 7.5 and 8.2 ppm confirms the presence of phenolic -OH groups [30-31].

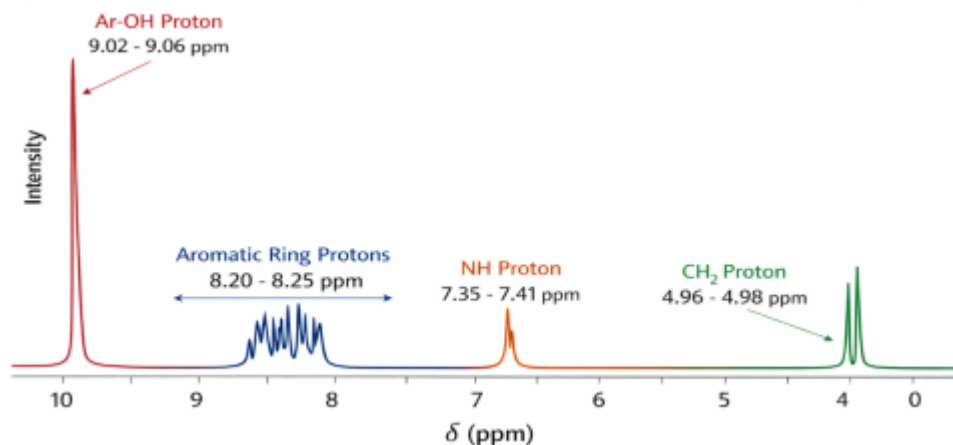


Figure 4: ^1H NMR Characterization of 2, 4-DBAF Copolymer

3.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to obtain the surface morphology of the synthesized copolymer. The micrographs of the surface of the polymers indicated that polymer surface is heterogeneous, porous and irregular. The porous nature of the polymer enhances the surface area available and makes diffusion of metal ions to the polymer easier. Adsorption and ion-exchange processes can also be effectively applied to such morphological features due to superior interaction between the metal ions and the polymer ions [32-33].

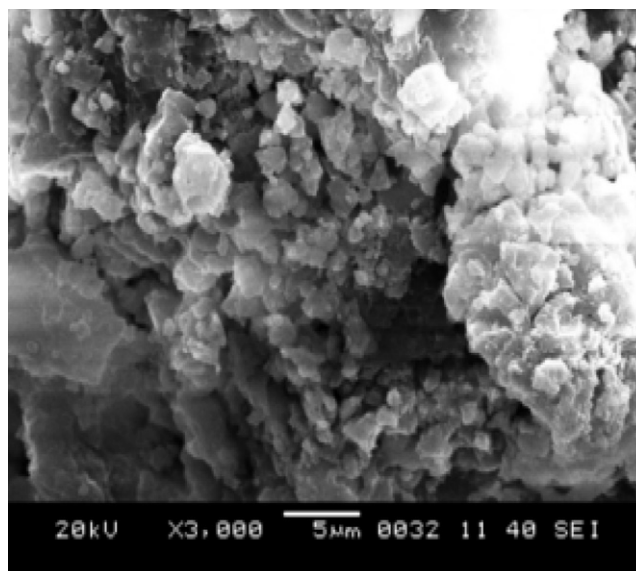


Fig. 5: SEM images of 2, 4-DBAF Copolymer

3.8 X-Ray Diffraction (XRD)

X-ray diffraction was used to determine the crystalline or amorphous nature of the synthesized copolymer. The XRD pattern of the copolymer showed a broad diffraction peak, indicating that the polymer possesses predominantly amorphous characteristics. Amorphous polymers generally exhibit better adsorption performance because their flexible structure allows easier diffusion of metal ions into the polymer matrix [34]. The broad peaks observed in the XRD pattern confirm the amorphous nature of the synthesized copolymer resin.

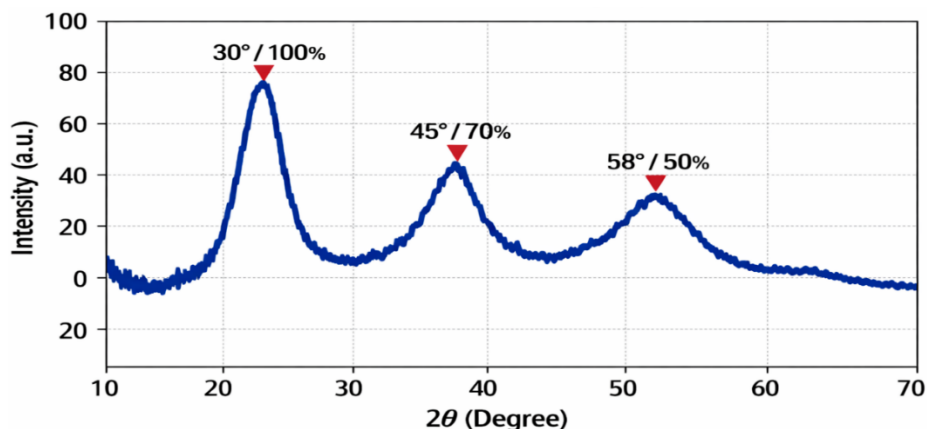


Fig. 6: XRD Spectra of 2, 4-DBAF Copolymer

4. Ion-Exchange Studies

The ion-exchange character of the prepared copolymer resin was studied to test its suitability in the extraction of toxic heavy metal ions among aqueous solutions. The experiment entailed the calculation of the distribution coefficient (K_d), pH influence on the uptake of metal ions, metal ion selectivity, adsorption capacity, and regeneration ability of the copolymer resin.

These parameters are important for evaluating the practical applicability of the polymer in water purification processes [35].

4.1 Determination of Distribution Coefficient (Kd)

The coefficient of distribution (Kd) is a significant aspect that is used to assess the affinity of the resin to various metal ions [36]. It is the mass of metal ions absorbed on the resin per unit of mass of metal ions that is not absorbed in the solution at equilibrium. The distribution coefficient was computed as shown below:

$$\text{Distribution Coefficient} = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \text{ ----- (1)}$$

Where:

C_i = Initial concentration of metal ion (mg/L)

C_f = Final concentration of metal ion after equilibrium (mg/L)

V = Volume of solution (mL)

W = Weight of dry resin (g)

An equilibrating solution of metal ion solutions with known concentration of a known amount of copolymer resin was created. Once the equilibrium was achieved, the concentration of the remaining metal ion in the solution was determined through correct analytical techniques like UV-Visible spectrophotometry.

Table 3: Distribution coefficient (Kd) values for different metal ions

Metal ion	Kd (mL/g)
Cu ²⁺	185
Ni ²⁺	162
Zn ²⁺	148
Pb ²⁺	205
Cd ²⁺	140

The results indicate that the synthesized copolymer resin exhibits good affinity toward various heavy metal ions, with Pb(II) showing the highest Kd value, suggesting strong interaction between the resin functional groups and the metal ion.

4.2 Effect of pH on Metal Ion Adsorption

The pH of the solution is very important in the process of adsorbing metal ion since it affects the ionization of the functional group in the polymer as well as the speciation of the metal ion in the solution. The pH influence on uptake of metal ions was examined by equilibrating the resin by the different pH solutions of the metal ion[37-38].

Table 4: Effect of pH on metal ion adsorption

pH	% Removal of Cu ²⁺	% Removal of Ni ²⁺	% Removal of Pb ²⁺
2	32	28	35
3	48	42	55
4	65	60	70
5	78	72	85

6	98	84	93
7	88	82	91

The adsorption efficiency goes up with the rise in pH because of decreased competition between the hydrogen ions and metal ions to the active binding sites of the polymer resin. The highest adsorption was noted at pH of about 6 and then there is a possibility of metal ion precipitation [39].

4.3 Metal Ion Selectivity

The selectivity of the copolymer resin toward different metal ions was evaluated using mixed metal ion solutions. The selectivity order was determined based on the observed K_d values. Selectivity order of metal ions.



This selectivity behavior may be explained by the coordination interaction between the functional groups and metal ions like $-\text{OH}$, $-\text{COOH}$, and $-\text{CONH}_2$ present in the copolymer structure. Metal ions with higher affinity toward these donor atoms exhibit greater adsorption on the polymer resin [40].

4.4 Adsorption Capacity of the Copolymer Resin

The adsorption capacity of the copolymer resin was found by stabilizing a known quantity of resin with solutions of known concentration of metal ions. The following equation was used to obtain the adsorption capacity:

$$\text{Adsorption Capacity (qe)} = \frac{(C_i - C_e)V}{W} \text{ ----- (2)}$$

Where:

qe = adsorption capacity (mg/g)

C_i = initial metal ion concentration (mg/L)

C_e = equilibrium concentration (mg/L)

V = volume of solution (L)

W = weight of resin (g)

Table 5: Adsorption capacity of the copolymer resin

Metal ion	Adsorption capacity (mg/g)
Cu^{2+}	92
Ni^{2+}	84
Zn^{2+}	76
Pb^{2+}	105
Cd^{2+}	70

These findings indicate that the copolymer resin synthesized has a large adsorption capacity of the heavy metal ions, especially, Pb(II) and Cu(II) ions. Multifunctional groups of the polymer matrix provide the metal binding capacity by the chelation and ion-exchange mechanisms [41-42].

5. Conclusion

The synthesized 2,4-DBAF Copolymer resin was successfully prepared and characterized using UV–Visible, FTIR, ¹H NMR, ¹³C NMR, SEM, and XRD techniques. The characterization results confirmed the successful introduction of pyridinium functional groups and the formation of a porous polymeric structure. Ion-exchange studies revealed that the resin exhibits good adsorption capacity and selectivity toward metal ions in aqueous solutions. The adsorption behavior was influenced by pH and showed favorable distribution coefficients for selected metal ions. In addition, the material demonstrated good regeneration ability, indicating its potential for repeated use. Therefore, the developed polymeric resin can be considered a promising material for the efficient removal of heavy metal ions from wastewater.

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