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Synthesis and Characterization of Copolymer Derived from 2-Amino 6-Nitrobenzothiazole, Biuret and Formaldehyde and Their study as Ion Exchange Resin for Toxic Cationic Elements

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Abstract: *The condensation of 2-amino 6-nitrobenzothiazole and biuret with formaldehyde at molar ratios of 1:1:2 of the reacting monomers within the sight HCl as a catalyst yielded a copolymer as an ion exchange resin. Electronic spectra, FTIR spectra, and 1H NMR spectra were used to analyze the resin. The batch equilibrium method was used to investigate the ion-exchange characteristics of this resin for Cu 2+, Ni2+, Zn2+, Co2+, and Pb2+ ions throughout a pH range of 2.0 to 6.0 and in fluids of varying ionic strengths. In the following order, the resin polymer demonstrated a better choosiness for removing these ions* $Pb^{2+} > Cu^{2+} > Ni^{2+}$*. The quantity of metal ion in use up by resin rises as the pH of the medium rises, according to analysis ratio of distribution as a function of pH. Scanning electron microscopy was used to analyze the surface morphology of the copolymer resin, which revealed the intermediate state among crystalline and amorphous nature. This research could be used to treat industrial waste water.*

Keywords: Copolymer; Resin; Polycondensation; Ion-exchanger; Heavy elements; Metal ion uptake; Distribution ratio.

I. INTRODUCTION

Poisonous and substantial metals found in industrial effluents are among the most dangerous contaminants, and adsorption, which is a major environmental problem, has a significant impact on their connection with water streams [1-2]. Since of their hazardous character and tendency to be maintained in living systems, the separation of heavy and poisonous metal ions from industrial effluents is of foremost attention. This emphasizes the use of specific functional polymeric sorbents to recover these hazardous ions from water [3-4].

Literature reviews have shown that copolymers made primarily of 4-hydroxybenzophenones and their derivatives are useful in many areas, along with unwanted water treatments, metal repairs, protective coatings and biological interests. It is known to be ion exchangers are used on a large scale to dispose of radioactive waste from nuclear power plants. [5]. Chelate ion interchange actions of poly (2-hydroxy, for acryloxybenzophenone) resins in the direction of divalent metal ions was investigated as time and pH characteristics using the batch equilibrium method [6]. The associated styrene / meric acid chelate matrix has been reported to be highly capable of removing metal ions along with Cr^{3+}, Fe^{3+}, Ni^{2+}, $Cu^{2+}$and Pb^{2+} [7]. An acidic polymer consisting of poly (methacrylic acid) and poly (acrylic acid) has an affinity for eliminating metal particles such as Co^{2+}, Ag^{2+}, Ni^{2+}, Cu^{2+}, and Cr^{3+} at a special pH and polymer metal ion ratio [8]. Melamine, salicylic acid including formaldehyde terpolymers has been shown to improve the selection of Cu2 +, Fe3 +, and Ni2 + ions, followed by improved selection of Cd2 +, Co2 +, Pb2 +, and Zn2 + ions [9]. Metal ion uptake increases as the molar ratio of terpolymers blended using substitute benzoic acid increases [11]. Using a batch equilibrium approach and several manufactured terpolymer resins, our research group has reported chelating ion-exchangers to remove dangerous producing metal ions from aqueous solution. The findings revealed that the synthetic glue has a high capability for removing certain metal ions [12-13]. Copolymers of 8-hydroxyquinoline, formaldehyde and catechol

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have low water content, which indicates excessive binding in the resin [14]. Still, no research work appears were carried out to blend and chelate ion interchange of copolymer resins blended from 2-amino-6-nitrobenzothiazole, biuret, and formaldehyde. The motivation for this study was the recently mixed copolymer resin ANBBF with eight metal ions Fe2 +, Cu2 +, Ni2 +, Co2 +, Zn2 +, Cd2 + Hg2 +, and Pb2 + at different pH values. It is to determine the adsorption behavior. The sorption activity of this steel ion is mainly derived from changes in the similarity of the chelate resin, such as pH value, electrolyte concentration, and shivering time. The most vital packages of chelating agents and useful polymers is the ability to get better metal ions after unwanted. Therefore, the chelate variability of ANBBF copolymer resin is also documented for the exact metal ions.

Pollution with dangerous serious metals have gained a immense deal of attention in current years due to its toxicity, low levels of consciousness, and the potential for bioaccumulation in ecosystems, agriculture and the human body. Many techniques have been developed to remove and recover metal ions from wastewater and commercial wastewater, including ion alternation, reverse osmosis, electrodialysis, precipitation and adsorption processes. Numerous research have attentive on metal ion elimination via adsorption on chelating polymers since they're recyclable, effortlessly separate, and have superior adsorption potential and selectivity with chemical and physical steadiness [15-20].

Current research focuses on the synthesis, characterization and use of ANBBF copolymer resins, and the chelate ion exchange properties of functional polymers, the ability to recuperate metal ions via effluents.

II. EXPERIMENTAL

The main chemicals utilized in the creation of novel ANBBF copolymer resin from the market, such as 2-amino 6-nitrobenzothiazole, biuret, and formaldehyde, were of chemically pure grade, and the purity was checked and validated by thin layer chromatography wherever necessary.

2.1 Synthesis of ANBBF Copolymer Resin

In a round bottomed flask, 2-amino6-nitrobenzothiazole (0.1mol) was dissolved in 30 mL glacial acetic acid, then biuret (0.1 mol) dissolved in 200 mL hydrochloric acid was slowly added. Dropwise additions of formaldehyde (0.2mol) dissolved in 200 mL HCl were made to the mixture, which was then refluxed for 6 hours at 120 ± 2 °C in an oil tub with constant stirring. The flask was then taken out of the oil bath and set aside to cool. With vigorous shaking, the mixture was placed into crushed ice and left overnight. To eliminate the brown colour, the product was separated, washed several times with warm water and methanol, then filtered and washed again with diethyl ether and petroleum ether. The yields of those copolymer resins found to be 89%. The synthesis of ANBBF copolymer resin is proven in Fig. 1.

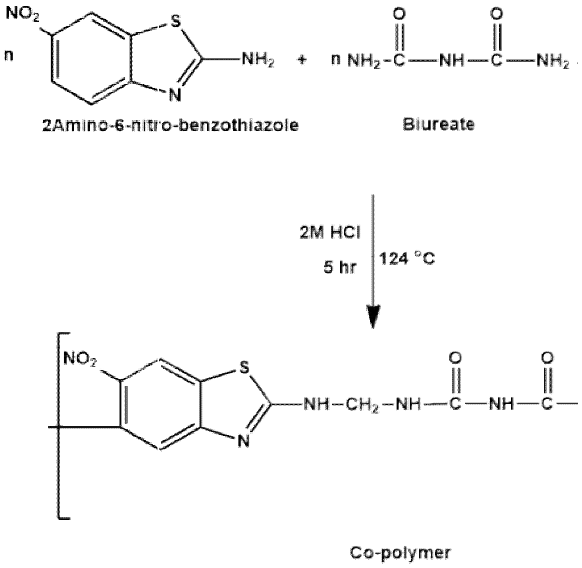

Figure 1: Synthesis and suggested structure of ANBBF resin

2.2 Ion-Exchange Properties

The batch equilibrium approach was used to determine the ANBBF resin ion exchange characteristics. The impact of diverse electrolytes, the charge of metal absorption, and dispersal of metallic ions among the copolymer and solutions were all investigated.

In an electrolyte solution, the copolymer (25 mg) is dissolved (25 ml). The suspension's pH was adjusted to the proper level using either 0.1 N HCl or 0.1 N NaOH, and it was spun for 24 hours at 25 degrees Celsius. This suspension was given 2 ml of a 0.1 M metal ion solution, and the pH was adjusted to the required level. Before filtering, the mixture was agitated for additional 24 hours at 25°C [21, 22]. Unlike regular EDTA, the product was cleaned, the rest and washings were collective, and a titration was performed to determine the metal ion level of the material. The ability of the polymer to absorb metallic ions. The polymer's ability to absorb metallic ions changed [23].

III. RESULTS AND DISCUSSION

The resin sample was light brown in color, unsolvable in usually used organic solvents, but was solvable in DMF, DMSO, THF, and concentrated H_2SO_4.

3.1 Spectral Investigation

Ultraviolet-Visible Spectra of ANBBF Copolymer Resin

Fig.2 shows the UV-Visible spectra of ANBBF copolymer resin. To identify the chromophores of matter qualitatively and quantitatively Ultraviolet–visible (UV–Vis) spectroscopy is very useful. UV–Vis spectra are quite large and usually contain only a modest number of peaks. The wavelengths at which maxima occur are referred to as peaks. At max = 280 nm, the copolymer has a strong absorption, whereas at max = 320 nm, it has a much reduced absorption. The shorter wavelength band corresponds to an electron transition, while the longer wavelength, lower intensity band corresponds to a nonbonding electron transition at the carbonyl oxygen atom [24-25].

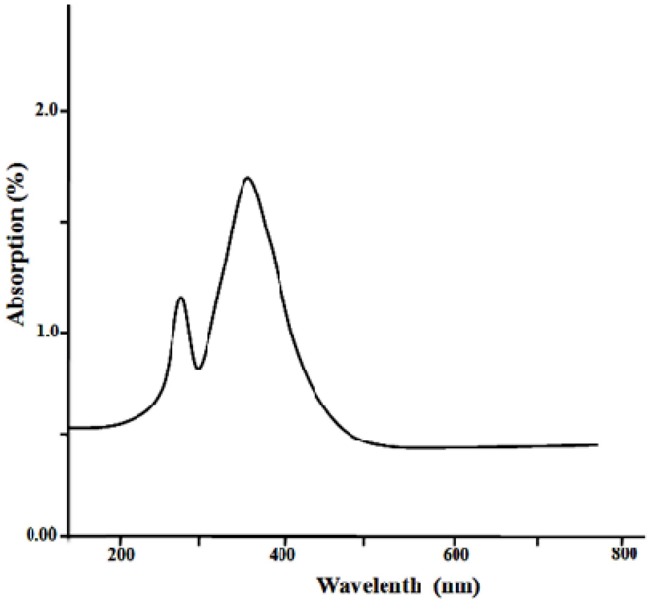

Figure 2: UV-Visible spectra of ANBBF copolymer

FT-IR Spectra of ANBBF Copolymer Resin

Figure 3 shows the IR spectrum of ANBBF copolymer resin, and the stretching vibrations of the NH group are responsible for an extensive absorption band occured in the range 3444 cm^{-1} [26-27]. The presence of methylene group ($-CH_2$) seen at 1372-1270 cm^{-1} and at 1499-1458 shows presence of methylene bridge in copolymer. Aromatic ring is represented by the bands 1411 cm^{-1} (Aryl C-H stretching) the bands seen at 788, 1045, and 1120 corroborated the 1,2,3,5 substitution in the aromatic ring. The -NH band (3200-3000 cm-1) appears to be elongated.

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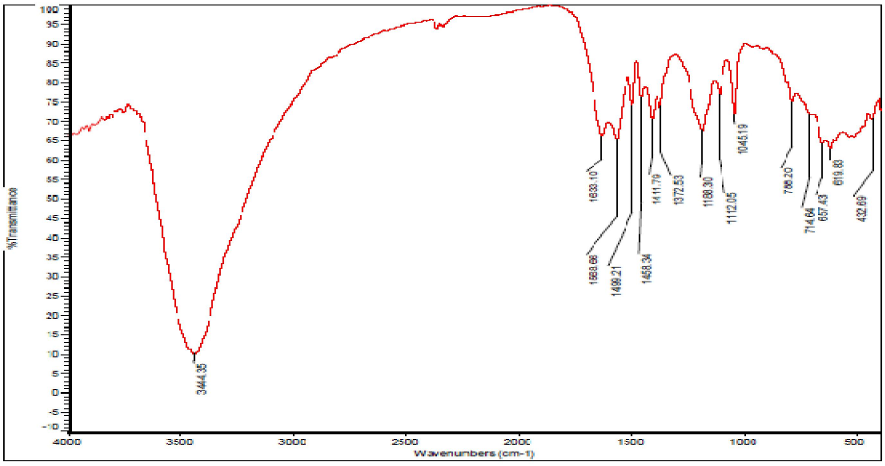

Figure 3: FT IR Spectra of copolymer resin

^{1}H NMR Spectra of ANBBF Copolymer Resin

In DMSO-d$_6$ solvent, the NMR spectrum of ANBBF polymer (Fig. 4) was scanned. The chemical shift (□) ppm observed is calculated using data from the literature [32-33]. The methylene proton of the Ar-CH2- moiety may be responsible for the singlet produced in the range 3.89-3.94 (□) ppm. Aromatic proton may be responsible for the faint multiple signals (unsymmetrical pattern) in the 8.23-8.18 (□) ppm range (Ar-H). NH protons may be responsible for the signals in the 9.11-9.16 (□) ppm range [34-35].

^{1}H NMR Spectra of ANBBF copolymer resin

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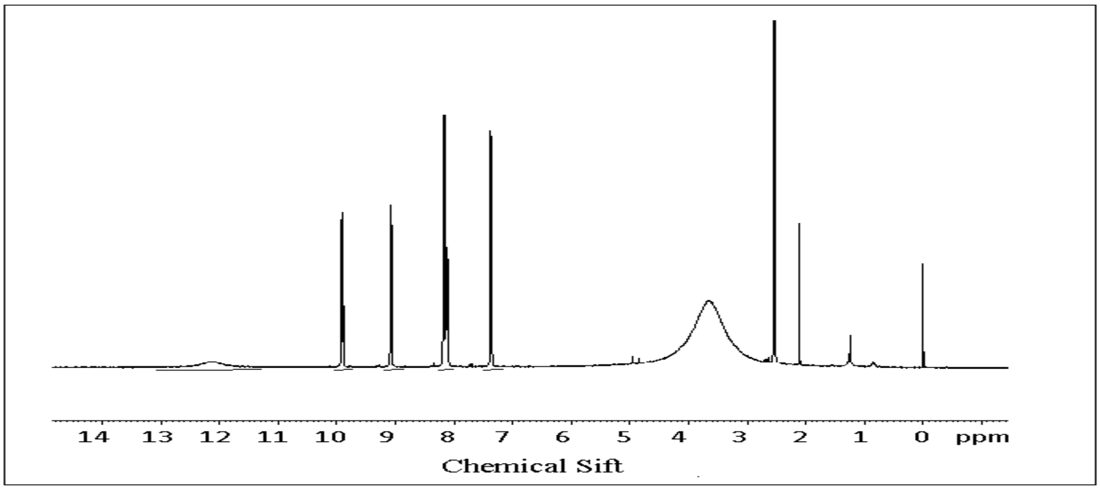

Figure 4: 1H NMR Spectra of ANBBF copolymer resin

SEM Analysis of ANBBF Copolymer

SEM was used to determine the morphology of the copolymer resin. Figure 4 shows pictures taken with a scanning electron microscope. The surface of the synthesized resin was discovered to be scattered, and the character of the prepared resin were determined to be uneven (Fig. 5). The copolymer showed atransitional state among amorphous and crystalline nature, as expected.

The crystallinity of monomers such as 2-amino6-nitrobenzaldehyde and biuret is lost during condensation polymerization, despite the fact that they are crystalline in nature. Because it is more amorphous than crystalline, it has a higher ion interchangecapability and extra reactive site for metal ion sorption [31-32]. ANBBF copolymer resin is extranebulous in nature, subsequently suggests greater ion change ability.

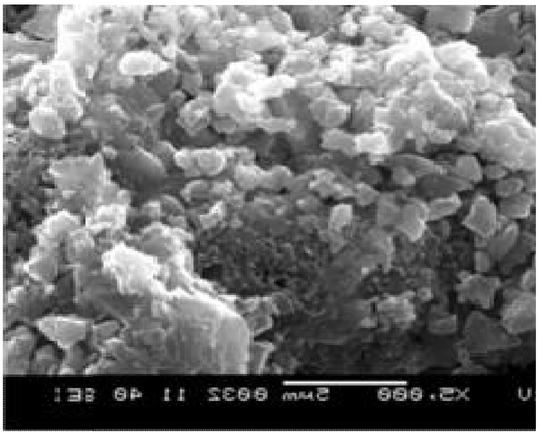

Figure 5: SEM of ANBBF resin

Ion Exchange Features

To determine the choosiness of the [33,34], the batch equilibrium method was used to examie the impact of various electrolytes on the selectivity of metallic ions, the value of metal absorption, and the distribution ratio of metallic ions between the copolymer and solution containing the metal ions. The findings of the experimental approach for through EDTA titration are shown in Table 4. The ANBBF copolymer has non bonding electrons pair in the OH and NH structures that could be donate to a metallic ion during complex formation. It possesses chelating characteristics as a result. This mechanism of metallic ion adsorption employing polymer ligands is understood when it comes to polymer metal absorption. Titration with a standard EDTA solution can be used to detect this since metal absorption diminishes the attention of metal ions in solution. The metal absorption potential of a polymer is different for each metal ion and is sometimes referred to as "metal absorption potential." Metal uptake by copolymers is influenced by three factors: electrolyte solution concentration, shaking time, and solution pH.

Electrolytes and their Concentrations have an Effect on Metal Ion Absorption Capability

At various concentrations, the impacts of NO^{3-}, Cl^-, SO_4^{2-}, and ClO_4^{2-} on the equilibrium of metallic resin contact at normal pH were investigated. Table 1 illustrates that thepH different metal ions in solution varies, meaning that the quantity of metal ions occupied up via a particular quantity of copolymer depends on the electrolyte's kind of attention. As people grow more aware of electrolytes, their absorption of Cu^{2+}, Zn^{2+} and Pb^{2+} ions rises in the incidence of NO_3^-, Cl^-, and $ClO4^{2-.}$

When sulphate ions are present the amount of above mentioned ions taken by the copolymer resin reduces as the electrolyte concentrations rises [35]. The aforesaid metal ions form vulnerable complexes with theNO_3-, Cl^-, and $ClO4^-$ ions, but SO_4^{2-} forms stronger complexes, causing the equilibrium to be disrupted. The stability constants of complexes with certain metallic ions, as well as the type of ligands, help explain this.

Table 1: Evaluation of Influence of Different Electrolyte on the Uptake of Several Metal Ions[a] of Resin

Metal Ions	pH	Conc.	$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
Cu^{2+}	4.5	0.01	1.27	1.08	1.15	3.15
		0.05	1.54	1.47	1.77	2.24
		0.10	1.83	1.75	2.33	1.68
		0.50	2.59	2.33	2.88	1.24
		1.00	3.13	3.29	3.13	0.35

Ni^{2+}	4.5	0.01	1.14	0.68	0.94	2.48
		0.05	1.45	1.13	1.25	2.16
		0.10	2.28	1.50	1.88	1.85
		0.50	2.57	1.87	2.18	0.94
		1.00	3.29	2.06	2.32	0.38
Co^{2+}	5.0	0.01	1.34	1.42	1.45	1.47
		0.05	1.22	1.24	1.32	1.24
		0.10	1.05	1.05	1.10	1.18
		0.50	0.63	0.79	0.85	0.68
		1.00	0.37	0.40	0.44	0.47
Zn^{2+}	5.0	0.01	1.57	1.30	1.75	1.68
		0.05	1.39	1.18	1.42	1.25
		0.10	1.17	1.03	1.26	1.13
		0.50	0.77	0.54	0.64	0.45
		1.00	0.42	0.27	0.43	0.14
Pb^{2+}	6.0	0.01	1.15	1.33	1.63	1.57
		0.05	1.03	1.15	1.38	1.35
		0.10	0.73	0.88	1.13	1.17
		0.50	0.68	0.64	0.75	0.68
		1.00	0.42	0.32	0.34	0.48

[a] $[M(NO_3)_2] = 0.1$ mol/l; Volume = 2 ml; Volume of electrolyte solution : 25 ml
Weight of resin = 25 mg; time: 24 h: Room temperature

Time Dependent Rate of Metal Ion Uptake

The amount of metallic adsorption was chosen to determine the quickest time for which equilibrium could be achieved while operating as close to equilibrium as possible. The attention of the metal ion and electrolyte solution, as well as the pH of the solution, remain constant during the charge of metal ion measurement, and the pH of each metal ion is unique, as indicated in Table 2. The polymer has more time to adsorb as the shaking period lengthens, resulting in higher metal ion uptake. Table 2 reveals the impact of metal ion sorption rate on ANBBF resin. The rate is defined as the change in metal ion concentration in the aqueous solution in contact with the metal.

The discovery demonstrates that the time it takes for one-of-a-kind metal ions to be taken up at a given level is dependent upon character of metal ions under precise situation. Cu2+ ions took around three hours to reach equilibrium, but Zn2+ and Pb2+ ions took approximately six hours. For the ANBBF copolymer, the price of steel ions uptake follows the order Cu2+> Pb2+ > Zn2+ > Ni2+ > Co2+ [36].

Table 2: Comparison of the Rate of Metal Ion Uptake[b] of Resin

Metal ions	pH	Percentage of the amount of metal ion[a] taken up[b] at different time (hrs)					
		1	**2**	**3**	**4**	**5**	**6**
Cu^{2+}	4.5	48.4	54.4	64.3	73.7	92.0	-
Ni^{2+}	4.5	51.5	54.3	62.9	74.7	89.6	-
Co^{2+}	5.0	36.6	42.4	51.8	69.5	89.2	-
Zn^{2+}	5.0	38.5	49.5	63.7	76.3	86.4	-
Pb^{2+}	6.0	31.5	51.5	62.6	73.9	82.9	93.7

[a] $[M(NO_3)_2]= 0.1$ mol/l; volume : 2ml; $NaNO_3 = 1.0$ mol/l; volume: 25ml, Room temperature.

[b] Metal ion uptake = (Amount of metal ion absorbed x 100) / amount of metal ion absorbed at equilibrium.

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Metal Ion Distribution Ratios at Various pH Levels

The solution pH affects the distribution of metal ions. Through rising pH, the H+ ion concentration in the solution reduce, allowing the best metallic ion in the solution to be available for adsorption, resulting in increased metal ion uptake.

The effects of pH on the quantity of metal ions dispersed among levels can be explained by the results in Table 3. According to the data on the distribution ratio as a function of pH, the relative amount of metallic ions taken up by the copolymers increases as the pH of the medium rises [36]. The significance of growth, on the other hand, differs for extraordinary metallic cations. To avoid metal ion hydrolysis at higher pH, the analysis was conceded out starting pH 2.0 to pH 6.0. In comparison to the other metal ions studied, the selectivity of Fe3+ ion for the ANBBF copolymer resin is higher. Within the range of 1.5 to 6.5, the order of distribution ratio of metallic ions is observed to beFe3+ > Cu2+ > Ni2+ > Zn2+. Thus the effects of such sort of have a look at where cooperative in choosing the most advantageous pH for a careful absorption of a exact metallic cation starting a combination of various metallic ions. In favor of illustration, the findings, reveals the best pH 2.0 for the separation of Fe3+ and Zn2+ with distribution ratio ‘D’ is 481 and 686.0 correspondingly the use of the ANBBF copolymer resin as ion exchange. The decreasing within the distribution ratios of Cu2+ turned into observed to be small for this reason, efficient separation may be done. The order of distribution ratio of metallic ions measured in pH variety 2.5 to 6.5 is found to be Cu2+ > Ni2+ >Zn2+ > Co2+ = Pb2+.

Table 3: Distribution Ratio ‘D’[a] of Different Metal Ions[b] as a Function of Different pH of Resin

Metal ions	Distribution ratios of different metal ions at different pH							
	1.5	2	2.5	3	3.5	4	5	6
Cu^{2+}	-	-	61.4	74.3	86.5	117.4	328.8	748.3
Ni^{2+}	-	-	56.6	68.6	73.3	112.4	278.4	584.9
Co^{2+}	-	-	26.5	54.8	73.4	112.3	143.4	213.4
Zn^{2+}	-	-	29.4	46.4	64.3	84.2	118.4	123.2
Pb^{2+}	-	-	27.3	47.4	62.7	88.4	112.3	158.3

IV. CONCLUSION

The condensation method is utilized to make copolymer resin from 2-amino6-nitrobenzothiazole and biuret with formaldehyde in hydrochloric acid medium. SEM tests revealed that the amorphous character of the ANBBF copolymer. The copolymer can operate as a potent ion exchange for divalent metal ions such as Cu2+, Ni2+, Pb2+, Zn2+, an Co2+ ions. This ion change observation demonstrates that ANBBF copolymer resin is environmentally friendly cation trade resin that may be used to remove unsafe metallic ions from the environmental area, to purify industrial waste solution and to purify desalinate water.

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