



Synthesis, Characterization and Ion-Exchange Properties of 2-Amino 6-nitro benzothiazole-Adpamide-Formaldehyde Resin

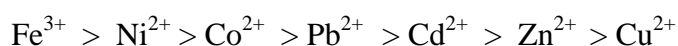
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Abstract

Copolymer resin (2-A6-NBAF) was synthesized by the condensation of 2-amino 6-nitrobenzothiazole, biuret and formaldehyde with varying the molar ratio of reacting monomers in the presence of acid catalyst. The composition of copolymer resin has been determined on the basis of their elemental analysis and the conductometric titration in non aqueous medium used to determine the number average molecular weight of their resin. The ion-exchange properties of newly synthesized copolymers proved to be selective for certain metals. The 2-A 6-NBAF copolymer resin was characterized with UV-visible, FTIR and ^1H NMR spectral data, employed to elucidate the structure. Chelating ion-exchange properties of the newly synthesized copolymer have also been studied employing batch equilibrium method. The chelating ion exchange properties of this copolymer was studied for Fe (III), Cu (II), Cd (II), Co (II), Zn (II), Ni (II), and Pb (II) ions. The study of this resin carried out over a wide pH range and in media of various ionic strengths. The overall rate of metal uptake by 2-A 6-NBAF copolymer resin follows the order :



Key words: Resins, Terpolymer, Polycondensation, NMR, FT-IR, Degree of polymerization , Ion-exchange.

Introduction

Recently many research works has been carried out on the synthesis and characterization of urea containing copolymers. The synthesis of polymeric chain, which is propagated by the preparation of metallic chelates. Phenols and diamides introduced for synthesizing efficient method. Copolymer is found very useful application as adhesive, fibers, coating materials, high temperature flame resistant, catalysis, semiconductors and ion exchange resins [1-5]. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal



recovery and for the identification of specific metal ions [6-7]. The polymer of poly[(2,4-dihydroxybenzophenone) butylene] has the chelating ion-exchange properties and its polychelates with transition metals are reported [8]. Copolymers involving 4-hydroxyacetophenone-biuret-formaldehyde [9] and 2,4-dihydroxy benzoic acid, ethylene diamine and formaldehyde [10] are reported for their ion-exchange characteristics. Copolymers involving 2-hydroxyethylmethacrylate and 2-methacryloyl-amidocysteine [11], polyacrylonitrile beads and 2-amino-2-thiazoline [12], 4-hydroxy acetophenone-biuret-formaldehyde [13] and o-aminophenol, urea and formaldehyde [14] are reported for their ion-exchange characteristics. However no work seems to have been carried out on synthesis and chelation ion-exchange studies of the copolymer resins synthesized from 2,4-dihydroxybenzoic acid, biuret and formaldehyde. The purpose of present study, is to explore the adsorption behavior of eight metal ions Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} on the newly synthesized copolymer resins 2,4-DHBBF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The adsorption tendency of the above metal ions are based on the affinity differences towards the chelating copolymer resins as functions of pH, electrolyte concentrations and shaking time.

The copolymer resins under investigations are found to be ion exchanger having both ion-exchange group and chelating group in the same polymer matrix and the resin can be used selectively for the purpose of purification of waste water.

Experimental

Starting Materials

Synthetic compounds utilized were all of AR or artificially unadulterated grade. 2-amino 6-nitrobenzothiazole, adipamide was purchased having 99% purity and formaldehyde (35%) procured from Merck.

Synthesis of 2-A 6-NBAF copolymer resin

The 2-A 6-NBAF copolymer resin was prepared by the condensation polymerization of 2-amino 6-nitro benzothiazole (0.1 mol), adipamide (0.1 mol) and formaldehyde (0.2 mol) with 1:1:2 mole ratio in hydrochloric acid medium at 124 ± 2 °C in an oil bath for 6 hrs. The solid precipitated was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water and then by hot water to remove excess of 2-amino 6-nitro benzothiazole - formaldehyde copolymer, which might be present along with the 2-A 6-NBAF



copolymer with cold water, dried and powdered. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yields of these copolymer resins found to be 76% and the melting point is between 385-389°K. The sieved resin was used for further characterization. The reaction sequence of the synthesis of 2-A 6-NBAF copolymer resin is shown in Fig. 1.

Fig.1 Reaction and Suggested Structure of Representative 2-A 6-NBAF Copolymer Resin.



Table 1. Synthesis and Physical Data of 2-A 6-NBAF Copolymer Resin

Copolymer Resin	Reactants			Molar ratio	Catalyst 2M/HCl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	2-Amino 6-nitro benzothiazole (mol)	Biuret (mol)	Formaldehyde (mol)						
2,4-DHBBF-I	0.1	0.1	0.2	1:1:2	200	397	6	76	385

Characterization of copolymer resin

The elemental analysis of 2-A 6-NBAF copolymer resin was subject to micro analysis for C, H and N on an Elementar Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight of 2-A 6-NBAF copolymer resin was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 gm of 2-A 6-NBAF copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation by this method is based on the following consideration [15-16] : (1) the first break corresponds to the stage at which the first acidic phenolic hydroxyl group is neutralized, and (2) the last break observed beyond the first break represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. On the basis of the average degree of polymerization, the average molecular weight has to be determined by following eq. (1)...

$$\overline{DP} = \frac{\text{(Total milliequivalents of base required for complete neutralization)}}{\text{(Milliequivalents of base required for smallest interval)}} \dots(1)$$

$$\overline{Mn} = \overline{DP} \times \text{molecular weight of the repeating unit}$$

Electronic (UV-visible) absorption spectra of the copolymer in DMSO was recorded with a double beam spectrophotometer fitted with an automatic pen chart recorder on themosensitive paper in the range of 200 – 850 nm at L.I.T. RTM , Nagpur University Nagpur. Infrared spectra of 2-A 6-NBAF copolymer resin was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of 4000 – 500 cm^{-1} at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR spectra and Carbon NMR spectra were recorded with Bruker Advance – II 400 NMR spectrophotometer using DMSO- d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The



surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur.

Ion-exchange properties

The ion-exchange properties of the 2-A 6-NBAF copolymer resin was determined by the batch equilibrium method. We studied the influence of various electrolytes, the rate of metal uptake and distribution of metal ions between the copolymer and solutions.

Determination of metal uptake in the presence of electrolytes of different concentrations

The copolymer sample (25 mg) was suspended in an electrolyte solution NaNO₃ (25 ml) of known concentration. The pH of the suspension was adjusted to the required value by using either 0.1 N HCl or 0.1 N NaOH. The suspension was stirred for a period of 24 hrs at 25°C. To this suspension was added 2 ml of a 0.1 M solution of metal ion and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 hrs and filtered [17,18]. The solid was washed and the filtrate and washings were combined and the metal ion content was determined by titration against standard EDTA. The amount of metal ion uptake of the polymer was calculated from the difference between a blank experiment without polymer and the reading in the actual experiments. The experiment was repeated in the presence of other three electrolyte such as NaCl, NaClO₄ and Na₂SO₄.

Evaluation of the rate of metal uptake

In order to estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type describe above were carried out, in which the metal ion taken up by the chelating resin was determined from time to time at 25°C (in the presence of 25 ml of 1 M NaNO₃ solution). It was assumed that under the given conditions, the state of equilibrium was established within 24 hrs. the rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain related to that at the state of equilibrium.

The percent amount of metal ions taken up at different time is defined as.

$$\text{Percentage of amount of metal ion taken up at different time} = \frac{\text{Amount of metal ion adsorbed}}{\text{Amount of metal ion adsorbed at equilibrium}} \times 100$$

Evaluation of the Distribution of Metal Ions at Different pH

The distribution of each one of the eight metal ions i.e. Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ between the polymer phase and the aqueous phase was determined at 25°C and in the presence of a 1M NaNO₃ solution.

The experiments were carried out from 1.5 to 6 pH for Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺. In case of Fe³⁺ the study was carried out from 1.5 to 3.0 pH. After 24 hrs the mixture was filtered, the filtrates and washing were collected. Amount of the metal ion which remained in the aqueous phase was estimated by back titration with standard EDTA solution using appropriate indicator. Similarly blank experiment was carried out without adding polymer sample. The amount of metal adsorbed



by the polymer was calculated from the difference between sample and blank reading. The original metal ion concentration is known and the metal ion adsorbed by the polymers was estimated. The distribution ratio 'D' is calculated from the following equation[19,20]-

$$D = \frac{\text{Amount of metal ion on resin}}{\text{Amount of metal ion in solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of resin (g)}}$$

If we consider

'Z' is the difference between actual experiment reading and blank reading,

'C' gm is the amount of metal ion in 2ml 0.1M metal nitrate solution,

'Y' gm of metal ion in 2ml of metal nitrate solution after uptake.

$$\text{Metal ion adsorbed [uptake] by the resin} = \frac{ZX}{Y} \frac{2}{0.025} = \left(\frac{ZX}{Y} \right) 133.33$$

Results and Discussion

The resin sample was light brown in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulphoxide and concentrated H₂SO₄. The resin synthesized do not show sharp melting point but undergo decomposition 385-390°K. Based on the analytical data, the empirical formula of the copolymer resin is found to be C₁₁H₁₁N₃O₆, which is in good agreement with the calculated values of C, H, N and O. The resin was analyzed for carbon, hydrogen, and nitrogen content.

Table 2: Elemental analysis data of 2-A 6-NBAF Copolymer Resin

Copolymer Resins	% of observed (Cal.)	C % of observed (Cal.)	H % of observed (Cal.)	N	Empirical formula of repeated unit	Empirical formula weight
2-A 6-NBAF	46.81 (55.04)	3.81 (3.97)	14.82 (21.40)		C ₁₅ H ₁₃ N ₅ O ₄	327

The number average molecular weight (\overline{M}^n) could be obtained by multiplying the \overline{DP} by the formula weight of the repeating unit. The calculated molecular weight for 2-A 6-NBAF resin is 3026.

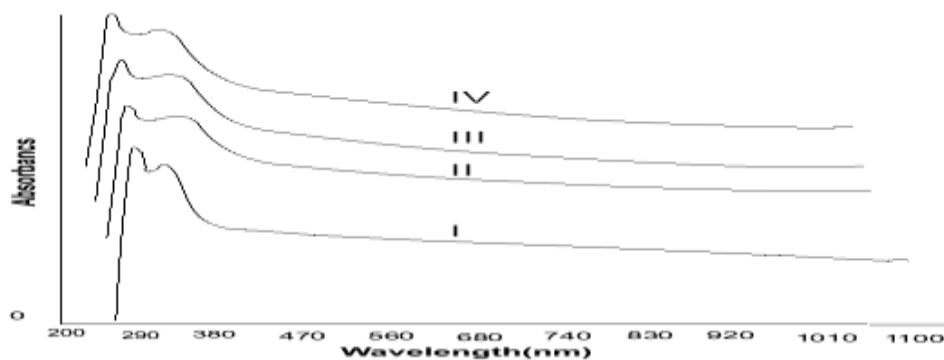


Fig. 2. UV-Visible Spectra of 2-A 6-NBAF Terpolymer Resin

The UV-visible spectra (Fig. 2) of all four 2-A 6-NBAF copolymer samples in pure DMSO were recorded in the region 200 – 850 nm at a scanning rate of 100 nm min⁻¹ and a chart speed of 5 cm min⁻¹. All of the four 2-A 6-NBAF copolymer resins displayed two characteristics broad bands at 310-370 nm and 270-300 nm. Both of these bands seem to be merged with each other because of their very broad nature. The band at 310-370 nm is the more intense band which may be accounted for a $\pi \rightarrow \pi^*$ transition while the less intense band at 270-300 nm may be due to $n \rightarrow \pi^*$ transition [23,24]. The basic value of transition for $>C=O$ group is nearly at 320 and 240 nm. The UV-visible spectra of 2-A 6-NBAF copolymer resins show bathochromic shift i.e. the shift towards the longer wavelength in which the value of λ_{max} increases.

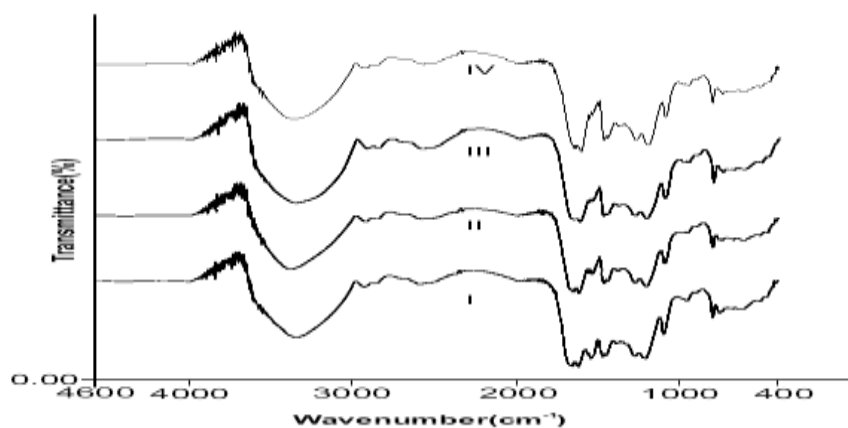


Fig. 3. Infra Red Spectra of 2-A 6-NBAF Copolymer Resin

Infrared spectra of 2-A 6-NBAF copolymer resin are shown in Fig. 3. From the IR spectral studies, it has been revealed that all the four 2-A 6-NBAF copolymer resin show nearly similar pattern of spectra. A very broad band appeared at the region 3225-3329 cm⁻¹ may be assigned to the stretching vibration of phenolic $-NO_2$ groups exhibiting intramolecular hydrogen bonding with carbonyl ($>C=O$) group and $-NH$ group[25]. The band at 3010-3011 cm⁻¹ may be due to Aryl C-H stretching. The band at 2816-2917 cm⁻¹ is due to stretching of $>CH_2$, $-NH$ etc. The band at 1742-1745 cm⁻¹ may be of $>C=O$ stretching. The band at 1606-1607 cm⁻¹ may be due to aromatic ring

(substituted). The band at $1480\text{-}1482\text{ cm}^{-1}$ may be due to -NH bending of secondary amide. The band at $1286, 1230$ and 783 or 812 cm^{-1} may be due to CH_2 bending (wagging and twisting) -CH_2 plane bending, -CH_2 bending (rocking). The band at $857\text{-}859\text{ cm}^{-1}$ may be due to tetrasubstituted benzene ring. 1,2,3,5 substitution in aromatic benzene ring may be due the bands appeared at $912\text{-}936\text{ cm}^{-1}$, $1097\text{-}1098\text{ cm}^{-1}$ and $1148\text{-}1149\text{ cm}^{-1}$ [26].

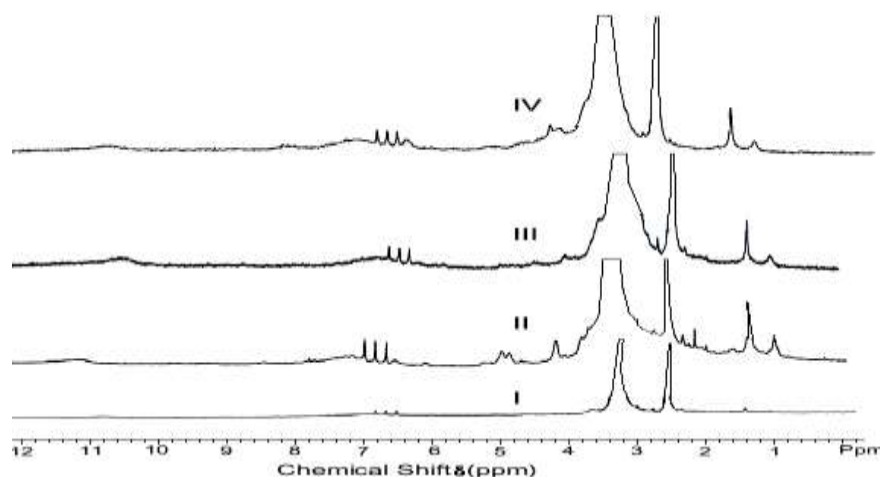


Fig. 4. ^1H NMR Spectra of 2-A 6-NBAF Copolymer Resin

The ^1H NMR spectra of all four 2-A 6-NBAF copolymer resins were scanned in DMSO-d_6 . The spectra are given in Fig. 4 and from the spectra it is revealed that all 2-A 6-NBAF copolymer resin possess set of proton having different electronic environment. The chemical shift (δ) ppm observed are assigned on the basis of data available in literature. The medium signal at $2.53\text{-}2.59$ (δ) ppm may be due to the methylene proton of Ar-CH_2 bridge. The signal obtained in the region of $3.45\text{-}3.47$ (δ) ppm may be due to the methylene proton of $\text{Ar-CH}_2\text{-N}$ moiety. The singlet in the region $5.22\text{-}5.25$ (δ) ppm may be due to the proton of -NH bridge. The weak multiplet signal (unsymmetrical pattern) in the region at $6.93\text{-}6.98$ (δ) ppm may be due to the aromatic proton of (Ar-H). The signals in the range at $8.3\text{-}8.9$ (δ) ppm may be due to phenolic hydroxyl proton [27,28]

Scanning Electron Microscopy (SEM)

Fig. 5 represent the scanning electron micrographs of 2-A 6-NBAF copolymer resin. The photographs of 2-A 6-NBAF copolymer exhibit sponge like structure derived from the aggregation of small granules. At lower magnification the resin shows spherulites in which the crystals are arranged smaller in surface area with more closely packed structures. This indicates the crystalline nature of the copolymer resin and this property shows the low ion exchange capacity for higher hydrated size metal ion. At different magnification the resins shows more amorphous character with less closed packed surface having deep pits. The amorphous character indicates that resin thus

possesses higher exchange for metal ions. The morphology thus identified by SEM as crystalline as well as amorphous or transition between crystalline and amorphous, showing more or less good ion-exchange capacity. The polymerization reaction proceeds by introducing amorphous character in the copolymer sample.

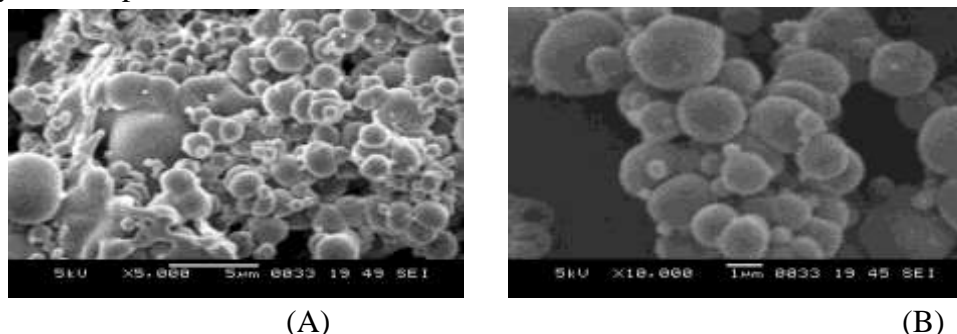


Fig. 5. SEM Micrographs of 2-A 6-NBAF Copolymer Resin

Effect of different electrolytes and their concentrations on metal ion uptake capacity

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} at various concentrations on the equilibrium of metal resin interaction. The Fig. 6 – 9 shows that the amount of metal ion taken up by a given amount of copolymers depends on the nature and concentration of the electrolyte present in the solution. In the presence of perchlorate, chloride and nitrate ions the uptake of Fe(III), Cu(II) and Ni(II) ions increase with increasing concentration of the electrolytes, whereas in the presence of sulphate ions the amount of the ions taken up by the copolymer decrease with increasing concentration of the electrolyte. Moreover, the uptake of Co (II), Zn (II), Cd (II) and Pb (II) ions decrease with increasing concentration of the chloride, nitrate, perchlorate and sulphate ions. This may be explained on the basis of the stability constants of the complexes with those metal ions. SO_4^{2-} may form strong complexes with Fe^{3+} , Ni^{2+} , Cu^{2+} ions while NO_3^- , Cl^- and ClO_4^- may form weak complexes therefore increases uptake by increasing concentration. While SO_4^{2-} , NO_3^- , Cl^- and ClO_4^- form rather strong complex with Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} chelates, therefore decreased uptake by increasing concentration. [17,18, 29].

Rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time where we find as close as equilibrium condition. Fig. 10 show the results of rate of uptake of metal ion on 2-A 6-NBAF copolymer. It is found that Fe (II) ions require about 3 hrs for the establishment of the equilibrium, where as Cu (II), Ni (II), Co (II) and Zn (II) requires 5 hrs and Cd^{2+} and Pb^{2+} require 6 hrs for the establishment of the equilibrium. Thus the rate of metal ions uptake follows the order $\text{Fe(III)} > \text{Cu(II)} \approx \text{Ni(II)} > \text{CO(II)} \approx \text{Zn(II)} > \text{Cd(II)} \approx \text{Pb(II)}$ for all four 2-A 6-NBAF copolymer resins[12,13, 30].

Distribution ratio of metal ions at different pH

The distribution ratio as a function of pH indicates that the distribution of each metal between the polymers phases and aqueous phase increase with increasing pH of the medium this effect shown in Fig. 11. For Fe^{3+} ion the highest working pH is 3. The results indicate the copolymer resin sample uptakes Fe^{3+} ion more selectively up to pH 3 and has comparatively lower



distribution ratio. The Fe^{3+} ion forms octahedral complexes with the ligands. Cu^{2+} and Ni^{2+} have highest distribution ratio at pH 3 to 6. The other four ions Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} have lower distribution ratio over pH range of 3 to 6. The different distribution ratio obtained for different metal ions may be due to the difference in stability of the complex formation during adsorption. The high distribution ratio may be due to higher stability constant of metal ligand complexes and vice versa. [20,31]. In the present investigation the observed order of distribution ratios of divalent ions measured in the range of pH 3 to 6 is found to be

$$Cu(II) > Ni(II) > Co(II) < Zn(II) > Cd(II) < Pb(II).$$

The results suggest the optimum pH 6.00 for separation of $Co(II)$ and $Ni(II)$ with distribution ratios 'D' are 278.6 and 783.4 respectively using 2-A 6-NBAF copolymer resin as ion-exchanger. Similarly for the separation of $Cu(II)$ and $Fe(II)$ the optimum pH is 3, at which the distribution 'D' of $Cu(II)$ is 885.4 and that of $Fe(III)$ is 331.4. Difference in the distribution ratio 'D' could be achieved efficient separation.

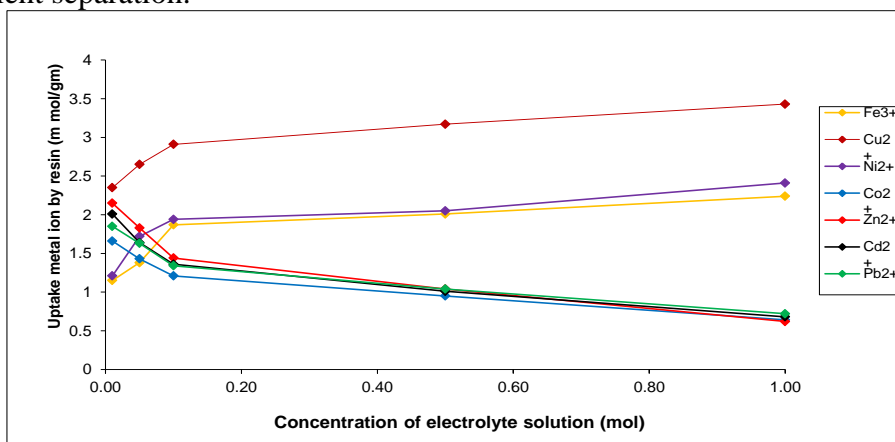


Fig. 6. Uptake of Several Metal Ions by 2-A 6-NBAF Copolymer Resin at Five Different Concentrations of Electrolyte Solution $NaNO_3$

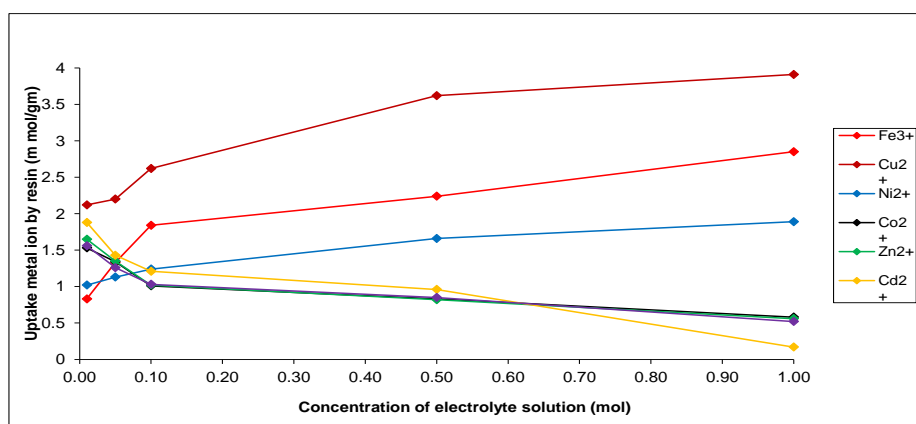


Fig. 7. Uptake of Several Metal Ions by 2-A 6-NBAF Copolymer Resin at Five Different Concentrations of Electrolyte Solution $NaCl$

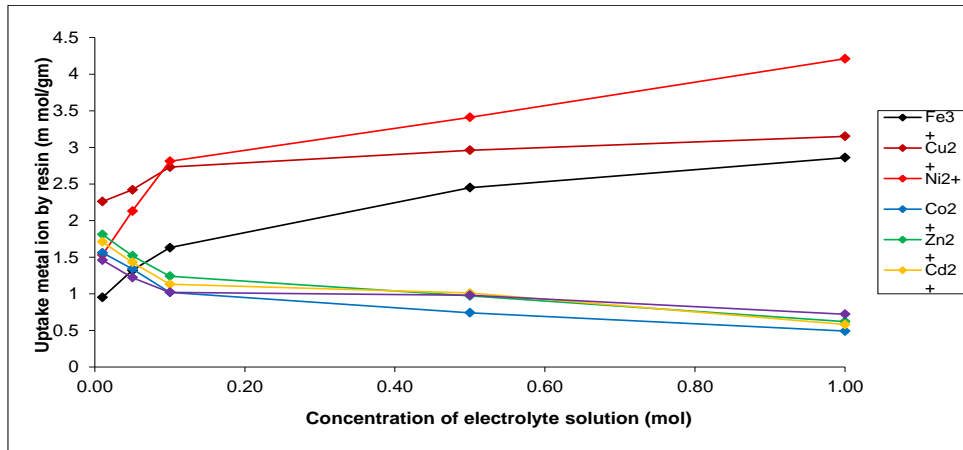


Fig. 8. Uptake of Several Metal Ions by 2-A 6-NBAF Copolymer Resin at Five Different Concentrations of Electrolyte Solution NaClO₄

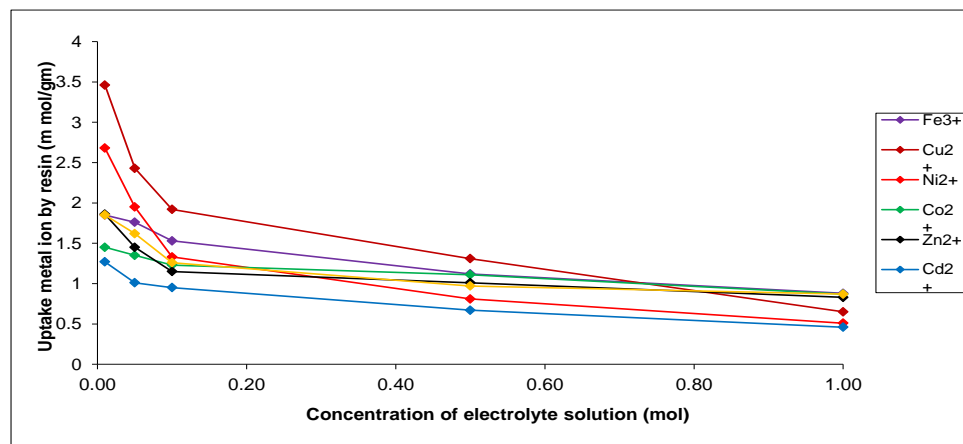


Fig. 9. Uptake of Several Metal Ions by 2-A 6-NBAF Copolymer Resin at Five Different Concentrations of Electrolyte Solution Na₂SO₄

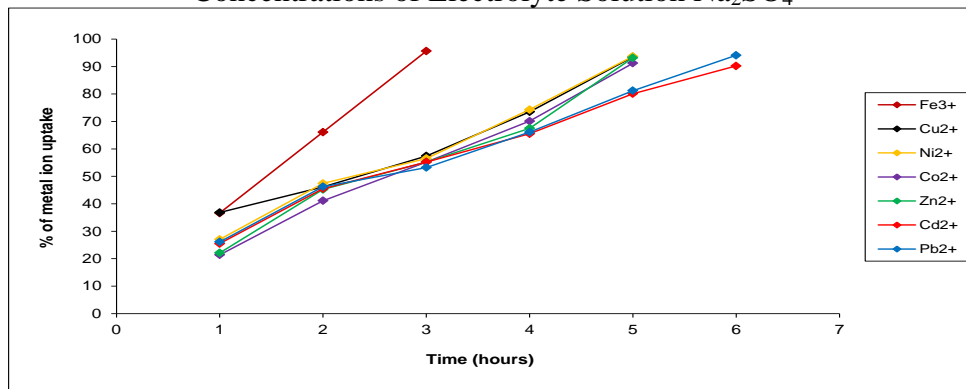


Fig. 10. Comparison of the Rate of Metal Ion Uptake by 2-A 6-NBAF Copolymer Resin

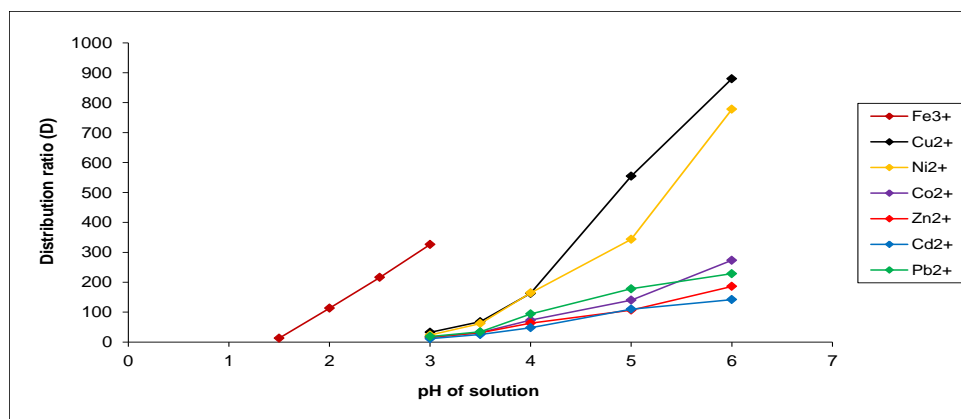


Fig. 11. Distribution Ratio (D) of Various Metal Ions as a Function of Different pH by 2-A 6-NBAF Copolymer Resin

Conclusion

The 2-A 6-NBAF copolymer based on the condensation polymerization of 2-amino 6-nitro benzothiazole and adipamide with formaldehyde in the presence of acid catalyst has been prepared. Since 2-A 6-NBAF copolymer contain phenolic ($-\text{NO}_2$) group and carboxylic ($-\text{CO}$) group, it play a key role in the ion exchange phenomenon, because of it higher tendency of capturing metal ions. Thus 2-A 6-NBAF copolymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. Due to considerable differences in the uptake capacities at different pH and media of electrolyte, and the rate of metal ion uptake and distribution ratios at equilibrium, it is possible to separate particular metal ions from their admixtures by this technique. The 2-A 6-NBAF copolymer is a selective chelating ion exchange polymer for certain metals. The copolymer showed a higher selectivity for Fe^{+3} , Cd^{+2} and Co^{+2} than for Cu^{+2} , Zn^{+2} , Ni^{+2} and Pb^{+2} ions.

Acknowledgement

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