Metal Ion Binding Properties of Copolymer Resin : Synthesis, Characterization and Its Application as an Ion- Exchanger

Punam G. Gupta¹, R. H. Gupta² and W. B. Gurnule¹*

¹Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur – 440 024, India . ²Department of Chemistry, K. Z. S. Science Collge, Brahmni, Kalmeshwar-441501, India E-mail: punamgupta04@gmail.com and wbgurnule@yahoo.co.in

Abstract--Copolymer was synthesized by the condensation of 2-amino 6-nitrobenzothiozol [2-A 6-NB] and melamine [M] with formaldehyde [F] in the presence of HCl catalyst using varied molar ratios of reacting monomers. A copolymer composition has been determined on the basis of their elemental analysis and the number average molecular weight of this copolymer was determined by conductometric titration in non-aqueous medium and by vapour pressure osmometry (VPO). The viscosity measurements in N, N-dimethyl formamide has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by FTIR spectra and ¹H NMR spectra. The copolymer has been further characterized by absorption spectra in non-aqueous medium to elucidate the structure. Ion-exchange properties of this resin was studied by batch equilibrium method for Fe³⁺, Cu²⁺, Ni²⁺, Cd²⁺ and Pb²⁺ ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. In the presence of nitrate, perchlorate and chloride ions the uptake of Fe(III), Cu(II), and Pb(II) ions increasing with increasing concentration of electrolytes, whereas in the presence of sulphate ions, the amount of above mentioned ions taken up by the copolymer resin decreases with increasing concentration of electrolyte. The resin shows a higher selectivity for Fe³⁺ ion over any other ions. Study of distribution ratio as a function of pH indicates that the amount of metal ion taken by resin is increases with the increasing pH of medium. The surface morphology of the copolymer resin was examined by scanning electron microscopy and it establishes the transition state between crystalline and amorphous nature.

Keywords: Copolymer resin; 4-Hydroxybenzophenone; Metal ion uptake; Batch equilibrium method; Ion-exchange capacity

I. INTRODUCTION

The discharge of heavy metals into watercourses is a seriousenvironmental problem that significantly affects the quality of the water supply. Increasing concentrations of these metals in the wastewater constitute a severe health hazard because of theirtoxicity, persistence in nature, and non-biodegradability, particularlywhen they exceed the permissible limits [1]. Heavy toxic metalions are generally found together in a hydrometallurgical, recycling or wastewater process, preliminary separation of thosemetals ions are very essential at this juncture. The awareness of the environmental dangers posed by the discharge of toxic heavymetals into the environment from the industries and the heavymetals in sewage sludge has been tremendously increased. The separation of metal ions present as contaminants in water is complicated by the number of variables that must be considered, including the solution composition, the pH, and the presence of organic substances. For example, the heavy metals such as Pb(II) andHg(II), which are toxic to most organisms. Hence, the chelatingresins can be used in the concentration and selective separation of heavy metal ions from the waste water and industrial wastes. Also, the ion exchange

resins can be used for the removal of toxicmetal ions, but the chelating resins are preferred instead of the ionexchange resins because of their selectivity [2].

Few of the synthesized copolymer derivatives possess potent antibacterial activity and some of the compounds were reported for its cytotoxic activity by Chaudhary et al. [3]. A series of cyano derivatives of N-alkyl and N-aryl piperazine were synthesized and their antimicrobial activities were evaluated against Gram-positive and Gram-negative strains Staphylococcus aureus, Pseudomonas aeruginosa, S. epidermidis, Escherichia coli and antifungal activities against Aspergillusflavus and Aspergillusniger [4-5].

Hence keeping in mind the properties of these monomers, we have planned to synthesize such polymers, which have combined properties of these monomers. The synthesized copolymer was characterized by elemental analysis, UV-VIS, FT-IR, ¹H NMR, ¹³C NMR, intrinsic viscosity and number average molecular weight.

The purpose of the selection of these monomers for the present study is to explore the adsorption behavior of seven metal ions Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} on the newly synthesized copolymer resins p-HBBF at different pH values, different concentrations of various electrolytes and at different shaking time intervals. Some commercially available ion-exchange resins are given in Table 1 [6-7].

conniciently available for exchange resins			
Trade name	Fuctional group	Polymer matrix	Ion-exchange
			Capacity (mmol.g ⁻¹)
Amberlite IR-120	$-C_6H_4SO_3H$	Polystyrene	5.0-5.2
Duolite C-3	-CH ₂ SO ₃ H	Phenolic	2.8-3.0
Amberlite IRC-50	-COOH	Methacrylic	9.5
Duolite ES-63	-OP(O) (OH) ₂	Polystyrene	6.6
Zeocarb-226	-COOH	Acrylic	10.00
Dowex-1	-N(CH ₃) ₃ Cl	Polystyrene	3.5
Amberlite IRA-45	$-NR_2$, $-NHR$, $-NH_2$	Polystyrene	5.6
Dowex-3	-NR ₃ , -NHR, -NH ₂	Polystyrene	5.8
Allassion A WB-3	$-NR_2, -N^+R_3$	Epoxy-amine	8.2

Table 1.Commercially available ion-exchange resins

II. EXPERIMENTAL

Starting Materials

The important chemicals (starting materials) such as 2-amino 6-nitrobenzothiozol, melamine and formaldehyde used in the preparation of new 2-A 6-NBMF copolymer resin were of chemically pure grade and, wherever necessary, the purity was tested and confirmed by thin layer chromatography.

Synthesis of 2-A 6-NBMFcopolymer resin

The 2-A 6-NBMFcopolymer resin was prepared by the condensation polymerization of 2amino 6-nitrobenzothiozol(0.2 mol) and melamine (0.1 mol) with formaldehyde (0.3 mol, 11.25 mL) in acidic hydrochloric acid medium at 126 ± 2 °C in an oil bath for 5 hrs. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of 2-amino 6-nitrobenzothiozol- formaldehyde copolymer, which might be present along with the 2-A 6-NBMFcopolymer. The dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1(v/v) HCl/water. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yields of these copolymer resins were found to be 81.5% and the melting point is between 450 - 455K. The sieved resin was used for further characterization.

Characterization of 2-A 6-NBMF copolymer resin

The copolymer resin was subject to micro analysis for C, H and N on an Elementary Vario EL III Carlo Erba 1108 elemental analyzer. The number average molecular weight $\overline{M} n$ 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 versus the milliequivalents of potassium hydroxide required for neutralization of 100 gm of copolymer was made. Inspection of such a plot revealed that there were many discontinuities in the plot. From this plot, the first break and the last break were noted. The calculation of \overline{Mn} by this method is based on the following considerations [8] : (1) the first break corresponds to the stage at which 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, (DP) the average molecular weight has to be determined by following eq. (1)...

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

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

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [9] at six different concentrations ranging from 0.3 wt % to 0.05 wt % of resin in DMSO at 30°C. Intrinsic viscosity (η) was calculated by the Huggin's eq.(2) [17] and Kraemer's eq.(3) [18]. In $\eta_{sp}/C = [\eta] + K_1 [\eta]^2$.C ------(2)

In
$$\eta_{rel}/C = [\eta] - K_2 [\eta]^2 .C$$
 -----(3)

Spectral Analysis

Electronic (UV-visible) absorption spectra of the copolymer in DMSO was recorded with a double beam spectrophotometer equipped with an automatic pen chart recorder on thermosensitive paper in the range of 200 - 850 nm at L.I.T. RTM, Nagpur University

Nagpur.Infrared spectra of 2-A 6-NBMFcopolymer resin was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of $4000 - 500 \text{ cm}^{-1}$ at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Proton NMR and ¹³C NMR spectra was recorded with Bruker Adanve – II 400 NMR spectrophotometer using DMSO-d₆ as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. Surface analysis was performed using a scanning electron microscope (SEM), JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur, at various magnifications.

Antimicrobial study by disc diffusion technique

Antibacterial activity was tested by the filter paper disc diffusion technique involving the cultures of the selected organisms for 24 h at P. G. and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli 620 020, Tamil Nadu, India. Mueller Hinton agar no.2 (Hi Media, India) was used as the bacteriological medium. The test solutions of the synthesized copolymers and their metal complexes were prepared in sterile dimethyl sulphoxide solvent for the study.

Antifungal activity was tested by the filter paper disc diffusion technique involving the cultures of the selected organisms for 24 h at P. G. and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Tiruchirappalli 620 020, Tamil Nadu, India. Sterile yeast nitrogen base (HI Media) with 2% agar was inoculated by a rotating swab (soaked in standard inoculums suspension) over the surface of the media. Fluconazole (100 mg/ml) was taken as the standard for antifungal activity. The test solution impregnated discs were placed on the agar and incubated at 37°C for 18 h. The zone of inhibition was measured by measuring the minimum dimension of the zone of fungal growth around the filter paper disc.

Ion-exchange properties

The ion-exchange properties of the 2-A 6-NBMFcopolymer 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 (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. 2 ml of a 0.1 M solution of metal ion was added to this suspension and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 hrs and filtered [10-11]. 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 [12]. The experiment was repeated in the presence of other three electrolytes 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 a percentage of the amount of metal ions taken up at the state of equilibrium.

Evaluation of the Distribution of Metal Ions at Different pH

The distribution of each one of the seven metal ions i.e. Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in 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 as described earlier at different pH values. The distribution ratio "D" is defined by the following relationship:

 $D = \frac{\{Wt. (in mg) of metal ions taken up by 1 gm of copolymer\}}{\{Wt. (in mg) of metal ions present in 1 ml of copolymer\}}$

III. Results and Discussion

The resin sample was light pink in color, insoluble in commonly used organic solvents, but was soluble in dimethyl formamide, dimethyl sulphoxide, tetrahydrofuran, pyridine and concentrated H₂SO₄. The synthesized resins do not show sharp melting point but undergo decomposition between 450-455 K. Based on the analytical data, the empirical formula of the copolymer resin is found to be $C_{19}H_{20}N_3O_7$, 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 C = 56.71% (Cal) and 56.22% (F); H = 4.97% (Cal) and 4.68% (Cal); N = 10.44% (Cal) and 10.11% (F).

Characterization of copolymer resin

Number average molecular weights Mnof these copolymers have been determined by conductometric titration method in non-aqueous medium and using standard potassium hydroxide (0.5 N) in absolute ethanol as a titrant. The specific conductance was plotted against milliequivalents of ethanolic KOH required for neutralization of 100 gm of each copolymer. There are several breaks before the complete neutralization of all phenolic hydroxyl groups. The first break in the plot was the smallest break and assumed that this corresponds to a stage in titration when an average one phenolic hydroxide group of each chain was neutralized. The average degree of polymerizationDpand hence the number average molecular weightMnof all copolymer resins have been determined using the formula:

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

$(\overline{Mn}) = \overline{DP} \times Repeat unit weight$

The number average molecular weight could be obtained by multiplying \overline{DP} by the formula weight of the repeating unit, i.e 4812 [13-14].Viscometric measurement was carried out in DMSO at 30°C. The intrinsic viscosity was determined by the Huggin's eq. (2) and

Kraemer's, eq. (3) which is 0.27 and 0.25 respectively. In accordance with the above relations, the plot of $\eta sp/C$ and $\eta rel/C$ versus C was linear giving slopes K₁ and K₂ (0.52)respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots [15-16]. The values of (η) obtained from both relations were in good agreement with each other.

Spectral Analysis

UV-visible spectrum of 2-A 6-NBMFresin has been recorded in pure DMSO in the wavelength range of 200 - 800 nm at a scanning rate of 100 nm min⁻¹ and at a chart speed of 5 c min⁻¹. The spectra of these copolymers exhibit two absorption maxima in the region of 280 nm and 320 nm. These observed positions of the absorption bands indicate the presence of carbonyl group (ketonic) processing double bond, which is in conjugation with the aromatic nucleus [26-27]. The appearance of former band (more intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the later band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition. The shift from the basic value (viz. 240 nm and 310 nm respectively) may be due to conjugation effect, and the presence of phenolic hydroxyl group (auxochromes) is responsible for hyper chromic effect i.e. Σ_{max} higher values.

Assignment	Observed wave
number (cm^{-1})	
-OH (phenolic)	3250-
3500 b,st	
>C=O	1615-
1640 sh,st (ketonic and biuret moity)	
Aromatic ring	1163
sh,w	
>CH ₂ (methylene bridges)	1374,
1273 sh,m	
1,2,3,4,5 substitution	815
sh,w	
in benzene skeleton	

Table 2.	
FTIR frequency signatures of 2-A 6-NBMF copolymer	resin

H¹ NMR spectrum of 2-A 6-NBMF copolymer data are specified in Table 3 [31-33].

Table 3.

¹H NMR spectral data of 2-A 6-NBMF copolymer resin in DMSO-d₆

Chemical shift (δ) ppm of copolymer	Chemical shift (δ) ppm of copolymer
7.5-7.8	Aromatic proton of Ar-H
6.86-7.14	Imido proton of -CO-NH-CO linkage
3.62-3.90	Proton of Ar-OH
5.15-5.45	Amido proton of -CH2-NH-CO- linkage
4.64	Methylene proton of Ar-CH2-NH moity
2.58-2.72	Proton of Ar – CO- C ₆ H ₅

Scanning electron microscopy

Surface analysis has found significant use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron microscopy. As can be seen in the figure, the resin appeared to be dark brown in color. The morphology of copolymer resin exhibited spherules and fringes. The spherulites indicate the crystalline nature of 2-A 6-NBMF copolymer resin sample. The morphology of resin polymer also shows fringes that are characteristic of the crystalline/amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the micrograph shows fringed and scattered nature having shallow pits representing the transition between crystalline and amorphous phase. The nature of the synthesized resin was found to be irregular and the surface was found to be scattered. As expected, an intermediate state between amorphous and crystalline nature was observed in the copolymer. Even though the monomers such as 2-amino 6nitro benzothiazole and melamine was crystalline in nature, it loses crystallinity during condensation polymerization. The more amorphous nature than crystalline will enhance the ionexchange capacity and shows more reactive sites for the adsorption with the metal ions. The resin exhibits more amorphous characters with close packed surface having deep pits. Due to deep pits, the resin exhibits higher exchange capacity for Pb²⁺ions (as well as many other metal ions). This could be due to bigger nitrated Pd²⁺ ions, which can easily penetrate into the deep pits. Thus by studying the SEM micrographs, the morphology of resin shows the transition between crystalline and amorphous phase. When compared to the other resin [17-18], the 2-A 6-NBMFcopolymer resin is more crystalline-and less amorphous in nature; hence it shows higher metal ion exchange capacity.

Antimicrobial testing

The results of microbial screening of the p-HBBF copolymer resin are presented in Table 4 for antibacterial and antifungal studies.

Compound (Copolymer resin)	Zone of inhibition (mm)				
	Bacteria			Fungi	
	E. Coli	Klebseilla	P. Aeruginosa	C. Albicans	Pencillium species
2-A 6-NBMF	29	19	19	21	16
Standard	28	26	25	20	22
Control (DMSO)	-	-	-	-	-

I able 4. Antibacterial and antifungal activity of the 2-A 6-NBMF copolymer re-	resin
---	-------

Antibacterial activity

An admirable result was obtained for 2-A 6-NBMF copolymer resins against *E. coli* bacterium which is markedly higher than the standard. E. coli, a gram negative rod-shaped bacterium that affects the urinary tracts in humans.*Klebsiella* is a genus of non-motile, gram-negative bacterium that causes a wide range of disease states, notably pneumonia, septicemia and

soft tissue infections. The results showed a good activity against Klebsiella. *P. aeruginosa*, a common bacterium which can cause diseases such as pulmonary tract and urinary tract burns and wounds in animals and human beings for which the 2-A 6-NBMFresins had moderate activity.

Antifungal activity

The antifungal activities of the 2-A 6-NBMF copolymer resins also provide appealing results against the chosen fungal strains. *Penicillium* sp. causes infection in humans and the resulting disease is known generically as penicilliosis. The resins had moderate activity against *Penicillium* sp. *C. albicans* is a diploid fungus and a causal agent of opportunistic oral and genital infections in humans and has also emerged as an important cause of morbidity and mortality in immune compromised patients. The 2-A 6-NBMFcopolymer resin exhibits a very good activity against *Penicillium* sp. *C. neoformans*, an encapsulated yeast-like fungus that can live in both plants and animals and cause lung infection.

Ion-exchange properties

With a view to ascertain the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the copolymer and solution containing the metal ions, by using batch equilibrium method [19-20] was investigated. Data of experimental procedure for direct EDTA titration is presented in Table 5.

n Buffer used	Indicator used	
Colour change		
Dil.HNO ₃ /dil.NaOHVariamin	ne blue	Blue-
Yellow		
Dil.HNO ₃ /dil.NaOH	Fast sulphon blac	ck
Purple-Green		
Aq.NH ₃ /NH ₄ Cl	Murexite	
Yellow-Violet		
Aq.NH ₃ /NH ₄ Cl	Salochrom	
Wine Red-Blue		
Hexamine	Xylenol orange	e
Red-Yellow		
Hexamine	Xylenol orang	e
Red-Yellow		
Hexamine	Xylenol orange	e
Red-Yellow		
	n Buffer used <u>Colour change</u> Dil.HNO ₃ /dil.NaOHVariamin Yellow Dil.HNO ₃ /dil.NaOH Purple-Green Aq.NH ₃ /NH ₄ Cl Yellow-Violet Aq.NH ₃ /NH ₄ Cl Wine Red-Blue Hexamine Red-Yellow Hexamine Red-Yellow	n Buffer used Indicator used <u>Colour change</u> Dil.HNO ₃ /dil.NaOHVariamine blue Yellow Dil.HNO ₃ /dil.NaOH Fast sulphon blac Purple-Green Aq.NH ₃ /NH ₄ Cl Murexite Yellow-Violet Aq.NH ₃ /NH ₄ Cl Salochrom Wine Red-Blue Hexamine Xylenol orange Red-Yellow Hexamine Xylenol orange Red-Yellow

Table 5. Data of experimental procedure for direct EDTA titration

The 2-A 6-NBMFcopolymer shows that the group -OH and -NH contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating behavior. When polymer is suspended in metal ion solution, the chelating tendency of copolymer forms the cyclic complex with the metal ion, which absorbs the metal ion from solution to the surface of the polymer. This mechanism of adsorption of metal ion by polymer ligands is known at metal uptake of polymer. The decrease in uptake concentration of metal ion

in solution can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ions due to the selectivity of polymer towards the uptake of metal ions. The metal uptake of copolymer depends on three variables: concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of 2-A 6-NBMFcopolymer was studied with these three variables by keeping two variables constant at each time.

 $Polymer + metal ion solution + shaking \rightarrow Polymer - metal ion chelate$ (Metal uptake capacity of polymer depends on stability of polymer - metal ion chelate)

The batch equilibrium technique developed by Gregor et al. and DeGeiso et al.[21] was used to study ion exchange property of 2-A 6-NBMFcopolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 2-A 6-NBMFis presented in Figs. 8-13. Seven metal ions Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Co²⁺ and Pb²⁺, in the form of aqueous metal nitrate solution, were used. The ion exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength (b) shaking time and (c) pH of the aqueous medium. Among three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the copolymer [22-23].

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

Figures 7-10 reveal that the amount of metal ions taken up for a given amount of 2-A 6-NBMFresin sample depends on the nature and concentration of electrolyte present in the solution. We examined the influence of NO_3^- , CI^- , CIO_4^- and SO_4^{-2-} at various concentrations on the equilibrium of metal-resin interaction at constant pH. Different metal ions have different pH in solution. Figures 8 to 11 show that the amount of metal ions taken up by a given amount of copolymer resins depends on the nature and concentration of the electrolyte present in the solution. Generally, as concentration of the electrolyte increases, the ionization decreases; the number of ligands which form the complex, with less metal ions, decreases in the solution and more ions are available for adsorption. The variable metal ion uptake capacity of 2-A 6-NBMF copolymer resins may be due to the strong and weak complex formation between electrolyte ligands and metal ions.

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 above mentioned ions taken up by the copolymer decreases with increasing concentration of the electrolyte. Among all the above four ligands, $SO_4^{2^-}$ is a strong ligand, due to having more number of electrons contributing to the meal ion during complex formation. It forms strong and stable complexes with all the seven metal ions considered in this study. Therefore, the overall metal uptake is less in sodium sulphate electrolyte and, on increasing the concentration of $SO_4^{2^-}$ ligand. Thus, less number of ions are left available for uptake of polymer, decreasing, thereby, the metal uptake capacity in $SO_4^{2^-}$ electrolyte [Fig. 1].



Fig.1 Uptake of Several Metal Ions by 2-A 6-NBMF Copolymer Resin at Five Different Concentrations of Electrolyte Solution (a)NaNO₃ (b) NaCl (c) NaClO4 and (d) Na₂SO₄

Evaluation of rate of metal ion uptake

The rates of metal adsorption by the 2-A 6-NBMF copolymer resins were measured for Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions in order to know the equilibrium time required. The data of metal uptake at various shaking time intervals is depicted in Fig.2. The rate of metal adsorption was determined to find out the shortest period for which equilibrium could be maintained while operating as close to equilibrium conditions as possible. During the rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant. The pH of each metal ion is different. As shaking time increases, the polymer gets more time for adsorption; hence uptake increases.



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

Distribution ratio of metal ions at different pH

Fig. 3 shows the results of the effect of pH on the metal binding capacity of the synthesized polymers. It is observed that the relative amount of metal ion adsorbed by the copolymer resin increases with increasing pH of the medium. The study was performed up to pH 6 to prevent hydrolysis of the metal ions at higher pH. The data of the distribution ratio, as a function of pH, indicates that the distribution of each metal between the polymer phase and aqueous phase increases with increasing pH of the medium. For Fe³⁺ ion, the highest working pH is 3. The results indicate that the copolymer resin sample uptakes Fe^{3+} ion more selectively than other metal ions under investigation up to pH 3. The Fe³⁺ has comparatively lower distribution ratio. The Fe³⁺ ion forms octahedral complexes with the ligands in aqueous layer at lower pH, which shows crowding effect; this steric hindrance may lower the distribution ratio of Fe³⁺ ions [3, 29]. Cu^{2+} and Ni²⁺ have highest distribution ratio at pH 3 to 6; therefore, these ions can be taken up more selectively between the range of pH 3-6. 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. Cu²⁺ and Ni²⁺ may form more stable complex, indicating that these ions are adsorbed more selectively to a higher extent, rather than Co^{2+} , Zn^{2+} , Cd²⁺ and Pb²⁺ which may form rather weak complexes with ligand during the course of time; therefore, these ions are adsorbed to a least extent over an entire pH range [24].





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) \approx Co (II) > Zn (II) > Cd (II) \approx Pb (II).

Hence, the results of this type of study are helpful in selecting the optimal pH for a selective uptake of a metal ion from a mixture of different ions. The ion-exchange capacity has been found to be 4.35 mili mol.g⁻¹, which indicates that the copolymer resin is a better ion-

exchanger for certain metal ions than some phenolic and polystyrene commercial ion-exchangers.

IV. Conclusions

2-A 6-NBMF copolymer resin was prepared from 2-amino 6-nitro benzothiazole and melamine with formaldehyde in hydrochloric acid medium by condensation technique. The spectral characteristics of the copolymer confirm the linear structure. The semi crystalline - amorphous nature of the 2-A 6-NBMF copolymer resin was confirmed by SEM studies and reveals that the copolymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe³⁺, Cd²⁺, Cu²⁺, Zn²⁺, Ni²⁺ and Pb²⁺ ions. This study of ion-exchange reveals that 2-A 6-NBMFcopolymer resin is an eco-friendly cation exchange resin and can be used for theremoval of hazardous metal ions from the environment, for the purification ofindustrial waste solution and for purification and desalination of water. Thus 2-A 6-NBMFcopolymer has significant applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. The 2-A 6-NBMF copolymer resin was found to have excellent antimicrobial activity against the chosen bacteria and fungi. Further, in the case of *C. albicans* and *E. coli*, the copolymer resin showed enhanced activity than the standard approach.

ACKNOWLEDGMENTS

The authors are thankful to the Principal, Kamla Nehru Mahavidyalaya, Nagpur, India, for providing the necessary laboratory facilities and also to SAIF, Punjab University, Chandigarh for carrying out the spectral analysis.

REFERENCES

- [1] S. D. Alexandratosand R. Chiarizia, Solv. Extr. Ion Exch, vol. 16(4), pp.951–966, 1998.
- [2] A. Singh, and S. K. Saraf, Int. J. Polym. Mater, vol. 58(10), pp. 499–508, 2009.
- [3] W. B. Gurnule, Y. U. Rathod, Curr. Appl. Polym. Sci., vol. 4, pp.1-8, 2020.
- [4] Q. J. Rong-jun, S. Chun-nuan, L. Yan-zhi, C. Zhong-fang, and S. Ren-feng, Chinese J. Polym. Sci, vol. 22(5), pp.469–475, 2004.
- [5] V. D. Mane, N. J. Wahaneand W. B. Gurnule, J. Appl. Polym. Sci., vol.111, pp. 3039–3049, 2009.
- [6] N. C. Das, W. B. Gurnule, Material Today Proceedings, vol.15, pp. 619, 2019.
- [7] R. N. Singruand W. B. Gurnule, Iran. Polym. J., vol.9(3), pp. 169–183, 2010.
- [8] P. Chaudhary, S. Nimesh, V. Yadav, A. K. Verma and R. Kumar, European Journal of Medicinal Chemistry, vol. 42, pp. 471, 2007.
- [9] S. Parveen, T. Ahamad, A. Malik and N. Nishat, *Polymers for Advanced Technologies*, vol.19, pp.1779, 2008.
- [10] H. Nawaz, Z. Akhter, S. Yameen, H.M. Siddiqi, B. Mirza and A. Rifat, J.Organo-metallic Chemistry, vol.604, pp. 2198, 2009.
- [11] M. M. Patel , M. M. Kapadia, Reactive and Functional Polymers, vol. 67, pp. 746, 2007.
- [12] J. M. Patel, M. G. Patel, H. J. Patel, K. H. Patel, JMac MolSci, vol.45, pp.281-288, 2008.
- [13] C. Kohad, W. B. Gurnule, Materials Today, Proceedings, vol.15, pp.446, 2019.
- [14] B. A. Shah, A. A. Shah, N. B. Patel, Iran PolymJ, vol. 17, pp.3-17, 2008.
- [15] P.E. Michael, J. M. Barbe, H. D. Juneja, L. J. Paliwal, EurPolym J,vol.43, pp.4995-5000, 2007.
- [16] A. Vogel, Text Book of Quantitative ChemicalAnalysis, 5th ed, Longman group, UK, 186-213, 1989.
- [17] R. N. Singru, A. B. Zade, W. B. Gurnule, *J ApplPolymSci*, vol.109, pp.859-868, 2008.
- [18] S. S. Rahangdale, A. B. Zade, W. B. Gurnule, Indian J. Chem, vol. 48A, pp.531-535, 2009.
- [19] D. B. Patle and W. B. Gurnule, Archives of Applied Science, vol.2 (1), pp.261-276, 2010.
- [20] R. N. Singru, W. B. Gurunule, A. B. Zade, Der PharmaChemica, vol.3(2), pp.257-262, 2011.
- [21] P.S Kalsi, Spectroscopy of Organic Compounds, 2nd ed., New Age International, New Delhi, 1005.
- [22] H. Kaur, strumental methods of chemical analysis, Arihant Electric Press: Meerut, 2009.
- [23] S. S. Butoliya, A. B. Zade and W. B. Gurnule, J. Appl. Polym. Sci., vol. 113(1), 1-9, 2009.

[24] D. B. Patle and W. B. Gurnule, Elixir Applied Chemistry, vol. 65, pp. 267, 2012.