Sorption Investigation on the Removal of Metal Ions from Aqueous Solution using Chelating Copolymer Resin

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Abstract-- Novel chelating copolymer (4-HBPBF-II) has been synthesized by the condensation of 4-hydroxybenzophenone [HBP] and biuret [B] with formaldehyde [F] in the presence of acid catalyst at 126 °C in the ration 2:1:3 was proved to be a selective chelating ion-exchange copolymer for certain metals. 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. The viscosity measurements in dimethyl sulphoxide (DMSO) has been carried out with a view to ascertain the characteristic functions and constants. The newly synthesized copolymer resin was characterized by UV-visible spectra, IR spectra, ¹³C NMR 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⁺, Zn²⁺, Co²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ ions over the pH range, 1.5 to 6.5 and in media of various ionic strengths. 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; Degree of polymerization; Polycondensation; Ion-exchanger; Synthesis, Resin

I. INTRODUCTION

Much research is being directed towards the preparation of polymeric chain, which is propagated by the formation of metallic chelates. Some success has been achieved in formation of polychelates derived from copolymer ligand. An efficient method for synthesizing such type of polymers by introducing phenols and diamides. The literature survey reveals that copolymers based on 4-hydroxybenzophenone and its derivatives have received attention due to their application in various areas such as in waste water treatment, for metal recovery, in protective coating and in biological activity [1-3]. Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations [4, 5]. The chelation ion-exchange behavior of poly (2-hydroxy, 4-acryloyloxybenzophenone) resin towards the divalent metal ions were studied by batch equilibrium method as a function of time and pH [6]. A cross linked styrene/meleic acid chelating matrix has been reported for its higher ability to removes the metal ions such as Cr^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Pb^{2+} [7]. Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency of removes the metal ions like Ag^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} at different pH and polymer-metal ion ratios [8]. Salicylic acid melamine with formaldehyde terpolymer found to have higher

selectivity for Fe³⁺, Cu²⁺ and Ni²⁺ ions then for Co²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ ions [9]. Resin synthesized by the condensation of a mixture of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported [10]. The metal ion uptake increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid [11]. o-nitrophenol and thiourea with p-formaldehyde terpolymer was identified as an excellent ion-exchanger for Zn²⁺ and Co²⁺ ions [12]. Salicylic acid – formaldehyde – resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixture [13]. 8-hydroxyquinoline formaldehyde – catechol copolymer found to have lower moisture content indicating the high degree of cross linking in the resin [14].

However no work seems to have been carried out on synthesis and chelation ionexchange studies of the terpolymer resins synthesized from 4-hydroxybenzophenone, biuret and formaldehyde. The purpose of present study, is to explore the adsorption behavior of eight metal ions Fe²⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ Hg²⁺ and Pb²⁺ on the newly synthesized copolymer resins 4-HBPBF at different pH values, different concentrations of different electrolytes and at different shaking time intervals. The adsorption behavior of these metal ions are based on the affinity differences towards the chelating resins as functions of pH, electrolyte concentrations and shaking time. One of the important applications of chelating and functional polymers is their capability to recover metal ions from waste solution. Hence the chelating ion exchange property of the 4-HBPBF-II terpolymer resin was also reported for specific metal ions. Pollution by toxic heavy metals due to their toxicities in relatively low concentration and tendency to bioaccumulation in the ecosystem, agriculture and human body has received wide spread attention in recent years. Various approaches such as ion-exchange, reverse osmosis, electro dialysis, precipitation and adsorption techniques have been developed for the removal and recovery of the metal ions from sewage and industrial wastewater. Among these techniques, many research works have focused on metal ions removal by adsorption on chelating polymers, because they are reusable, easily separable, and with higher adsorption capacity and selectivity having physical and chemical stabilities [15-16].

II. EXPERIMENTAL

Chemicals

Chemicals (starting materials) like 4-hydroxybenzophenone, biuret and formaldehyde used in the preparation of new 4-HBPBF-II copolymer resin were procured from the market and were of chemically pure grade, and wherever necessary the purity was tested and confirmed by thin layer chromatography.

Synthesis of 4-HBPBF-II copolymer resin

The 4-HBPBF-II copolymer resin was prepared by the condensation polymerization of 4-hydroxybenzophenone (0.2 mol) and biuret (0.1 mol) with formaldehyde (0.3 mol) in hydrochloric acid medium at 124 ± 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 4-hydroxybenzophenone - formaldehyde copolymer, which might be present along with the 4-HBPBF-II copolymer. 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 a vacuum over silica gel. The yields of these copolymer resins found to be 87% and the melting point is between 420-425°K. The sieved resin was used for further characterization.

Characterization of copolymer resin

The 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 $\overline{M}n$ 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 against the milliequivalants of potassium hydroxide required for neutralization of 100 gm of 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 of $\overline{M}n$ by this method is based on the following consideration [17] : (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, (\overline{DP}) the average molecular weight has to be determined by following eq. (1)...

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

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

The intrinsic viscosity was determined using a Tuan-Fuoss viscometer [18] 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) [19] and Kraemer's eq.(3) [20].

In
$$\square \square_{sp}/C = [\square] + K_1 [\square] \stackrel{?}{f.C}$$
-----(2)
In $\square_r/C = [\square] - K_2 [\square] \stackrel{?}{f.C}$ -----(3)

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 4-HBPBF-II 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 Adanve – II 400 NMR spectrophotometer using DMSO-d₆ 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 scnanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at VNIT, Nagpur. *Ion-exchange properties*

The ion-exchange properties of the 4-HBPBF-II 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 (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 [21, 22]. 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 [23]. 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.

Percentage of amount of metal ion taken up at different time = <u>Amount of metal ion adsorbed at</u> x 100 equilibrium

Evaluation of the Distribution of Metal Ions at Different pH

The distribution of each one of the eight metal ions i.e. Fe^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} Hg²⁺ 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 Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} . 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-

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

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.

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

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 resin synthesized do not show sharp melting point but undergo decomposition 420-425°K. Based on the analytical data, the empirical formula of the copolymer resin is found to be $C_{17}H_{17}N_3O_5$, 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 =69.53% (Cal) and 69.15% (F), H=4.67% (Cal) and 4.48% (F), N =7.85% (Cal) and 7.75% (F). The number average molecular weight ($\overline{M}n$) could be obtained by multiplying the \overline{DP} by the formula weight of the repeating unit [24, 25]. The calculated molecular weight for 4-HBPBF-II resin is 10329.

Viscometric measurement was carried out in DMSO at 30°C. 4-HBPBF-II resin showed normal behavior. The intrinsic viscosity was determined by the Huggin's eq. (2) and Kraemer's, eq. (3) which is 0.28 and 0.26 respectively. In accordance with the above relations, the plot of $\eta_{sp/c}$ and $\eta_{rel/c}$ against C was linear giving as slopes K₁ and K₂ (0.54) respectively. The intercept on the axis of viscosity function gave the (η) value in both the plots [26]. The values of (η) obtained from both relations were in good agreement with each other.

Spectral Analysis

UV-visible spectra of 4-HBPBF resin has been recorded in pure DMSO in the region of 200 – 800 nm at a scanning rate of 100 nm min⁻¹ and at a chart speed of 5 cm min⁻¹. The spectra of these copolymers exhibit two absorption maxima in the region 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 [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 presence of phenolic hydroxyl group (auxochromes) is responsible for hyperchromic effect i.e. Emax higher values. The FTIR spectrum of 4-HBPBF-II copolymer resin shows a broad absorption band appeared in the region 3550-3200 cm⁻¹ may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding. The peak, at 3200-3000 cm⁻¹ and indicate the presence of -NH stretching (imides). The peak at 3200-3000cm⁻¹ (-CH stretching), 1300-1280 cm⁻¹ (-CH₂ bending wagging and twisting), 1390-1270 cm⁻¹ (-CH₂ plane bending), indicate the presence of methylene (-CH₂) group and 1367-1369 cm⁻¹ methylene bridge in copolymer chain. The bands appeared at 3200-3000 cm⁻¹ (Aryl C-H stretching) and 950-1125 cm⁻¹ (substituted aromatic ring) may be ascribed to aromatic ring. The band at 600-800 cm⁻¹ indicates the presence of tetra substituted aromatic ring. 1,2,3,5 substitution in aromatic ring was confirmed by the bands appeared at ~ 950, 1058, 1125. The band of -NH stretching (3200-3000 cm⁻¹) seems to be merged with very broad band of phenolic hydroxyl group[28].

 H^1 NMR spectra of 4-HBPBF-II copolymer shows a weak multiplicity signals (unsymmetrical pattern) in the region 7.52 to7.88 (δ) ppm may be due to the aromatic protons. A weak signal appeared in the region of 6.86 – 7.14 shows the presence of imido proton of – CO-NH-CO- linkage. The weak multiply signals appearing at 5.15 – 5.45 (δ) ppm may due to the amido –CH₂ -NH-CO linkage. A signal appeared in the region 4.07 – 4.98 (δ) ppm may be due to proton of methelenic bridges (Ar – CH₂ – N) of polymer chain. The signal in the range of 3.62 – 3.90 (δ) ppm is attributed to phenolic -OH proton[29].

A ¹³C NMR spectrum of 4-HBPBF-II copolymer resin shows peaks appeared at 121.14, 127.71, 129.09, 131.88 and 155.94 ppm may be corresponded to carbons present in aromatic benzophenone ring. The peak appeared at 162.11 ppm of may be correspond to carbonyl group of biuret moity. The medium peak appeared at 115.33 ppm may be confirmed the presence of -C-NH group of terpolymer resin. The peak appeared at 65.56 ppm may be due to the presence of -C-OH group in aromatic benzophenone group. The peaks appeared at 38.91 to 40.17 ppm may be due to the $-CH_2$ – bridge in copolymer resin. All these peaks confirmed that the 4-HBPBF-II copolymer resin must have linear structure.

Scanning electron micrographs

Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported resin sample was investigated by scanning electron micrographs at different magnification. It gives the information of surface topology and defect in the structure. The resin appeared to be dark drawn in colour. The morphology of polymer resin shown spherule and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of 4-HBPBF-II copolymer resin sample. The morphology of resin polymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The resin exhibits more amorphous characters with closed packed surface having deep pits. Due to the deep pits, resin exhibits higher exchange capacity for Pb²⁺ ions (as well as other many metal ions). This could be the reason of bigger nitrated Pd²⁺ ions, which can easily penetrate in to the deep pits. Thus by SEM micrographs morphology of the resin shows the transition

between crystalline and amorphous nature. When compare to the other resin [30], the 4-HBPBF-II copolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

Ion-exchange properties

With a view to ascertain the selectivity of the studied 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 [31]. Data of experimental procedure for direct EDTA titration is presented in Table 4.

The 4-HBPBF-II copolymer 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 surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known at metal uptake of polymer. Due to metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution. The metal uptake capacity of polymer is different for different metal ion, is also known as selectivity of polymer towards the uptake of metal ion. The metal uptake of copolymer depends on three variables, concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of 4-HBPBF-II copolymer was studied with these three variables by keeping two variable constant at each time.

Batch equilibrium technique developed by Gregor et al. and DeGeiso et al. was used to study of ion exchange property of 4-HBPBF-II copolymer resin. The result of the batch equilibrium study carried out with the copolymer resin 4-HBPBF-II is presented in Fig. 1-6. eight metal ions Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Hg^{2+} and Pb^{2+} 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 evaluable its effect on metal uptake capacity of the polymer [32].



M(NO₃)₂]=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH: Fe(III) = 2.5; Cu(II) = 4.5; Ni(II) = 4.5; Co(II) = 5.0; Zn(II) = 5.0; Cd(II) = 5.0; Hg(II) = 6.0; Pb(II) =





 $M(NO_3)_2$]=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)=6.0; Pb(II)=6.0 Fig. 2. Uptake of several metal ions by 4-HBPBF-II copolymer resin at five different concentration of electrolyte solution NaCl



 $M(NO_3)_2$ =0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)=6.0; Pb(II)=6.0 Fig. 3. Uptake of several metal ions by 4-HBPBF-II copolymer resin at five different concentration of electrolyte solution NaClO₄



 $M(NO_3)_2$]=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)= 6.0; Pb(II)=6.0 Fig. 4. Uptake of several metal ions by 4-HBPBF-II copolymer resin at five different concentration of electrolyte solution Na₂SO₄

Effect of electrolytes and their concentration on the metal ion uptake capacity

We examined the effect of NO_3^- , CI^- , SO_4^{-2-} and CIO_4^- at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been mentioned in [Fig.1-4], which shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe³⁺, Cu²⁺, Zn²⁺ and Pb²⁺ ions increasing with increasing concentration of electrolytes. Whereas in the present of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte [33]. Above NO_3^- , Cl⁻, and ClO₄⁻ ions form weak complex with the above metal ions, while SO_4^{-2} form stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands.



 $M(NO_3)_2$]=0.1 Mol/l; Volume = ml; Volume of electrolyte solution : 25 ml; Weight of resin = 25 mg; time : 24 hrs: Room temperature.

pH : Fe(III) =2.5; Cu (II) = 4.5; Ni(II)=4.5; Co(II)=5.0; Zn (II)=5.0; Cd(II)=5.0; Hg(II)=6.0; Pb(II)=6.0 Fig. 5. Uptake of several metal ions by 4-HBPBF-II copolymer resin at five different concentration of

electrolyte solution Na₂SO₄

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 for which equilibrium could be carried out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution remain constant and pH of each metal ion is different, which is given in Fig 5. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. Fig.5 shows the results of rate of uptake of metal ion on 4-HBPBF copolymer resin. The rate refers to the change in the concentration of the metal ions in the aqueous solution which is in contact with the given copolymer. The figure shows that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Fe³⁺ ions required about 3 hrs for the establishment of the equilibrium, whereas Cu²⁺, Zn²⁺ and Pb²⁺ ions required about 6 hrs. Thus the rate of metal ions uptake follows the order Fe³⁺ > Cu²⁺ > Hg²⁺ \approx Pb²⁺ > Zn²⁺ > Ni²⁺ >Cd²⁺ > Co²⁺ for the 4-HBPBF-II copolymer [34].



D= weight (mg) of metal ions taken up by 1 g of copolymer/weight (mg) of metal ions present in 1ml of solution.

 $[M(NO_3)_2]=0.1 \text{ mol/l};$ volume of metal nitrate=2ml; NaNO₃= 1.0 mol/l; volume of electrolyte= 25ml, time=24hrs (equilibrium state) at Room temperature.

pH : Fe(III) = 2.5; Cu(II) = 4.5; Ni(II) = 4.5; Co(II) = 5.0; Zn(II) = 5.0; Cd(II) = 5.0; Pb(II) = 6.0; Hg(II) =

Fig 6. Distribution ration (D) of various metal ions as function of different pH by by 4-HBBF-II Copolymer resin

Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions.

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results given in [Fig.6]. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the copolymers increase with increasing pH of the medium [35]. The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of Fe^{3+} ion is more for the 4-HBPBF-II copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be $Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$ [38]. Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [36]. For example, the result suggests the optimum pH 2.5 for the separation of Fe^{3+} and Zn^{2+} with distribution ratio 'D' is 480.2 and 685.7 respectively using the 4-HBPBF-II copolymer resin as ion exchange. Similarly for the separation of Fe³⁺ at the optimum pH is 2.5 with distribution ratio is 480.2 for 4-HBPBF-II copolymer. The lowering in the distribution ratios of Fe³⁺ was found to be small hence, efficient separation could be achieved. The order of distribution ratio of metal ions measured in pH range 2.5 to 6.5 is found to be Fe $^{2+}$ > Cu^{2+} > Ni^{2+} \Box $\Box Cd^{2+}$ $> \Box Zn^{2+} > Co^{2+} \Box \Box Pb^{2+}.$

IV. CONCLUSIONS

4-HBPBF-II Copolymer resin was prepared from 4-hydroxybenzophenone and biuret with formaldehyde in hydrochloric acid medium by condensation technique. The amorphous nature of the 4-HBPBF-II copolymer resins were confirmed by the SEM studies and reveals that the copolymer can act as an effective ion exchanger for trivalent and divalent metal ions such as Fe³⁺, Cd²⁺, Cu²⁺, Zn²⁺, Ni²⁺ Co²⁺, Hg²⁺ and Pb²⁺ ions. This study of ion-exchange reveals that 4-HBPBF-II copolymer resin is proved to be an eco-friendly cation exchange resin and can be used for the removal of hazardous metal ions from the environmental area,

for the purification of industrial waste solution and for the purpose of purification and desalination of water.

REFERENCES

- [1] N. Angelova, N. Manolova, I. Rashkov, Eur polym J, vol.31(8), pp.741, 1995.
- [2] N. C. Das, W. B. Gurnule, *Material Today Proceedings*, vol.15, pp.619, 2019.
- [3] N. C. Das, W. B. Gurnule, Int. J. Curr. Engg. Sci. Res., vol.6(1), pp.1425, 2019.
- [4] W. B. Gurnule, Y. U. Rathod, Curr. Appl. Polym. Sci., vol. 4, pp.1-8, 2020.
- [5] R. M. Zalloum, S. M. Mubarak, J. Appl Polym Sci, vol.109, pp.3180-3184, 2008.
- [6] P. K. Roy, A. S. Rawat, P. K. Rai P. K, J. Appl Polym Sci, vol. 94, pp. 1771-1779, 2004.
- [7] C. G. Kohad, W. B. Gurnule, Ajanta, vol.8, pp.148-153, 2019.
- [8] W. B. Gurnule, H. D. Juneja, L. J. Paliwal, React Funct Polym, vol. 50, pp.95-100, 2002
- [9] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, Synth React Inorg Met. Org Chem, vol. 33, pp.1187-1205, 2003.
- [10] M. M. Yeole, S. Shrivastava, W. B. Gurnule, Der Pharma Chemica., vol.7(5), pp.129, 2015.
- [11] M. B. Thakre, W. B. Gurnule, Materials Today, Proceedings, vol.15, pp.525, 2019.
- [12] C. G. Kohad, W. B. Gurnule, Materials Today, Proceedings, vol.15, pp.446, 2019.
- [13] B. A. Shah, A. V. Shah, B. N. Bhandari, J Iran Chem Soc, vol.5, pp. 25-22, 2008.
- [14] D. Feng, C. Aldrich C, H. Tan, *Miner Eng*, vol.13, pp.623-642, 2000.
- [15] B. A. Shah; A. V. Shah; B. N. Bhandari, Asian J Chem, vol.13, pp.1305-1308, 2001.
- [16] W. B. Gurnule, H. D. Juneja, L. J. Paliwal, Reactive and Funtional Polymers, vol.55, pp. 255-265, 2003.
- [17] W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat; J. Appl Polym Sci. vol.89, pp.787–790, 20003.
- [18] S. S. Rahangdale, W. B. Gurnule, A. B. Zade, J. Appl. Polym. Sci, vol. 108, pp.747-756, 2008.
- [19] M. V. Tarase, W. B. Gurnule, A. B. Zade, J. Appl. Polym. Sci, vol.116, pp.619-627, 2010.
- [20] V. D. Mane, W. B. Gurnule, A. B. Zade, J. Appl. Polym. Sci, vol.111, pp.3039-3049, 2009.
- [21] B. A. Shah, A. V. Shah, P. M. Shah, Iran Polym J, vol.15, pp.809-819, 2006.
- [22] J. D. Joshi, N. B. Patel, S. D. Patel, Iran Polym J, vol.15, pp.219-226, 2006.
- [23] M. M. Jadhao, L. J. Paliwal, N. S. Bhave, Ind J of Chem, vol. 44, pp.656, 2005.
- [24] B. A. Shah, A. V. Shah, P. M. Shah, Iran Polym J, vol. 13, pp. 445-454, 2004.
- [25] S. S. Katkamwar, W. B. Gurnule, A. B. Zade, J Appl Polym Sci, vol.113, pp. 3330-3335, 2009.
- [26] R. N. Singru, W. B. Gurnule, A. B. Zade, J Appl Polym Sci, vol.109, pp.859-868, 2008.
- [27] S. Dutta, A. K. Das, J Appl Polym Sci, vol.103, pp. 2281-2287, 2007.
- [28] Zalloum R. M.; Mubarak S. M.; J Appl Polym Sci, 109, 2008, 3180-3184.
- [29] S. S. Rahangdale, W. B. Gurnule, A. B. Zade, E-Journal of Chemistry, vol.6(3), pp.835-843, 2009.
- [30] S. S. Rahangdale, W. B. Gurnule, A. B. Zade, Indian J Chem. Vol.48A, pp.531-535, 2009.
- [31] R. M. Silverstein, F. X.Webster, Spectrometric identification of organic compounds John Wiley and Sons, New York, 1998.
- [32] D Gruyter Walter; Ion Exchangers (K. Dorfner, ed.), Berlin, 1991.
- [33] R. H. Gupta, W. B. Gurnule, A. B. Zade, J Appl Polym Sci, vol.109(5), pp. 3315-3320, 2008.
- [34] D. B. Patle and W. B. Gurnule, Archives of Applied Science Research, vol.2 (1) pp. 261-276, 2010.
- [35] D. B. Patle and W. B. Gurnule, Polymer Bulletin, vol. 66(6), 803-820, 2011.
- [36] R. N. Singru, W. B. Gurunule, A. B. Zade, Der Pharma Chemica, vol.3(2), pp.257-262, 2011.