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UPTAKE OF HEAVY METAL IONS BY CHELATING ION-EXCHANGE RESIN DERIVED FROM P-HYDROXYBENZOIC ACID-FORMALDEHYDE-RESORCINOL: SYNTHESIS, CHARACTERIZATION AND SORPTIONDYNAMICS

(Pengambilan Ion Logam Berat oleh Resin Penukar Ion Terbitan Asid p-Hidroksibenzoik-Formaldehid-Resorsinol: Sintesis, Pencirian dan Dinamik Erapan)

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Abstract

Chelating ion-exchange resin (pHFR) has been synthesized by condensing p-hydroxybenzoic acid with formaldehyde employing resorcinol as cross linking agent at 80 ± 5 ^{o}C using DMF as a solvent. The resin was characterized by elemental analysis, FTIR, ^{1}H-NMR and XRD. The thermal analysis (TGA, DTA and DTG) was done at the heating rate of 10 ^{o}C/min in N_2 atmosphere. The morphology of the resin was studied by optical photographs and scanning electron micrographs (SEM) at different magnifications. The physico-chemical properties have been studied. The uptake behaviour of various metal ions viz. Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) towards pHFR resin have been studied depending on contact time, pH, metal ion concentration and temperature. The maximum uptake capacity for Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) are found 1.310, 2.304, 1.690, 1.591 and 2.020 mmol/g respectively. The selectivity order is: Cu(II)>Pb(II)>Zn(II)>Cd(II)>Ni(II). The intra-particle diffusion rate constant (K_{id}) and external diffusion rate constant (K_s) are calculated by Saphn-Schlunder and Weber-Morris models respectively. Equilibrium adsorption data were analyzed by Langmuir and Freundlich equations. The adsorption process follows first order kinetics and specific rate constant K_r was obtained by the application of Lagergan equation. Thermodynamic parameters viz. ΔG^o, ΔS^o and ΔH^o have also been calculated for the metal-resin systems.

Keywords: Chelating resin, thermal study, SEM, Thermodynamics, optical photograph, kinetics

Abstrak

Satu resin penukar ion kelat (pHFR) telah disintesis melalui kondensasi asid p-hidroksibenzoik dengan formaldehid menggunakan resorsinol sebagai agen taut silang pada suhu 80 ± 5 ^{o}C dan DMF sebagai pelarut. Resin ini telah diciri menggunakan analisis unsur, FTIR, ^{1}H-NMR dan XRD. Analisis terma (TGA, DTA dan DTG) telah dilakukan pada kadar pemanasan 10^{o}C/min dalam atmosfera N_2. Morfologi resin telah dikaji menggunakan fotograf optik dan mikrograf electron imbasan (SEM) pada pelbagai pembesaran. Sifat fiziko-kimia telah juga dikaji. Perlakuan pengambilan pelbagai ion logam seperti Ni(II), Cu(II), Zn(II), Cd(II) dan Pb(II) terhadap resin pHFR telah dikaji pada pelbagai masa sentuhan, pH, kepekatan ion logam dan suhu. Muatan maksimum pengambilan bagi Ni(II), Cu(II), Zn(II), Cd(II) dan Pb(II), masing-masing ialah 1.310, 2.304, 1.690, 1.591dan 2.020 mmol/g. Tertib selektiviti ialah : Cu(II)>Pb(II)>Zn(II)>Cd(II)>Ni(II). Pemalar resapan intra-zarah (K_{id}) dan pemalar kadar resapan luaran (K_s) dikira menggunakan model Saphn-Schlunder dan Weber-Morris. Data jerapan keseimbangan dianalisis berdasarkan persamaan Langmuir dan Freundlich. Proses jerapan didapati mengikut kinetik tertib satu dan pemalar kadar tentu K_r didapati melalui persamaan Lagergan. Parameter termodinamik seperti ΔG^o, ΔS^o dan ΔH^o telah juga dikira bagi sistem logam-resin yang dikaji.

Kata kunci: Resin kelat, kajian terma, SEM, termodinamik, fotograf optik, kinetik

Introduction

Removal, separation and enrichment of trace metals in aqueous solutions play an important role for the analysis of wastewaters, industrial and geological samples. Many separation techniques such as solvent extraction and ion-exchange chromatography have been applied for this purpose. Ion exchange is a popular method owing to its applicability to both pre-concentration and separation. The ion-exchange resin from salicylic acid and formaldehyde was derived by DeGeiso et al [1] in 1962. They have studied the ion exchange capacity and selectivity of salicylic acid-formaldehyde copolymer with Fe^{3+}, UO_2^{2+} ions as a function of pH. Patel et al [2, 3] have prepared the terpolymer of salicylic acid/p-hydroxy benzoic acid and thiourea with trioxane in the presence of acid catalyst with different molar proportions of monomers. Shah et al have been synthesized chelating resin from o-substituted benzoic acid and studied its ion-exchange properties [4]. The micro-wave assisted synthesized phenolic-formaldehyde polymers were prepared and their ion exchange properties towards the heavy metal ions were studied using a static batch equilibrium technique at 25 ^oC as a function of contact time, pH and concentration [5]. The sorption capacity of salicylic acid-formaldehyde condensate towards Al(III), Cu(II), Ni(II), Zn(II) and Co(II) were studied. The resin was found selective for Cu(II) ion with highest exchange capacity of 0.7 mmol/g [6].

Kapadia et al [7-9] prepared ion exchange resins from various phenolic derivatives like salicylic acid, gallic acid, β-resorcylic acid, anthranilic acid, 8-hydroxyquinoline and hydroquinone using DMF as a solvent. They have studied their anion as well as cation exchange properties towards various metal ions. Mubarak and coworkers [10] have studied the chelation behavior of the phenolic-formaldehyde polymers towards the trivalent lanthanide metal ions such as La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} and Tb^{3+} by a static batch equilibrium technique at 25 ^oC as a function of contact time, pH and concentration. Samal et al [11] prepared resins from the diazonium salt of aniline with phenol/resorcinol coupled with formaldehyde in alkaline medium. They have studied the uptake behavior of alkali and alkaline earth metal ions by the resin. The optimum conditions for effective separation of Cu^{2+} from UO_2^{2+} were also determined.

Recently, in 2006, Burgeson et al [12] evaluated resorcinol-formaldehyde resin for cesium removal and cesium elution characteristics. A new spherical form of resorcinol-formaldehyde resin [13] was also tested for efficiency of cesium removal from the complex mixture of radioisotopic liquid wastes. Resin from salicylic acid and formaldehyde with resorcinol [14] in DMF media has also been prepared and studied for its chelation ion-exchange properties. Shah et a [15] synthesized ion-exchange resin from anthranilic acid and formaldehyde with resorcinol in DMF media. They have separated transition and post transition metal ions from synthetic binary mixtures using tartaric acid as eluting agent.

So far no resin based on p-hydroxy benzoic acid-formaldehyde-resorcinol in DMF media has been reported with its morphology and thermal characteristics along with its kinetic and thermodynamic parameters. As industrial effluents are often rich in transition and post transition metal ions, removal and recovery of these metals is an important task for industries. In this paper, synthesis, characterization and different physico-chemical and chelation properties of the resin are reported along with its thermal and morphological studies. Various diffusion models and isotherm equations were employed to analyze the sorption data.

Materials and Methods

Materials and Reagents

Analytical grade chemicals such as p-Hydroxybenzoic acid (Ranbaxy fine chemicals S.A.S. Nagar), formaldehyde (37%) (Qualigens fine chemicals, Mumbai) and catechole (SRL Mumbai, extra pure) used as received without further purification. Solutions of acids and alkalies were prepared by dissolving appropriate amount of the particular compound in double distilled water and standardized by the literature methods [16]. Stock solution of metal salts under study were prepared by dissolving appropriate amount of metal acetates in double distilled water and standardized by EDTA titration [16]. Stock solution of EDTA (0.1M) was prepared and standardized against a solution of $MgSO_4$ using Ereochrome Black T (EBT) indicator. Buffer of acetic acid/sodium acetate (pH 3.0-6.0) was used for the batch experiments carried out to study uptake behaviour of metal ions. Mureoxide indicator was used for the estimation of Ni(II), Ereochrome Black T was used for Zn(II), Xylenol orange was used for Cd(II) and Pb(II), Fastsulphon Black F was used for Cu(II) estimation [16]. Glasswares were cleaned by overnight soaking in nitric acid (1:1) followed by multiple rinsing with water. All the other reagents used were of analytical grade and were used as such. Double distilled and deionized water was used throughout the research work. All pH measurements were carried out with digital pH meter (Elico CL-44) equipped with a combine glass/calomel electrode.

Resin Synthesis

p-Hydroxybenzoic acid (13.5 g, 0.1 mole) was taken in 250 ml round bottom flask and dissolve in DMF solvent (20 ml) to give clear solution. A solution of resorcinol (11 g, 0.1 mole) in 10 ml DMF was added to above solution and stirred for two hours. Formaldehyde (0.3 mole as 37%) was added and stirred for an hour. Then mixture was refluxed on a water bath at 80 ± 5 ^{o}C for 2-3 h with constant stirring during which the mixture gelled to a soft mass, which was dark brown in colour. A gel was separated from the reaction vessel and cured in an oven at 80-90 ^{o}C for 12 h. As carboxylic acid group normally get decomposed above 100 ^{o}C, the resin was cured below 90 ^{o}C. The resulting resin was washed with DMF to remove monomer impurities and finally with deionised water. After complete washing cycle, the yield of the resin was found to be 63 % (13.7 g). This purified and dry resin sample was finely ground and passed through 20 mesh screen and then 50 mesh screen to get uniform particle size (20 to 50 mesh). This sieved resin was again washed with water, air dried at room temperature and stored in polyethylene bottle. The solubility test of resin in different solvents was performed at room temperature and pressure with intermittent shaking. It was found non-melting and insoluble in almost all common organic solvents like acetone, ethanol, benzene, DMF, chloroform etc and also in acids and alkalies of higher strength (up to 6 M). But the resin exhibits poor solubility in DMSO-d_6 solvent. This sieved resin was characterized using different instrumental techniques and was used for all the experiments during the research period. The resin obtained from pHydroxybenzoic acid-fromaldehyde-resorcinol is abbreviated as pHFR (Scheme-I).

The particle size was measured by Malvern particle size Analyzer (Mastersizer-2000). The elemental analysis was carried out on Elemental Analyser (Carlo Erba, model 1160). Infra-Red spectra of the synthesized resin sample had been scanned in KBr pallets on FTIR Spectrophotometer (Shimadzu model-8201PC). The ^{1}H-NMR spectra was scaned in DMSO-d6 solvent on NMR Specrometer (Bruker DPX-200) at 200 MHz with a seep time of 10 min. at room temperature. The x-ray diffraction analysis (XRD) was performed by advanced Diffractometer (Bruker AXE D8). The thermograms (TGA, DTG and DTA) of the present resin sample were taken on TG/TGA instrument (Perkin Elmer Pyris Damond) at constant heating rate of 10 ^{o}C/min. in N_2 atmosphere. The surface analysis was done using an optical photograph (Olympus SZX12) and scanning electron microscope (Philips XL30) at different magnifications.

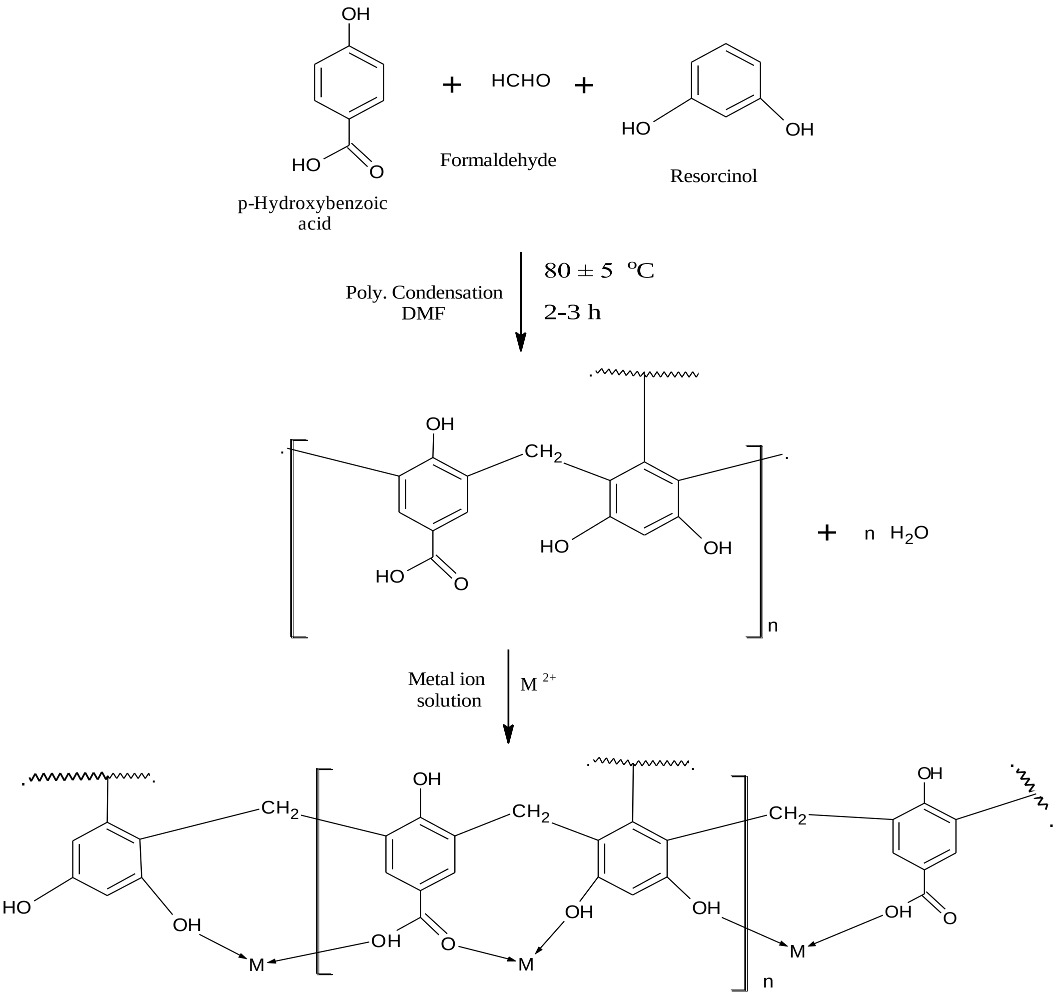
To convert the resin sample in H^+ form, resin sample having uniform particle size (20-50 mesh) was equilibrated with 1M HCl solution for 24 h and washed with deionized water till it was free from chloride by testing with silver nitrate solution. This H^+ form of resin was used for further studies. The batch equilibrium method was adopted to study the ion-exchange properties. The surface area of the resin was calculated using the following equation:

$$A_s = \frac{G\, N_{AV}\, \phi\, 10^{-20}}{M\, Mw} \qquad (1)$$

where, A_s is the resin surface area in m^2/g, G is the amount of methylene blue adsorbed (g), N_{AV} is the Avogadro's number (6.023 x 10^{23} mol^{-1}), ϕ is the methylene blue molecular cross section (197.2 ^{o}A), Mw the molecular weight of methylene blue (373.9 g.mol^{-1}) and M is the mass of the resin (g).

The surface area of pHFR is found to be 143.2 m^2/g.

The sorption properties such as effect of pH, contact time, metal ion concentration, temperature, and distribution coefficient (K_d) for different metal ions as a function of pH and concentration of tartaric acid were studied according to literature methods [17, 18].



Scheme–I. Route of synthsis of pHFR resin.

Batch sorption experiments

To study the effect of important parameters like pH, contact time and metal ion concentration on uptake of various metal ions, batch experiments were conducted at room temperature (30 ± 2 °C). To study the effect of pH on the metal ion uptake, it is necessary to buffer the resin and the solutions used. Different sets of accurately weighed (0.250 ± 0.001 g) dry resin having uniform particle size (20-50 mesh) were equilibrated with buffer in different stoppered bottles for 24 h, so that resin attained desired pH value. After 24 h buffer solutions were decanted and 50 ml of 0.2 M metal ion solutions of varying pH from 3-6 were added. Metal ion solutions were equilibrated at room temperature (30 ± 2 °C) for 24 h with intermittent shaking. After 24 h solutions were filtered with 0.02 µm membrane to separate the resin and solution. The pH of the filtrate was measured and it was found that pH remain stable throughout the experiment (± 0.2). From the filtrate unadsorbed metal ions were estimated by complexometric titration with 0.1 M EDTA solution using appropriate indicator. To study the effect of contact time on sorption of metal ions, H^+ form of accurately weighed (0.250 ± 0.001 g) dry resin samples were taken in different glass stoppered bottles and equilibrated with buffer solutions of optimum pH value (pH of highest exchange) for 24 h. For Ni(II) and Pb(II) pH was maintained 5.0, for Cu(II) and Cd(II) pH audjusted to 5.5 and for Zn(II) ph was adjusted to 6.0. After decanting buffer solution, 50 ml (0.2 M) metal ion solution of the same pH was added. The amounts of unadsorbed metal ions were determined by complexometric titration at fixed time intervals. To study the effect of metal ion concentration on uptake of different metal ions by the resin, the resin was equilibrated with acetate buffer at desired pH values (pH value of highest exchange) for 24 h and then buffer solutions were decanted. The accurately weighed (0.250 ± 0.001 g) dry resin were equilibrated with metal ion solutions (50 ml) of varying molar concentration i.e. 0.05 M, 0.1 M, 0.15 M, 0.20 M, 0.25 M and 0.30 M at the same pH value at room temperature for 15 h with intermittent shaking. After 15 h metal ion solutions were filtered and unchelated metal ions were estimated. The study the effect of temperature was performed at fixed metal ion concentration (0.15 M) for fixed resin loading (0.250 ± 0.001 g) and initial pH (different optimum pH for dofferent metal ions) at four different temperatures i.e. 20, 30, 40 and 50 °C.

Results and Discussion

Elemental analysis

The %C, %H and %N were calculated from the general formula ($C_{14}H_{11}O_7$) of the repeating unit of the assumed structure (scheme-I) of the resin. The value obtain are 64.15% (64.85%) and 3.91% (4.11%) for %C and %H respectively. The results of the elemental analysis are good agreement with calculated values of %C, %H and %N. The values of elemental analysis confirm the proposed structure of the resin presented in scheme-I.

Spectral characterization of resin (FTIR, ^{1}H-NMR, XRD)

The FTIR spectrum of pHFR resin is exhibited in Figure 1. The strong band at 3446.9 cm^{-1} is due to the υ(O-H) stretching of phenolic group. The presence of medium band at 2983 cm^{-1} is due to the υ(C-H) stretching of methylene group [15, 19]. The presence of broad band at 2612.4 cm^{-1} is due to υ(C-OH) stretching of carboxylic group. The medium strong band at 1639.0 cm^{-1} can be assigned to υ(C=O) stretching of aromatic acid group. The weak band at 1410 cm^{-1} is due to δ(C-H) deformation of methylene group [20]. The weak medium band at 1392.9 cm^{-1} can be assigned to δ(C-O-H) bending of aromatic –OH group. The band at 1235.5 cm^{-1} can be assigned to the aromatic δ(O-H) bending of phenol. The medium band at 775.2 cm^{-1}, is due to the δ(C-H) bending of 1,2,3,4-tetra substituted benzene ring [21]. The medium band at 664.3 cm^{-1}, is due to the δ(C-H) bending of poly ethylene –(CH_2)– bridges.

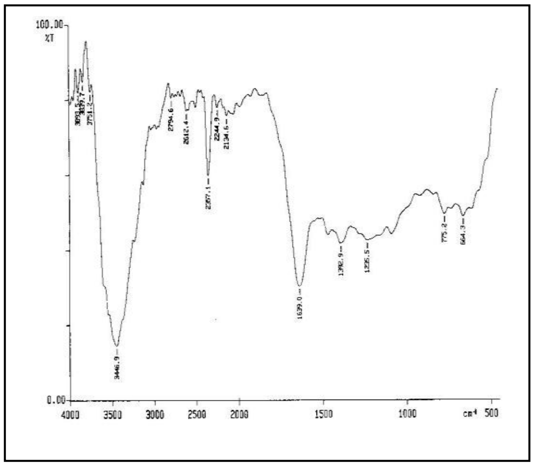


Fig. 1. FTIR spectrum of pHFR

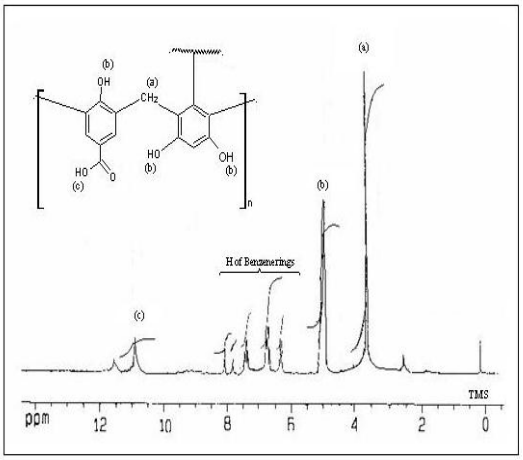


Fig. 2. ^{1}H-NMR spectrum of pHFR

The ^{1}H-NMR spectra of synthesized resin (pHFR) is shown in Figure 2. The peak observed at 10.9 ppm is due to the H of carboxylic acid group (Ar-COOH). The peaks observed at 6.2 ppm to 8.12 ppm are due to the H of benzene ring. The peak observed at 3.86 ppm is due to the 2H of methylene group (Ar-CH_2-Ar) [19]. The sharp singlet peak at 5.2 ppm is due to the H of phenolic (–OH) group.

The XRD pattern of the compound provides information whether the compound is crystalline or amorphous or crystalline and amorphous region co-exist in he same compound [21]. The XRD pattern of pHFR is shown in Figure 3. No sharp peaks are observed in the difractogram of the resin. The pHFR resin exhibits irregular pattern, which is a characteristic of the amorphous compound [21, 22]. Phenol-formaldehyde resin [23] also exhibited similar XRD pattern, which confirms the amorphous nature of the pHFR resin.

Thermal analysis (TGA, DTG, DTA)

The examination of the result of the thermograms (TGA, DTG and DTA) (Fig 4) reveals that resin sample undergoes degradation in two steps like salicylic acid-formaldehyde-resorcinol [14]. In the beginning of TGA curve, weight loss of 8.2 % was observed at 57 to 142 °C, this may be due to the loss of surface water which is loosely bound and evolved slowly. The maximum rate of weight loss was at 113 °C , which is observed in DTG curve. This is further confirmed from the DTA curve, which shows endothermic moisture loss at 113 °C. The second step decomposition of polymeric material starts at 400 °C which extends upto 800 °C involving 66 % (2.58 mg) weight loss. The DTG curve reveals that at 492 °C the rate of weight loss is highest. The first step DTA curve of pHFR exhibits broad endotherm at 112 °C with enthalpy 542 mJ/mg while in second step the exothermic peak observed at 493 °C with enthalpy -398 mJ/mg. The thermal degradation of the resin may be due to the random cleavage of polymeric resin affording simpler degradation products [3, 23]. It is very difficult to draw any conclusion from the magnitude of the thermal activation because the decomposition mechanism is expected to be very difficult [24]. The typical observations from the TGA are that the thermal degradation is steep and almost no left over residue is seen and similar observation was reported for salicylic acid-formaldehyde-resorcinol resin [14] and anthranilic acid-formaldehyde-resorcinol [15].

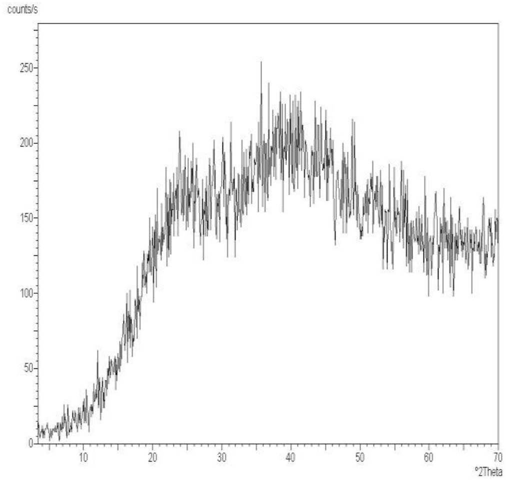


Fig. 3. XRD pattern of pHFR

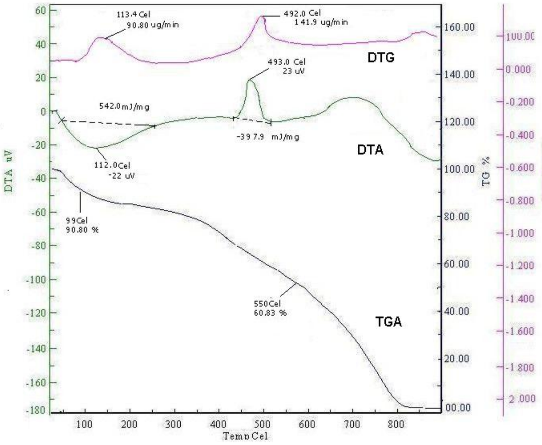


Fig. 4. TGA, DTG and DTA of pHFR resin at heating rate of 10 °C/min. in N_2 atmosphere

Surface Analysis (Optical and SEM photographs)

Surface analysis has been found to be of great use in understanding the surface features of the material. The morphology of the reported resin sample was investigated by optical photographs and scanning electron micrographs to characterize particle shape, size and surface morphology which are shown in Figure 5 and 6 respectively. Several observations were made of the resin before the micrographs (optical and SEM) were taken to ensure that the photographed regions were representative of the overall resin sample [12]. The optical and SEM photographs were taken at different magnifications, here in the present communication optical photograph of 110X (Fig. 5a) and 290X (Fig. 5b) magnifications and SEM photograph of 200X (Fig. 6a) and 500X (Fig. 6b) magnifications have been presented. The white bar at the bottom of the SEM micrographs represents the scale. Resin appeared dark brown with rough surface in optical photograph. From the SEM photographs it is observed that the resin exhibits angular edges with regular fringes. The fringes represent the transition material between crystalline and amorphous phases [15, 21]. The morphology of the resin shows a fringed micelle model of the crystalline-amorphous structure, similar observation was obtained for salicylic acid-formaldehyde-resorcinol resin [14].

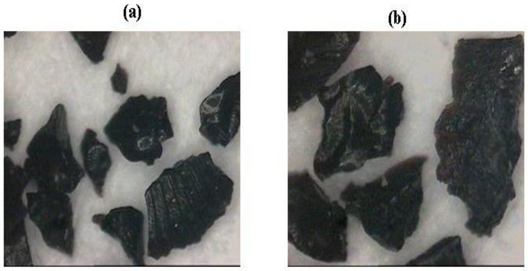


Fig. 5. Optical photographs of pHFR
(a)110X (b) 290X magnifications

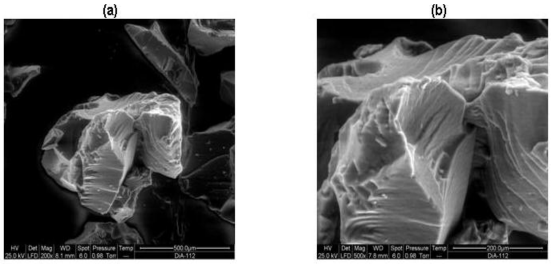


Fig. 6. SEM photographs of pHFR
(a) 200X (b) 500X magnifications

Sorption dynamic studies

Effect of pH on exchange capacity

The removal of metal ions from aqueous solution by sorption is highly dependent on pH of the solution that affects the surface charge of the sorbent [3]. Chelating ligand forms complexes with various metal ions at specific pH conditions [4]. Therefore, the effect of variation in pH on chelating ability of the resin has been studied. The results are presented as exchange capacity against pH for different metal ions in Figure 7. The results show that adsorption of metal ions were increased with increase in pH upto a certain value and thereafter decreased. From the nature of the trend observed indicates that the cation exchange behaviour of this resin is similar to weak acid cation exchangers [1, 14]. Because in weak acid cation ion exchanger, exchange capacity is pH dependent [17]. The maximum adsorption for Ni(II) and Pb(II) took place at pH 5, for Cu(II) and Cd(II) it was at pH 5.5 and for Zn(II) it was at pH 6. The selectivity order for metal ions is Cu(II) > Pb(II) > Zn(II) > Cd(II) > Ni(II).

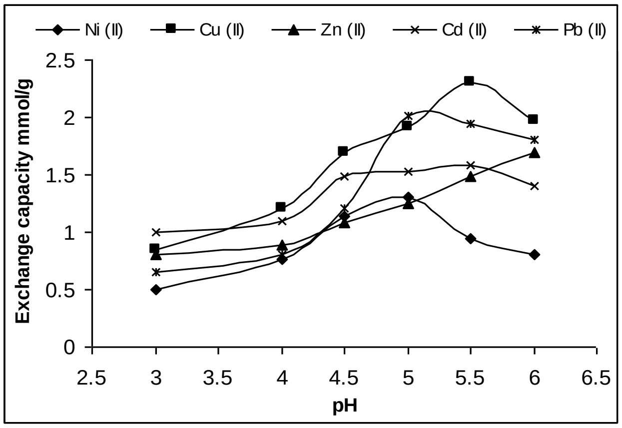


Fig. 7. The metal uptake capacity of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)on pHFR resin as a function of pH [initial metal ion conc. = 0.2 M, amount of resin = 0.250 g, vol. of metal ion solution = 50 ml, temp.= 30 ± 1 ^{o}C]

An increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positively charged metal ions and negatively charged sorbent and results in increase in the adsorption of metal ions. The decrease in the removal of metal ions at lower pH is due to the higher concentration of H^+ ions present in the reaction mixture which compete with the metal ions for the sorption sites on the sorbent surface. Meanwhile the observed decrease in sorption at higher pH is due to the formation of insoluble hydroxy complexes of the metal ions [25]. Therefore, pH 5 is taken as the optimum pH for Ni(II) and Pb(II), pH 5.5 is considered optimum pH for Cu(II) and Cd(II), pH 6 is considered optimum pH for Zn(II). The further sorption experiments were carried out at these different pH conditions for different metal ions.

Rate of exchange for metal ions

The exchange of metal ions on resin exhibits the time dependant phenomenon. The rate of exchange for different metal ions is illustrated in Figure 8. The rate of metal ion adsorption of the resin was determine to ascertain the shortest time period for which equilibrium could be carried out [3]. The graph shows that the time required for 50 % exchange ($t_{1/2}$) for zinc(II) and lead(II) is about 55 min., for cadmium(II) and nickel(II) is 2.5 h, for copper(II) is 48 min. respectively. The fast rate of exchange in the beginning can be explained on the basis of law of mass action [6]. The faster rate of exchange facilitates column chromatographic separation. Kinetics of metal ion exchange mainly depends on the various physical properties like particle size distribution, pore size, physical core structure and diffusion of counter ion [14, 15].

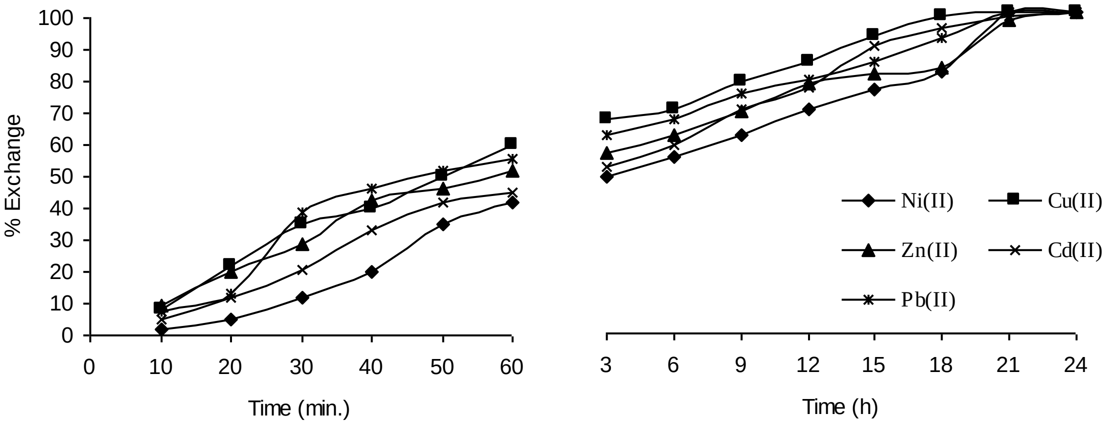


Fig. 8. Rate of metal ion exchange on pHFR resin

Time dependence of the fraction of metal uptake on resin

Time dependence is determined by poltting the fraction of adsorption, Y_t against the retention time, $t^{1/2}$. The Y_t is define as[27]:

$$Y_t = C_o\text{-}C_t / C_o\text{-}C_e \tag{2}$$

where, C_o denotes the initial concentration of metal ions, C_t is the concentration of metal ions at time 't' and C_e is the equilibrium concentration.

The rate of fraction of adsorption Y_t expressed as square root of time is estimated from the three staged curve illustrated in Figure 9. The initial steep sloped portion is attributed to the transfer of metal ions from the bulk of the solution to the boundary film of the adsorbent and later to its surface. The second stage corresponds to the transfer of the metal ions from the surface to the intraparticular active sites of the resin. This stage is slow and the rate determining step of the reaction. The final stage shows the completion of sorption reaching equilibrium [26]. At equilibrium there is a definite distribution of the solute particle between the solution and the resin particle. Karthikeyan et al [27] reported similar observation while studying the adsorption of reactive dye and Zn (II) ion respectively over chitosan.

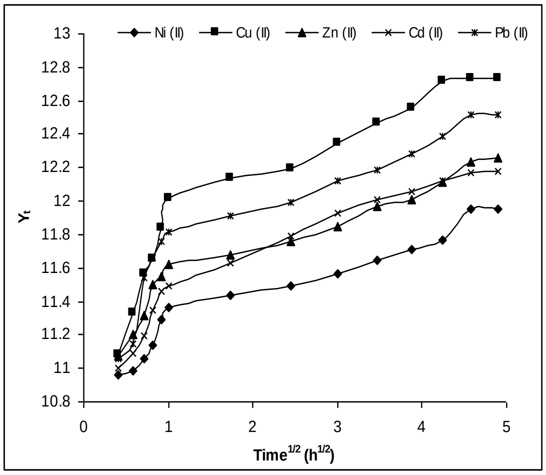


Fig. 9. Time dependence of the fraction of adsorption of metal ions on pHFR resin

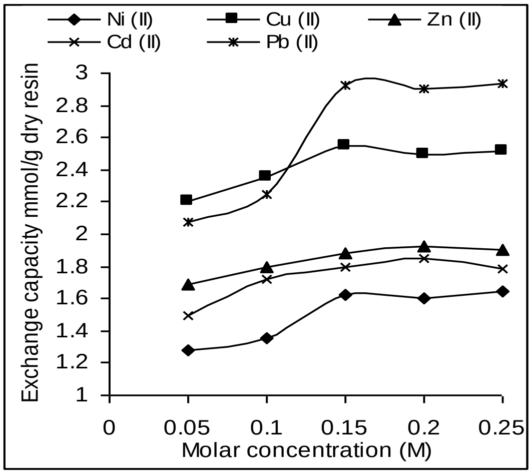


Fig. 10. The metal uptake capacity of pHFR resin as a function of metal ion concentration

Effect of metal ion concentration on exchange capacity

The examination of data presented in Figure 10 reveals that the amount of adsorbed metal ion increases with the increase in concentration of metal ions in solution until a maximum value, and will remain constant upon further increase in metal ion concentration. At lower concentration of metal ions the number of metal ions available in solution is less as compared to the available sites on the sorbent [28]. However, at higher concentration the available sites of sorption remain same whereas more metal ions are available for sorption and subsequently the sorption becomes almost constant thereafter [14, 15]. Therefore 0.15 M is consider as optimum concentration and used for all further experiments.

Effect of temperature and thermodynamic parameters

The effect of temperature on the adsorption of various metal ions on pHFR resin was also studied using the optimizing conditions. The temperature was varied from 20 to 50 °C. It was observed that the adsorption of metal ions increase with the increase in temperature (Table 1). This is due to the endothermic ion-exchange reaction of divalent cation [20]. The working of an ion-exchange depends on metal ion concentration and temperature. The surface energy of the pHFR resin increases with temperature. Similar results have also been reported for the adsorption of Ni(II), Cu(II), Zn(II),Cd(II) and Pb(II) with Dowex 50 [20] and Amberlite IR 120 [29].

Table 1. The metal uptake capacity of pHFR resin as a function of temperature

Metal ions	Exchange capacity at various temperature (mmol/g)			
	293 K	303 K	313 K	323 K
Ni(II)	1.37	1.41	1.46	1.49
Cu(II)	1.28	1.35	1.44	1.47
Zn(II)	1.78	1.80	1.84	1.87
Cd(II)	1.56	1.59	1.63	1.68
Pb(II)	2.21	2.27	2.31	2.35

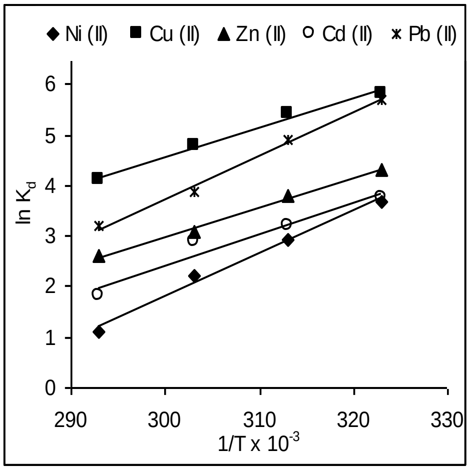


Fig. 11. Van't Hoff plot for the adsorption of metal ions on pHFR resin

Table 2. Thermodynamic parameters for metal ion adsorption on pHFR resin.

Metal ions	**Temp K**	**ΔG° kJ mol^{-1}**	**ΔH° kJ mol^{-1}**	**ΔS° J K^{-1} mol^{-1}**
Ni	**293**	**-2.588**	**7.021**	**19.56**
	303	**-2.591**		
	313	**-2.607**		
	323	**-2.615**		
Cu	**293**	**-4.803**	**4.794**	**10.57**
	303	**-4.812**		
	313	**-4.835**		
	323	**-4.853**		
Zn	**293**	**-3.845**	**4.819**	**11.97**
	303	**-3.892**		
	313	**-3.911**		
	323	**-3.923**		
Cd	**293**	**-3.701**	**5.135**	**13.39**
	303	**-3.722**		
	313	**-3.735**		
	323	**-3.739**		
Pb	**293**	**-4.371**	**7.113**	**18.23**
	303	**-4.391**		
	313	**-4.406**		
	323	**-4.409**		

The values of ΔH^o, ΔS^o and ΔG^o were also calculated from the slope and intercept of the Vant' Hoff plot of the adsorption of metal ions on pHFR resin, i.e. the linear variation of $\ln K_d$ with reciprocal temperature 1/T (Fig. 11) using the following relation:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (3)$$

where K_d is the distribution coefficient (cm^3/g), ΔS^o is the entropy change for the process, ΔH^o is the enthalpy change for the process.

The free energy of the adsorption and ΔG^o was calculated using the following Van't Hoff equation (4):

$$\Delta G^o = -RT\ln K_d \quad (4)$$

The thermodynamic parameters for the adsorption of various metal ions on pHFR resin are given in Table 2. The value of ΔH^o is positive which indicates an endithermic adsorption process and it is likely that the chelation mechanism dominates [30]. The entropy (ΔS^o) is positive corresponding to an increase in degree of freedom of the system due to release of two hydrogen ions for the divalent metal ions under study [31]. The negative value of ΔG^o indicate the feasibility of the process and also the spontaneity of the adsorption process. The amount of metal ions adsorbed at equilibrium must increase with increasing temperature, because ΔG^o decrease with the rise in temperature of the solution [27].

Sorption Isotherms

Equilibrium is described by usual isotherm equations such as Langmuir and Freundlich isotherms. A preliminary screening of the corresponding equations has shown that Langmuir and Freundlich models best fit the experimental data and the following equations are used for the modeling of results.

Langmuir model: $$(C_e/Q_e) = (1/Q^o b) + (C_e/Q^o) \quad (5)$$

where C_e is the equilibrium constratin (mmol/L), Qe is the amount of adsorbed at equilibrium (mmol/g) and Q^o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The liner plot (Fig. 12) C_e/Q_e versus C_e shows that adsorption obeys Langmuir model. These constant were calculated as 101.32, 352.46, 211.24, 119.41 and 249.19 mg/g as maximum capacity for Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) respectively. The results were comparable with commercial resin Duolite GT-73. The Q_{max} of Duolite GT-73 for Cu(II), Cd(II) and Pb(II) were 62, 106 and 122 mg/g respectively. Prasad et al [28] reported Q_{max} values for synthetic resin (methacrylic acid-co-ethyleneglycol dimethacrylate) were 416.67 and 588.24 mg/g for Cu(II) and Ni(II) respectively. Sorption energy constant for Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) are 0.0714 L/mg, 0.1131 L/mg, 0.0912 L/mg, 0.0883 L/mg and 0.1081 L/mg respectively. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L [32]. The values indicates the isotherm to be either unfavourable ($R_L < 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L obtained for the metal-resin system are shown in Table 3. The R_L value for all the metals under study are lying between 0 and 1 indicate favourable adsorption.

This adsorption was confirmed by Freundlich model (eq. 6):

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

where C_e is the equilibrium concentration (M) and q_e is the amount adsorbed (mmol/g). A linear plot (Figure 13) of log qe versus log C_e shows the applicability of Freundlich isotherm. The adsorption capacity (K_f) and the adsorption intensity (1/n) are directly obtained from the slope and the intercepts of the linear plot respectively and data are given in Table 3. The determined value of 1/n is of the same magnitude as those reported by Vaughan et al [33] for a commercial macrorecticular chelating resin Duolite GT-73. The higher fractional values of 1/n signify that strong adsorption forces are operative on the system. The magnitude of 1/n also gives indication of the favourability and capacity of the adsorbent/adsorbate system. Treybal [34] has reported that 'n' values between 1 to 10 represents favourable adsorption. For all the systems reprted here, the exponent is $1 < n < 2$ showing beneficial adsorption. Freundlich constants K_f were calculated as 83.34, 236.71, 172.39, 150.67, 209.11 and 1/n were calculated as 0.5213, 0.8731, 0.6543, 0.6376, 0.8044 for Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) respectively. The values of Freundlich constant are given in Table 3.

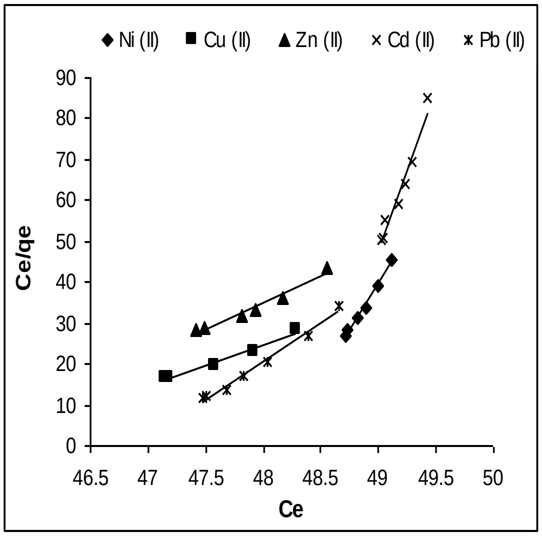


Fig. 12. Langmuir isotherm for the adsorption of metal ions on pHFR resin

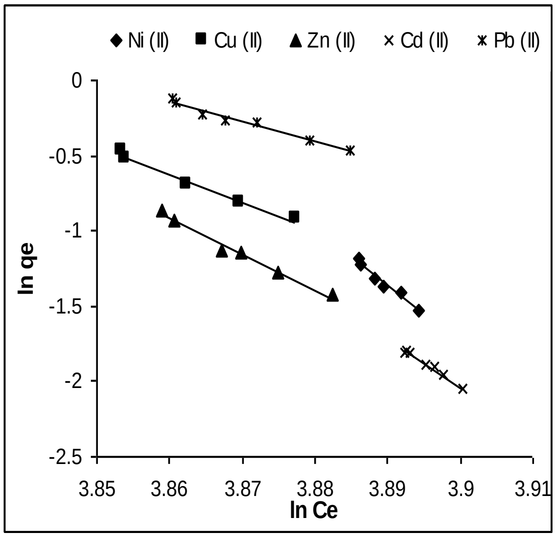


Fig. 13. Freundlich isotherm for the adsorption of metal ions on pHFR resin

Table 3. Langmuir and Freundlich constants for metal ions.

Metal ion	Langmuir constant				Freundlich constant		
	b (L mg^{-1})	Q^o (mg g^{-1})	R_L	R^2	K_f	1/n	R^2
Ni(II)	0.0714	101.32	0.327	0.9917	83.34	0.5213	0.9686
Cu(II)	0.1131	352.46	0.235	0.9797	236.71	0.8731	0.9834
Zn(II)	0.0913	211.24	0.208	0.9681	172.39	0.6543	0.9862
Cd(II)	0.0883	119.41	0.198	0.9644	150.67	0.6376	0.9912
Pb(II)	0.1081	249.19	0.216	0.9863	209.11	0.8044	0.9725

Kinetic model (Langargren equation)

It is well established fact that the ion-exchange phenomenon follows reversible first order kinetics, when a single species is considered on a heterogenous surface [20]. The specific rate constant K_r for the sorbent was determined by Lagergren equation (7) [28].

$$\text{Log}\,(q_e - q) = \log q_e - (K_r \times t) / 2.303 \qquad (7)$$

where q_e and q (mg/g) are the amounts of metal ions adsorbed at equilibrium and time, t (min) respectively. The straight line plot (Figure 13) of the log (q_e-q) versus time, t (at 30 ± 2 ^{o}C) indicates the validity of the Lagergran equation for the system and explains that process follows first order kinetics. The values of K_r were calculated from the slop of the plot (Fig. 14) and found to be 4.145 x 10^{-3}, 4.606 x 10^{-3} , 4.375 x 10^{-3}, 8.290 x 10^{-3} and 5.987 x 10^{-3} min^{-1} for Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) respectively. Anand et al [28] reported similar K_r values viz. 11.3 x 10^{-3} min^{-1} for Cu(II) and 9.9 x 10^{-3} min^{-1} for Ni(II) with synthetic resin (methacrylic acid-co-ethyleneglycol dimethacrylate).

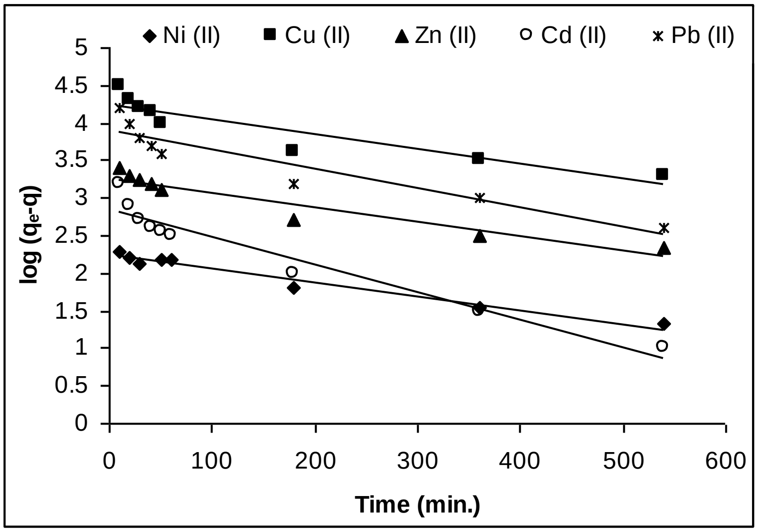


Fig. 14. Langergan plot for specific rate constant of metal ions on pHFR resin

Diffusion models

Sorption kinetics are usually controlled by various factors including, (i) Solute transfer from the solution to the boundry film of the particle (bulk diffusion) (ii) diffusion from the film to the surface of the sorbent (external diffusion) (iii) diffusion from the surface to the intraparticular sites (intraparticle diffusion) (iv) Solute adsorption by complexation or physico-chemical sorption or ion exchange.

By providing sufficient agitation to avoid particle and solute gradients in the batch reactor makes it possible to ignore bulk diffusion [28]. The process of intraparticle diffusion and external diffusion are the possible rate controlling steps. Several models have been used to described the effect of external diffusion and intraparticle diffusion of solute on adsorbent. In the present work Spah and Schlunder model [35] and Weber and Morris model [36] have been chosen to describe the external diffusion and intraparticle diffusion respectively on the resin.

Spahn and Schlunder model

If external diffusion of metal cations (within the diffuse layers outside the sorbent) is the rate limiting step then the sorption data can be fitted into the following equation [35].

$$\ln (C_t/C_o) = -K_s (A/V) \times t \qquad (8)$$

where K_s is external diffusion coefficient, C_o is initial metal ion concentration, C_t is concentration at time t, A/V is external sorption area to the total solution volume, t is sorption time. The external diffusion coefficient can be calculated from the slope of the straight line obtained from the plot of ln (C_t / C_o) versus t (Fig 15).

The external diffusion model shows excellent correlation with the sorption data, with high correlation coefficients obtained. This would indicate that the sorption of metal ions under study is a probably a surface process occurring on the exterior of the sorbent particle. The external diffusion coefficient (K_s) values of Ni(II), Cu(II), Zn(II) , Cd(II) and Pb(II) for pHFR was calculated, the values are given in the Table 4. The value for external diffusion coefficient (K_s) for pHFR is in the range of 0.00193-0.00276 mmol/h. Similar type of results were reported by Prasad et al [28], while studying uptake behaviour of copper and nickel on methacrylic acid-co-ethylene glycol dimethacrylate polymer.

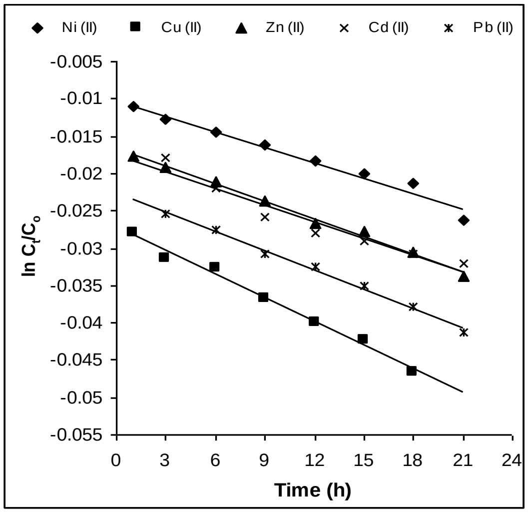


Figure 15. External diffusion plot for the sorption of metal ion exchange of pHFR resin

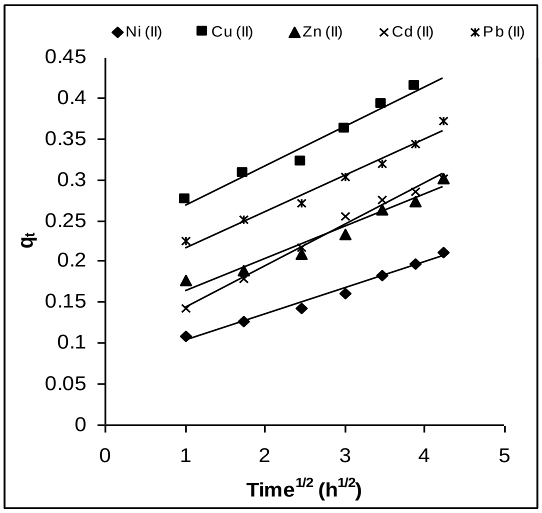


Figure 16. Intra-particle diffusion plot for the sorption of metal ion exchange of pHFR resin

Weber and Morris model

An empirically found functional relationship, common to the most sorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber and Morris plot [36], rather than with the contact time, t .

$$q_t = k_{id}\, t^{1/2} + I \tag{9}$$

where, q_t is amount of sorbate retained at time t, k_{id} is intra-particle diffusion rate constant, I is thickness of the boundary layer.

According to above equation (9), a plot of q_t versus $t^{1/2}$ should be a straight line (Fig 16) with a slope k_{id} and intercept I when sorption mechanism follows the intraparticle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., larger the intercept the greater is the boundary layer effect [27].

The plot of q_t versus $t^{1/2}$ is presented in Fig. 16. The values of I for pHFR for various metal ions under study are found in the range of 0.071-0.222 mmol/L $h^{1/2}$, Weber and Morris [36] pointed out that a functional relation common to the majority of the intraparticle diffusion treatment is that the uptake varies almost proportionately with the half power of the time. The values intraparticle coefficient (K_{id}) and I are given in Table 4. From the external diffusion and intraparticle diffusion data, it can be concluded that diffusion process is mainly controlled by intraparticle diffusion.

Table 4. Data of external and intra-particle diffusion rate constant

Metal ions	External Diffusion		Intra-particle diffusion		
	K_s	R^2	K_{id}	I	R^2
Ni (II)	0.00193	0.912	0.0319	0.071	0.983
Cu (II)	0.00276	0.921	0.0477	0.222	0.969
Zn (II)	0.00220	0.914	0.0390	0.125	0.963
Cd (II)	0.00193	0.938	0.0504	0.094	0.992
Pb (II)	0.00249	0.903	0.0443	0.173	0.979

Conclusion

The elemental analysis, FTIR and 1H-NMR confirmed the assumed structure of terpolymeric resin mentioned in scheme-I. No sharp peaks are observed in the difractogram of the resin confirms the amorphous nature of the pHFR resin. Thermogravimetric analysis suggests that the decomposition reaction is first order, exothermic and slower one. The pH titration study of the resin was carried and results are studied. The pH titration study of the resin was carried and results are studied. General trend of chelating ability of resin is Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II). Thus, resin can be used for removal of heavy toxic metals. From the result of rate of exchange it is observed that the time required for 50 % exchange ($t_{1/2}$) for zinc(II) and lead(II) is about 55 min., for cadmium(II) and nickel(II) is 2.5 h, for copper(II) is 48 min. respectively. The data obtained from Langmuir and Freundlich equations indicating beneficial adsorption occurring through monolayer mechanism involving chemisorption (ion-exchange/chelation). Thermodynamic parameters shows that adsorption process is exothermic and spontaneous, which implies increased sorption at higher temperature. From the results of various diffusion models, it can be concluded that diffusion process is mainly controlled by intra-particle diffusion.

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