



A Benign Approach of Microwave Assisted Synthesis of Copolymeric Resin with Improved Thermal, Spectral and Ion-exchange Properties

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ABSTRACT

Microwave irradiation (2.46 GHz, 300 W) was utilized to produce salicylic acid-formaldehyde-resorcinol (SFR-M) chelating resin in DMF media at $80\pm 2^\circ\text{C}$ with ecofriendly approach involving shorter time as compared to conventional method. The resulting resin was characterized by FTIR, ^1H NMR, and elemental analysis. The investigation of the surface characteristics of the resin was carried out by examination of resin morphology using scanning electron microscopy (SEM) at different magnifications. Broido and Horowitz-Metzger methods were used to calculate the energy of activation (E_a) from TGA. The chelating properties of synthesized resin such as total ion-exchange capacity, effect of pH, concentration and time for different metal ions Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) were also studied by employing batch equilibrium method. The quantitative separations of metal ions from binary [Ni(II)-Cd(II)] and ternary [Ni(II)-Zn(II)-Cd(II)] synthetic mixtures were performed by column chromatography at $25\pm 2^\circ\text{C}$. The constituents of brass were also analyzed by selective sorption on column at optimized distribution coefficient (K_d) values. Microwave assisted chelating resin is specific for transition metal ions rather than selective as compared with the resin synthesized by conventional method.

Key Words:

microwave irradiation;
chelating resin;
batch equilibrium;
morphology;
column chromatography.

INTRODUCTION

The analyses of trace elements in natural and waste water, biological, industrial and geological samples in complex mixtures are the challenging problem in analytical chemistry. The heavy metals such as Pb, Cd, Hg, etc. are toxic to most organisms [1]. The production of nuclear weapons has also resulted in dangerous waste problems.

Burning of coal in power station, industries or other combustion units emits particulate matter that carries hazardous substances like toxic metals. In addition, there is a growing interest to recover the precious metals due to both environmental and economic reasons. During the recovery process, the important problem arises that the

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target elements present in environment are in such low concentration that many sophisticated instruments fail to measure accurately. The rapid development of electronic instrumentation has created powerful analytical tools but it can give erroneous result due to the presence of matrix elements. To obtain reliable data, the best course is to separate the analytes of interest from the matrix constituents and to determine them in isolated state. Thus, preconcentration and separation followed by analysis is mandatory particularly when analyte is present at trace level.

Solvent extraction [2] and ion-exchange resin [3] are the two most common methodologies for the preconcentration and separation of trace elements from various matrices. Solvent extraction is inefficient due to the requirement of large volume of solvent which may create health problem. Solid phase extraction using chelating resins is the method of choice due to its high separation efficiency, good reproducibility of retention parameters and high sensitivity. They have found widespread applications in the enrichment of metals from various sources.

Chelating resin is basically an organic copolymer containing donor atoms which can successfully interact with the metal ions through coordinate bond whereas polymer backbone makes them more efficient by offering large surface area. It has some advantages over solvent extraction such as higher preconcentration factor, better efficiency, greater reproducibility and greater simplicity in handling [4].

The preparation of such chelating resins were carried out in two different ways, first of which involves the physical adsorption of chelating ligand on the support such as polystyrene-divinyl benzene whereas the second one involves the incorporation of such ligand through covalent linking into the matrix. The adsorbed resin has little stability in high ionic strength as well as in organic solvent. The partial elution of the chelating ligand with the high concentration of perchloric or hydrochloric acid makes the use of the column impossible for several sorption-elution processes. Thus the functionalization of the chelating ligand is a promising technique. In recent years, the developments of suitable functionalized chelating resin for trace metal preconcentration and separation provide a new impetus to extraction approach. Kantipuly et al. [5] discussed the usefulness of the

chelating polymers including some commercial resin based polystyrene, silica gel, cellulose, etc. in chemical analysis with special emphasis on uranium preconcentration. Bilba et al. [6] and Garg et al. [7] also focused on the application of chelating sorbents to various samples. Beauvais et al. [8] reviewed the analytical applications of chelating resins in chemical analysis.

A wide range of chelating ion-exchange resins has been prepared from different monomers containing epichlorohydrin and related monomers [9]. A chelating resin based on 2,4-dihydroxypropiononeoxime-urea-formaldehyde reported by Patel et al. [10]. Ion-exchange resins have proved to be of great importance due to its applications. There are many useful reports on ion-exchange separation methods in chemical processes [11-12].

A number of investigations on chelating resins has been reported. A chelating resin based on salicylic acid functionalized polystyrene sorbent Amberlite XAD-2 is reported by Singh et al. [13]. Salicylic acid anchored Amberlite XAD-2 was used by Singh et al. [14] for Zn (II) and Pb (II) recovery.

Roy et al. [15] synthesized chelating polymer sorbent through the copolymerization of styrene and maleic anhydride in the presence of divinylbenzene as a cross-linking agent, followed by hydrolysis. This polymeric resin, bearing O donor groups, had the advantage of being stable in basic and saline media, unlike its linear analogue. Jadhao et al. [16] synthesized resin by condensation of 2,2'-dihydroxybiphenyl and urea with formaldehyde in 2:1:3 molar ratio in presence of 2 M HCl as a catalyst. Joshi et al. [17] used poly[2,4-dihydroxybenzophenone]butylenes resin which is selective for transition metal ions. This polymeric ligand forms 1:2 metal-ligand complexes with Ni (II), Co (II), Cu (II), and Zn (II). All the chelates are paramagnetic in nature except Zn (II) chelate which is diamagnetic. The ion-exchange study of the resin was checked by batch equilibrium method with selected metal ions at varying electrolyte concentration, pH and time. It is found that resin can be used as an ion-exchanger. Dutta et al. [18] synthesized resin containing poly[(2,4-dihydroxybenzophenone)butylene] and its polychelates with transition metals.

Microwave assisted synthesis of the chelating resin was introduced first by Mondal et al. who mod-

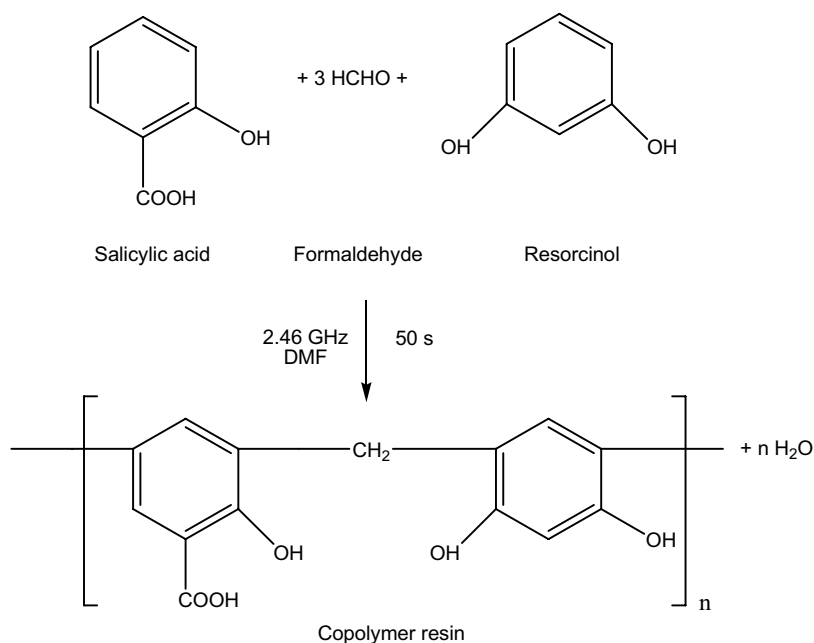


Figure 1. Synthesis of copolymer by microwave irradiation.

ified chloromethylated polystyrene DVB (2%) with *o*-aminothiophenol S-acetic acid under a microwave irradiation for 45 min at 180 W power level [19] instead of classical 40 h refluxing. The resin thus obtained was compared with resin obtained by classical heating in terms of yield, IR and elemental analyses and it was found that the products are identical. By using the same technique, an adenine anchored polystyrene DVB (2%) was also synthesized by the same group of workers [20].

Microwave assisted synthesis is a green, ecofriendly and a short-time process. In the present communication, an attempt has been made to compare the thermal, spectral and ion-exchange properties of microwave assisted synthesized SFR-M resin with conventional SFR resin (SFR-C) [21].

The present work concerns the study of ion-exchange efficiency of transition and post-transition metal ions. The exchange behaviour of the various metal ions is dependent on the physical properties, morphology and method of synthesis.

EXPERIMENTAL

Apparatus

C, H and N elements were analyzed on a Carlo Erba

Elemental Analyzer Model 1106 at Saif, Mumbai. Fourier transform infrared spectra of the microwave assisted synthesized resin sample has been scanned in the region of 400-4000 cm^{-1} in KBr pellets on Shimadzu FTIR spectrophotometer model 8201 pc at Saif, Mumbai. ^1H NMR Spectrum was scanned at 300 MHz with deuterated dimethyl sulphoxide (DMSO-d_6) solvent on Bruker-DPX-200 spectrometer with a sweep time of 10 min at Saif, Mumbai. The morphology of SFR-M resin was examined by micrographing its surface using scanning electron microscopy at 200 \times and 1000 \times magnifications with a Philips XL30, Japan at Saif, Mumbai. The non-isothermal thermogravimetric measurement of the tercopolymer was performed at Saif, Mumbai. Mettler TA 4000 System with Pt-Pt Rh thermocoupled from 20-1000 $^\circ\text{C}$ at a linear heating rate of 10 $^\circ\text{C}/\text{min}$ in atmospheric air was used to obtain the thermogram of present SFR-M resin. The pH was measured with an Elico pH meter (Hyderabad, India, Model LI-120-digital). The metal sorption studies of the chelating resin SFR-M were generally carried out on columns of 1 cm in diameter and length of 17 cm. The batch method was also employed.

Materials

Stock solution (0.1 mol.L^{-1}) of nickel (II), zinc (II),

copper (II), cadmium (II) and lead (II) were prepared by dissolving appropriate amounts of analytical grade acetate salts in deionized water acidified with 10 mL of the corresponding acid. These were standardized [22] before use. Working solution of these metal ions was obtained by dilution of the above solution with double distilled water. The pH of the solutions during each experiment, whenever required, was adjusted with 0.1 mol.L⁻¹ HCl and 0.1 mol.L⁻¹ NaOH or buffer solutions. For pH 3.0-5.0, acetate buffers were prepared from 0.1 mol.L⁻¹ acetic acid and 0.1 mol.L⁻¹ sodium acetate. For preparing buffer solution of pH 6.0-7.0 solution of 0.5 mol.L⁻¹ sodium acetate was used. Salicylic acid was used as received from Ranbaxy Fine Chemicals (purity>99%) purified by rectified spirit. Resorcinol was obtained from SRL Mumbai (extra pure 99%) purified by rectified spirit. Formaldehyde (Qualigens Fine Chemicals, Mumbai, 37%) was used as received. Unless otherwise stated, all the reagents were of analytical reagent grade. The glassware used was washed with chromic acid, ethanol and finally soaked in nitric acid overnight and thoroughly washed with distilled water.

Synthesis of Microwave SFR-M Resin

In the first step, salicylic acid (13.8 g, 0.1 mol) was taken in a 250 mL three-necked round bottom fitted with a stirrer, a thermometer and a condenser and was dissolved in DMF solvent (20 mL). To that formaldehyde (0.3 mol as 37%) and a solution of resorcinol (11 g, 0.1 mol) in 10 mL DMF were added simultaneously dropwise giving a clear solution and was stirred for 1 h. The mixture was refluxed in microwave oven using irradiation of 2.46 GHz at 80±2°C for 50 s until a viscous solution was obtained with the formation of a hard mass of resin. The colour of resultant resin is red-brown.

The resin was washed with DMF and finally with water to remove monomer impurities. The resin was then sealed and cured at 70-75°C for 12 h stored in polyethylene bottle. As carboxylic acid groups normally are decomposed above 100°C, the resin was cured below 90°C. After complete washing, the yield of the resin was found to be 67%.

The dry resin sample free from impurities was directly examined for FTIR, ¹H NMR, SEM, elemental and thermogravimetric analysis. The reaction

scheme is shown in Figure 1 [20].

Resin Pretreatment

To convert the SFR-M resin sample in H⁺ form, the resulting hard mass was crushed to -20+30 or -60 +100 BSS mesh size as needed. The resin was conditioned by alternate treatment with 4% NaOH and 0.1 N HCl solutions. After several alternate regeneration cycles, the resin was washed until free from regenerant and finally with distilled water. The resin was air dried to remove surface moisture.

Physico-chemical Properties

Total ion-exchange capacity and moisture content of the SFR-M resin were determined by the method reported by Kunin et al. [23]. The pH titrations for the SFR-M resin was carried out according to the procedure described by Kunin [24]. True density, apparent density, void volume fraction, concentration of ionogenic groups, and volume capacity were determined as per the method reported by Helfferich [25]. The rate of ion-exchange and thermal stability of the SFR-M resin was determined according to the procedure described by Krishnaswamy et al. [26]. The adsorption properties such as the effect of pH on metal ion-exchange capacity, effect of concentration for different metal ions and the effect of time were also studied [27].

Column Packing

A calibrated 50 mL burette was used as chromatographic column of 1 cm in diameter, in which a thoroughly mixed and well soaked hydrated resin in H⁺ form having uniform particle size was to be packed. The formation of air pockets in the column should be avoided during the filling and therefore deionized water was added in the column to a depth of several inches before the resin slurry was passed into the column. For resin handling procedures, the use of deionized water was recommended to prevent the occurrence of ion-exchange under uncontrolled conditions.

The water swollen resin having uniform particle size (20-50 mesh) was transferred to a beaker and covered with deionized water. The excess water was decanted from the resin so that the mixture was thick slurry. The slurry (1:2 resin:water) was poured along

the walls of the column, allowing the particles to settle so as to form the compact resin bed free from any air pockets. The column length was 17.0 cm. The resin bed was then back washed for several times at 50% expanded height. The back wash flow was then stopped and the resin was allowed to settle. When the resin had settled, the effluent screw clamp was opened and water was allowed to flow down upto 1.0 cm on the top of the resin bed. The above back wash and drain procedures were repeated until the resin bed of 17.0 cm depth was reproducible. After the column was filled, the resin was kept covered with the water. This column was used for the binary mixture, ternary mixture and Brass constituents' analysis.

RESULTS AND DISCUSSION

Physico-chemical Properties

The percentage moisture of the SFR-M resin in the H⁺ form is 7.02. The known values of percentage moisture for the commercial resins (cationic form) are 43-53% for IRC-50/75 (weak acid, active group, COO-) and 42-50 for IRC-84 (weak acid, active group, COO-). Thus, the resins under investigation have very low range of percentage moisture. This may be attributed to high degree of cross-linking.

The value of d_{res} of SFR-M resin is 1.27 g/cm³. The true density of commercial resin generally lies between 1.10 to 1.50 g/cm³. Known values of density for commercial resins in H⁺ form are 1.25 g/cm³ for IRC-50/75 (weak acid, active group, -COO-), 1.19 g/cm³ for IRC-84 (weak acid, active group, -COO-) and 1.16 g/cm³ for IRC-72 (weak acid, active group, -COO-). The result obtained indicates that the resin has density comparable to that of commercial samples and the value is adequate to avoid the floating of resin particles. Floating of resin particles is undesirable in chromatographic study, as it hampers the formation of compact columns.

The value of d_{col} of SFR-M resin is 0.69 g/mL and it shows that this resin has comparatively low apparent density than the commercial resins (IRC-84). It may be because of change in polymeric matrix, difference in functional groups and the method of synthesis. The void volume fraction was calculated as:

$$\text{Void volume fraction} = 1 - d_{col}/d_{res}$$

Table 1. Physico-chemical properties of SFR-M resin.

Properties	Value (SD)*
Moisture content (%)	7.02 (± 0.05)
True density (d_{res})	1.27 (± 0.01) g/cm ³
Apparent density (d_{col})	0.69 (± 0.01) g/mL
Void volume fraction	0.45 (± 0.01)
Sodium ion-exchange capacity	5.97 (± 0.05) meq/g
Concentration of fixed ionogenic group	7.03 (± 0.05)
Volume capacity	3.87 (± 0.05) meq/cm ³

(* Average of 5 times determinations.

The value of void volume fraction of SFR-M resin synthesized in our laboratory is 0.45. The appreciable value of void volume fraction helps the diffusion of the exchangeable ions on the resin and hence increases the rate of exchange of ions. The sodium exchange capacity of the reported SFR-M resin is 5.97 meq/g of dry resin. It is due to high value of void volume fraction and also the existence of versatile groups like carboxylic acid (-COOH) and hydroxyl (-OH) of polymeric matrix present in the resin. The physico-chemical data of SFR-M resin is given in Table 1.

Resin Stability

The resin stability is usually expressed in terms of copper ion-exchange capacity of the resin. To study the stability of the SFR-M resin, 0.25 g of the moist exchanger was equilibrated at pH 5.0 with acetate buffer solution for 12 h. After decanting the buffer solution, the resin was equilibrated for 24 h with 50.0 mL of 0.1 M cupric acetate solution of pH 5.0. The copper exchange capacity of the resin was determined by the estimating amount of copper taken up by the resin. The metal was eluted with 1.0 M HCl and the resin was regenerated. Again the same resin was used for determination of copper exchange capacity. The procedure was repeated twenty times to study the resin stability.

It was observed that up to 12 loadings and acid washing cycles, sodium exchange capacities and copper ion-exchange capacity of reported resin varied by less than 2%. The SFR-M resin shows good stability indicating the greater chemical stability.

Thermal Stability

From the data regarding the thermal stability of the

Table 2. Thermal stability data of SFR-M resin.

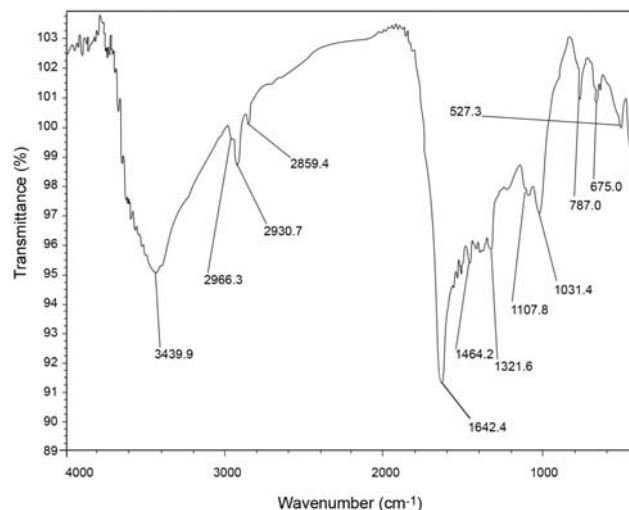
Temperature (°C)	Capacity (meq/g dry resin) (SD)*
40	5.97 (±0.03)
60	5.97 (±0.03)
80	5.97 (±0.03)
100	5.97 (±0.03)
120	5.97 (±0.03)
140	5.80 (±0.03)
160	5.72 (±0.03)

(* Average of 5 times determinations.

SFR-M resin (Table 2), it is revealed that there is no change in the total capacity of the resins up to 120°C. Hence this resin can be safely used upto 120°C. Above this temperature, they show a decrease in the capacity when the heated resin is regenerated and tested, this could be due to distortion of some of the -CH₂- bridges, creating more gaps in the polymeric matrix thus reducing the chelating tendency of the functional groups.

Spectral Characterization of SFR-M Resin

Although the tercopolymer SFR-M resin is partly soluble in DMSO-d₆, it is however, insoluble in most of the organic solvents. The composition of the polymeric unit was assigned on the basis of detailed study of the elemental analysis of the polymer, FTIR and ¹H NMR spectral studies and thermogravimetric analysis (TGA). The morphology of tercopolymer is examined by scanning electron micrographs (SEM).

**Figure 2.** FTIR Spectrum of the SFR-M resin.

FTIR Spectra

FTIR Spectrum data are presented in Table 3 and the spectrum is shown in Figure 2. IR Spectrum recorded in a KBr matrix for the SFR-M tercopolymer showed a peak in the range of 3500 to 3200 cm⁻¹ [27], attributed to the stretching vibration of the -OH group of the polymeric associated phenolic group and the intermolecular H bonding between the hydroxy group of -COOH from different acid units in the polymeric chain. The band at 1642.4 cm⁻¹ was observed because of >C=O (carboxylic ketonic) stretching [28]. A sharp peak at 2930.7 cm⁻¹ may have been due to aromatic skeletal ring stretching modes [29]. The band observed between 1200 cm⁻¹ and 800 cm⁻¹ may have been caused by a 1, 2, 3, 5-tetra substituted benzene ring [28-29]. The inflections around 1464.2 cm⁻¹,

Table 3. FTIR Spectra of SFR-M resin.

Vibrational mode	Frequency (cm ⁻¹)	
	Reported	Observed
Phenolic (-OH) stretching	3500 - 3200	3439.9
Aromatic ring stretching (C-H)	2700 - 3000	2930.7
Methylene(-CH ₂) stretching	3000 - 2850	2859.4
>C=O stretching (carboxylic ketone)	1690 - 1650	1642.4
Methylene bridge (-CH ₂) modes		
Bending	1450	1464.2
Rocking	760	787
Wagging	1300 - 1200	1321.6
1,2,3,5-Substituted benzene ring	1200 - 800	1107.8 & 1031.4

Table 4. ^1H NMR Spectra of SFR-M resin.

Nature of proton assigned in the NMR spectrum	Expected chemical shift (ppm)	Chemical shift (δ) of the terpolymer (ppm)
Aromatic (Ar-H)	7.3 - 8.8	7.4
Phenolic (Ar-OH)	7.5 - 7.12	7.8
Carboxylic (Ar-COOH)	7.41	7.41
Ar - CH_2 - Ar	3.7 - 3.10	3.74

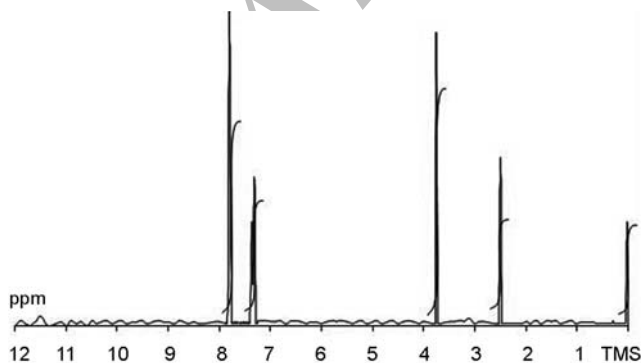
787 cm^{-1} and 1321.6 cm^{-1} were due to the stretching, rocking and twisting modes of $-\text{CH}_2$ which suggested the presence of methylene bridges in the tercopolymer [29-30].

NMR Spectra

^1H NMR Spectrum of SFR-M tercopolymer shown in Figure 3 exhibited signals in the region of 7.4-7.8 δ (ppm) which may have been due to the proton of the aromatic ring (Ar-H) and the signal in the region of 7.8 δ (ppm) may have been due to phenolic -OH proton in the hydrogen bonding (Ar-OH) [27-29]. The signal displayed at 7.41 δ (ppm) may have been due to the carboxylic proton of Ar-COOH [29-30]. A methylene proton Ar- CH_2 -Ar is inferred by the appearance of a weak singlet signal at 3.74 δ (ppm) [28-30]. The spectral data are presented in Table 4.

SEM Studies

The scanning electron micrographs of SFR-M resin exhibit spherulites. The spherulites are typical crystalline formations and they grow in high viscous and concentrated solutions. In the present case, the spherulites are complex polycrystalline formation composed of simplest structural forms having smoother surface free from defects' growth. The

**Figure 3.** ^1H NMR Spectrum of SFR-M resin.

crystals are smaller in surface area with more closely packed structures with no visible pits. This could be the reason of low ion-exchange capacity of higher hydrated size of lead ion.

The white bar at the bottom of the SEM microphotographs represents the scale. The two different magnifications are represented as follows: Figure 4a exhibits two magnifications 200x and 1000x for SFR-M resin.

The SFR-M resin appears to be reddish-brown in colour. The morphology of the SFR-M resin exhibits the crystalline structure with deep corrugations which is clearly visible in SEM photographs of SFR-M resin (Figure 4a). Figure 4b exhibits two magnifications, 200 \times and 1000 \times for SFR-C resin. For the same magnification, it is observed that particle size for SFR-M resin is smaller than SFR-C resin. In Figure 4b of SFR-C resin, there is evidence of more amorphous character with less closed packed surface having deep pits. The resin thus possesses higher ion-exchange capacity for lead ions.

Elemental Analysis

The %C, %H, and %N were calculated from the general formula ($\text{C}_{14}\text{H}_{11}\text{O}_7$) of the repeating unit of the assumed structure of the SFR-M resin. The results of the elemental analysis are in good agreement with calculated values of %C, %H, and %N, which are shown in Table 5.

Thermogravimetric Analysis

Thermal stability has been defined in many different qualitative and arbitrary ways. Arbitrary methods to assess the thermal stability of polymers from the TG traces have briefly been described by Reich et al. [31]. Several temperature characteristics used for the qualitative assessment of relative thermal stability of polymers are initial decomposition temperature (T_1), tem-

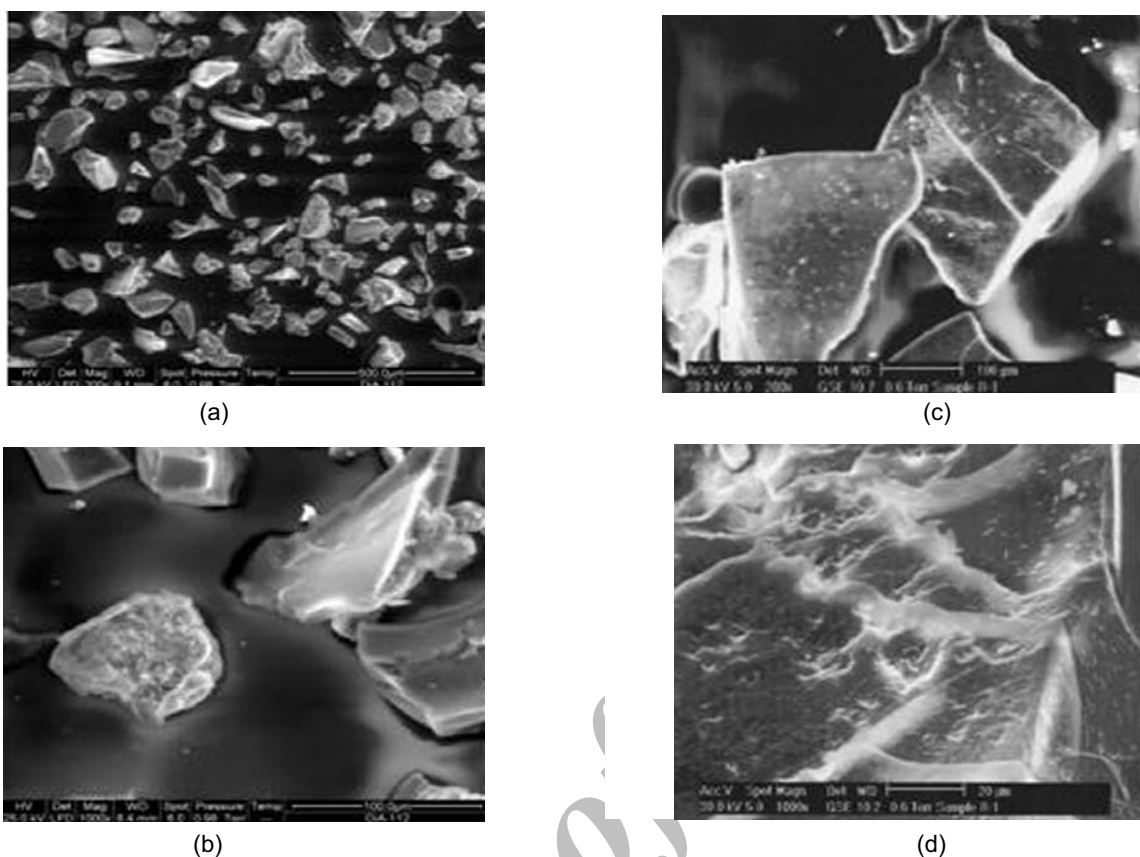


Figure 4. SEM Photographs of: (a) SFR-M resin at 200 \times , and (b) SFR-M resin at 1000 \times , (c) SFR-C resin at 200 \times , and (d) SFR-C resin at 1000 \times magnifications.

perature for maximum rate of decomposition (T_{max}) and half volatilization temperature (T_{50}). These parameters have proved to be very useful to assess, at least qualitatively, the thermal stability of polymers. The values of these characteristic parameters are summarized in Table 6.

The thermograms of SFR-M and SFR-C indicate (Figure 5) that both conventional SFR-C and microwave assisted synthesized SFR-M resin exhibit a two-step degradation. The first step decomposition starts at 190 $^{\circ}$ C which extends up to 290 $^{\circ}$ C involving 20% weight loss in both types of resin samples. The weight loss may be due to the removal of carboxylic

group (-COOH) as CO_2 . But the second step decomposition in conventional method begins at 400 $^{\circ}$ C and extends up to 600 $^{\circ}$ C and in microwave method the second step decomposition begins at 750 $^{\circ}$ C and extends up to 925 $^{\circ}$ C with 68% weight loss and considerably a good thermal stability is observed. The maximum rate of weight loss occurs at 240 $^{\circ}$ C and 600 $^{\circ}$ C for the steps one and two, respectively. In microwave conventional method the same occurs at 240 $^{\circ}$ C and 800 $^{\circ}$ C for the steps one and two, respectively.

Table 5. Elemental analysis of SFR-M resin.

Resin	Analysis (%) calculated (found)		
	C	H	N
SFR-M	61.34 (61.58)	6.26 (6.08)	Nil

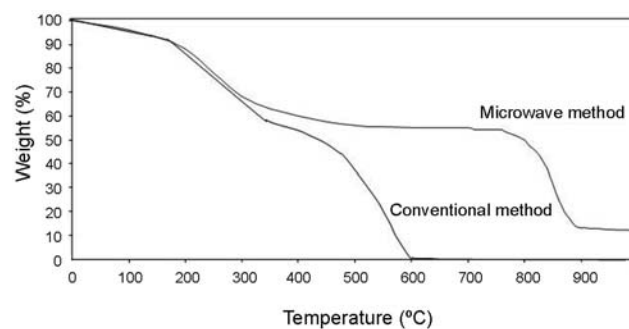


Figure 5. Thermograms of SFR-M resin and SFR-C resin.

Table 6. Thermal behaviour of SFR-M resin and SFR-C resin.

Polymer	Step	T_i	T_{max}	T_{50}	T^f	ipdt
SFR-M	I	190	240	540	290	345
	II	750	800		925	
SFR-C	I	190	240	426	290	315
	II	400	426		600	

The activation energies of SFR-M resin for Broido method [32] step-I is $E_a = 25.71$ kJ/mol and for step-II is $E_a = 59.676$ kJ/mol (Figure 6a) and for Horowitz-

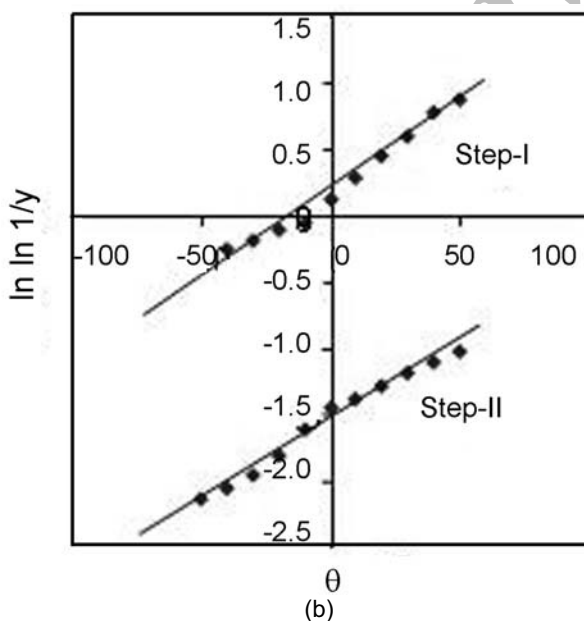
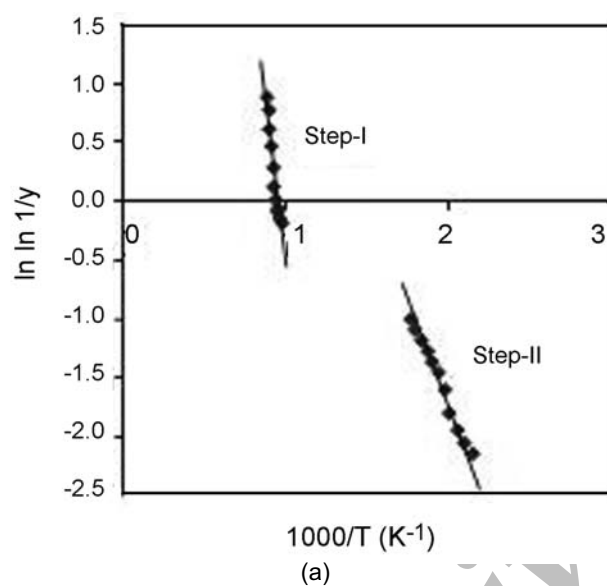


Figure 6. (a) Broido plot for SFR-M, and (b) Horowitz-Metzger plot for SFR-M resin.

Metzger method [33] step-I is $E_a = 26.12$ kJ/mol and for step-II is $E_a = 60.534$ kJ/mol (Figure 6b) which are shown in Table 7.

The magnitude of the activation energies of thermal degradation satisfactorily corresponds to the activation energy of polymeric network rupture.

The SFR-M resin undergoes the polymeric network formation under the influence of polarized condition of monomeric molecules. Hence orientationally, the SFR-M resin macromolecules are arranged parallel to one another and therefore their intermolecular bond interactions are summed up along the length of macromolecular network.

Since there are very many interactions, the total interchain interaction grows very sharply and becomes commensurable with the chemical bonds. To rupture the more oriented intermolecular bonds, a higher energy is required. Therefore, the second step energy of activation of SFR-M resin $E_a = 59.676$ kJ/mol (Broido) and 60.534 kJ/mol (Horowitz-Metzger) is higher than the conventionally synthesized SFR-C resin $E_a = 32.98$ kJ/mol (Broido) and 33.17 kJ/mol (Horowitz-Metzger) [21].

Between the two methods, the Broido method is expected to provide reliable estimates of E_a , since no other temperature characteristics are involved. The value of activation energies calculated according to

Table 7. Activation energy in kJ/mol of degradation of SFR-M and SFR-C resins.

Resin	Energy of activation (E_a) (kJ/mol)			
	Broido method		Horowitz-Metzger method	
	Step-I	Step-II	Step-I	Step-II
SFR-M	25.71	59.676	26.12	60.534
SFR-C	25.71	32.980	26.12	33.170

the Broido method and Horowitz-Metzger method are in good agreement.

Optimum Conditions for Sorption of Metal Ions

An amount of 0.25 g SFR-M resin was taken in a 100 mL beaker and it was treated with 25 mL of 2 mol.L⁻¹ HCl and washed with double distilled water until free from acid. A set of solutions of 50 mL volume, each containing each of the five metal ions in the concentration range of 0.05-0.25 mol.L⁻¹, was taken. The pH of the solution was varied and adjusted in the range of 3.0-7.0. The effect of pH on sorption is shown in Figure 7. The use of 2-4 mL of acetate buffer solution to adjust the pH of all metal ion solutions (50 mL) in the range of 3.0-6.0 did not affect their sorption behaviour. The optimum pH for nickel (II) was at 7.0, for copper (II) at 5.5, for zinc (II) at 6.0, for cadmium (II) at 5.5 and for lead (II) at 6.0.

The sorption capacity (maximum amount of metal sorbed per gram of resin) of each metal was determined by saturating 0.25 g of SFR-M resin in the glass stopper bottle with a metal ion solutions at room temperature for 24 h with intermittent shaking. After 24 h the solutions were decanted and the non-adsorbed metal ions were estimated by complexomet-

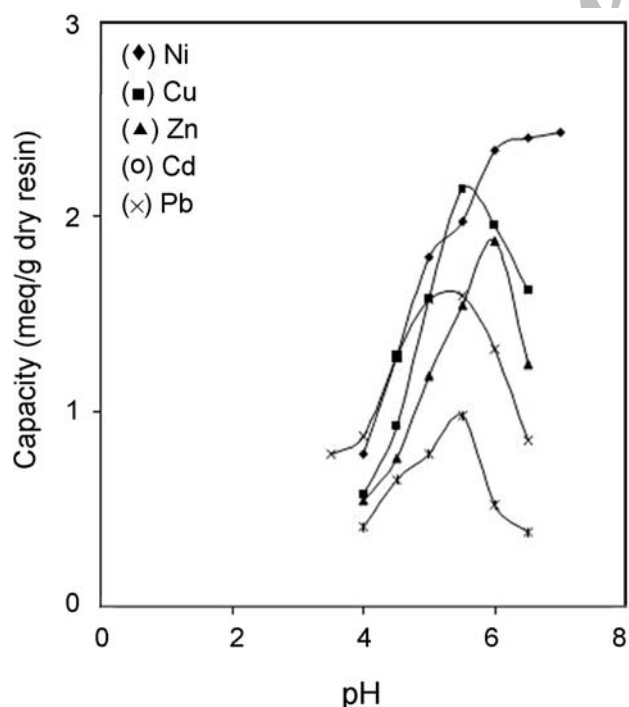


Figure 7. Effect of pH on metal ion capacity for SFR-M resin.

Table 8. Maximum metal ion capacity of optimized pH for SFR-M resin.

Metal ion	pH	Capacity (meq/g)	
		SFR-M	SFR-C
Nickel (II)	7.0	2.43	1.95
Copper (II)	5.5	2.43	2.28
Zinc (II)	6.0	2.93	1.87
Cadmium (II)	5.5	1.59	2.57
Lead (II)	6.0	0.97	3.06

ric titration with 0.1 M EDTA solution using appropriate indicators. A blank experiment was also run simultaneously. The metal uptake was calculated by a different method [25]. The result is shown in Table 8. The difference in the sorption capacities of the various metal ions is due to the difference in their sizes (also caused by the varying degree of hydration) and in their binding constants with SFR-M resin. Table 8 shows the value of optimum pH exhibiting maximum capacities for each metal ion to be 0.25 mol.L⁻¹. The SFR-M resin exhibits greater capacities for Ni (II), Cu (II), Zn (II) (transition metal ions) as compared to heavier metal ions [Pb (II) and Cd (II)] at its optimum pH. Thus the microwave assisted resins are more specific rather than selective for transition metal ions. Thus separation and recovery of transition metal ion from matrix containing heavy metal is possible.

The higher capacity of transition metal ions is due to its smaller hydrated size as compared to the hydrated ionic size of heavy metal ions. The size of Pb(II) is greater and the SFR-M resin being more crystalline cannot be exchanged easily on microwave assisted SFR-M resin. This is in contradiction to SFR-C resin exhibiting higher capacities for Pb(II) due to its more amorphous character [21]. Also the difference in capacities for these metal ions is due to its particle size. SFR-M exhibits a smaller particle size and hence greater surface area as compared to SFR-C with larger particle size.

Hence in case of SFR-M smaller particle size, greater the surface area and the crystalline nature of the resin from Table 6, it shows that T_{max} (step-II) of SFR-M is higher at 800°C as compared to T_{max} (step-II) of SFR-C which is 426°C. Therefore, the thermal

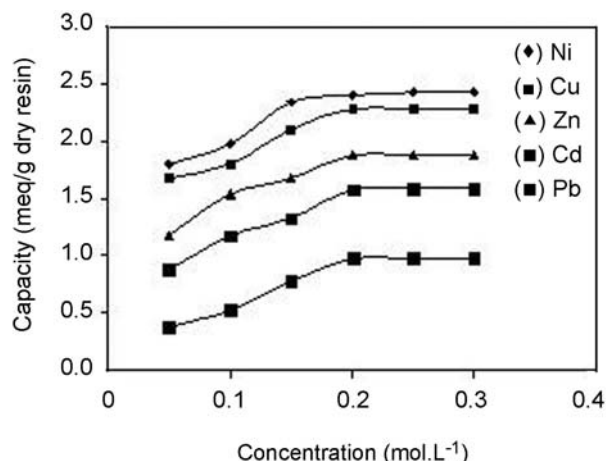


Figure 8. Effect of metal ion concentration on exchange capacity.

degradation (Figure 5) is quite steep in SFR-C resin which is being more amorphous while the thermogram of SFR-M is less steep and it possesses the left out residue unlike SFR-C resin.

Effect of Metal Ion Concentration on Exchange Capacity

The experimental data presented in Figure 8 shows the effect of metal ion concentration on its uptake by sorbent. The examination of data reveals that the amount of adsorbed metal ion increases with the increase in concentration of metal ions up to a particular limit and then becomes constant. 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. However, at higher concentration the available sites of sorption remain constant whereas, more metal ions are available for sorption and subsequently from then the sorption becomes almost constant. For this SFR-M resin, saturation occurs for nickel (II), copper (II), and zinc (II) at 0.25 M and cadmium (II) and lead (II) at 0.2 M concentration of metal ion solution.

Rate of Exchange for Metal Ions

To determine the rate of loading of Ni (II), Cu (II), Zn (II), Cd (II) and Pb (II) on the SFR-M resin, batch experiments were carried out as detailed below. The SFR-M resin (0.25 g) was stirred with 50 mL of solution containing each of the five metal ions (0.2 mol.L⁻¹) at room temperature for different

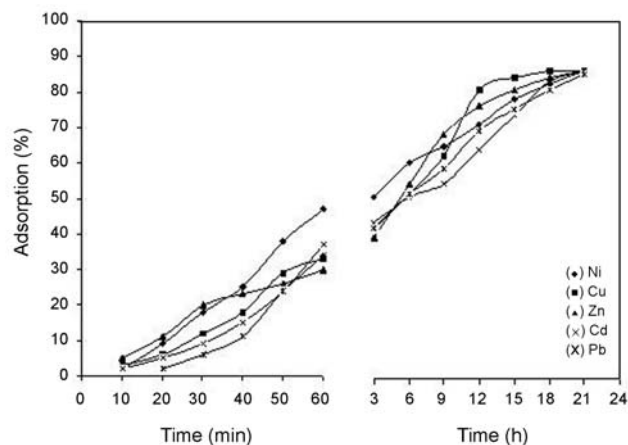


Figure 9. Rate of exchange of SFR-M resin for metal ions.

periods of time. The concentration of metal ions in the supernatant solution was calculated by complexometric titration with 0.1 M EDTA solution using appropriate indicators. The loading half time needed to reach 50% of the total loading capacity was estimated from the curve (Figure 9). The $t_{1/2}$ values were found to be 3 h for Ni (II) and 6 h for Cu (II), Zn (II), Cd (II), and Pb (II). The complete exchange occurs in 24 h for all metal ions.

Effect of Electrolyte Concentration and pH on Distribution Coefficients of Metal Ions

The distribution coefficient values of the metal ions as a function of pH and concentration of electrolyte solution were studied. The K_d value decreases with increasing electrolyte concentration and increases with increase in pH, which is presented in Table 9. The present investigation limits the distribution studies up to a certain pH for each metal ion to prevent the

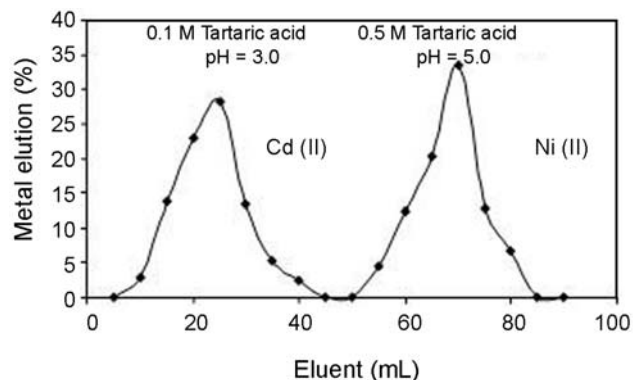


Figure 10. Separation of Ni (II) and Cd (II) on SFR-M resin.

Table 9. K_d Values of metal ions on SFR-M resin in tartrate media at various molarities and pH.

Metal ion	Tartaric acid concentration (M)	K_d values in tartaric acid at different pHs				
		3.0	3.5	4.0	5.0	6.0
Ni (II)	0.1	57.77	38.59	19.80	9.45	3.68
	0.2	24.23	13.48	5.57	1.82	-
	0.3	11.45	7.49	-	-	-
	0.5	-	-	-	-	-
	1.0	-	-	-	-	-
Cu (II)	0.1	48.50	32.80	16.72	6.35	1.80
	0.2	19.40	11.30	3.57	-	-
	0.3	11.87	5.72	1.28	-	-
	0.5	-	-	-	-	-
	1.0	-	-	-	-	-
Zn (II)	0.1	14.34	9.83	6.93	4.10	1.35
	0.2	12.82	8.37	2.71	-	-
	0.3	5.50	-	-	-	-
	0.5	-	-	-	-	-
	1.0	-	-	-	-	-
Cd (II)	0.1	11.71	8.66	5.69	2.81	-
	0.2	7.17	4.24	-	-	-
	0.3	-	-	-	-	-
	0.5	-	-	-	-	-
	1.0	-	-	-	-	-
Pb (II)	0.1	11.54	9.24	4.29	1.85	-
	0.2	4.12	2.76	-	-	-
	0.3	-	-	-	-	-
	0.5	-	-	-	-	-
	1.0	-	-	-	-	-

hydrolysis of metal ions at higher pH. The K_d values decrease with increase in electrolyte concentration and they decrease with increase in pH of the electrolyte. To achieve a more distinct separation of metal ion in a shorter time, the maximum K_d value difference should be selected for optimized condition of chromatography.

Among all the metal ions under investigation, Ni (II) ion shows higher K_d values, whereas lead (II) exhibits lower K_d values. It is because of the larger size of hydrated Pb (II) relative to Ni (II) and the more crystalline structure of SFR-M resin. From Table 8 it is clear that Cd (II) has distribution coefficient of 11.71 as compared to 57.77 for Ni (II) at pH = 3 indi-

cating the possibilities of chromatographic separation of these two ions employing this SFR-M resin at pH=3. Chromatographic separation of these metal ions was achieved and it is presented in Figure 10.

Analytical Applications

Separation of Binary Mixture

Separation of Ni (II) and Cd (II) from equimolar synthetic mixture (2 mL of 5 mg/mL solution of each metal) was achieved by selective desorption. All fractions were individually analyzed for each of the metal ion i.e., Cd (II) and Ni (II). Initially the column was eluted with 0.1 M tartaric acid at pH 3.0. Cd (II) was eluted from 0 to 45 mL of eluate and then Ni (II) was

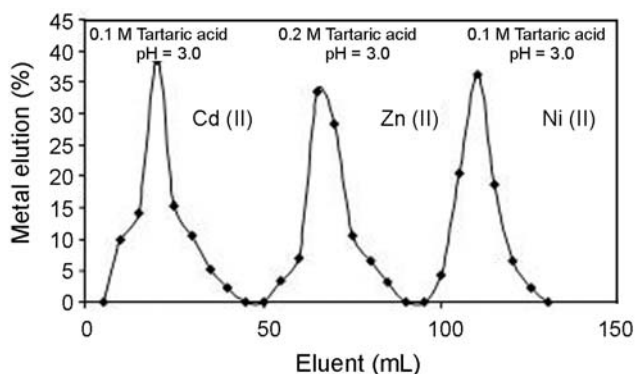


Figure 11. Separation of Ni (II), Zn (II), and Cd (II) on SFR-M resin.

eluted by 0.5 M tartaric acid at pH 5.0. These fractions contain only Ni (II). No cross-contamination was observed for this separation. The recovery of Cd (II) was 90.7% and Ni (II) was 96.20%, which is shown in Figure 10.

Separation of Ternary Mixture

Separation of Ni (II), Zn (II), and Cd (II) from equimolar synthetic mixture (2 mL of 5 mg/mL solution of each metal) was achieved by selective desorption. In this case Ni (II) was eluted by 0.1 M tartaric acid at pH 3.0, Zn (II) was eluted by 0.2 M tartaric acid at pH 3.0 and Cd (II) was eluted by 0.2 M tartaric acid at pH 3.0. For this ternary system the recovery of Ni (II) was 94.3%, Zn (II) was 89% and Cd (II) was 84%. No cross-contamination was observed for this separation, which is shown in Figure 11.

Analysis of Brass

A 100 mg sample of brass was dissolved in about

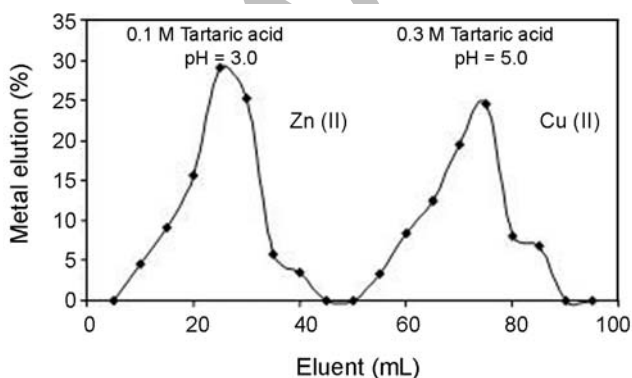


Figure 12. Separation of Brass components on SFR-M resin.

2 mL of concentrated nitric acid and the solution was evaporated just to dryness. The residue was dissolved in 5.0 mL of 0.1 M hydrochloric acid and the solution was filtered. The pH of the filtrate and washings were adjusted to pH 5.0 and made exactly to 50 mL. This aliquot was directly passed through the resin column at a flow rate of 0.3 mL/min. The elution was carried out with 0.1 M tartaric acid solution at pH 3.0. Zn (II) does not form the chelate at pH 3.0 in 0.1 M tartaric acid. Thus Zn (II) was separated from Cu (II). Then Cu (II) was eluted with 0.3 M tartaric acid at pH 5.0. No cross-contamination was observed for this separation. The recovery of Zn (II) was 92% and Cu (II) was 96%, which is shown in Figure 12.

CONCLUSION

The following conclusions have been drawn from the above investigations:

1. Microwave assisted synthesis of the resin (SFR-M) is a green, ecofriendly and big time saver. This is clearly seen from the fact that where the classical method needs 40 min of refluxing it can be synthesized in only 50 s using microwave assistance.

2. With respect to elemental analysis, FTIR, ^1H NMR and physico-chemical properties like moisture content, true density, apparent density, void volume fraction, resin stability and thermal stability it was found that both the products, classically synthesized and microwave assisted synthesized resins were identical.

3. The morphology of the SFR-M resin exhibits a more crystalline structure rather than SFR-C resin. The crystals are smaller in surface area with more closely packed structures with no visible pits. This could be the reason of low ion-exchange capacity of higher hydrated size of metal ions (cadmium and lead).

4. From the study of thermograms of SFR-M resin and SFR-C resin, it clearly shows that higher degree of polymerization could have occurred in SFR-M. This is confirmed by their complete decomposition temperatures. SFR-M completely decomposes at 900°C while SFR-C resin completely decomposes at 600°C . Moreover some left out residues remain at the end of decomposition of SFR-M resin.

5. A perusal of the trends in the rate of exchange clearly indicates that the resin under study shows rapid rates of exchange in the beginning followed by slower rates of exchange, which may probably be due to surface exchange and exchange in the interior due to diffusion. Relatively long times for 50% exchange may probably be due to weakly acidic nature of these SFR-M resin.

6. The SFR-M resin is more selective for transition metal ions rather than post-transition metal ions.

7. The yield of SFR-M resin is slightly greater (67%) than SFR-C resin (64%).

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