Microwave Assisted Benign Method of Chelating Resin Synthesis Having Different Thermal and Ion Exchange Properties

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Summary: Microwave irradiation method was used for synthesis of chelating ion exchange resin derived fom Salicylicacid-Formaldehyde-Resorcinol (SFR-M). The resin was characterized by Elemental analysis, FTIR, TGA and SEM. The Broido and Horowitz-Metzger method were used to calculate the energy of activation (Ea) from TGA. The microwave assisted chelating resin has different thermal behaviour as compared to conventional resin (SFR-C). The sorption capacities of microwave SFR resin for transition metal ions are higher than conventional SFR resin. The separation of binary mixtures [Cu (II) and Zn (II)] in brass and [Ni (II) and Cd (II)] were successfully carried out using Kd value.

Keywords: chelating resin; column chromatography; microwave; morphology

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 target elements present in environment are in so 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 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.

Microwave assisted synthesis of the chelating resin was introduced first by Mondal et al. who modified chloromethylated polystyrene DVB (2%) with o-aminothiophenol S-acetic acid under a microwave irradiation for 45 minute at

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180W power level[4] in stead of classical 40 hour 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 adenine anchored polystyrene DVB(2%)[5] was also synthesized by the same group of workers.

Microwave assisted synthesis is a green, ecofriendly and short time synthesis. 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).[6]

The present work concerns with 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 Part

Synthesis of Microwave (SFR-M) Resin

In the first step, salicylic acid (13.8g, 0.1 mole) was taken in 250 ml three necked round bottom three necked flask fitted with a stirrer, a thermometer and a condenser and was dissolved in DMF solvent (20 ml). To that formaldehyde (0.3 mole as 37%) and a solution of resorcinol (11g, 0.1 mole) in 10 ml DMF were added simultaneously drop wise giving a clear solution and was stirred for an hour. The mixture was refluxed in microwave oven using irradiation of 2.46 GHz at $80 \pm 2\,^{\circ}C$ for 50 seconds 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 hours stored in polyethylene bottle. As carboxylic acid groups normally get 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, ^{1}H-NMR, SEM, elemental and thermogravimetric analysis. The reaction scheme is shown in below Figure 1.[6]

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 0.1N HCl solution. After several alternate regeneration cycles, the resin was washed until free from regenerant and finally with

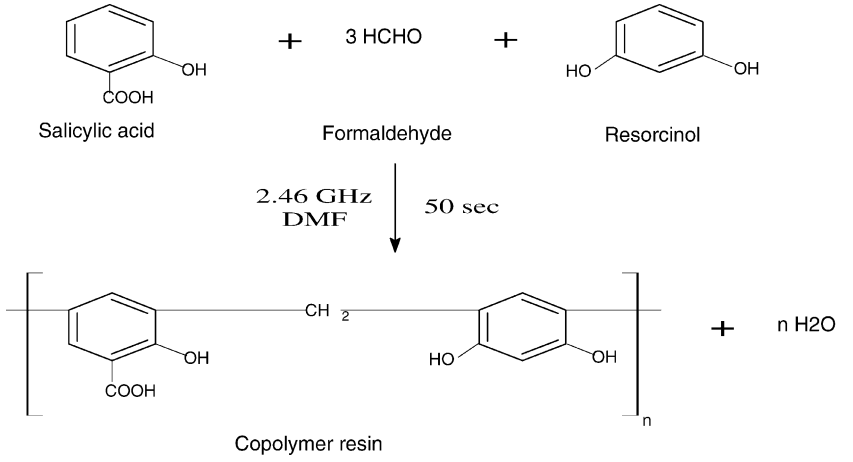

Figure 1.
Synthesis of copolymer by microwave irradiation.

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.[7] pH titrations for the SFR-M resin was carried out according to the procedure described by Kunin.[8] True density, apparent density, void volume fraction, concentration of ionogenic groups, and volume capacity were determined as per the method reported by Helfferich.[9] The rate of ion exchange and thermal stability of the SFR-M resin was determined according to the procedure described by Krishnaswamy and Trivedi.[10] The adsorption properties such as effect of pH on metal ion exchange capacity, effect of concentration for different metal ion and effect of time were also studied.[11]

Results and Discussion

Physico-Chemical Properties

The % moisture of the SFR-M resin in the H^+ form is 7.02. The known values of % 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 % moisture. This may be attributed to high degree of cross linking.

The value of d_{res} of SFR-M resin is 1.27 g/cm^3. The true density of commercial resin generally lies between 1.10 to 1.50 g/cm^3. Known values of density for commercial resins in H^+ form are 1.25 g/cm^3 for IRC-50/75 (weak acid, active group –COO-), 1.19 g/cm^3 for IRC-84 (weak acid, active group –COO-) and 1.16 g/cm^3 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 floting of resin particles. Floting of resin particles is undesirable in chromatographic study, as it hampers 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:

$$\text{Void volume fraction} = 1 - \frac{\text{dcol}}{\text{dres}}$$

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 reported SFR-M resin is 5.97 meq/g dry resin. It is due to high value of void volume fraction and also present versatile groups like carboxylic acid (–COOH) and hydroxyl (–OH) in polymeric matrix present in the resin. The physico-chemical data of SFR-M resin is given in Table 1.

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

Properties	Value (SD)[a)]
Moisture content (%)	7.02 (±0.05)
True density (dres)	1.27 (±0.01) g/cm^3
Apparent density (dcol)	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

Spectral Characterization of SFR-M Resin

FTIR Spectra

The FTIR spectrum of the SFR-M tercopolymer shown in Figure 2. The spectral data is tabulated in Table 2.

SEM Studies

The Scanning Electron Micrographs of SFR-M resin exhibits 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 more smooth surface free from growth of the defects. The crystals are smaller in surface area with more close 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 are as follows: Figure 3a 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 3a). Figure 3b exhibits two magnifications, 200X and 1000X for SFR-C resin. For the same magnification, it is seen that particle size is for SFR-M is smaller than SFR-C. In Figure 3b of SFR-C exhibits more amorphous character with less closed

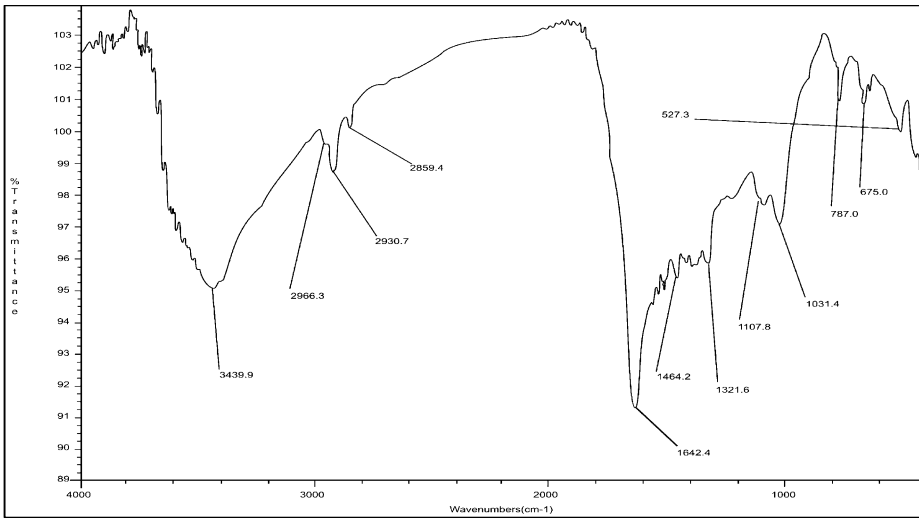

Figure 2.
FTIR spectrum of SFR-M resin.

Table 2.
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	1450	1464.2
1,2,3,5-substituted benzene ring	1200–800	1107.8 & 1031.4

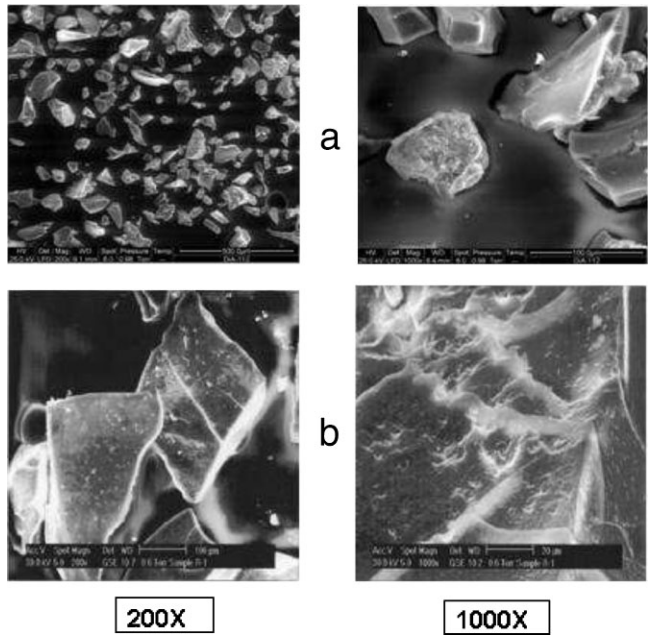

Figure 3.
SEM photograph of (a) SFR-M and (b) SFR-C at 200X and 1000X magnification.

packed surface having deep pits. The resin thus possesses higher ion exchange capacity for lead ions.

Elemental Analysis

The %C, %H and %N was calculated from the general formula ($C_{14}H_{11}O_7$) of the repeating unit of the assumed structure of the SFR-M resin. The results of the elemental analysis are good agreement with calculated values of %C, %H and %N, which is shown in Table 3.

Thermogravimetric Analysis

The thermograms of SFR-M and SFR-C indicate (Figure 4) that both conventional SFR-C and Microwave assisted synthesized SFR-M resin exhibit two step degradation. The first step decomposition starts at 190 °C which extends up to 290 °C involve 20% weight loss in both types of resin samples. The weight loss may be due to the removal of carboxylic group (–COOH) in form of CO_2. But the second step decomposition in conventional method begins at 400 °C and extends up to 600 °C and in microwave method the second step decomposition begins at 750 °C and extends up to 925 °C with 68% weight loss and considerably good thermal stability is observed. The maximum rate of weight loss occurs at 240 °C and 600 °C for step one and two respectively in conventional method the same occurs at 240 °C and 800 °C for the step one and two respectively in microwave method.

The activation energies of SFR-M resin for Broido method[12] step-I is Ea = 25.71 KJ/mol and for step-II is Ea = 59.676 KJ/mol (Figure 4a) and for Horowitz-Metzger method[13] step-I is Ea = 26.12 KJ/mol and for step-II is Ea = 60.534 KJ/mol (Figure 4b) which are shown in Table 4.

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

Table 3.
Elemental analysis of SFR-M resin.

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

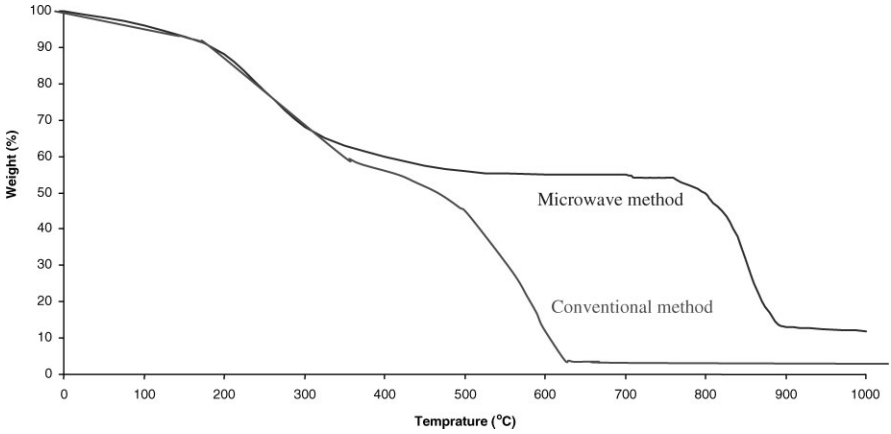

Figure 4.
Thermogram of microwave and conventional SFR resin.

Table 4.
Activation Energy in KJ/mole of Degradation of SFR-M and SFR-C resin.

Resin	Energy of Activation (Ea) K.J/mole			
	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	32.98	26.12	33.17

The SFR-M resin undergoes the polymeric network formation under the influence of polarized condition of monomeric molecules. Hence in orientation view point, 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 of them, the total interchain interaction grows very sharply and becomes commensurable with the chemical bonds. To rapture the more oriented intermolecular bonds, it requires higher energy. Therefore, the second step energy of activation of SFR-M resin Ea = 59.676 KJ/mol (Broido) and 60.534 KJ/mol (Horowitz-Metzger) is higher than the conventionally synthesized SFR-C resin Ea = 32.98 KJ/mol (Broido) and 33.17 KJ/mol (Horowitz-Metzger).[6]

Between the two methods, the Broido method is expected to provide reliable estimates of Ea, since no other temperature characteristics are involved. The value of activation energies calculated according to the Broido method and Horowitz-Metzger method are in good agreement.

Optimum conditions for sorption of metal ions
The 0.25g of SFR-M resin was taken in 100 ml beaker and it was treated with 25 ml of 2 mol l^{-1} HCl and washed with doubly

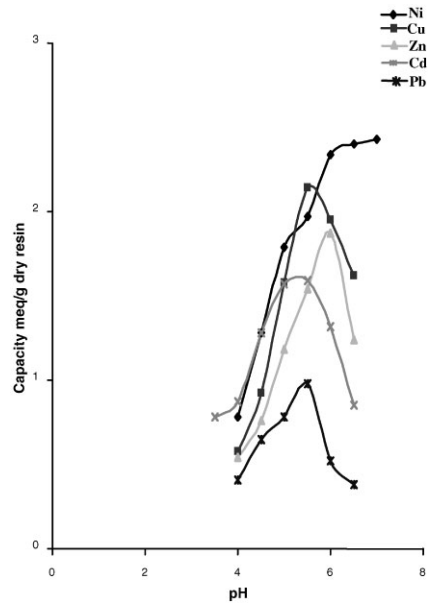

Figure 5.
Effect of pH on metal ion capacity for microwave SFR resin.

Table 5.
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

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 0.05–0.25 mol l^{-1}, was taken. The pH of the solution was varied and adjusted in the range 3.0–7.0. The effect of the pH on the sorption is shown in Figure 5. The use of 2–4 ml of acetate buffer solution to adjust the pH of all metal ion solutions (50 ml) in the range 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 0.25g of SFR-M resin in the glass stopper bottle with a metal ion solutions at room temperature for 24 hours with intermittent shaking. After 24 hours solutions were decanted and unadsorbed metal ions were estimated by complexometric titration with 0.1 M EDTA solution using appropriate indicators. A blank experiment was also run simultaneously. The result is shown in Table 5. 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 5 shows the value of optimum pH exhibiting maximum capacities for each metal ion for 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 is more specific for transition metal ions rather than selective. 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) being greater and the SFR-M resin being more crystalline do not get 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.[6] 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 more is the crystalline nature of the resin. The thermal degradation (Figure 4) is quite steep in SFR-C resin which 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 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 become 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 same whereas more metal ions are available for sorption and subsequently the sorption becomes almost constant then after. For this SFR-M resin, saturation occurs for nickel (II), copper (II) zinc (II) at 0.25M and cadmium (II) and lead (II) at 0.2M 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-

Table 6.
K_d values of metal ions on SFR-M resin in tartrate media at various molarities and PH.

Metal ion	Tartaric acid Conc.(M)	K_d values in tartaric acid at different pH				
		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	–	–	–	–	–

M resin (0.25g) was stirred with 50 ml of solution containing each of the five metal ions (0.2 mol l^{-1}) at room temperature for different period of time. The concentration of metal ions in the supernatant solution was calculated by complexometric titration with 0.1M 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 hours for Ni (II) and 6 hours for Cu(II), Zn(II), Cd(II) and Pb(II). The complete exchange occurs in 24 hours 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 the function of pH and concentration of electrolyte solution were studied. The K_d value decreases with increasing electrolyte concentration and increasing with increasing in pH, which is presented in Table 6. The present investigation limits the distribution studies up to a certain pH for each metal ion to prevent the hydrolysis of metal ions at higher pH. The K_d values decreases with increase in electrolyte concentration and also decrease with increase in pH of the electrolyte. To achieve more clear separation of metal ion in shorter time maximum K_d value difference should be selected for optimized condition of chromatography.

Among the all metal ions under investigation, nickel (II) ion shows higher K_d

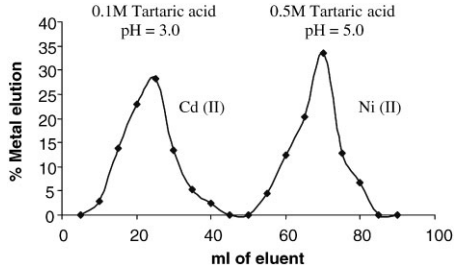

Figure 6.
Separation of Ni (II) and Cd (II) on microwave SFR resin – Binary System.

values, whereas lead (II) exhibits lower K_d values. It is because of the larger size of hydrated Pb(II) than Ni(II) and more crystalline structure of SFR-M resin. From Table 6 it is clear that Cd(II) has distribution coefficient of 11.71 as compared to 57.77 for Ni(II) at pH = 3 indicating 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 result is shown in Figure 6.

Analytical Applications

Separation of Binary Mixture

Separation of nickel (II) and cadmium (II) from equimolar synthetic mixture (2 ml of 5 mg/ml solution of each metal) was achieved by selective desorption. All fractions were individually analysed for each of the metal ion i.e. Cd (II) and Ni (II). Initially the column was eluted with 0.1M tartaric acid at pH 3.0. Cadmium (II) was eluted from 0 to 45 ml of eluate and then nickel (II) was eluted by 0.5M tartaric acid at pH 5.0. These fractions contain only Nickel (II). No cross contamination was observed for this separation. The recovery of cadmium (II) was 90.7% and nickel (II) was 96.20%, which is shown in Figure 6.

Analysis of Brass

A 100 mg sample of brass was dissolved in about 2ml of concentrated nitric acid and the solution was evaporated just to dryness. The residue was dissolved in 5.0 ml of 0.1M 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 0.1M tartaric acid solution at pH 3.0.

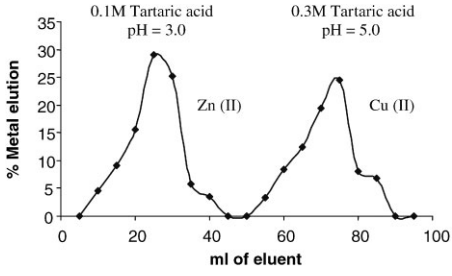

Figure 7.
Separation of Brass components on microwave SFR resin.

Zinc (II) does not form the chelate at pH 3.0 in 0.1M tartaric acid. Thus zinc (II) was separated from copper (II). Then copper (II) was eluted with 0.3M tartaric acid at pH 5.0. No cross contamination was observed for this separation. The recovery of zinc (II) was 92% and copper (II) was 96%, which is shown in Figure 7.

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 minute of refluxing it can be synthesized in only 50 second using microwave assistance.
2. With respect to elemental analysis, FTIR, ^{1}H-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 the more crystalline structure rather than SFR-C resin. The crystals are smaller in surface area with more close 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 more 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. More-

over some left out residues remain at the end of decomposition of SFR-M resin.

5. A perusal of the trends of the rate of exchange clearly indicates that resin under study show 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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