Sorption Isotherms and Column Separation of Cu(II) And Zn(II) Using Ortho Substituted Benzoic Acid Chelating Resins.

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ABSTRACT

Four synthesized resins (AFR, PFR, SFM, and AFM), derived from o-substituted benzoic acid were used for adsorption of sodium ion. It is in the range of 5.50 mmol/g to 7.76 mmol/g. pH study reveals that resins exhibit a good sodium exchange capacity above pH 12.0. Thermal stability of resins show that the sodium exchange capacity remains unaltered up to 373 K. Langmuir isotherm and Freundlich isotherm was used for sorption of three metal like Cu(II), Zn(II) and Pb(II). The adsorption follows Freundlich isotherm model and Langmuir isotherm for all four resins.. These resins were used for chromatographic column separation of Cu(II) and Zn(II) from brass sample using distribution coefficient value (K_d). The resin was experienced for separation of ternary synthetic mixture of [Cu(II)-Zn(II)-Pb(II)]. The developed procedure was also tested for the removal of Cd(II) and Pb(II) from natural water of Purna river near by Navsari, Gujarat, India.

Keywords: Chelating Resin, Chromatographic Column Separation, Langmuir Isotherm, Freundlich Isotherm.

INTRODUCTION

Nowadays heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Industrial and municipal waste waters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water [1]. The heavy metal ions are stable and persistent environmental contaminants, since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life, and water contaminated by toxic metal ions remains a serious public health problem for human health. There are many different methods for treating wastewaters. Current methods for wastewater treatment include precipitation, coagulation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, ion exchange, biological processes, and chemical reactions. Ion exchange resins have been developed as a major option for treating

327

wastewaters over the past few decades [2, 3]. Selective resins reduce the residual concentration of heavy metal to below the maximum limits [4-6]. The influence of complex formation on ion exchange sorption equilibrium and on the distribution of metal ions between the liquid and resin phases has been extensively studied [7, 8].

Solvent impregnated resins have been extensively used for separating and recovering valuable metals. Among the separating methods porous resins impregnated with extracting solvents have offered many advantages over the use of liquid-liquid extraction, due to characteristics of the solid phase. These advantage include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristics. Many studies on the adsorption of metal ions on ion exchange resins such as Dowex A-1 [9], and Duolite GT-73 [10], have been reported.

Bhavna et al [11-15] had synthesized four chelating ion exchange resins (AFR, PFR, AFM, SFM) from o-substituted benzoic acid. These resins had been studied as chelating sorbent for several metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)].The studies of total ion exchange capacity, effect of pH, and concentration for different metal ions were carried out. Column separations of metal ions from their binary mixtures were achieved in tartaric acid media at optimized (K_d) values.

In present study same resins (AFR, PFR, AFM, and SFM) were used for sorption of sodium ion. Different studies like effect of pH, salt splitting capacity, and thermal stability was carried out. Sorption isotherms like Langmuir and Freundlich were carried out for three metal ions [Cu(II), Zn(II) and Pb(II)]. These four resins were used for chromatographic column separation of Cu(II) and Zn(II) from brass sample using distribution coefficient value (K_d). The separation of heavy metal ions from synthetic mixture [Cu(II)-Zn(II)-Pb(II)] was also tested. The removal of Cd(II) and Pb(II) from natural water was also carried out.

MATERIALS AND METHODS

Materials
All the reagents were of analytical grade. Phthalic Acid, Anthranilic acid, Salicylic acid (Ranbaxy fine chemicals, S.A.S. Nagar) were used as received. Formaldehyde, M-cresol (Qualigence fine chemicals, Mumbai) was used as received. Resorcinol: (Glaxo extra pure) was purified by rectified spirit. Metal ion solutions were prepared by dissolving appropriate amount of metal acetates in double distilled water and standardized by complexometric titration [16].

Synthesis of Resins
Four resins AFR (Anthranilic acid- Formaldehyde- Resorcinol), PFR (Phthalic acid- Formaldehyde- Resorcinol), AFM (Anthranilic acid- Formaldehyde- M-Cresol) and SFM (Anthranilic acid- formaldehyde- M-Cresol) were synthesized according to early research literatures. [11, 12, 13, 14, 15] Recrystallised (0.1mole) Anthranilic acid (13.7g) / Phthalic acid (16.6g) / Salicylic acid (13.8 g) (A.R. grade) was ground to fine powder and was taken in to a 250 ml four-necked flask. It was fitted with a condenser, thermometer, stirrer and addition funnel containing 20 ml of DMF, which was added dropwise at room temperature. After the addition of DMF, 37% w/v 25ml formaldehyde (0.3 mole) was added from addition funnel with constant stirring. It was stirred for 1h at room temperature. Then, the solution of resorcinol (11.0 g, 0.1 mole) / m-cresol (10.8 g, 0.1 mole) in 20 ml DMF was added from addition funnel at the rate of 2 ml/min. The mixture was heated on water bath at 100 ^{o}C ± 6 ^{o}C temperature with stirring for about 2-3 h till soft jelly type material was obtained.

The cured mass was then crushed to 20 – 50 mesh size particles and it was washed with methanol and finally with hot double distilled water to remove unreacted monomers. The resin was dried in vacuum oven at 100 °C. The sieved resins were used for all of the experiments during the research period. Physico-chemical properties of four synthesized resins were summarized in Table-1. The possible structure of resins was exhibited in Figure-1.

Adsorption of metal ion on Synthesized resin
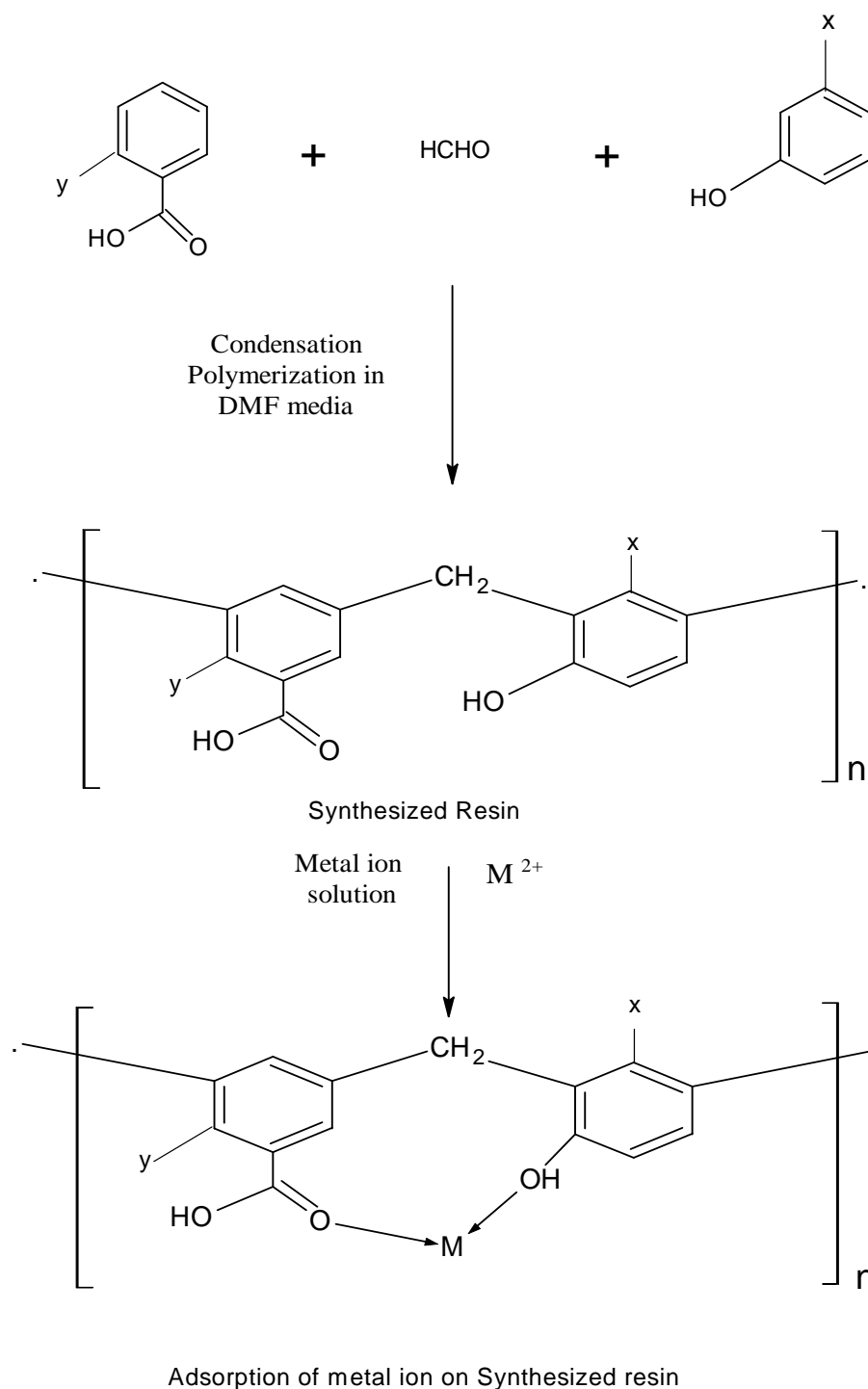
Where, X = -NH₂, -COOH or –OH and Y= -OH or –CH₃ M⁺² Metal Ion [Zn(II),Cu(II), Pb(II)]

Figure 1 Structure of synthesized resins.

METHODS

Sodium Exchange Capacity
Approximately 10 g of each sample of dry resin was weighed and taken in a beaker to convert it into H^+ form with 2 M hydrochloric acid. Each resin sample was filtered, washed with distilled water for neutrality and dried in air. Exactly one gram of each sample of resin in H^+ form was taken in a dry 250 ml Erlenmeyer flask. To the sample in the Erlenmeyer flask, 200 ml standardized 0.1 M sodium hydroxide solution was added. Each mixture was equilibrated for 24 hours with intermittent stirring. 50 ml aliquot of the supernatant liquid was titrated with standard 0.1 M HCl. The sodium exchange capacity was calculated by following formula:

$$\text{Sodium Exchange Capacity} = \frac{(200 \text{ } \mathbf{X} \text{ Normality of NaOH}) - 4 \text{ (ml of acid } \mathbf{X} \text{ Normality of HCl)}}{\text{Weight of sample } \mathbf{X} \text{ (\% solid /100)}}$$

SEC=milli equivalents of cation exchange capacity/g of dry resin in H^+ form.

Effect of pH
The H^+ form of each resin sample (0.2 g) was accurately weighed into different glass bottle. To each bottle, 100 ml of the solution of pH ranging from 10.0 to 12.5 was added which was prepared by varying the quantities of 0.1 M NaOH solution prepared in 1 M NaCl solution. The resin was kept for equilibrium with the mixture for 24 h and then residual basicity was determined.

Rate of Exchange
For H^+ form of each resin (0.25 g) was accurately weighed into twelve different glass bottles. 100 ml of 0.1 M sodium hydroxide was added to each bottle and resin was allowed to remain in contact for different period of the time with intermittent shaking. At definite pre-determined interval, the solutions were decanted and aliquots were titrated against standard acid and from this, capacity released at different time intervals were calculated. The values of the capacities were converted into percentage exchange and were plotted against time.

Salt Splitting Capacity
Each H^+ form of the resin (0.25 g) was accurately weighed into twelve different glass stopper bottle. 10 ml of 1 M NaCl was added to each bottle and the resin was allowed to remain in contact for different periods of time with intermittent shaking. At definite pre-determined intervals, the solutions were decanted and aliquots were titrated against standard alkali.

Thermal Stability
Thermal stability of the cation exchange resin in the free acid form was determined by the following procedure: Each resin (H^+ form of known capacity) about 1.0 g was heated in electric oven at a pre-determined temperature for eight hours. The capacity of portion of the heated sample (0.25 g) was determined by directly equilibrating with standard alkali solution (0.1M). Another portion of the heated resin (0.25g) was regenerated with acid, washed thoroughly with distilled water and its capacity was determined. The experiments were repeated by heating the resin to different temperatures in the range of 313 K to 393 K for each resin sample.

Adsorption Isotherm for Metal Ions
Adsorption isotherm studies were carried out in a series of 100 ml reaction bottles. Each bottle was filling with 25ml of different initial concentration of different metal ion solution [Cu(II),

Zn(II) and Pb(II)] while maintaining the resin dosage at constant level (0.25g). After equilibration, the solution was separated and analyzed by complexometric titration. The initial concentration of solution taken for the studies was 10, 15, 20 and 25 mg/L. The equilibrium adsorption capacity was calculated using following equation,

$$qt = \frac{(Co - Ct)V}{M}$$

Where qt (mg/g) is the equilibrium adsorption capacity, Co and Ct the initial and equilibrium concentration (mg/L) of metal ion in solution, V(L) the volume, and M(g) is the weight of adsorbent.

The amount of material adsorbed is determined as a function of the concentration at a constant temperature that could be explained in adsorption isotherms. Equations that are often used to describe the experimental isotherm data were developed by namely, Freundlich [17] and Langmuir [18]. The Freundlich isotherm model was also used to explain the observed phenomena.

$$\ln qe = \ln K_F + 1/n \ln Ce$$

Where K_F (mg/g) is the Freundlich constant and '*n*' the Freundlich exponent. Where, *C*e is the equilibrium concentration (mg/L), *q*e the amount of metal ion adsorbed by per gram of the ion exchange resins and K_F and *n* are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. K_F and *n* were calculated from the intercept and slope of the plot.

The Langmuir sorption isotherm is often used to describe sorption of a solute from a liquid solution as

$$\frac{1}{qe} = \frac{1}{Q^o} + \frac{1}{bQ^oC_e}$$

Where Ce is the equilibrium concentration (mg/L), *q*e the amount adsorbed at equilibrium (mg/g) and Q^o and *b* is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The value of Q^o and b were determines from the slope and intercepts of the Langmuir slope.

Chromatographic Column Separation of Brass Sample
Brass is an alloy containing 60 % Cu and 40 % Zn. Brass sample (0.25 g) was dissolved in about 10.0 ml of concentrated nitric acid and the solution was evaporated to dryness. The residue was dissolved in 10.0 ml of 0.1 M hydrochloric acid. Solution was filtered and made it up to 25.0 ml by addition of distilled water in standard measuring flask. From this, 5.0 ml of solution was taken for column separation. This aliquot was directly passed through each of the column of synthesized resins. The chelating resin in H^+ form was packed into a chromatographic column to form a compact resin bed of 15 cm height and 0.4 cm diameter. This aliquot was directly passed through each of the column of synthesized resins at a flow rate of 0.5 ml/min. The elution was carried out with tartaric acid solution at different optimized conditions [11, 12, 13, 14, 15]. The plot of % metal elution versus ml of eluate is shown in Figure-4-7.

Separation of Ternary Mixture

Separation of ternary mixture [Cu(II)-Zn(II)-Pb(II)] by AFR resin has been carried out using their corresponding conditions of K_d values. The different conditions for the separation like pH and molar concentration of tartaric acid are taken from early publications [11, 12, 13, 14, 15].

Recovery for Heavy Metal Ions from Purna River Water

20 liter of Purna River water sample from Navsari city was collected in polythene container. The water sample contains Cd(II) and Pb(II). The concentration of Cd(II) and Pb(II) varies from 0.01 ppm to 0.7 ppm and 0.01 to 0.4 ppm respectively which is higher than the Indian Standard Desirable Limit. It exhibits higher concentration of these metal ions at Jalalpor. This may be due to industry effluent of sewage waste in the river water. A one liter water sample was recycled through the resin (AFM) columns for the preconcentration of these metal ions at flow rate 1 ml/min.

RESULTS AND DISCUSSION

Physico-Chemical Properties

The physico-chemical properties of synthesized resins are presented in Table 1. Water content of resin is the ability of resin to hold the moisture. The moisture content of a resin furnishes a measure of its water loading capacity or its swelling capacity. Many ion exchangers are very hygroscopic and lose all its water only after prolonged heating. Moisture content depends on many factors such as, on the composition of the resin matrix, the degree of cross-linking or the nature of the active groups and the ionic form of resins. When resin sample is heated up to 100 ^{o}C, initially they lose some weight; soon weight is regained after exposing it in the air for 24 h. This indicates that resin sample contain percentage of moisture. The percentage of moisture content of synthesized resins is in range of 8.6 to 10.0. The value were calculated in hydrogen ion form and water associated with 1.0 g of dry resin. It has been observed that these resins have low range of percentage moisture content compared to the commercial resins. Moisture content is an essential component of ion exchange resins, for example; strong acid cation resins contain about 50% moisture. The amount of cross linking in the bead has an impact on the moisture content of the bead and the moisture content in turn has an impact on the selectivity. A bead with high moisture content has a high porosity and the active groups are spaced further apart from each other. The difference in moisture content may be due to the different experimental conditions like medium in which the resins are synthesized, polymeric backbones and functional groups involved.

Table -1 Physico-Chemical property of Ion Exchange Resins

Properties	AFR	PFR	AFM	SFM	SD
% moisture	10.0	9.6	8.6	9.4	± 0.5
% solid	90.0	90.4	91.4	90.5	± 0.5
True density (dres) g/cm^3	1.11	1.16	1.15	1.22	± 0.03
Apparent density (dcol) g/ml	0.7010	0.7027	0.6848	0.7653	± 0.0060
Void volume fraction	0.3642	0.3973	0.4045	0.3727	± 0.0050
Concentration of fixed ionogenic group mmol/cm^3	6.1048	5.7670	6.5503	7.7605	± 0.2000
Volume capacity mmol/cm^3	3.82	3.47	3.71	4.86	± 0.05
Sodium exchange capacity mmol/g dry resin	6.10	5.50	6.24	7.76	± 0.20

True density of synthesized polymers is shown in Table 1 which is in range of 1.11 to 1.22 g/cm^3. The true density of commercial resins generally lies between 1.1g/cm^3 to 1.7 g/cm^3. To avoid the floating of resin particles, true density must be more than one. Floating of resin particles is undesirable in chromatographic study, as it hampers formation of compact column.

Optimum density and uniform particle size gives perfect column packing and performance of the column. The measurement of column density or apparent density is necessary because commercially it is sold on volume basis and packed on weight basis. Apparent density of synthesized resins is between 0.68 and 0.76 which is given in Table 1, which is comparable to the density of commercial resins. It may be because of charge in polymeric matrix, different functional group and the method of synthesis.

The apparent density parameter gives an idea of probable length of the packed column for an ideal column chromatography study. The value of void volume fraction of resin is in range of 0.36 to 0.40, which is represented in Table 1. The appreciable values of void volume fraction help the diffusion of the exchangeable ion on the resin and hence increase the rate of exchange of ions. Minimum essential void volume provides better diffusion of exchangeable ions and thus feasibility of column operation.

Sodium Exchange Capacity
It is one of the most important chemical properties of an ion exchange resin. It shows the number of groups capable of entering into ion exchange phenomenon. The values of sodium exchange capacities are shown in Table-1.The capacities in increasing order, as shown below, is in the range of 5.50 mmol/g to 7.76 mmol/g. PFR < AFR < AFM < SFM. The type of o- substituted group (acid group, amino group or phenol group) plays role in establishing different sodium exchange capacity. Sodium exchange capacity of resin is dependent upon the number of ion active site per unit weight of material. The greater the number of active ions, the greater will be the capacity. The adsorption of sodium ion also depends upon the degree of cross linking, as the degree of cross linking is increase, resin become more selective towards ion of different sizes. The comparative results are obtained with SFR and SFR-M resin [19, 20].

Effect of pH
The results of effect of pH on sodium exchange capacity are given in Figure-2. It reveals that resins exhibit a good sodium exchange capacity above pH 12.0. The low capacity may be due to the unionizable phenolic –OH group at pH- 4 to pH-10. From the graphs, it is observed that sodium exchange behaviours of these resins are similar to weak acid cation exchangers.
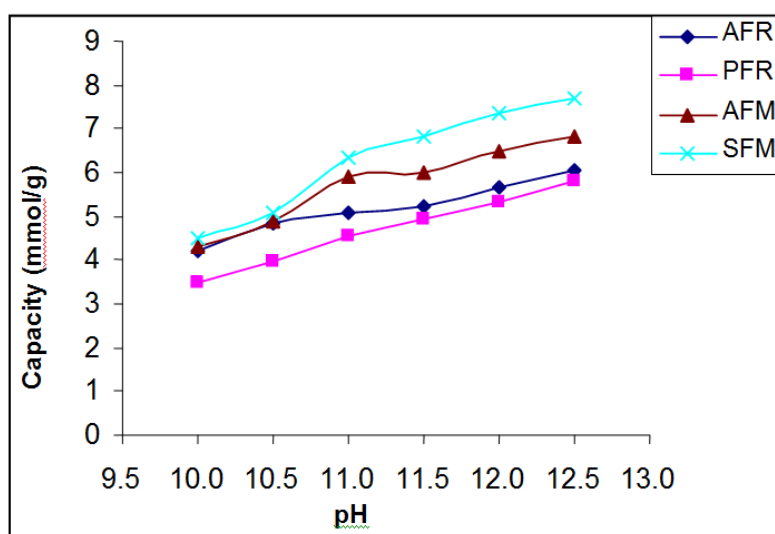

Figure 2 Effect of pH on sodium exchange capacity on synthesized resins.

333

Ion exchange capacity is higher for monovalent ions than divalent ions. This may be due to the preferential uptake of the monovalent Na^+ ion by highly cross-linked system.

Rate of Exchange

The utility of resin in chromatography depends on the faster rate of ion exchange. Therefore, determination of rate of ion exchange reaction can be of practical significance. If the velocity of the flow to be maintained in the column is same as the rate at which these reactions occur, then ion exchange processes are more economic. The rate of exchange of sodium ion is shown in Figure-3. It reveals that for comprehensive exchange of sodium ions, 18 h to 24 h are required. For 50 % exchange, AFR takes 50 min, PFR takes 3 h, AFM takes 50 min and SFM takes 6 h. PFR and SFM take more time for half exchange. It may be due to shell diffusion or particle diffusion. The faster rate of exchange for AFR and AFM may be due to presence of $-NH_2$ group, which favours the ion exchange. In the beginning the rate is fast which may be due to the law of mass action and gradually the rate of diffusion of ions towards the interior of the resins show slow exchange.
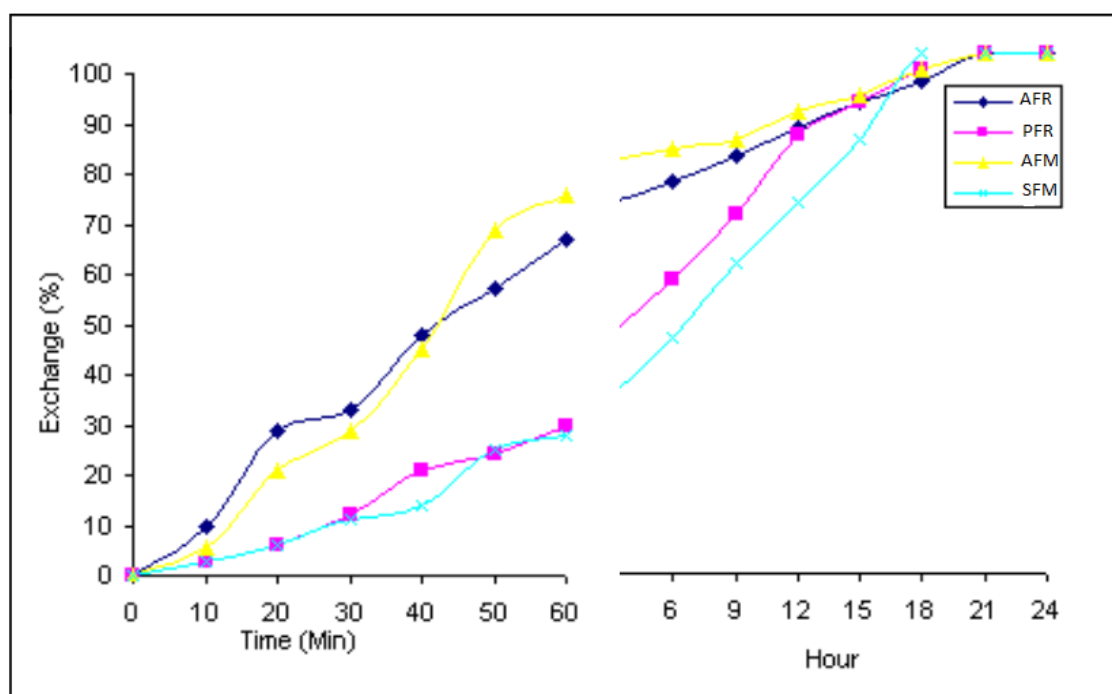

Figure 3 Rate of exchange for sodium ion on synthesized resins

Salt Splitting Capacity

The salt splitting capacities of the resins are almost zero, which suggest that ion exchange with neutral salt like 1 M sodium chloride solution is zero.

Thermal Stability

Thermal stability tests give significant information for cation exchange resins. When resins are heated from 313 K to 393 K temperature for 8 h, it is observed that the sodium exchange capacity remains unaltered up to 373 K. This may be due to cross-linking between monomers, which produces tough resin. The results are given in Table-2. Each resin shows little increase in the capacity when heated to above 373 K. This is due to (1) destruction of some of -CH$_2$- bridge between aromatic ring, and (2) removal of the decomposed products which had neutralized the ionogenic groups. The thermal stability of resin makes resins useful for ion exchange

334

chromatography at high temperature. The thermal stability also affects chemical and physical properties, which are important for exchange capacity.

Table-2 Thermal stability data

Sodium Exchange Capacity (mmol/g dry resin)				
Temp. (K)	AFR	PFR	AFM	SFM
313	6.05	5.65	6.11	7.71
333	6.10	5.77	6.23	7.70
353	6.12	5.77	6.25	7.70
373	6.15	5.76	6.27	7.73
393	6.30	5.82	6.44	7.85

Adsorption Isotherm for Metal Ions

A sorption process could be preceded by the following mechanisms: (1) ion-exchange reaction, (2) physical adsorption, (3) molecular sorption of electrolytes, (4) complex formation between the counter ion and the functional group, and (5) hydrate formation at the surface or in the pores of the adsorbent. The quantity of metal that could be taken up by a resin is a function of both the concentration of the metal and the temperature. Linear plots of ln$q$e versus ln$C$e show that the adsorption follows Freundlich isotherm model. The constants K_F and n for Zn(II) , Cu(II) and Pb(II) metal ions on different chelating resin systems are presented in Table 3. The correlation coefficients (R^2) are considerably higher for Zn(II) and Cu(II). The value of 1/n thus determined is of the same magnitude as those of commercial macrorecticular chelating resin Amberlite IR-120 [21].

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 favorability and capacity of the adsorbent/adsorbate system. The values of n lie between 1 and 10 indicating favorable adsorption [22]. For all four resin, Pb(II) shows less than 1 value for n. Due to electrostatic effects, the metal binding strength increases with decrease of the radius of hydrated metal ion and increase of charge of the metal ion. If a strange field is present, electrostatic effects may be come the dominant factor, such that small ions which have a higher charge density are bound more strongly. Due to higher ionic radius of Pb(II), adsorption of Pb(II) on resins is very difficult and for this reason it may shows less exchange capacity. [11, 12, 13, 14, 15]

Adsorption obeys Langmuir isotherm model for all four resins. The correlation coefficients (R^2) are more than 0.9 for Zn(II), Cu(II) and Pb(II) . The values of Q^o and *b* were determined from the slopes and intercepts of the Langmuir plots and represented in Table 3. The Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbet molecule on to the surface has equal sorption activation energy. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter, RL [23].

$$R_L = \frac{1}{1+bC_o}$$

Where b is the Langmuir constant and C_o is the initial concentration of metal ions.

Table 3 Langmuir and Freundlich Isotherm Constant

Resin	Metal ion	Langmuir isotherm			Freundlich isotherm			Exchange Capacity* (mmol/g)
		Q^o (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2	
AFR	Zn(II)	0.5199	0.1542	0.9825	0.1820	4.2337	0.9000	0.9473
	Cu(II)	1.0028	0.0400	0.9952	0.0759	1.7313	0.9792	0.8884
	Pb(II)	-0.9916	-0.0094	0.9903	0.0024	0.6568	0.9720	0.5277
PFR	Zn(II)	1.3931	0.0196	0.9846	0.0385	1.3104	0.9880	1.0210
	Cu(II)	3.9900	0.03290	0.9725	0.0800	1.0463	0.9276	0.9736
	Pb(II)	-28.010	-0.0004	0.9823	0.0114	0.9900	0.8720	0.2914
AFM	Zn(II)	1.9766	0.0062	0.9940	0.0153	1.1325	0.9966	0.2574
	Cu(II)	3.4083	0.02009	0.9686	0.1105	1.3888	0.9852	0.6315
	Pb(II)	-3.8350	-0.0046	0.9852	0.0013	0.5840	0.9618	0.1957
SFM	Zn(II)	1.1596	0.0251	0.9152	0.0394	1.3320	0.9480	0.5319
	Cu(II)	20.876	0.0041	0.9997	0.0773	1.0000	0.9990	0.6315
	Pb(II)	-2.2210	-0.0045	0.9935	0.0048	0.7856	0.9877	0.2659

* Results are taken from literatures [11-15]
The values indicates the isotherm to be either unfavorable ($R_L >1$), linear ($R_L = 1$), favorable ($0 < R_L <1$) or irreversible ($R_L = 0$). The values of R_L can be calculated from result obtained from the Langmuir isotherm. The R_L value for both the metals Cu(II) and Zn(II) under study are lying between 0 and 1 indicate favorable adsorption [24]. The negative value of Langmuir constant (b) for Pb(II) suggest that it gives R_L value more than 1 and adsorption of Pb(II) on synthesized resins were very difficult. It may be due to, As ionic radius increases, charge density decreases, the adsorption capacity of synthesized resins decrease as for Pb(II).

Chromatographic Column Separation of Brass Sample

An effective way of separating solute particles and capable of extracting positively charged ions is ion exchange technique. Quantitative binary separations of metal ions were performed by column chromatography using elution technique. These separations are based on the exploitation of the difference in the exchange potential of different ions with respect to the resin. Certain ions were capable of forming anionic complexes; passed through the column unabsorbed leaving behind the second metal ions on the column. This was later eluted with suitable eluent. The metal ions adsorbed by the resin were then eluted with different eluents depending on the K_d values. After the metal elutions were complete the resin was regenerated to hydrogen form using mineral acids such as HCl. The results of K_d values presented in Table 4. The reason for selective sorption and desorption of certain metal ions can be attributed to the larger difference in K_d values.

The superior selectivity towards multivalent cations exhibited by chelating resin has been demonstrated in column experiments by using K_d values. [11, 12, 13, 14, 15]. An ideal situation would be such that one K_d values is ten times greater than the K_d value for other ions, while the other approaches zero. The first eluting fractions of tartaric acid carry one metal ion, which has a smaller K_d values. The second metal ion can be eluted by changing the tartaric acid concentration to a level that has a lowest K_d values for second metal ion.

Separation of Cu(II) from Zn(II) by AFR was performed, at initial pH 3.0 by selective elution of Cu(II) with 0.3 M tartaric acid solution and Zn(II) with 0.5 M tartaric acid solution at pH 5.0, which is shown in Figure-4. The elution percentage of Cu(II) and Zn(II) was found to be 85% and 70% respectively. In case of separation of Zn(II) from Cu(II) by PFR, the resin column was equilibrated at pH 3.0. Zn(II) was eluted with 0.1 M tartaric acid. The first few fractions contained only Zn(II) and the later fractions contain only Cu(II) which was eluted with 0.5 M tartaric acid at pH 5.0. There was no cross contamination in the separation which is shown in Figure-5.

336

Table 4 K_d values of metal ions on synthesized resins in tartaric acid media at different pH

Resin	Metal ion	Tartaric acid Conc.(M)	K_d values at different pH				
			3.0	3.5	4.0	5.0	6.0
AFR	Cu(II)	0.1	44.4	61.5	67.5	24.6	37.5
		0.2	9.6	60.0	99.9	52.8	24.6
		0.3	70.5	84.3	99.9	108.6	99.9
		0.5	150.0	84.3	99.9	150.0	70.5
		1.0	70.2	60.0	87.5	102.2	69.3
	Zn(II)	0.1	11.4	14.4	17.4	26.7	83.1
		0.2	48.6	55.2	61.8	68.7	75.6
		0.3	232.8	160.8	101.5	133.2	154.4
		0.5	62.7	43.1	28.5	38.4	57.4
		1.0	28.5	30.6	33.3	36.0	38.4
PFR	Cu(II)	0.1	300.0	225.0	150.0	24.0	-
		0.2	100.0	33.2	33.0	15.6	145.0
		0.3	90.0	70.5	-	-	-
		0.5	-	-	-	-	-
		1.0	-	-	-	-	-
	Zn(II)	0.1	45.0	30.2	45.0	51.3	105.0
		0.2	21.0	60.8	27.6	21.8	45.0
		0.3	420.0	9.1	-	12.6	-
		0.5	18.0	24.0	9.6	420.0	-
		1.0	48.0	27.0	36.2	21.0	-
AFM	Cu(II)	0.1	90.0	90.5	54.0	39.0	150.0
		0.2	150.0	210.3	370.0	-	103.5
		0.3	90.0	215.9	51.3	100.2	75.8
		0.5	-	75.8	-	132.0	-
		1.0	-	-	-	-	-
	Zn(II)	0.1	-	75.6	90.0	71.0	99.5
		0.2	99.5	75.0	100.0	90.0	-
		0.3	51.6	45.0	85.6	30.5	60.3
		0.5	30.4	18.2	45.0	12.3	-
		1.0	90.5	55.0	24.0	24.5	51.2
SFM	Cu(II)	0.1	205.3	157.6	-	-	20.0
		0.2	300.2	100.2	69.0	-	-
		0.3	-	-	-	-	290.3
		0.5	-	-	-	-	2.0
		1.0	-	-	-	-	-
	Zn(II)	0.1	-	6.3	90.4	45.6	75.0
		0.2	10.0	-	-	-	21.0
		0.3	27.6	45.0	21.3	33.6	-
		0.5	63.5	60.0	51.6	-	-
		1.0	150.2	-	60.0	-	-

The elution percentage of Zn(II) and Cu(II) was found to be 92% and 65% respectively. In the separation of Cu(II) from Zn(II) by AFM, Cu(II) was eluted first at 3.0 pH and 1.0 M tartaric acid concentration and then Sorbed Zn(II) was eluted with 0.2 M tartaric acid at pH 4.0 which is shown in Figure-6.
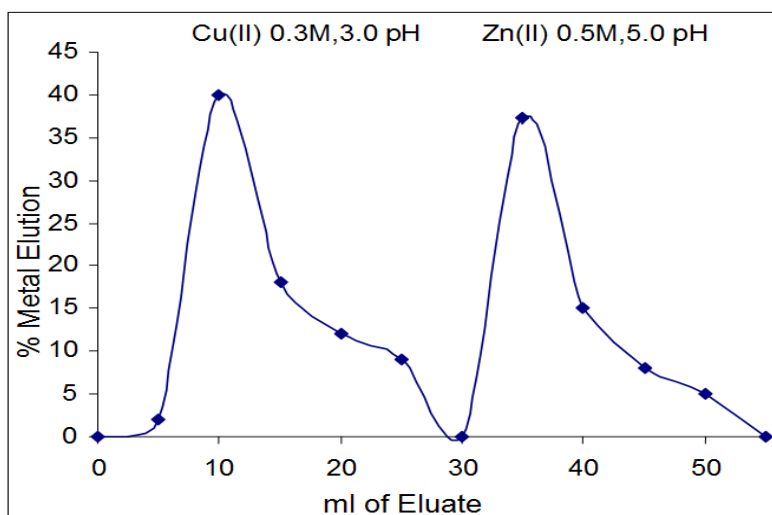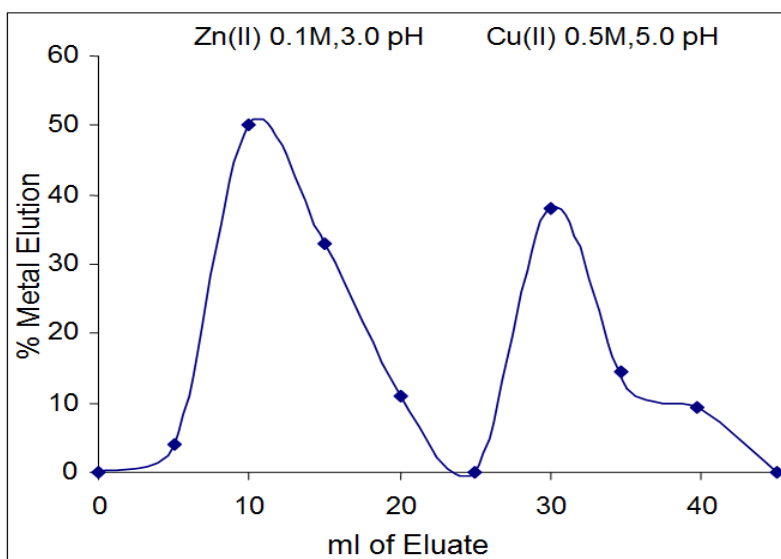
Figure 4 Separation of Brass sample on AFR.
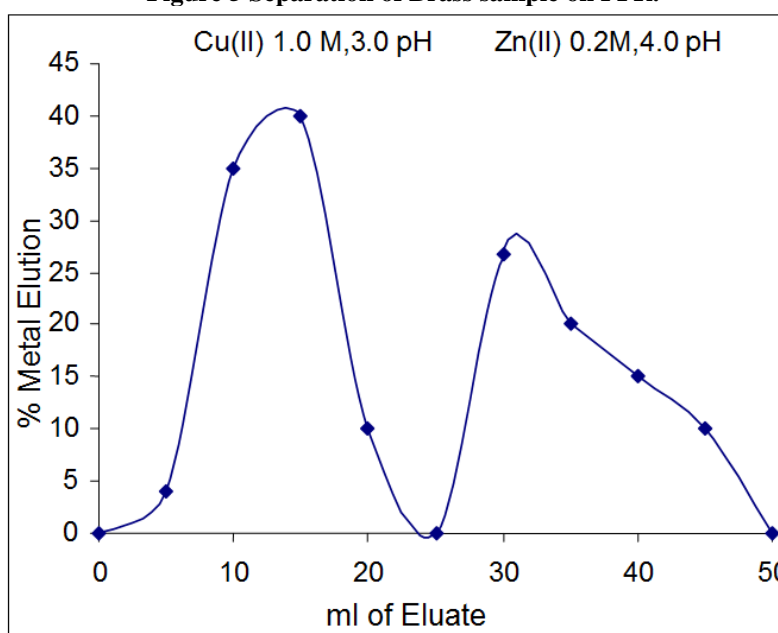

Figure 5 Separation of Brass sample on PFR.

Figure 6 Separation of Brass sample on AFM.

The elution percentage of Cu(II) and Zn(II) was found to be 86 % and 76 % respectively. Separation of Cu(II) from Zn(II) by SFM was carried out, at initial pH 3.0 by selective elution of Cu(II) with 1.0 M tartaric acid solution and Zn(II) with 0.2 M tartaric acid solution at pH 3.0, which is shown in Figure-7. The elution percentage of Cu(II) and Zn(II) was found to be 75% and 70% respectively.
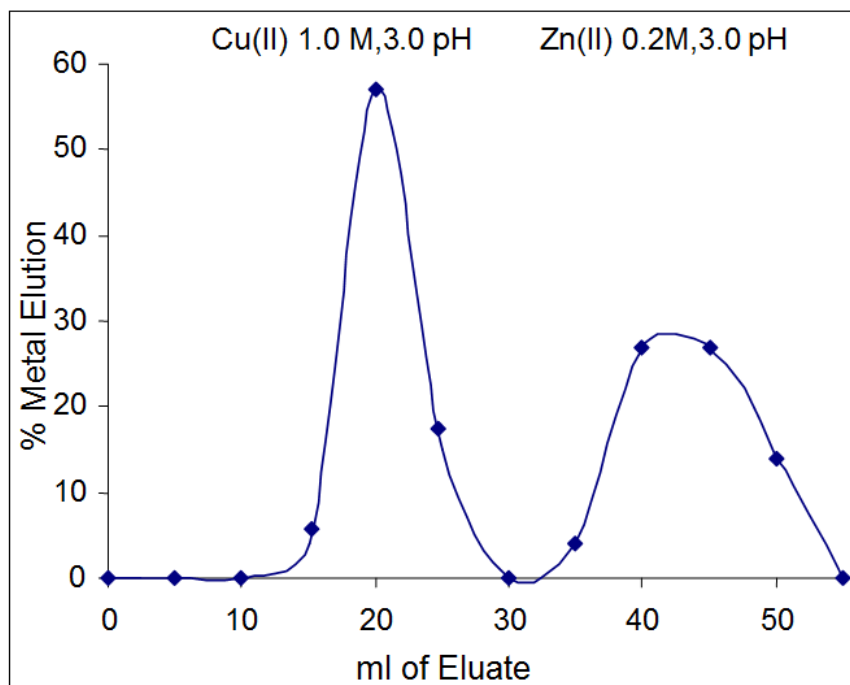

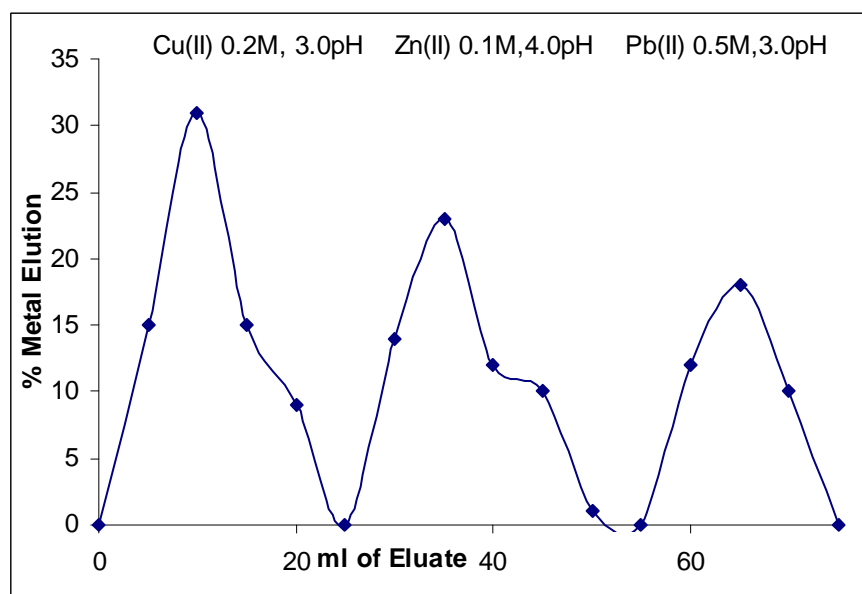**Figure 7 Separation of Brass sample on SFM.**

Figure 8 Separation of Ternary Mixture on AFR.

Separation of Ternary Mixture.

Separation of ternary mixture [Cu(II)-Zn(II)-Pb(II)] by AFR resin has been carried out using their corresponding conditions of K_d values. First Cu(II) was eluted at 3.0pH and 0.2M concentration of tartaric acid. Then Zn(II) was eluted by changing pH to 4.0 and concentration of tartaric acid at 0.1M . Finally at 3.0 pH and 0.5M concentration of tartaric acid Pb(II) was eluted.

The recovery of Cu(II), Zn(II) and Pb(II) was found to be 70% , 65% and 45% respectively. The plot of % metal elution versus ml of eluate is shown in Figure-8.

Recovery for Heavy Metal Ions from Purna River Water
To verify the applicability of AFM chelating resin using preconcentration of trace metal ions like Cd(II) and Pb(II) from river water sample, the extraction and elution of metal ions was studied. The metal ion concentration of Cd(II) and Pb(II), in river water and after preconcentration was determined by Atomic Absorption Spectroscopy. The recovery of heavy metal ion from column was carried out using 2M HCl solution. The recovery of Cd(II) and Pb(II) ions was 85 % and 84 %. The results indicate that the extraction and elution of Cd(II) and Pb(II) is little affected by the coexistence of salt matrices.

CONCLUSION

Various study like exchange capacity, rate of exchange, thermal behavior for sodium ion has been carried out. Sodium exchange capacity for synthesized resins is comparative with other commercial resins. [25] AFR resin shows rapid exchange for sodium ion, which is very important for chromatographic separation. All resins shows good sodium exchange capacity above 12 pH. All resins were thermally stable so they can be used up to 373 K. The Freundlich and Langmuir adsorption models were applied for mathematical description of synthesized resins equilibrium data. The present results demonstrate that both isotherm models fit fairly to the adsorption equilibrium data in the examine concentration range for Cu(II) and Zn(II). Heavy metal ion like Pb(II) was not fit with both this isotherm. So these resins may be very useful for the analytical separation of heavy metal ion from transition metal ions. Using distribution coefficient value (K_d) of synthesized resin binary mixture can be easily separated. These resins may be also used for wastewater treatment in industry. Use of chelating resin is the method of choice due to its high separation efficiency and good reproducibility; therefore, these resins can be used in enrichment of metals from various sources by adopting preconcentration and separation from various matrices.

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