

The Effect of Chelating Agent on the Separation of Some Metal Ions from Binary Mixture Solution by Cation-Exchange Resin

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Abstract: The need to clean-up heavy metal contaminated environment cannot be over emphasized. This paper has been studied the distribution coefficients of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) on cation exchange resin Purolite C100 in the presence of some chelating agent at 25°C. Sodium nitrate, citric acid and ethylene diamine tetraacetic acid (EDTA) were tested as eluants. The relative efficiency of the eluants has been discussed in terms of their elution constants. A rapid ion-exchange method was proposed for the separation of lead cations. The method has depended on the selective complexing of metal ions by a chelating agent as achieved by control of pH. Several binary separations of metal ions have been achieved on the basis of their k_d values [Nature and Science . 2010; 8(10): 16-25]. (ISSN: 1545-0740).

Keywords: Ion exchange; Separation ; Heavy metals; Distribution coefficient.

1. Introduction

The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems. The heavy metals are of special concern because they are non-degradable and therefore persistent. These metals are toxic in both their chemically combined forms as well as the elemental form. Exposure to these contaminants present even in low concentration in the environment can prove to be harmful to the human health [1]. Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photo- graphic materials and explosive manufacturing. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis, nephritic syndrome and can interfere with enzyme activities. It can affect nerves and brain [2 and 3]. Most of the heavy metal salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical separation methods. Conventional techniques for removing dissolved heavy metals include precipitation, adsorption and ion exchange [4].

For the separation of various elements, ion-exchange has been used more extensively than any other technique, because it has been preferred by many researchers on account of the fast, simple and higher preconcentration factors, rapid phase separation, time and cost saving [5 and 6]. The separations were performed using cation-exchange or anion-exchange resins. As elution agents, different acid solutions, acid containing organic solvent some mixtures like

hydrobromic-nitric acid, tartaric acid-nitric acid and tartaric acid-ammonium tartarate, thiourea-hydrochloric acid solutions were used [7]. The effective separation of cation exchange resin can be increased by using complexing agents. Ethylenediamine tetraacetic acid (EDTA) forms very stable complexes with the transition metals and this fact has been used to develop separation techniques based on ion-pair or ion exchange chromatography [8-10]. The purpose of the present work is to explore the possibility of a few analytical separations of metal ions from synthetic binary mixtures, namely Pb(II)-Ca(II), Pb(II)-Ba(II), Pb(II)-Fe(III), Pb(II)-Bi(III), Pb(II)-Ce(IV), Ca(II)-Ba(II) and Fe(III)-Ba(II). Distribution coefficient values of ions in the presence of various complexing agents have been studied. Also the recovery % for ion exchange separation of some metal ions in the presence of different eluent has been calculated.

2. Materials and Methods

All chemicals were of analytical reagent grade. Distilled water was used throughout the study. Each metal ion stock solution (1000 ppm) was prepared by dissolving a calculated amount of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) as nitrates, EDTA and citric acid used for elution, concentrated hydrochloric acid from Merck, Darmstadt. They were used without further purification. The working solutions were prepared by diluting the stock solution to appropriate volumes.

The pH of solution was adjusted to the desired pH values using 0.1M citric and 0.2M

disodium hydrogen phosphate buffer.

Purolite C100 is a high capacity premium grade bead form conventional gel polystyrene sulphonate cation exchange resin. The exchange capacity was 2.2 mequiv./g and its particle size was 0.42-1.2mm. Purolite C100 was procured from Purolite international Limited, Hounslow, UK. Prior to use, the resins were washed with HCl (1.0 mol/dm³) and were washed with deionized water until all chloride ions removed and were dried in a vacuum oven at 25°C.

Apparatus

Thermo Jarrell Ash atomic absorption spectrophotometer (AAS) model (POEMS III) USA was used to analyze the concentration of metals in solutions. The pH values of all prepared solution were measured using pH meter OP-021/2 (Germany) with combined electrode.

Batch exchange and elution experiments

In the batch exchange experiments, an aliquot of dry resin (1.0 g) and 40 cm³ of the aqueous solution containing 26.5ppm of each metal ion were placed in a 100-cm³ glass-stopper for 24 h. at temperatures (25°C). After equilibrium, the resin was separated and the concentrations of metals in the aqueous phase were analyzed by an atomic absorption spectrophotometer.

Experiment to study the quantitative elution of lead ions were performed by adding 9.23g resin in a 100 ml solution containing 26.5 ppm of PbNO₃ was passed through the column at a rate of 1 ml/min, resin bed (1.4 x 12.9 cm). The resin was washed with 50 ml, of water and then the Pb(II) was eluted with 200 ml of different eluents. The latter include 0.01 M EDTA and 5% citric acid at different pH's. In each case the elation rate was 1 ml/min and the eluting agent was collected in 10 ml. The elution constant, E, for each eluting agent is calculated, from the relation[11].

$$E = d.A/V \quad (1)$$

Where V is the volume of eluent, which is required to displace Pb(II) under essentially equilibrium conditions through a distance d cm in a column of cross sectional area A cm², the free column volume in this work was found to be 13 ml.

3. Results and Discussion

3.1. Determination of the equilibrium distribution coefficient, k_d

The distribution coefficient, k_d is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution and can be used as a valuable tool to study metal cation mobility. High values of

distribution coefficient, k_d indicate that the metal has been retained by the solid phase, while low values of, k_d indicate that a large fraction of the metal remains in solution. The distribution coefficient k_d were calculated using the equation [12].

$$K_d = \frac{\text{amount of metal ion in adsorber}}{\text{amount of metal ion in solution}} \times \frac{V}{m} \text{ ml/g} \quad (2)$$

where V is the volume of the solution (ml) and m is the weight of adsorbent (g).

3.2. Effect of ethylene diamine tetraacetic acid and citric acid on distribution coefficient, k_d

Systematic information on ion exchange equilibrium distribution coefficient is very useful for planning separations. For this reason, a batch equilibrium method was employed for the determination of the distribution coefficient of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) on cation exchange resin Purolite C100 in the presence of some chelating agent such as EDTA and citric acid at 25°C.

The presence of chelating agent such as Ethylenediamine tetraacetic acid, EDTA in solution considerably changes the metal ion sorption ability of resin. It was able to change the surface characteristics of the adsorbent. In the reaction between EDTA and metal ion, donor atoms of EDTA molecule shield metal ion as a substitute for six water molecules. It means the transition from aqua complex to EDTA metal complex. Complex structures of M (III) and EDTA are shown in Fig. (1).

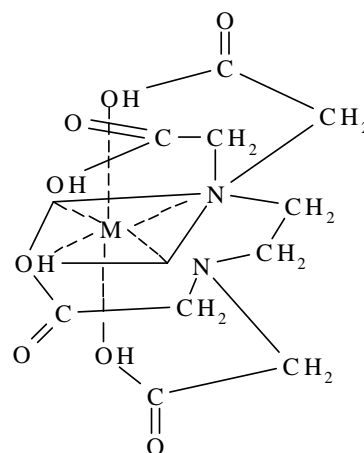
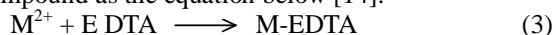


Fig. 1. The structure of M-EDTA complex.

The shape of metal complex with EDTA becomes octahedral (sp^3d^2 hybrid orbit) since six donor atoms shield one metal ion. An asterisk attached oxygen and nitrogen (O* and N*) means a donor atom with unshared electron pair, which can coordinate a metal ion. Each complex has different valency against

pH because hydrogen of aqua ion ($-\text{OH}_2$) or carboxylate ion ($-\text{COOH}$) is removed as pH increases. For example, EDTA has four carboxyl groups ($-\text{COOH}$) and then existence ratios of each component are obtained from dissociation constants, K e.g. EDTA; $K_1=1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$ and $K_4 = 5.50 \times 10^{-11}$. Each component is abbreviated as H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} and Y^{4-} . In the case of EDTA, H_2Y^{2-} is the most dominant form when the experimental condition is at pH = 4.6 [13].

These K values show that the first two protons come off easier than the last two protons. In an acid solution, EDTA has structure of a neutral ion. Lone pair electrons in hydroxyl groups and nitro groups cause EDTA molecules to become hexadentate ligands that can assemble with metal ions. Thus, EDTA reacts with metal ions, and forms a metal EDTA complex compound as the equation below [14].



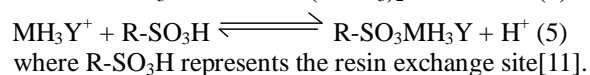
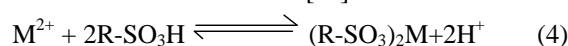
A batch equilibrium method was employed for the determination of distribution coefficient of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) on cation exchange resin Purolite C100 in the presence of 0.01M EDTA at different pH's values ranging from 2.2 to 9.0 at 25°C. Studies were performed in order to verify the effectiveness of the cation-exchange for metal-EDTA complex separation. The distribution coefficients were determined and presented in Table (1). As can be seen from this table, there were enough differences between the distribution coefficients for the separations of the elements. Since the stability of EDTA complexes vary with pH's. It was to be expected that change of pH would have considerable effect on the distribution coefficient for all metal ions. The results indicate that Ba(II)-EDTA complex was less stable than of Pb(II) - EDTA complex at pH 4.0-4.5. It seen from the results that Fe(III) and Bi(III) have lower k_d values at pH 2.2, so the value of pH 2.2 was considered most suitable for the stabilities of Fe(III) and Bi(III). Pb(II) form more stable complex at pH 4.5, on other hand k_d value for Ba(II) very high at pH 2.2 while it have lower k_d at pH 9.0. The result in Table (2) designate the separation of Fe(III) and Al(III) from the alkaline earth metals because the multivalent metals form stronger EDTA complexes than do the alkaline earth. The barium complex of EDTA is much weaker than the corresponding complexes of Fe (III), Al (III) and Bi (III). It was therefore, considered possible to effect complete separation of Ba(II) from Fe(III), Al(III) and Bi(III) on cation exchange resin purolite C100, making use of this difference in stabilities of the EDTA complexes.

The distribution coefficient of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) on cation exchange resin Purolite C100 in the presence of 5%

citric acid at different pH's values ranging from 2.2 to 6.4 at 25°C were determined. Table (1) indicate that k_d values for all metal ions vary with the change of pH. Lead ions form more stable anionic complex and has noticeable decrease in k_d values. The difference between k_d values for Ca(II), Ba(II) and Pb(II) should be fairly enhanced at pH 5.2. Where as at pH 2.2 the difference between k_d values for Pb(II) and Ce(IV) should be enhanced. Bi(III) forms more stable complex than Pb(II) at $\text{pH} < 4$. The highest separation factor for Al(III) and Pb(II) is obtained at pH 4.5, Table (2) furthermore Ca(II) and Ba(II) have some what lower separation factors at pH 6.4 therefore the cation exchange resin purolite C100 in the presence of citric acid was unsatisfactory for the separation of calcium and barium ions.

3.3. Quantitative elution of lead ions.

If cationic complexes are present, e.g. in the case of M-EDTA chelates, more than one positively charged species exists. The chromatographic system contains several ionic species, such as Na^+ , H^+ , EDTA in the eluent and different complex forms in the sample. Furthermore, the eluted metal ions are partly complexed and partly exist in solution as free metal cations. In order to have a reliable retention model all forms of cationic species in the system must be considered in the same run [15]:



The behaviour of lead ions towards various eluting agent using cation exchange resin Purolite C100 was studied. Quantitative elution of lead ions were possible with 200 ml of different eluents. The elution curves in the presence of sodium nitrate 2M, mixture of sodium nitrate 2M and 0.5M nitric acid, 0.01 M EDTA and 0.005 M EDTA at pH 4.5 were illustrated in Fig. (2a and b). EDTA used as complexing agent for lead ions. It was eluted as lead - EDTA complex at pH 4.0-4.5. The results indicate that the elution peak is seen to be gradually shifting towards the left with increasing EDTA concentrations. Where the elution peak was observed in the second fraction. The elution constant and total lead recovery % were presented in Table (3). The elution of lead was found 94.10% in the presence of 2M sodium nitrate but in the presence of 2M sodium nitrate and 0.5M nitric acid the elution of lead increased to 99.10% and sodium nitrate efficiency was greater than EDTA.

3.4. Quantitative separations of metal ions from binary mixtures.

A rapid ion-exchange method is proposed for the separation of metal cations. The separation of

Table (1). Values of distribution coefficient (k_d) for different metal ions in the presence of 0.01M EDTA or 5% citric acid at different pH's, the concentration of metal ions was 26.5 ppm using cation exchange resin purolite C100 (H^+ form) at $25^\circ C \pm 0.1^\circ C$.

pH's	k_d													
	Pb(II)		Ca(II)		Fe(III)		Al(III)		Bi(III)		Ce(IV)		Ba(II)	
	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric
2.2	405.58	1535.08	395.29	369.00	2.28	66.17	19.32	3136.70	3.34	71.09	25.61	4.16	11604.07	773.37
2.7	201.20	913.73	247.63	256.00	3.56	123.06	22.42	1447.50	3.42	80.00	42.82	2.02	11293.30	4318.30
3.4	100.10	494.29	210.22	174.00	3.79	135.59	19.83	765.00	3.62	96.64	58.93	6.58	10960.00	548.50
4.0	40.34	253.08	160.25	118.63	9.37	173.78	21.60	230.97	17.39	95.85	63.40	33.41	10715.50	270.79
4.5	6.98	18.86	120.00	72.00	10.07	190.15	16.96	146.19	19.30	97.71	48.61	36.32	10200.00	144.17
5.2	17.07	11.17	9.68	34.01	69.74	195.04	-	94.90	55.58	98.59	46.80	96.51	9269.09	96.35
5.8	70.33	33.41	6.13	22.63	50.80	80.50	-	61.75	39.40	75.64	47.01	116.30	561.25	37.80
6.4	191.05	152.02	0.70	46.52	43.79	77.46	-	-	36.37	55.29	-	130.40	361.25	23.73
7.0	-	-	-	-	-	-	-	-	-	-	-	-	34.61	-
7.6	-	-	-	-	-	-	-	-	-	-	-	-	14.01	-
8.2	-	-	-	-	-	-	-	-	-	-	-	-	4.70	-
9.0	-	-	-	-	-	-	-	-	-	-	-	-	2.10	-

Table (2). Separation factors of some metals in presence of 0.01M EDTA or 5% citric acid at different pH's using cation exchange resin purolite C100 (H^+ form) at $25^\circ C \pm 0.1^\circ C$.

Cations	Separation factors		pH's
	EDTA	Citric	
Pb(II) — Ba(II)	1461.30	7.60	4.5
Pb(II) — Ca(II)	17.20	3.80	4.5
Pb(II) — Fe(III)	177.90	23.30	2.2
Pb(II) — Al(III)	2.40	7.75	4.5
Pb(II) — Bi(III)	121.43	12.86	2.2
Pb(II) — Ce(IV)	15.84	369.01	2.2
Ba(II) — Ca(II)	957.55	-	5.2
Al(III) — Ce(IV)	-	452.34	2.7

Table (3). Behaviour of lead ions towards various eluting agents using cation exchange resin purolite C100 (H^+ form) at $25^{\circ}+01^{\circ}C$.

Eluting agents		Elution constant E	Total lead recovery %
$NaNO_3$	2M	0.232	94.10
$NaNO_3 + HNO_3$	(2M + 0.5M)	0.769	99.10
EDTA at pH 4.5	0.005M	0.232	53.00
EDTA at pH 4.5	0.01M	0.769	89.21

Conc. of lead (II) 26.5 ppm

wt. of dried resin = 9.23g

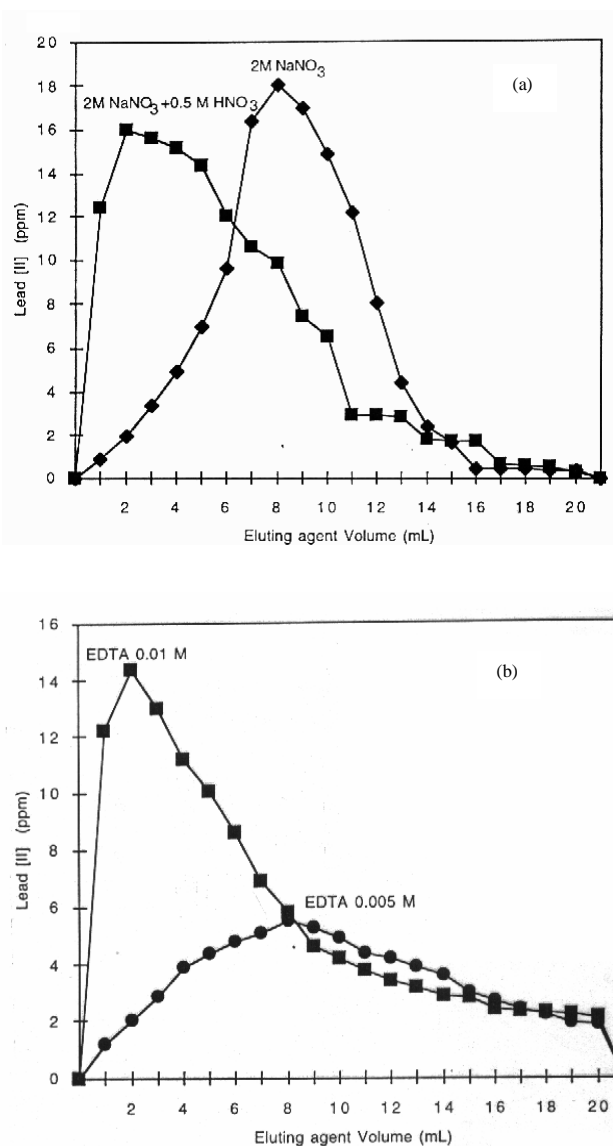


Fig. 2a,b. Elution of lead ions by eluting agents 2M $NaNO_3$, 2M $NaNO_3$ + 0.5 M HNO_3 , 0.01M EDTA and 0.005M EDTA at pH 4.5 using cation exchange resin purolite C100. Conc. Lead (II) = 26.5 ppm. Wt. of dried resin = 9.23 g.

M-EDTA can be carried out with a cation-exchange column. The retention mechanism of analytes involves the cation exchange of free metal ions which are present at low pH values [16]. Theoretical approaches to the retention behaviour of anionic metal complexes, taking into account only negatively charged species, have been developed for anion exchange [17], for cation exchange and for dynamic ion exchange. In fact at slightly basic or acidic pH values, the negatively charged species generally represent the total molar fraction. Nevertheless, if cation exchange is selected as separation method, not only the free metal but also the neutral, positive and negative species must be considered [18-22]. The method depends on the selective complexing of metal ions by a chelating agent as achieved by control of pH. To accomplish this separation, an excess of EDTA is added to the metal ion solution. The solution is buffered at a pH where the EDTA complex of one metal is quantitatively formed, while the complex of the other metal ion is largely dissociated. The solution is, then passed through a previously buffered column containing cation exchange resin Purolite C100. The uncomplexed metal ion is quantitatively removed from solution by the resin while the complexed ion passes through the column. The method has been applied with good results to several binary mixtures of metal ions.

Studies of the distribution of Ce(IV), Al(III), Fe(III), Bi(III), Ca(II), Ba(II) and Pb(II) between the cation exchange resin Purolite C100 in the presence of ethylene diamine tetraacetic acid (EDTA) or citric acid show the existence of separation factors between members of this metal ions. Separation of the metal ions was performed by an elution technique. A glass column 1.4x12.9 cm was packed with a known amount of resin (5 g) in the hydrogen form. After washing the resin with distilled water the sample solutions containing the metal ions desired to be separated were passed through the column at a flow rate of 1 ml/min. The quantitative separation Pb(II)-Ca(II), Pb(II)-Ba(II), Pb(II)-Fe(III), Pb(II)-Bi(III), Pb(II)-Ce(IV), Ca(II)-Ba(II) and Fe(III)-Ba(II) ions has been achieved. The effluent fractions were collected in 10 ml portion and analysed for the metal ions inside it using atomic absorption spectrophotometer. Results of the possible separation achieved on the column from synthetic solutions are given in Figs. (3a-d and 4a-d).

The separation of lead are based on that it doesn't form complex with EDTA and citric acid at pH 2.2. Hence cations which give rise to anionic complexes with these reagents at a proper pH can be separated from lead by passage through a cation exchange column. The separation of lead from calcium ions is facilitated by the eluant which has much greater complexing ability toward lead ions than calcium ions. In Pb(II)-Ca(II) the excellent separation

are obtained with 0.0 1M EDTA at pH 4.5, Table (2). EDTA complex of calcium is less stable than that of lead and it completely dissociated at pH 4.0-4.5 while lead complex doesn't. Calcium ion can be quantitatively eluted with 4MHCl. The separation of Pb(II) from Ba(II) is significance since the later is principle interference in the routine analysis of Pb(II). EDTA complex of Ba(II) is less stable than that of Pb(II) and it is completely dissociate at pH 4.0-4.5, even as Pb(II) complex dose not dissociate. In Pb(II)-Ba(II) binary mixture lead ions was selectively eluted with 0.01M EDTA at pH 4.5 followed by barium was eluted with 0.0 1M EDTA at pH 9.0. Mixtures of lead ions with bismuth or iron ions were treated with 0.01M EDTA and adjusted to pH 2.2. This transformed the cation other than lead into anionic complexes rending the separation quite easy. The most effective separation of Pb(II)-Fe(III) and Pb(II)-Bi(III) synthetic binary mixture is obtained with 0.0 1M EDTA at pH 2.2. In Pb(II)-Ce(IV) ions can be eluted very easily with 5% citric acid at pH 2.7 and separated from lead.

Calcium ion can be quantitatively eluted with 200 ml. of 0.0 1M EDTA at pH5.2 which fails to elute barium ions in Ba(II)-Ca(II) binary mixture; this provides an easy method of separation, barium ions can later be eluted with 200ml. 4M HCl or 0.01M EDTA at pH 9.0.

From the values of distribution coefficient, it appears that 0.01M EDTA at pH 2.2, give the most favorable conditions for the separation of iron ions which give rise to anionic complexes from barium ions the finally barium ions were eluted with 200 ml. of 4MHCl. The recovery % was calculated from the equation [23].

$$\text{Recovery \%} = \frac{[\text{M}^{n+}] \text{ eluted}}{[\text{M}^{n+}] \text{ fixed}} \times 100 \quad (6)$$

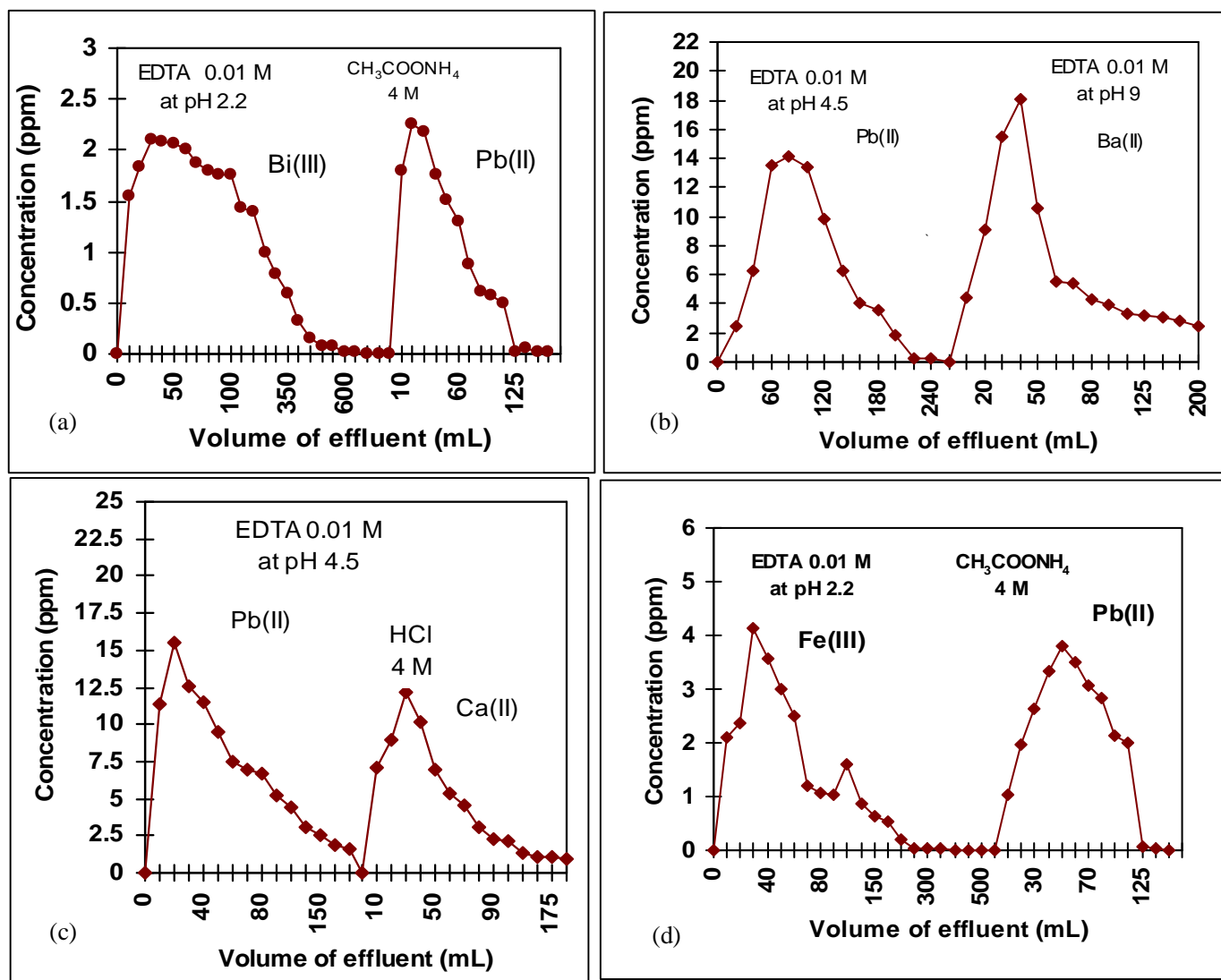
Table (4) represented in the recovery % of some metal ions in the presence of different eluent using cation exchange resin purolite C100.

4. Conclusion

The effects of EDTA chelating agent on separation of some metal ions were studied at 25°C. The cation exchange resin has been shown to be efficient stationary phase for the separation of many metal ions .It has been demonstrated that cation exchange resin Purolite C100 having sulfonic acid functional groups are able to separate Pb(II)-Ca(II), Pb(II)-Ba(II), Pb(II)-Fe(III), Pb(II)-Bi(III), Pb(II)-Ce(IV), Ca(II)-Ba(II) and Fe(III)-Ba(II) synthetic binary mixtures. From an experimental point of view, the behaviour of Pb-EDTA complexes

Table (4). Recovery percent % of some cations from a binary mixtures in the presence of different eluent using cation exchange resin purolite C100 (H⁺ form).

No	Mixture	Taken, (ppm)	Eluting agent	Found, (ppm)	Recovery %
1	Pb(II)	26.50	0.01M EDTA at pH 4.5	25.28	95.40
	Ba(II)	26.50	0.01M EDTA at pH 9.0	21.87	82.53
2	Pb(II)	5.30	0.01M EDTA at pH 2.2	5.30	100.00
	Fe(III)	5.30	4M CH ₃ COONH ₄	5.23	98.68
3	Pb(II)	2.65	0.01M EDTA at pH 2.2	2.62	98.87
	Bi(III)	2.65	4M CH ₃ COONH ₄	2.33	87.92
4	Pb(II)	26.5	0.01M EDTA at pH 4.5	22.79	86.00
	Ca(II)	26.5	4M HCl	14.77	55.74

**Fig. 3a-d. Elution curves for separation of some cations by different eluents using cation exchange resin purolite C100 (5g) (H⁺ form).**

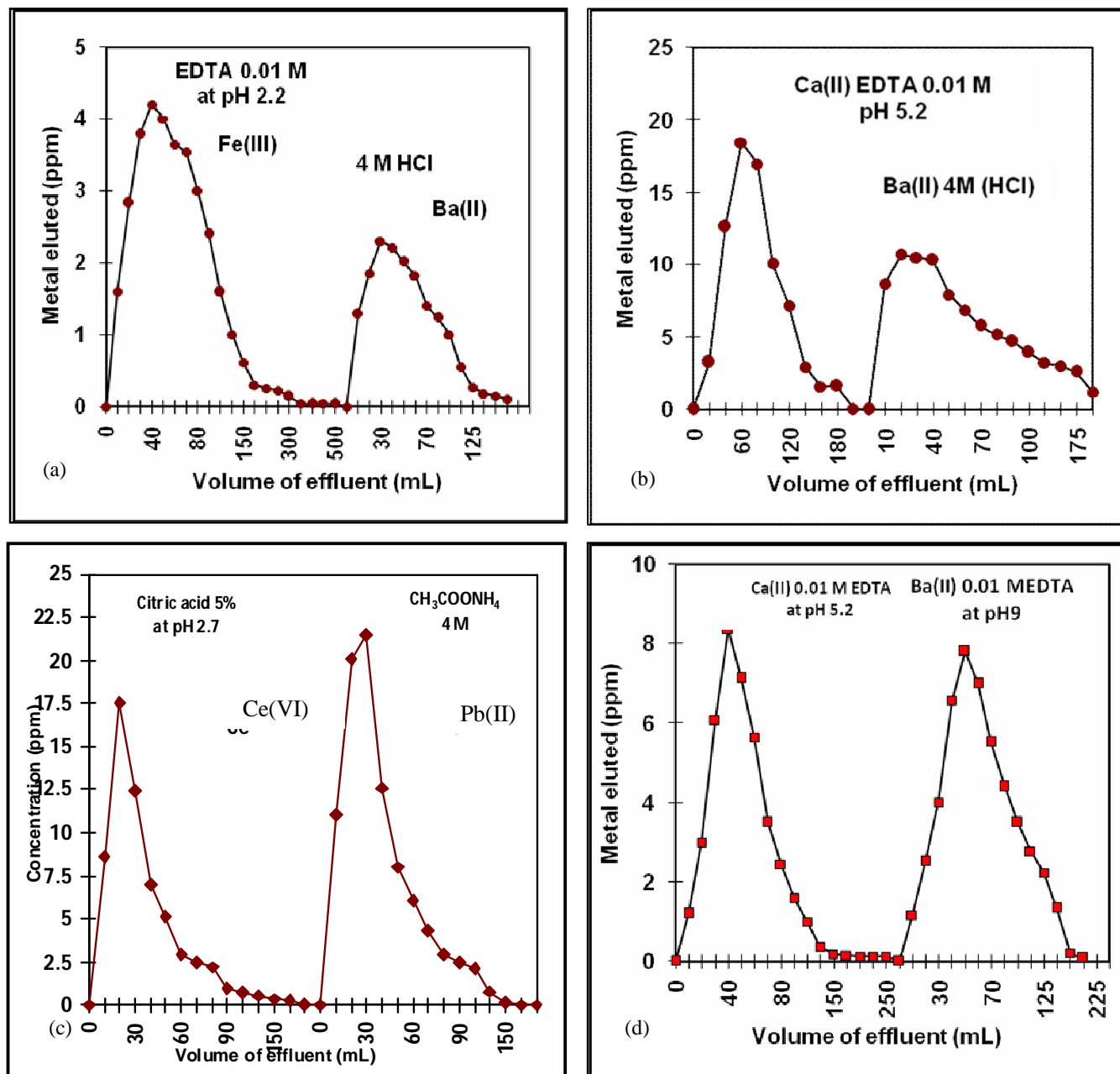


Fig. 4a-d. Elution curves for separation of some cations by different eluents using cation exchange resin purolite C100 (5g) (H^+ form)

provide data that can be used to develop a selective method for separation of lead ions. The separation of lead ions from metal ions was facilitated by the eluent which has much greater complexing ability towards it. The most effective separation of Pb(II)-Fe(III) and Pb(II)-Bi(III) synthetic binary mixture was obtained with 0.01M EDTA at pH 2.2 while the successful separation of Pb(II)-Ca(II), Pb(II)-Ba(II) synthetic binary mixture was obtained with 0.01M EDTA at pH 4.5.

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6/1/2010