

Chromatographic Column Separation of Rare Earth Elements by Resorcinol Formaldehyde Cationic Exchanger Resin

M. F. Attallah*, R. S. Hassan and S. A. Shady

Hot Laboratories Center, Atomic Energy Authority, P.O. 13759 Cairo, Egypt

Received: 15/2/2012

Accepted: 28/5/2012

ABSTRACT

Due to increase use of rare earth elements (REEs) in modern technology in the world over the past years, alternative separation method is essentially requested. Therefore, the main objective of this study is oriented to find efficient process for individual separation of light REEs from each other using resorcinol formaldehyde organic resin. In this investigation different type of eluent namely, oxalic acid, sodium hexameta phosphate and hydrazine have been tested for separation process of REEs. Optimizations of some parameters that affect on separation of REEs such as eluent concentration, flow rate and bed height of column have been performed. The results indicated that, 0.08M of hydrazine as novel eluent at 1ml/min is efficient for individual separation of REEs. Thus the improved successfully the separation process that more efficiently recovers the economically valuable REEs. The preliminary investigation has given promising results for lanthanides separation and production using resorcinol formaldehyde resin as stationary phase and hydrazine as novel eluent.

Keywords: Chromatographic Separation/ Rare Earth Elements REEs/ Resorcinol Formaldehyde Resin/ Efficient Eluent.

INTRODUCTION

All lanthanide elements except promethium occur in nature. Several lanthanide elements are more abundant than many better known metals. Among the lanthanides the relative natural abundance varies widely, the most abundant being cerium and the least thulium. However, more than an element estimated average crystal abundance, the nature and extent of its concentration in mineral deposits influence its commercial availability. Chemically the mineral monazite is an important source of lanthanides especially the light lanthanides ^[1]. It is a phosphate mainly of the cerium group (La-Nd) and thorium. Most of the traditional applications of lanthanides in industry are based on their similar chemical properties. Lanthanide elements are used in the medical, pharmaceutical, rubber, photographic, space, oil and lubrication, instrumentation, polymer and other industries ^[2,3]. The use of these metal ions in the technical and medical fields is growing annually. Lanthanide elements and compounds have found a variety of applications in nuclear uses, e.g in nuclear fuel control, where europium is used as control rods in compact nuclear reactors because it exhibits a high capture cross-section of the natural isotopes. Gd oxide is one of the largest elements used in the nuclear power as shielding and fluxing devices. It is used in general electric's boiling water reactor as burnable poison ^[4]. It mixed directly with uranium to achieve a uniform neutron flux during the life time of a fuel element. Pr is used in production of atomic battery. Ce and Y hydrides are useful as neutron moderation. Gd₂O₃ and Sm₂O₃ are used for glasses protecting eyes from neutron radiation. Radioisotopes of Nd and Eu are used as burn-up monitors to evaluate the performance and characteristics of reactors fuels ^[5]. Separation of lanthanides poses one of the most challenge problems in the analytical chemistry. Their separation as a group or as individual elements requires costly separation techniques and fractionation processes. The great similarity in chemical and physical properties of the lanthanides, which is often emphasized, can be ascribed to their similar ionic sizes

^[6]. Therefore, separation of trivalent lanthanides is still a very important and serious problem. The commercial production of these elements commonly employs solvent extraction processes ^[7-9]. An interesting alternative to traditional liquid–liquid solvent extraction is the use of aqueous polymeric solutions as environmentally safe liquid–liquid extraction media was increased ^[10].

Investigation of synthesis materials for separation of lanthanides was interested in researcher in last few decades. Ismail et al. ^[11] studied the use of some Mannich-type polymers in the separation of La^{3+} , Nd^{3+} , Sm^{3+} , and Gd^{3+} from each other. Draye et al. ^[12] synthesized some phenolic resins which were selective to lanthanides. Ion-exchange materials based on phenol–formaldehyde condensation polymers were described in the literature together with details of their chelating behavior toward various metal ions, and their selectivity to lanthanides was tested. In similar studies, the separation of La^{3+} , Ce^{3+} , Nd^{3+} , Pr^{3+} , and Sm^{3+} using a resin impregnated with 2-ethylhexyl hydrogen 2-ethyl hexylphosphonate [PC88A] impregnated resin was examined ^[11, 13-16]. This study represents a part of our systematic evaluation of the distribution behavior of light rare earth elements [Ln(III)] with resorcinol–formaldehyde (RF) polymeric material. Previously, we described the sorption behavior of light rare earth elements (La, Ce, Nd, Sm) on RF resin using batch experiments ^[17]. In the present work, the main goal is oriented to investigate the potential application of RF resin for individual separation of REEs using column experiments. In this concern, oxalic acid, sodium hexa meta phosphate (SHMP) and hydrazine have been investigated as eluent. The optimization of separation process of REEs has been performed.

EXPERIMENTAL

Chemicals and Materials

In this study all chemicals were used as analytical grad and used without further purification. Salts of lanthanide oxides and resorcinol were purchased from Merck with a chemical purity of 99.9%. Oxalic acid that used as eluent, 4-(pyridyl-(2)-azo)-resorcinmonohydrate (PAR) that used as the post column reagent and sodium hexametaphosphates were supplied from Fluka.

Preparation of resorcinol-formaldehyde resin (RF)

Resorcinol-formaldehyde resin was previously prepared ^[17,18] in our laboratory by condensing resorcinol ($\text{C}_6\text{H}_6\text{O}_2$), which was dissolved in a potassium hydroxide (KOH) solution, with 37% formaldehyde.

Column set-up

About 1.0 gm (1 cm height) Resorcinol formaldehyde in hydrogen (H^+) form was weighted in a beaker and twice the volume of distilled water was added then the beaker was shaken and the resin was allowed to settle. The liquor was decanted off and this process was repeated until the liquor is clear. Carefully the resin was poured in the form of slurry so that column is packed. From this point the resin must always be covered with liquid to avoid air bubbles getting into the column. The prepared resin was washed into the glass column, which should have a glass wool plug, with a small volume of dilute hydrochloric acid (0.1M) to ensure that resin is in H^+ form, and then wash with distilled water. All experiments were done at room temperature and at pH 4.5 that the high stability lanthanides complexes were performed ^[19]. The effect of column length on the retention volume of the five light lanthanide elements was investigated with three different bed height. The column was packed with 1, 2 and 3 cm of resin separately. The affinity of each column length was determined through two parameters resolution and distribution coefficient. The effect of flow rate on the

separation of light lanthanide elements was investigated at three different flow rates 1, 5 and 10 ml/min.

Break-through capacity of RF resin

One gram of the resin was taken into the glass column (1.0x20cm) fitted with glass wool support at the bottom. The bed length was approximately 1.0 cm of column height. Various mixture samples contains La, Ce, Pr, Nd and Sm were loaded with fixed concentration of 50 mg/L and collected individually in 10 mL vial. The effluents were measured using ion chromatographic system and the resin capacity was determined by usual column process. The breakthrough capacity (Q_{0.5}) of the cationic exchange resin (RF) is calculated according to the following equation:

$$\text{Breakthrough capacity (Q}_{0.5}\text{)} = V(50\%) \times C_o/m$$

Where, V(50%) is the volume to breakthrough at 50 % uptake in L, C_o is the initial concentration in mg/L, and m is the weight of the RF resin in grams.

Mathematical Chromatographic Parameters

Three different eluents namely oxalic acid, sodium hexa meta phosphate and hydrazine hydrochloride were used individually to elute mixture of lanthanide elements. Resolution factor (R) is used for comparative study of three eluents to express the separation between two adjacent lanthanide element peaks. Resolution can be calculated from the Gaussian-fitted curves using the following equations:

$$R = 1.18[(t_{R2}-t_{R1})/W_{1/2(1)}+W_{1/2(2)}]$$

Where t_{r1} and t_{r2} are the retention time of two adjacent peaks 1 and 2 respectively with their peak width at half maximum height w_{1/2(1)} and w_{1/2(2)} respectively.

Effect of different concentration of hydrazine hydrochloride on the separation process of REEs was carried out. The effluent was collected in 5 ml vials and measured using ion chromatography. The elution efficiency for each concentration was frequently represented with the resolution and selectivity factors. Resolution can be calculated as above and separation factor can be calculated from the Gaussian-fitted curves using the following equations:

$$\text{Separation factor (a)} = K_2' / K_1'$$

Where K₁' and K₂' are the capacity factors of element 1 and 2 respectively.

Capacity factor of an element K' can be calculated from the Gaussian-fitted curves using the following equations:

$$K' = (V_r - V_0) / V_0$$

Where V_r and V₀ are the retention volume and dead volume respectively.

RESULTS AND DISCUSSION

Break-through capacity

The loading behavior of La, Ce, Pr, Nd and Sm are depicted in Fig. (1) showing the breakthrough curves that are expressed in terms of normalized concentration which, defined as the ratio of the effluent concentration (C) to the original concentration (C_o) as a function of effluent volume. The figure shows that La has lower breakthrough volume than that of the other REEs. The breakthrough capacity (Q_{0.5}) of cationic exchanger (RF) towards La, Ce, Pr, Nd and Sm are 6.5, 7.5,

9.5, 10.2 and 10.5 mg/g, respectively. The capacities sequence for the studied elements is presented according to the following order:

Sm > Nd > Pr > Ce > La

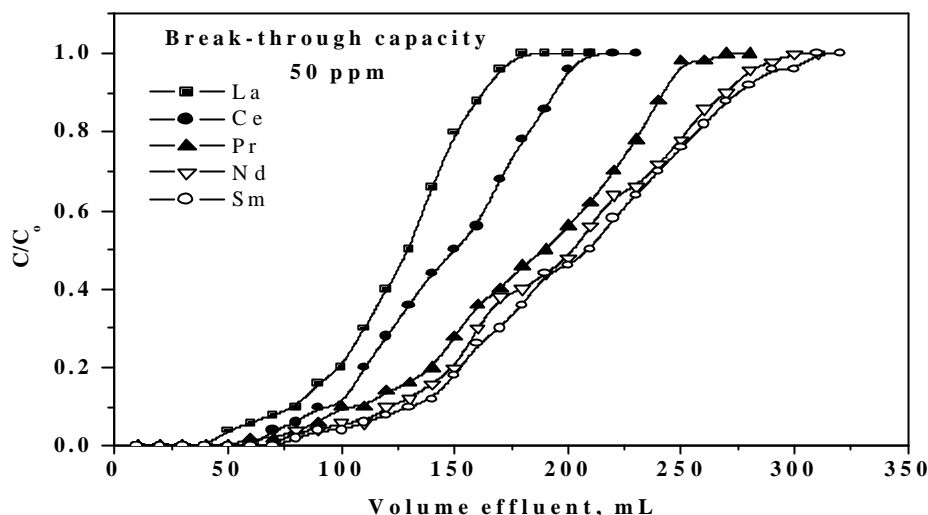


Fig. (1): Break-through curve for loading La, Ce, Pr, Nd and Sm onto RF resin.

Effect of eluent type

The influence of eluent type (oxalic acid, SHMP and hydrazine) on separation of REEs using RF cation exchanger was investigated as shown in Fig (2). The figure showed that, elution order was found from La to Sm with the three different eluents. It can be seen the sequence of elution order is consistent with the effective ionic radii of the lanthanides that monotonically decreases with atomic number from 1.320 Å for La to 1.194 Å for Lu [20,21]. Furthermore, this sequence is consistent with capacity order of REEs which is directly correlated to affinity of RF resin towards REEs, i.e., low sorption of REEs has found faster elution than other REEs under investigation.

For comparison between the elution performances of the three eluents, chromatographic parameters such as resolution and recovery % of REEs were calculated and presented in Table (1-2). The obtained data indicated that high resolution of REEs was obtained by hydrazine and the sequence of resolution is taking the following order: hydrazine > oxalic acid > SHMP. On the other hand range of recovery % of REEs was found 52-71, 58-70, 81-95% for oxalic acid, hydrazine and SHMP, respectively. The results indicated that SHMP has the highest recovery percent; therefore it can be used for preconcentration rather than for separation of REEs. In this respect, development of REEs separation using hydrazine as eluent has been studied in details in the next part.

Table (1): Comparison of resolution of separation of REEs using different type of eluent.

Adjacent REEs	Resolution		
	Oxalic acid	SHMP	Hydrazine
La/Ce	0.42	0.14	1.77
Ce/Pr	0.20	0.17	2.53
Pr/Nd	0.24	0.21	1.73
Nd/Sm	0.33	0.13	2.48

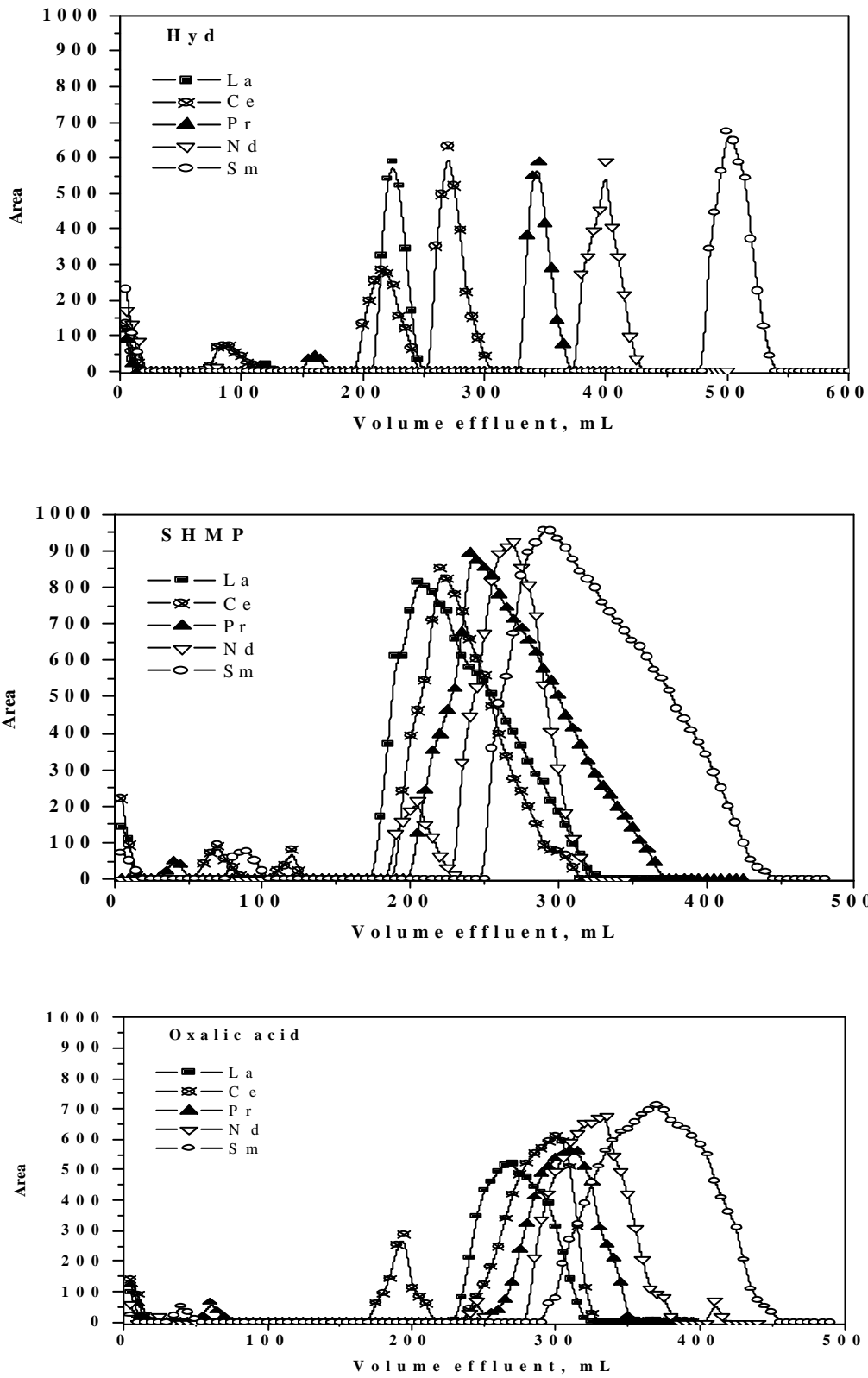


Fig. (2): Effect of oxalic acid, SHMP and hydrazine as eluent on separation of REEs. Eluent conc. 0.08M, flow rate 1 ml/min, pH 4.5, column length 1 cm.

Table (2): Recovery percent of REEs separation using different type of eluent.

REEs	*Recovery %		
	Oxalic acid	SHMP	Hydrazine
La	52	81.4	58.9
Ce	61	85.2	63.3
Pr	56	89.2	58.7
Nd	67.5	92.4	59.1
Sm	71.2	95.5	69.4

* Recovery percent = C_f/C_o %

Effect of hydrazine concentration

Effect of different concentration (0.05-0.1M) of hydrazine on the separation of REEs was studied. This feature was examined in Fig. (3) by plotting area under peak of the individual REEs with different eluent concentrations. It can be seen that, generally, an increase in eluent concentration decrease elution time (faster elution) and increase area under peak without any change in the elution pattern (sequence) for all REEs.

The data of recovery %, resolution and separation factor of REEs are listed in Table (3-5). Data demonstrated that, recovery % of REEs was increased with increasing of hydrazine concentration as a result of increasing ionized species of the eluent and there is no significant change in selectivity factor. At 0.05M concentration, elution peaks show some broadening (no sufficient ionized species). This broadening affected on the resolution data (decrease resolution). Although 0.1M concentration show the highest peak areas and shorter elution time but elution peaks show splitting phenomenon, it is consistent with another column studied ^[22]. At 0.08M concentration, resolution shows the highest values as a result of the base line separation between each two neighboring elements with good recovery %. Therefore, 0.08M hydrazine was selected as optimum eluent concentration for good separation and was used in further experiment.

Effect of flow rate

Figure (4) shows effect of different flow rate (1-10 ml/min) on the separation process of REEs using 0.08M hydrazine as eluent. The results indicated that increasing in the flow rate decrease retention time (faster elution) and without any change in the elution sequence of REEs. It can be also seen that, resolution of REEs was increased with decrease of flow rate as reported in Table (6). Thus individual REEs separation was optimized using 0.08M hydrazine at 1 ml/min.

Effect of column length

Different column length (1, 2, 3 cm) was investigated for the separation process of REEs at 0.08M hydrazine and 1ml/min as given in Fig. (5). From gaussian fitted curves it can be concluded that with increasing column length leads to increase the retention volume as well as increasing distance traveled by elements. Resolution data is increasing with column length increasing as represented in Table (8-9). The results indicated that, non significant effect of increasing column length for separation sequence of REEs under study.

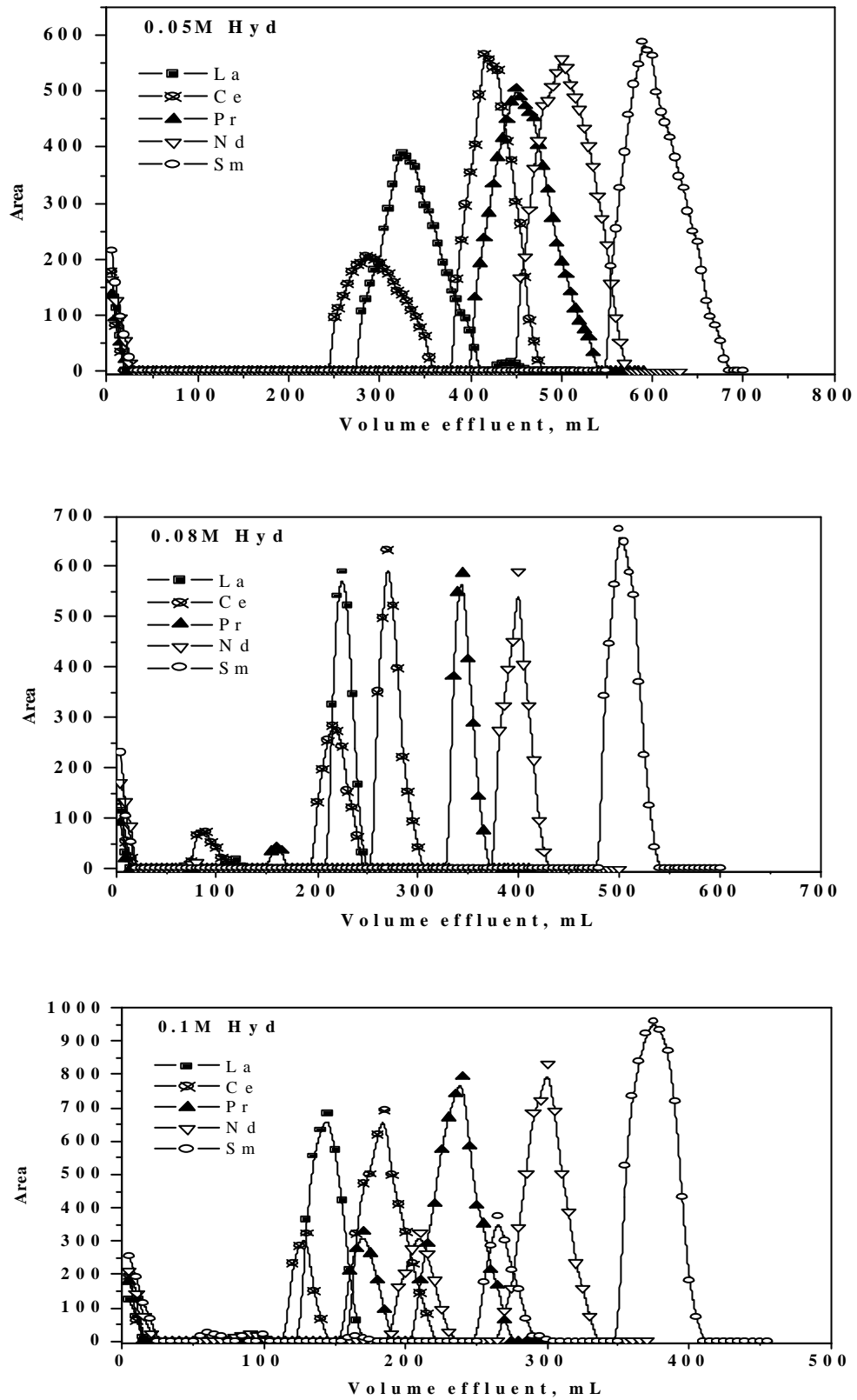


Fig. (3): Effect of hydrazine concentration as eluent on separation of REEs at flow rate 1 ml/min and pH 4.5.

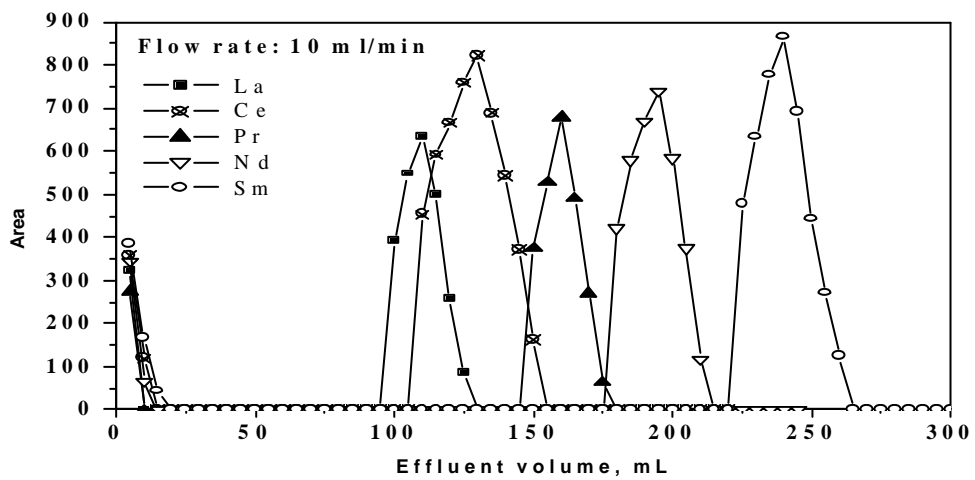
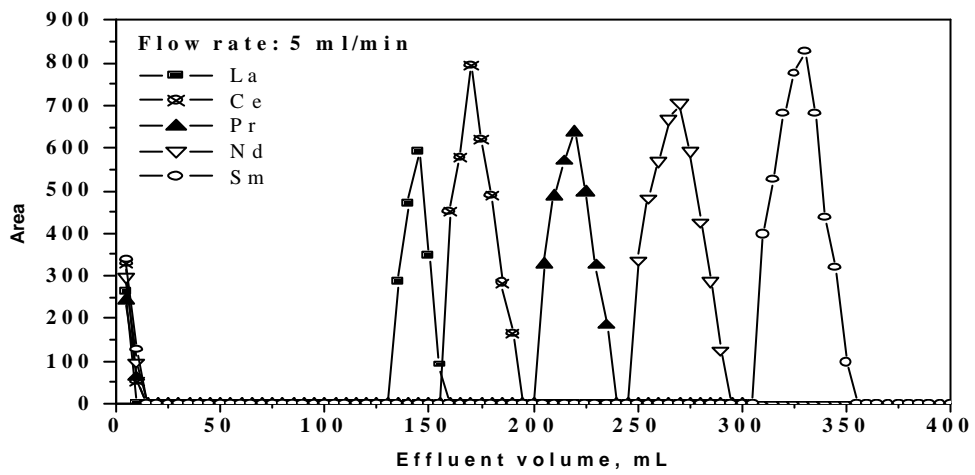
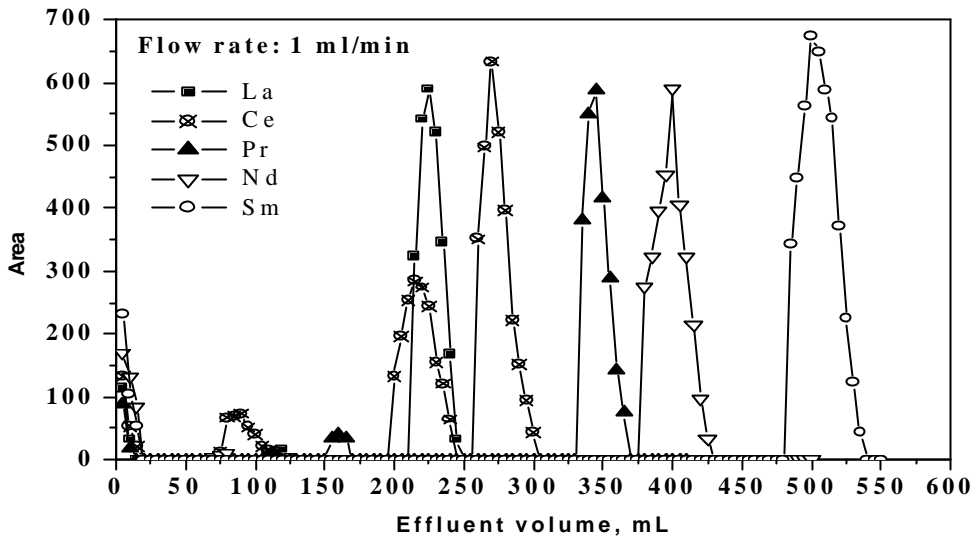


Fig. (4): Effect of flow rate on separation of REEs using hydrazine as eluent at pH 4.5.
 Table (3): Recovery percent of REEs using different concentration of hydrazine.

REEs	Recovery % for different concentrations of Hydrazine		
	0.05M	0.08M	0.1M
La	38.9	58.9	68.2
Ce	56.7	63.3	69.0
Pr	50.5	58.7	79.2
Nd	55.7	59.1	83.4
Sm	58.9	69.4	95.7

Table (4): Resolution of REEs separation using different concentration of hydrazine.

Adjacent elements	Resolution		
	0.05M	0.08M	0.1M
La/Ce	0.99	1.77	1.1
Ce/Pr	0.38	2.53	1.2
Pr/Nd	0.48	1.73	1.2
Nd/Sm	0.89	2.48	1.6

Table (5): Separation factor (a) of REEs using hydrazine as eluent at different concentration.

REEs	a		
	0.05M	0.08M	0.1M
La/Ce	0.85	0.69	0.84
Ce/Pr	1.10	1.29	1.32
Pr/Nd	1.11	1.17	1.27
Nd/Sm	1.21	1.26	1.26

Table (6): Resolution of REEs separation using hydrazine as eluent at different flow rate.

Adjacent elements	Resolution		
	1 ml/min	5 ml/min	10 ml/min
La/Ce	1.77	1.18	0.73
Ce/Pr	2.53	1.97	1.09
Pr/Nd	1.73	1.68	1.50
Nd/Sm	2.48	1.77	1.63

Table (7): Recovery percent of REEs separation using hydrazine as eluent at different flow rate.

Elements	Recovery %		
	1 ml/min	5 ml/min	10 ml/min
La	58.9	59.0	63.2
Ce	63.3	79.4	82.1
Pr	58.7	63.7	67.9
Nd	59.1	70.5	73.9
Sm	69.4	82.5	86.4

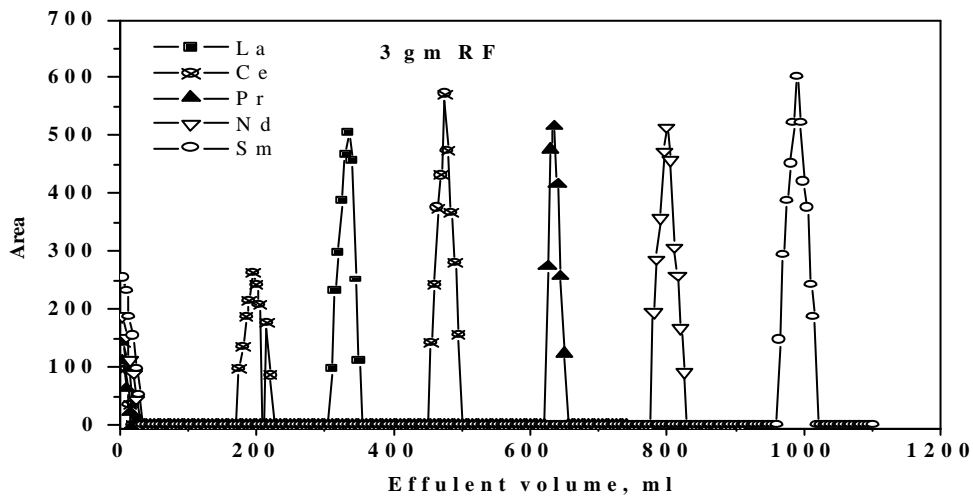
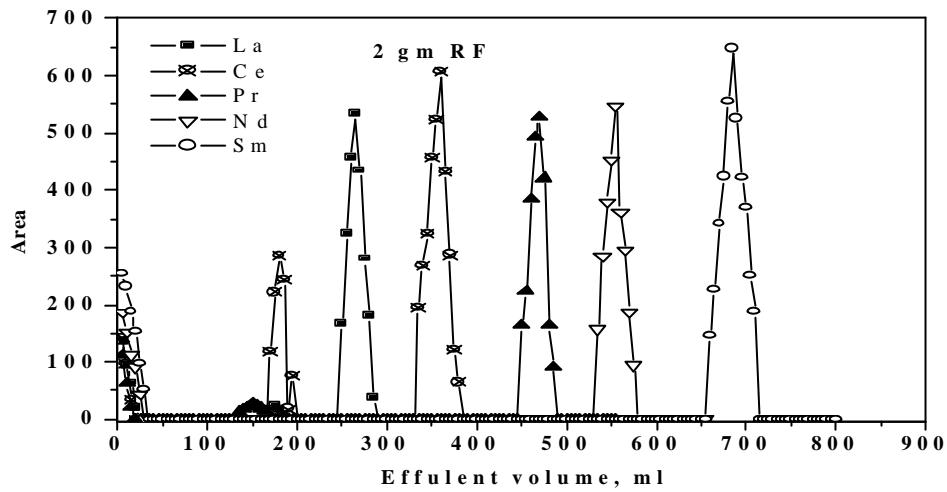
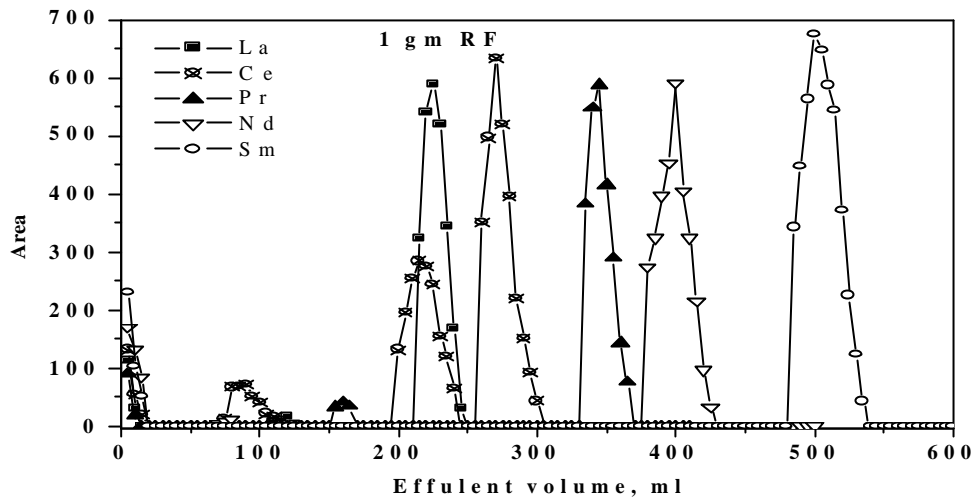


Fig. (5): Effect of bed height on separation of REEs using hydrazine as eluent.

Table (8): Resolution of REEs separation using hydrazine as eluent at different column length.

Adjacent elements	Resolution		
	1 gm	2 gm	3 gm
La/Ce	1.77	2.36	3.77
Ce/Pr	2.53	3.44	4.01
Pr/Nd	1.73	2.8	3.15
Nd/Sm	2.48	3.02	3.20

Table (9): Recovery % of REEs separation using hydrazine as eluent at different column length.

elements	Recovery % for different amount of RF resin		
	1 gm	2 gm	3 gm
La	58.9	53.4	50.4
Ce	63.3	60.8	57.2
Pr	58.7	52.7	51.7
Nd	59.1	54.7	51.4
Sm	69.4	64.7	60.2

CONCLUSION

The extraction chromatographic of REEs namely La, Ce, Pr, Nd and Sm from aqueous solution using resorcinol–formaldehyde (RF) resin has been studied. This study has demonstrated that, RF resin is suitable stationary phase for selective and sequential separation of REEs that eluted with oxalic acid, SHMP and hydrazine. Elution of REEs with hydrazine is desired as best eluent rather than oxalic acid and SHMP. The separation order of REEs are found La, Ce, Pr, Nd and Sm, it gives important information to support the separation mechanism. The sequence of elution order is consistent with the effective ionic radii of the REEs that monotonically decrease with atomic number from 1.320 Å for La to 1.194 Å for Lu. Furthermore, this sequence is consistent with capacity order of REEs which is directly correlated to affinity of RF resin towards REEs. RF resin has some advantages such as low cost, short equilibration time and high affinity for lanthanide elements. It is promising ion exchanger for determination and separation of lanthanides as convenient method.

ACKNOWLEDGMENT

The authors intended a grateful thank to Prof. Dr. E.H. Borai, Hot Laboratories and Waste Management Center, for his kind help and continuous support during this study.

REFERENCES

- (1) K. Miura, J. Qiu, S. Fujiwara, S. Sakaguchi, and K. Hirao, Appl. Phys. Lett.; 80, 2263 (2002).
- (2) L Eyring; Pergamon Press;New York, 2 (1966).
- (3) K.A.J. Gschneidner, "Industrial applications of the rare earth elements", (1981).
- (4) L. Goldstein, and A. F Strasser, Nucl. Tech.; 60, 352 (1983).
- (5) M. B. Farr, Mineral, Ann, Rev.; 94, (1982).
- (6) I. Otmez, and G.E. Gordon; Science; 229, 966 (1985).
- (7) K.L. Nash; Solvent Extr. Ion Exch.; 11, 729 (1993)
- (8) M.L.P. Reddy, M.S. Murali, and J.N. Mathur, J. Radioanal. Nucl. Chem.; 230, 29 (1998).
- (9) Danuta Czakis-Sulikowska and Natalia Pustelnik; Solvent Extr. Ion Exch.; 21, 751 (2003).

- (10) Alain Favre-Réguillon, Micheline Draye, Gérard Lebusit, Sylvie Thomas, Jacques Foos, Gérard Cote, and Alain Guy; *Talanta*; 63, 803 (2004).
- (11) A.I. Ismail, K.A.K. Ebraheem, M.S. Mubarak, and F.I. Khalili; *Solvent Extr. Ion Exch.*; 21, 125 (2003).
- (12) M. Draye, K.R. Czerwinski, A. Favre-Reguillon, J. Foos, A. Guy and M. Lemaire; *Sep. Sci. Technol.*; 35, 1117 (2000).
- (13) G.S. Lee, M. Uchikoshi, and K. Mimura; *Sep. Purif. Technol.*; 67, 79 (2009).
- (14) N. Dumont, A. Favre-Reguillon, B. Dunjic, and M. Lemairc; *Sep. Sci. Technol.*; 31, 1001 (1996)
- (15) S.K. Samanta, M. Ramaswamy, and B.M. Misra; *Sep.Sci. Technol.*; 27, 255 (1992).
- (16) S.K. Samanta, M. Ramaswamy, and B.M. Misra; *Radiochim. Acta*; 57, 205 (1992).
- (17) S. A. Shady, M. F. Attallah, and E. H. Borai *Radiochemistr*; 53, 396 (2011).
- (18) S.A. Shady; *Journal of Hazardous Materials*; 167, 947 (2009).
- (19) J. Schijf, and R.H. Byrne; *Geochimica et Cosmochimica acta*; 65, 1037 (2001).
- (20) *CRC Handbook of Chemistry and Physics*, 66th ed., CRC Press, Boca Raton, FL, (1985).
- (21) P.N. Nesterenko, and P. Jones; *J. Chromatogr. A* 804, 223 (1998).
- (22) Katty R. Echols, Robert W. Gale, Kevin Feltz, Jerome O. Laughin, Donald E. Tillitt, and Ted R. Schwartz; *Chromatography; A.*, 135 (1998).