



## The Utmost Extraction of some individual rare earth elements from Monazite Mineral Acidic Leach Liquor by solvent and ion exchange techniques

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### Abstract

This paper focused on the extraction of Nd (III) from acidic leach liquor obtained after monazite mineral opening by concentrated H<sub>2</sub>SO<sub>4</sub> solution. The behaviors of REEs extraction were studied by examining the extractant concentration and the effectiveness of other experimental parameters. Solvent extraction process is used to separate the total dissolved REEs in the Pregnant Leach Solution (PLS) as Ce, La, Nd and Pr into the organic phases using tri butyl phosphate (TBP) as the most effective extractant. By the 5th stage of SX process, 55.94, 11.48, 14.97 and 7.61 % purity of Ce, La, Nd and Pr were separated from the (PLS) respectively using 50 vol. % TBP diluted in kerosene, at 0.2 pH for 5 minutes then stripped by 3M NH<sub>4</sub>NO<sub>3</sub> solution at room temperature. Extraction mechanism of REEs was studied for the separation of light REEs and middle REEs from the pregnant leach solution. The produced LREEs were dissolved in concentrated HCl followed by pH adjustment to 1.8 passed in column of Dowex 50 -X8. REEs load is then eluted through the Cu-form resin column using 0.5 M Citric acid solution adjusted to pH of 3.9. Neodymium concentrates with ~ 99.9, 99.5, 98, 97.1% purity and 50, 80, 81, 82.5 % recovery can be obtained according to marketing or further chemical or technical approaches for the fractions obtained.

**Keywords:** Monazite, Rare earth Elements (REEs), Solvent extraction, TPB, ion exchange process, Dowex 50 -X8..

### 1. Introduction

Rare earth (RE) elements are group of 15 elements in the periodic table known as the lanthanide series as well as Sc and Y, which categorized into two groups according to their ionic radius; light rare earth elements (LREEs) from La to Sm and heavy rare earth elements (HREEs) from Eu to Lu. From a point of view, these metals possess similar chemical and physical properties and universally originate in the same mineral assemblies. Given their particular spectroscopic and magnetic properties, REEs play an imperative role from industrial to advanced material sciences that include electric and hybrid automobiles, electrical assemblies, metal alloys, critical military applications, fluorescent lights and in the manufacturing of high intensity magnets, etc.[1]

Among 250 recognized REEs minerals occurring in the crust, there are only three major sources of REMs which are monazite, bastnasite and xenotime. However, weathered crust elution-deposited rare earth ores known popularly as ion-adsorbed ore of rare earth is also workable for the recovery of RE. Monazite is one of the most abundant beach sand mineral found in vein deposits and acidic igneous rocks which

containing mainly 20–30% Ce<sub>2</sub>O<sub>3</sub>, 4–12% ThO<sub>2</sub> and 10–40% La<sub>2</sub>O<sub>3</sub>. [2]

Digestion for low grade monazite sand of different grain size is recommended via the acid route using sulphuric acid due to its advantages which include their availability, low cost and plant corrosion to its higher boiling point.

Recovery of rare earths from the leach liquor solution by solvent extraction is followed by precipitation of these elements from the strip solution in the form of rare earth oxalates. Also, separation of rare earths individually can be carried out by fractional precipitation, ion exchange and selective reduction or oxidation. The distribution between the two immiscible liquid phases of the individual rare earths controls the separation process of rare earth elements during the solvent extraction process. [3]

A critical factor that affects the rare earth extraction process is the selection of the most suitable extractant. Various solvents have been vastly used in the solvent extraction technique of rare earths such as: TBP, Aliquat 336 D2EHPA, HEHEHP and Versatic 10.

In solvent extraction, active extractants usually have chelating properties in the organic phase that

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dissolved in aromatics or Kerosene. Organophosphorus acids such as di-ethylhexyl phosphoric acid (DEHPA, D2EHPA, and others) are ordinary solvation agents. As the REE atomic number increases the distribution coefficient in such a system also increased. Other permissible solvation agents include other P-containing extractants such as: quaternary ammonium salts (Aliquat 336), tri-n-octyl phosphine oxide, tri-butyl phosphate (TBP, which can extract REE nitrates) and long-chained amines such as 2-aminononadecan (N1923) [4].

The cation exchange resins are the earliest applications for the separation of rare earth elements as a group. Generally used strong cation exchange resins include Dowex AG 50 W-X8 [5], Dowex AG 50WX12 [6], Bio Rad AG 50-X8 [7], Ostion LGKS 0800, sulphonated polystyrene and bonded-phase silica [8] and Amberlite IR-120 [9]. A common method for cerium ions sorption from solutions can be the use of commercially available and inexpensive ion exchangers: for example, KU-2-8 and AV-17-8 [10–13]. The Dowex 50WX8 and Lewatit MDS 200 H resins represented favorable sorption profiles to REE, evidenced by equilibrium factor values ( $R_L$ ) and higher values of the Langmuir constants (b) [14].

The aim of this study is to separate some individual REEs from pregnant leach liquor obtained from monazite leaching in nitric acid solution by solvent extraction and stripping processes followed by ion exchange process. The optimum separation of LREEs from the pregnant leach solution obtained from acid leaching of monazite was investigated using different strippers followed by ion exchange separation process and the obtained results are summarized in the next sessions.

## 1. Experimental

### 1.1. Materials

Monazite beach mineral about ~ 85% from black sand (Rosetta area on Mediterranean coast), sulfuric acid (TEDIA, 97-99%), sodium hydroxide (ADWIC, 96%), ammonia solution (ADWIC, 33%), tri-butyl phosphate (TPB) (LOBA Chemie, 99%), kerosene (Misr Petroleum Co.), ammonium nitrate (ADWIC, 98%), nitric acid (BDH, 65%), sodium nitrite (ADWIC, 99%), Dowex 50 -X8 (Fluka AG, 99%) in sodium form, citric acid (ADWIC, 99.9%), hydrochloric acid (SRL, 37%).

### 1.2. Instrumentation

Samples used in this investigation were weighed using an analytical balance (AND, Japan). The pH of the different solutions was measured using pH meter (inoLab, WTW, Germany). The determination of chemical composition of samples were done by X-ray fluorescence spectrometry using a Rigaku spectrometer (NEX CG) [15]. The mineralogical composition of the produced precipitates were

determined using X-ray diffractometer with  $\text{CuK}\alpha$  radiation tube source as X-ray source. Elements concentrations in the aqueous phases acquired from acid leaching, extraction and stripping were measured by using inductively coupled plasma (Prism ICP-high dispersion). Environmental scanning microscope (ESEM), Philips XL30 is used in the investigation of composition of REEs cake.

### 1.3. Feed solutions:

Egyptian monazite upgraded to about ~ (85%) mineralogical grade without grinding (-125 mesh) is used as a starting material of this study. The remainder included minerals such as zircon mainly, rutile, and ilmenite and silicates. It is obtained from black sands deposited at Rosetta area on Mediterranean coast. Monazite mineral digested with 97% conc.  $\text{H}_2\text{SO}_4$  with ratio equal 1:2 for 2.5 hours at 200-220°C. After that, the gray paste was dissolved by ice water (1:20) with continuous stirring for 1 hour followed by decantation, filtration. The acidic filtrate was precipitate first at pH1 by ammonia solution to produce thorium pyrophosphate. The produced filtrate was precipitated completely by sodium hydroxide then dissolve gradually by sulfuric acid till pH 1.75 followed by filtration. The produced precipitate after analysis contains the light and middle rare earth elements without any contamination with thorium and uranium. 150g of this L+MREEs was totally dissolved by concentrate nitric acid and completed to 1L by distilled water. Ammonium nitrate, (3M) solution, is prepared by dissolving about (240 gm) of analytical grade in 1 liter of distilled water. Sodium nitrite solution, 0.1N solution, is prepared by dissolving about 7.5 gm in 800 ml of distilled water then complete up to 1 liter. Nitric acid, (1 / 3 / 5M) solutions, are prepared by dissolving about (70 / 210 / 350 ml) respectively in 1 liter of distilled water.

### 1.4. Solvent Extraction and stripping processes:

The organic extractant is mixed with the pregnant leach solution which contains efficient amounts of REEs at volume ratio (1:1) using a mechanical shaker in shaking the sample for 5 minutes at room temperature then the separation of the 2 phases is obtained by separation funnels. After that, analyze the REEs concentrations found in the aqueous phase. The extracted REEs concentrations in the organic phase were calculated by mass balance while the extraction efficiencies of REEs in the organic phase were calculated by the following equation (equation 1);

$$E \% = (CT - CR) / CT * 100\% \quad (1)$$

Where; E % is the percentage of REE extracted into the organic phase, CT – Total REE concentration in the PLS, CR – REE concentration remained in the

aqueous phase (raffinate) after the extraction of REE into the organic phase.

Then, rare earth elements were stripped using different strippers as ammonium nitrate, nitric acid and sodium nitrite for 5 minutes at room temperature. After specifying the optimal extraction conditions, stripping of the rare earth elements into the new aqueous phase is done for further processing.

### 1.5. Ion exchange process

Cation exchange process for individual rare earth elements separation after the separation by solvent to achieve a good percent of purity. For the separation process, 2 g of REE concentrate are dissolved in concentrated HCl followed by pH adjustment to 1.8 and the volume is made up to 250 ml to give a concentration of about 8 g/l REEs.

## 2. RESULTS AND DISCUSSION

The pregnant acidic leach solution containing efficient amounts of REEs is analyzed and shown in table (1).

**Table (1):-** The analysis of the mother sample containing efficient amounts of REEs

Element Oxide	Concentration [% (w/w)]
La <sub>2</sub> O <sub>3</sub>	21.81
Ce <sub>2</sub> O <sub>3</sub>	40.93
Pr <sub>2</sub> O <sub>3</sub>	9.04
Nd <sub>2</sub> O <sub>3</sub>	20.34
Sm <sub>2</sub> O <sub>3</sub>	3.71
Gd <sub>2</sub> O <sub>3</sub>	4.17

### 2.1. Effect of TBP Concentration with different strippers:

TBP and TBP diluted with kerosene (1:1) after equilibration with 1N HNO<sub>3</sub> were used. At first, the reaction was carried out between the extractant and the pregnant solution and the scrubbing was done by hot water before the stripping process this is according to Jorjani, E., Shahbazi, M., [16] whom used hot water at 70°C as a scrubber, but the removal of impurities at one stage was inadequate. So, the removal of impurities increased as the scrubbing was repeated from one to four times. By repeating the scrubbing three times, more than 81, 27, 30, and 15 wt% of calcium, iron, magnesium and phosphorus were respectively removed while there were not significant loss of REEs (2.6%, 3.2%, 1.5% and 1.6% for Nd, Y, Ce and La respectively). When the scrubbing was done more than three times, the harmful elements removal only increased slightly while the loss of REEs increased significantly. The experimental works and the results show that scrubbing with hot water uptakes the most of REEs without any separation of individual elements or groups.

20 ml TBP are added to 20 ml pregnant solution and shake for 5 minutes at room temperature, then add 20 ml hot H<sub>2</sub>O and shake for 5 minutes as a scrubber, add 20 ml 3M NH<sub>4</sub>NO<sub>3</sub> then shake for 5 minutes as stripper and repeated twice. From the results, it was seen that in the first stage all the REEs elements was extracted totally by hot water with percent extraction equal 37.78, 16.07, 25.99, 8.08, 7.19 and 4.89 % for Ce, La, Nd, Pr, Sm and Gd respectively. This stage followed by stripping with 3M NH<sub>4</sub>NO<sub>3</sub>, which extracted Ce, La, Nd, Pr and Sm in two stages without Gd. The second, third, fourth and fifth extraction stages give almost the same results of the second stage with small gradual increase of La, Ce and Pr followed by decrease in Nd, Sm and Gd extraction percentages in hot water scrubbing stage. The best results were obtained in the third and fifth stage of extraction, where Ce and Nd were extracted by 50.76 and 49.24% respectively but La and Ce were extracted in the fifth stage by 48.88 and 51.12% respectively. The same results were mostly obtained using hot water as a scrubber with nitric acid and sodium nitrite as strippers in the two cases even with TBP or (1:1) TBP diluted in kerosene. According to the results obtained, we repeated the experimental work starting by nitric acid and ammonium nitrate for the reaction of the extractant in different concentrations with the pregnant solution as strippers.

#### 3.1.1. Ammonium nitrate as a stripper:

REEs are stripped in the three stages during the five stages of extraction with 100% TBP as shown in table (2). In Table (3), total REEs are separated in the five stages of extraction with 50% TBP diluted in kerosene, except the first step of the fifth stage of stripping there is a separation of 55.94, 11.48, 24.97 and 7.61 % purity of Ce, La, Nd and Pr respectively. Also, each first stage of stripping with 3M NH<sub>4</sub>NO<sub>3</sub> contains the total REEs but it is found that Pr is separated only from the second stage of stripping. LREEs ions in aqueous system bound strongly with the capping water molecules in comparison with hydrated middle REEs ions as the result of the ionic radii of REEs is decreased. It can be deduced that the importance of the bond strength of the hydrated REEs ions presented in the aqueous solution on the separation of LREEs and middle REEs into the organic phase from a PLS.

#### 3.1.2. Nitric acid as a stripper:

Gd is separated from the first stage of extraction by using 5M HNO<sub>3</sub> as a stripper in case of TBP after equilibration with 1N HNO<sub>3</sub> as presented in table (4). While, no separation is obtained in the other TBP concentration as found in table (5).

#### 3.1.3. Sodium nitrite as a stripper:

Sodium nitrite with low concentration used for the separation of light REEs from middle REEs, as shown

in tables (6-7). TBP pure and 50 % diluted in kerosene are used to extract REE's, and it is noticed that 50 % is revealed good removal than 100 % and this is in accordance to Gupta [17]. In Table (6), it was found that there isn't any separation till the second stage of stripping; the light rare earth was separated with 45.53, 27.61, 17.89 and 8.17 % purity for Ce, La, Nd and Pr respectively. In Table (7), there isn't any separation for the rare earth elements in all the stripping stages.

## 2.2. Effect of ammonium nitrate concentration as stripper:

In order to improve the stripping process, experiments were performed with different concentrations of ammonium nitrate within range 0.2-2M. Table (8) shows increasing in the extraction percentage for La and Sm only and decreasing in case of Ce, Pr, Nd and Gd till the third stage while at the fourth and fifth stages all light REEs are extracted as a group in the first time of stripping. No precipitate is formed in the scrubbing step. According to table (9), REEs are extracted as a group without any separation as individual elements. In table (10), La extraction percentage is increased at the first and second stages after that decreased till the fifth stage while Nd is increased all over the stages.

From all the previous stages of the experimental work, it was found that the best condition for light rare earth separation was TBP:Kerosene (1:1), contact time of 5 minutes, pH 0.2, with phase ratio (1:1), at room temperature, using 3M  $\text{NH}_4\text{NO}_3$  as stripper and hot  $\text{H}_2\text{O}$  as scrubber. The produced product considers the mother ore for ion exchange separation process.

## 3.4. Ion exchange for lanthanon separation:

In this part, we can use the cation exchange process for individual rare earth elements separation after the separation by solvent to achieve a good percent of purity. For the separation process, 2 g of REE concentrate produced from stage five of solvent extraction process, are dissolved in concentrated HCl followed by pH adjustment to 1.8 and the volume is made up to 250 ml to give a concentration of about 8 g/l REEs. The composition of the first REEs concentrate is mainly 55.94, 11.48, 14.97 and 7.61 % of Ce, La, Nd and Pr respectively. The partial separation of some individual REEs from such mixture was tried for member's fractionation via common applied cationic exchange resin.

A column (1.2 cm internal diameter) is packed with (Dowex 50 -X8), with size 100-200 mesh in the sodium form. Then, it is subjected to the prepared REEs' solution until saturation. The achieved saturation capacity is about 91.4 g  $\text{RE}_2\text{O}_3$ ; a value which matches with the theoretical capacity of the working resin (1.7meq/ml) and calculated using a mean molecular weight of 145 for the mixed REEs.

The used development column is packed by 2.5 multiples of the resin volume (about 26 ml weight settled resin) in the loading column but in the copper II state. The two columns are then coupled together and the REEs load is then eluted through the Cu-form resin column using 0.5 M Citric acid solution adjusted to pH of 3.9 with a contact time of 150 min.

A volume of as much as 1150 ml of the Citrate eluent is passed for Cu displacement and before Ln breakthrough. Thereafter, the Ln content of each collected fraction (25ml) was analyzed for individual REEs using the same preparation and analytical procedures used previously. From figure (1), it is clearly evident that the achieved partially separation of individual REEs is fairly moderate. This can actually be attributed to a number of reasons; namely,

- i ) The variable separation factors of the RE-citrate complexes.
- ii ) The presence of REEs beside Y.
- iii)The relatively wide range of concentrations of the component individual REEs in the working feed solution.
- iv) The eluent flow rate that did not permit adequate diffusion.
- v) The inadequate length of the retaining resin bed which controls the number of displacements of the working Ln mixture.

These reasons are indeed reflected in varying degrees in the composition of the collected eluate fractions which were found to represent single beside binary, triple and quadruple mixed REEs.

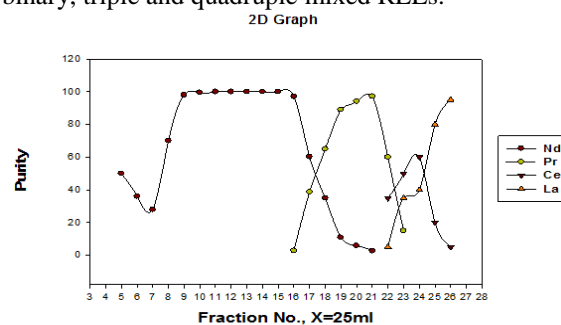


Figure (1):-Elution profile of REE Mixture by 0.5 M Citric acid from a column packed with Dowex 50-X8.

Separation of Nd individually from lanthanon is done using 0.5 M citric acid as eluent. The stock solution dissolved in concentrated HCl is transferred to a column packed with Dowex 50W-X8. Many neodymium fractions can be obtained started from ultrapure fraction with > 99.99 purity from the collected eluate in the effluents no. 11, 12, 13, 14, 15 in which no any other trace quantities of REEs are detected with total percent recoveries nearly ~ 50% of Nd content in the starting loading group REEs solution.

**Table (2)** : Extraction percentage of REEs by TBP, [H<sup>+</sup>]:0.63 mol/L (pH 0.2), phase ratio 1:1, contact time 5min. at 25°C.Nil.:  
No

Elem- ents	Stripping by 3M NH <sub>4</sub> NO <sub>3</sub> \ Scrubbing by Hot H <sub>2</sub> O																			
	% E Stage (1)				% E Stage (2)				% E Stage (3)				% E Stage (4)				% E Stage (5)			
	Stripping			Scrubbing	Stripping			Scrubbing	Stripping			Scrubbing	Stripping			Scrubbing	Stripping			Scrubbing
	1	2	3	H <sub>2</sub> O	1	2	3	H <sub>2</sub> O	1	2	3	H <sub>2</sub> O	1	2	3	H <sub>2</sub> O	1	2	3	H <sub>2</sub> O
La	15.91	13.79	12.92	Nil.	19.05	16.07	12.57	Nil.	22.90	18.43	14.85	Nil.	24.86	21.82	18.37	Nil.	24.79	21.77	17.86	Nil.
Ce	40.34	38.92	37.55	Nil.	42.14	40.41	39.67	Nil.	39.06	37.30	36.74	Nil.	39.76	38.36	37.65	Nil.	41.70	39.27	37.15	Nil.
Pr	8.04	9.45	10.28	Nil.	7.04	8.58	9.96	Nil.	8.05	9.06	10.63	Nil.	6.71	7.98	8.38	Nil.	7.63	8.45	10.86	Nil.
Nd	24.28	25.14	26.42	Nil.	21.17	23.60	25.95	Nil.	19.61	23.28	25.24	Nil.	17.36	20.26	23.95	Nil.	14.61	20.22	22.05	Nil.
Sm	7.46	8.82	9.84	Nil.	6.44	7.10	8.51	Nil.	5.23	6.58	8.99	Nil.	5.60	6.88	8.20	Nil.	5.46	6.03	8.99	Nil.
Gd	4.97	3.88	2.99	Nil.	4.16	4.24	3.34	Nil.	5.15	4.35	3.55	Nil.	5.71	4.70	3.45	Nil.	5.81	4.26	3.09	Nil.

precipitated is formed after addition of 3M NH<sub>4</sub>NO<sub>3</sub> and adjustment by fractional precipitation by ammonia**Table (3)** : Extraction percentage of REEs by TBP:Kerosene (1:1), [H<sup>+</sup>]:0.63 mol/L (pH 0.2), phase ratio 1:1, contact time 5min. at 25°C

Elem- ents	Stripping by 3M NH <sub>4</sub> NO <sub>3</sub> \ Scrubbing by Hot H <sub>2</sub> O																	
	% E Stage (1)			% E Stage (2)			% E Stage (3)			% E Stage (4)			% E Stage (5)					
	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing			
	1	2	1	1	2	1	1	2	1	1	2	3	1	2	3	1		
La	18.16	12.91	Nil.	14.71	12.77	Nil.	18.04	13.90	Nil.	18.36	17.56	14.19	Nil.	11.48	Nil	Nil	Nil.	
Ce	37.96	35.03	Nil.	39.10	34.16	Nil.	38.08	37.55	Nil.	40.18	37.79	36.23	Nil.	55.94	Nil	Nil	Nil.	
Pr	7.17	0.00	Nil.	8.05	0.00	Nil.	8.72	0.00	Nil.	9.23	0.00	0.00	Nil.	7.61	Nil	Nil	Nil.	
Nd	27.37	34.01	Nil.	29.30	36.44	Nil.	25.17	30.95	Nil.	24.95	29.99	30.77	Nil.	24.97	Nil	Nil	Nil.	
Sm	7.27	12.95	Nil.	6.75	11.42	Nil.	5.73	11.18	Nil.	3.54	9.73	12.83	Nil.	0.00	Nil	Nil	Nil.	
Gd	2.07	5.10	Nil.	2.09	5.21	Nil.	4.26	6.42	Nil.	3.74	4.93	5.98	Nil.	0.00	Nil	Nil	Nil.	

Nil.: No precipitated is formed after addition of 3M NH<sub>4</sub>NO<sub>3</sub> and adjustment by fractional precipitation by ammonia.**Table (4)** : Extraction percentage of REEs by TBP, [H<sup>+</sup>]:0.63 mol/L (pH 0.2), phase ratio 1:1, contact time 5min. at 25°C.

Elem- ents	Stripping by 5M HNO <sub>3</sub> \ Scrubbing by Hot H <sub>2</sub> O																	
	% E Stage (1)						% E Stage (2)			% E Stage (3)			% E Stage (4)			% E Stage (5)		
	Stripping			Scrubbing			Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing
	1	2	3	4	5	6	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2
La	26.24	24.84	28.54	20.25	18.21	17.07	15.71	24.72	22.76	18.23	25.15	25.57	Nil.	35.13	Nil.	Nil.	Nil.	
Ce	46.71	44.71	44.29	40.86	42.06	39.63	36.55	44.55	39.39	41.73	41.47	44.61	Nil.	42.22	Nil.	Nil.	Nil.	
Pr	5.51	7.35	6.08	7.54	7.75	7.93	8.39	8.68	10.59	9.49	9.32	8.41	Nil.	7.41	Nil.	Nil.	Nil.	
Nd	19.67	16.99	19.10	24.66	25.93	23.38	29.16	15.17	17.43	25.19	12.93	17.66	Nil.	10.19	Nil.	Nil.	Nil.	
Sm	1.87	6.11	1.99	6.69	6.05	8.60	7.74	6.88	9.83	5.36	5.16	3.75	Nil.	5.02	Nil.	Nil.	Nil.	
Gd	0.00	0.00	0.00	0.00	0.00	0.00	2.45	0.00	0.00	0.00	5.97	0.00	Nil.	0.00	Nil.	Nil.	Nil.	

Nil.: No precipitated is formed after addition of 5M HNO<sub>3</sub> and adjustment by fractional precipitation by ammonia.

**Table (5)** : Extraction percentage of REEs by TBP+Kerosene(1:1), [H<sup>+</sup>]:0.63 mol/L (pH 0.2), phase ratio 1:1, contact time 5min. at 25°C.

Elements	Stripping by 5M HNO <sub>3</sub> \ Scrubbing by Hot H <sub>2</sub> O														
	% E Stage (1)			% E Stage (2)			% E Stage (3)			% E Stage (4)			% E Stage (5)		
	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing	Stripping		Scrubbing
	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O	1	2	H <sub>2</sub> O
La	17.50	11.92	Nil.	16.42	11.02	Nil.	17.21	12.40	Nil.	17.22	13.60	Nil.	18.34	Nil.	Nil.
Ce	35.64	23.53	Nil.	36.09	29.92	Nil.	41.15	31.67	Nil.	43.62	33.48	Nil.	41.84	Nil.	Nil.
Pr	7.60	11.66	Nil.	7.89	9.49	Nil.	7.69	10.82	Nil.	7.70	8.06	Nil.	9.63	Nil.	Nil.
Nd	26.63	27.35	Nil.	27.79	28.64	Nil.	27.17	28.32	Nil.	25.97	26.50	Nil.	22.48	Nil.	Nil.
Sm	7.16	14.98	Nil.	7.03	12.32	Nil.	5.13	10.38	Nil.	4.10	10.81	Nil.	4.70	Nil.	Nil.
Gd	5.47	10.56	Nil.	4.78	8.61	Nil.	1.65	6.41	Nil.	1.39	7.55	Nil.	3.01	Nil.	Nil.

Nil.: No precipitated is formed after addition of 5M HNO<sub>3</sub> and adjustment by fractional precipitation by ammonia.

**Table (6)** : Extraction percentage of REEs by TBP, phase ratio 1:1, [H<sup>+</sup>] : 0.63 mol/L (pH 0.2), contact time 5min. at 25°C.

Elements	Stripping by 0.1N NaNO <sub>2</sub> \ Scrubbing by Hot H <sub>2</sub> O																										
	% E Stage (1)					% E Stage (2)					% E Stage (3)					% E Stage (4)					% E Stage (5)						
	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing		
	1	2	3	4	5	1	1	2	3	4	1	1	2	3	1	1	2	3	1	1	2	3	1	1	2	3	1
La	22.84	21.89	19.82			Nil.	22.74	27.61			Nil.	29.76			Nil.	Turbide				Turbide							
Ce	44.48	42.85	41.26			Nil.	46.44	45.53			Nil.	44.98			Nil.												
Pr	5.20	5.23	6.82			Nil.	5.96	8.17			Nil.	8.99			Nil.												
Nd	22.60	21.09	25.31			Nil.	22.46	17.89			Nil.	13.92			Nil.												
Sm	3.88	5.63	5.38			Nil.	2.40	0.00			Nil.	1.19			Nil.												
Gd	0.99	3.31	1.41			Nil.	0.00	0.00			Nil.	1.16			Nil.												

Nil.: No precipitated is formed after addition of 0.1N NaNO<sub>2</sub> and adjustment by fractional precipitation by ammonia.

**Table (7)** : Extraction percentage of REEs by TBP:Kerosene(1:1), [H<sup>+</sup>]:0.63 mol/L (pH 0.2), phase ratio 1:1, contact time 5min. at 25°C.

Ele-Ments	Stripping by 0.1N NaNO <sub>2</sub> \ Scrubbing by Hot H <sub>2</sub> O																										
	% E Stage (1)					% E Stage (2)					% E Stage (3)					% E Stage (4)					% E Stage (5)						
	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing	Stripping				Scrubbing		
	1	2	3	4	5	1	1	2	3	4	1	1	2	3	1	1	2	3	1	1	2	3	1	1	2	3	1
La	20.42	15.16	17.07	16.53	15.74	Nil.	16.10	18.18	21.66	19.94	Nil.	27.06	26.44	24.37	Nil.	27.13	26.50	24.34	Nil.	28.23	27.03	28.40	Nil.	28.40	28.40	28.40	Nil.
Ce	46.16	44.99	39.30	37.05	40.79	Nil.	56.10	41.44	44.95	45.04	Nil.	48.60	48.80	48.97	Nil.	49.20	48.17	44.04	Nil.	46.14	46.01	45.87	Nil.	45.87	45.87	45.87	Nil.
Pr	5.15	6.48	8.38	23.88	20.18	Nil.	5.15	9.17	19.11	21.89	Nil.	7.53	7.10	17.03	Nil.	6.48	5.84	17.54	Nil.	9.15	8.29	14.62	Nil.	14.62	14.62	14.62	Nil.
Nd	22.56	24.03	22.11	9.87	8.42	Nil.	17.04	20.45	7.69	7.99	Nil.	14.34	15.26	5.98	Nil.	13.47	15.10	8.59	Nil.	14.22	15.21	6.58	Nil.	6.58	6.58	6.58	Nil.
Sm	1.49	4.23	8.02	7.11	9.40	Nil.	2.09	8.43	4.08	2.45	Nil.	1.22	1.12	2.18	Nil.	1.19	2.04	1.94	Nil.	1.11	2.21	3.04	Nil.	3.04	3.04	3.04	Nil.
Gd	4.22	5.11	5.12	5.55	5.47	Nil.	2.53	2.33	2.50	2.69	Nil.	1.25	1.28	1.47	Nil.	2.53	2.35	3.55	Nil.	1.15	1.25	1.49	Nil.	1.49	1.49	1.49	Nil.

Nil.: No precipitated is formed after addition of 0.1N NaNO<sub>2</sub> and adjustment by fractional precipitation by ammonia.

The many other fractions for Nd can be collected through addition of the previous five eluent cuts and the next three cuts to reach maximum recovery >98% of the eluent content but it was against the purity. In other words neodymium concentrates with ~ 100, 99.5, 98, 97.1% purity and 50, 80, 81, 82.5 % recovery can be obtained on the desire for marketing or further chemical or technical approaches for the fractions obtained. The elution profile for neodymium is presented in figure (2).

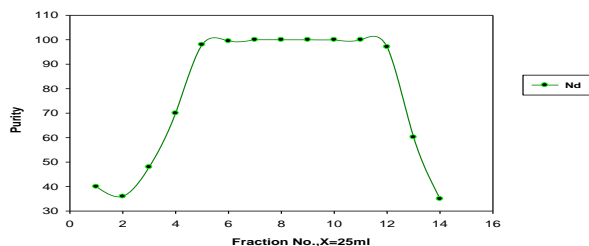


Figure (2):- Elution profile of neodymium with different purities using 0.5 M Citric acid from a column packed with Dowex 50W-X8.

#### 4. Conclusions

The separation of some individual rare earth elements by solvent extraction followed by ion exchange separation process were investigated by tri-butyl phosphate and Dowex 50 -X8. The results were obtained as follows:

- Solvent TBP is promising in extracting the Ce, La, Nd and Pr from a nitrate solution of light and middle REEs. About 55.94, 11.48, 14.97 and 7.61 % purity of Ce, La, Nd and Pr were separated respectively from the PLS by 50 vol. % TBP diluted in kerosene, stripped by 3 M  $\text{NH}_4\text{NO}_3$  solution, at 0.2 pH for 5 minutes at room temperature.
- Separation of neodymium concentrates with ~ 99.9, 99.5, 98, 97.1% purity and 50, 80, 81, 82.5 % recovery after using Dowex 50W-X8 as cation exchanger which eluted by 0.5 M citric acid.

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