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RESEARCH ARTICLE

Recovery of Rare earth elements using ethanolic extractant of aerial part of *Helianthus annuus* plant from their sulfate leach liquor

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Abstract

The possibility of using *Helianthus annuus* extractant (sun flower) as a solvent for Rare earth elements (REEs) extraction from its sulfate liquor for their recovery has been studied. Several experiments were conducted to determine the relevant factors affecting both the extraction and stripping of the REEs from a synthetic solution. Under the optimum conditions, the achieved REEs capacity has attained about 12 mg/g for the ethanolic extractant via 10 vol. of ethanolic extractant, O/A ratio of 1:1 for a shaking time 10 min. at the pH of 0.1. The optimum stripping conditions for REEs content from the loaded ethanolic extractant using 1M NaCl /1M HCl were aqueous to organic phase ratio (A/O) 1:3, stripping time 15 minutes and at room temperature (25^{o}C). From the prepared sulfate leach liquor of Abu Zeneima raw material (South Eastern Sinai, Egypt), REEs has then been recovered using the working ethanolic extractant under the previously studied optimum conditions, with an efficiency of 82% The obtained strip liquor was then subjected to precipitation using 20 % oxalic acid to precipitate REEs as lanthanides oxalate. The obtained precipitate has been confirmed using EDAX analysis.

INTRODUCTION

In the twenty one century, highlights were focused now upon the environmental concerns. One of the important concerns is the useful employment and recycling of the plant and animal remains, on their burning, cotton stalk, rice husk, sun flower stalk and plant cellulosic remains….etc. are essential pollutants to the atmosphere. Thus, the possibility of using the sunflower as extractant for the recovery of lanthanides could be considered as one of improvement of using waste management.

Perennial sunflower species are not as popular for gardens due to their tendency to spread rapidly and become invasive. **Subashini and Rakshitha 2012** evaluated the methanolic extract seeds of Helianthus annuus L. For the phytochemical present in the plant and results shown that, the carbohydrates, flavanoids, tannins, alkaloids, sapanins, phytosterols, steroids and fixed oils were present in the extract. **(Macias et al. 2008)**.

The lanthanides are group of 15 chemical elements with atomic numbers 57 to 71 and to which the two other elements, scandium and yttrium, having a similar physiochemistry, therefore referred to as the rare earth elements (REEs). The latter are indeed required in several photoelectronic and metallurgical industries as well as in nuclear energy programs (**Zhou et al., 2007**). Among the large number of REE minerals only three were actually rich enough to warrant their use as ores (**Subbarao and Wallace, 1980**). These include bastnasite (La, Ce) FCO_3, (60-70% RE_2O_3), monazite (Ce, La, Y, Th) PO_4 which represents the second main source (RE_2O_3 55-60 %) and xenotime (Y) PO_4 (42-50% RE_2O_3). Other commercial sources of REEs were apatite, REE bearing laterites, allanite, zircon, euxenite, clay and loparite (**KanaZawa and Kamitanai, 2006).** The recovery of mixed REEs was generally accomplished by a variety of methods including the mineral acids or else sodium hydroxide at high temperature including proper fusion or roasting with sodium carbonate.

Rare earth elements (REEs) are vital to the proper functioning of our computer's memory, hydrogen storage, nuclear reactors, fluorescent lighting, TV's, cell phones, DVD's, re-chargeable batteries, fiber optic lasers, as well as car catalytic converters, and nickel-metal hydride batteries. Magnets made from REEs are the most powerful on the planet. Without REEs our hi-tech environment would quickly grind to a halt **(Degraaf, 2006).**

The separation of REEs by solvent extraction technique depends on the slightly difference in the distribution coefficient of individual REEs between two immiscible liquid phases (aqueous and organic phases). The main advantage of this technique is the loading of very high contents of REEs reached to 180g RE_2O_3/ l. Also, the complete separation of Ce (IV) from trivalent cations in aqueous HNO_3 using TBP was reported **(Bauer, 1959)**. The extraction process depends on the transfer of metal ion from aqueous phase into organic one (scrubbing) and stripping by contacting the scrubbed organic phase with an aqueous solution to recover the main extracted species of REEs from organic phase.

Different organic solvents were used for investigating the separation of individual REEs, one of these is tri-butyl phosphate (TBP) which has been investigated for the separation of REEs from monazite **(Bochinski et al., 1958)**. In addition, the separation of REEs by solvent extraction was investigated by **Callow, 1967**. However, the separation of REEs away from terbium was difficult. Uses of di-2-ethylhexyl phosphoric acid (D2EHPA) as organic solvent **(Deshpande, et al., 1979)** for rapid initial concentration of low HREEs content of India monazite's to obtain concentrates of Sm, Eu, Gd and Y with concentrations varying from 60 to 90 % while leaving the light REEs in the raffinate that are reprocessed by diluted and undiluted TBP to the prepared concentrates of La, Nd, Pr, and Sm as illustrated in figs. (10 and 11). Quaternary ammonium compounds were used to extract Y with purity 99.999% from Y concentrate assaying 60 % Y_2O_3 which was prepared from xenotime. According to **Gupta and Krishnamurthy, 1992** the solvent extraction technique was expanded to commercial separation and purification of at least 11 of 15 REEs occurring in bastnasite, xenotime and monazite minerals.

The solvent extraction of several rare earth ions from sulfate liquors was extensively reported. Prominent extractants that have been employed are high molecular weight amines (**Desai and Shinde, 1985**), carboxylic acids (**Singh et al., 2006**), tri-n-butyl phosphate (TBP) (**Mathur and Choppin, 1998**) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) (**Panturu et al., 2000 ; Zhou et al., 2007**) mixtures of 8-hydroxyquinoline with Cyanex 301 or Cyanex 302 (**Tian et al., 2013**), and phosphonic/phosphinic acid mixtures (**Quinn et al., 2015**). Also, (**Masson and Cunha, 2002**) could investigate rare-earth elements (from terbium to ytterbium, plus yttrium) in hydrochloric acid aqueous solution by using D2EHPA as the solvent extraction. Efficiencies of chitosan nanoparticles and crab shell particles in europium uptake from aqueous solutions were studied by **Cadogan et al., 2014**. Recovery of lanthanum(III) from aqueous solution using biosorbents of plant and animal origin was investigated by **Das et al., 2014**.

The possibility of using the Helianthus annuus as a solvent extractant for REEs from its sulfate liquor has been detailed studied. The work has then been shifted to investigate the potentially of this extractant for the recovery of REEs from an actual acidic leach liquor originated from Abu Zeneima ore material (South Eastern Sainai, Egypt) as a case study .

2- Materials and Methods

2-1 Materials

2.1.1. Plant materials.

The aerial part of Helianthus annuus were collected on April (2013) and identified by Botany department, Faculty of Science, Zagazig University.

2.1.2. Extraction of the ethanolic extractant

The aerial part are dried in the shadow in air draft were comminuted to powder (2 kg) and exhaustively extracted under reflux over a boiling water bath with 5 liters of ethanol(80%) for 3 hours. The extract was filtered; the process was repeated 3 times. The solvent was removed under reduced pressure at about 60 °C. The process yielded finally 150 g of a sticky dark brown material.

2.1.3. Preparation of Rare earth elements (REEs) Synthetic Solutions

Synthetic solutions of REEs have been prepared from their proper salts. REEs solutions were thus prepared by dissolving analytical grade metal salts in distilled water to obtain accurate concentration 200 ppm (mg/L) solution. The pH of this solution was measured and adjusted at 0.1 using sulfuric acid and all the adsorption experiments were run at room temperature.

2.2. Experimental procedures

2.2.1. REEs extraction procedures from their sulfate solutions by the ethanolic extractant

In this work, the ethanolic extractant in carbon tetra chloride 10 vol % as solvent extraction has been applied for extraction of REEs from their sulfate solution. Several experiments were conducted to determine the relevant factors affecting the extraction of REEs from either the synthetic solution or that of Abu Zeneima leach liquor as the effect of diluent type, ethanolic extractant concentration, A/O ratio, contact time, pH value, temperature and interfering ions.

2.2.2. REEs stripping procedure loaded upon ethanolic extractant

A number of mineral acids, alkalis and acidified NaCl solutions have been used for studying REEs stripping efficiency from REEs –loaded upon the ethanolic extractant. For choosing the eluent, both the shaking time and temperature together with the A/O phase ratio have been studied.The resultant strip solution is treated in subsequent circuit to produce a metal concentrate while the stripped solvent is returned for cycle to extraction circuit.

2.3. Analytical procedures

2.3.1. Ethanolic extractant characterization

As mentioned above, *Helianthus annuus* extractant (HAE) was analyzed for its acid content in the quality control laboratory of Hashem Brothers for Essential & Aromatic Products using the Gas Chromatography Mass Spectrometry (GC-MS) HP 6890 Series A (Agilent). On the other hand, an infrared analysis was achieved for the ethanolic extractant using (FTIR) model Thermo Scientific Nicolet IS10, Germany.

2.3.2. Control Analysis for REEs

For analysis of total REE in aqueous solutions, a visible- ultra violet spectrophotometer (Shimadzu UV-160A) was used for its quantitative analysis using 0.05 % arsenazo III at 654 nm using a mixture of light and heavy REEs as reference, **(Marczenko, 1986).** On the other hand, analyses of the studied possible interfering base metals as well as individual REEs were achieved by prism ICP-OES, Teledyne technologies (Inductively Coupled Plasma Optical Emission Spectrometer) for analysis.

Gibbsite ore sample was subjected to complete chemical analysis for the major components according to **Shapiro and Brannock procedure (1962).** Thus, SiO_2, Al_2O_3, TiO_2 and P_2O_5 were determined using relevant spectrophotometic methods while the contents of Na and K were determined by the flame photometric technique. Total Fe as Fe_2O_3, MgO and CaO were analyzed by titration methods. The estimated error for major constituents is not more than ±1 %.

3-Results and Discussion

3.1 Characteristics of the ethanolic extractant

3.1.1. I.R spectrum of the ethanolic extractant

From the achieved IR spectral analysis of the the ethanolic extractant shown in Table (1) and plotted in Fig.(1) before complexation with REEs it is clearly evident that a number of characteristics peaks have been obtained.

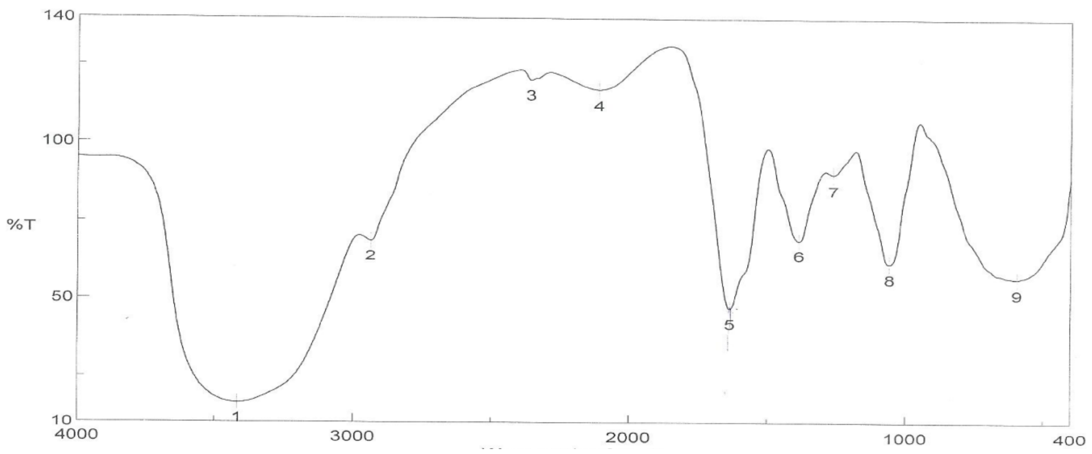


Fig.(1) : IR characteristic spectrum of the ethanolic extractant

Table (4) : IR spectral analysis of the ethanolic extractant

Peak No	Spectra Value (cm^{-1})	Functional Group
1	3400	OH alcohol
2	2890	C-H
3	2350	X=C=Y (C,O,N,S)
4	2100	C=C
5	1750	C=O
6	1390	C-C
7	1250	C-N
8	1050	C-O

3.1.2. Chromatographic analysis

The separated organic compounds were analyzed on gas chromatography mass spectrometry (GC-MSD). Retention time indices for all compounds were determined while identification of the components was based on comparison of their mass spectra with those of internal (computer) library W9N11.L (Minimum Quality: 50) and NIST11.L (Minimum Quality: 50) libraries and some reference compounds. As shown in **Fig.(2)** the major components are 55% benzyl acetate , 16% Linalool and 9% Sotalol (Methane sulphonamide benzene methanol)

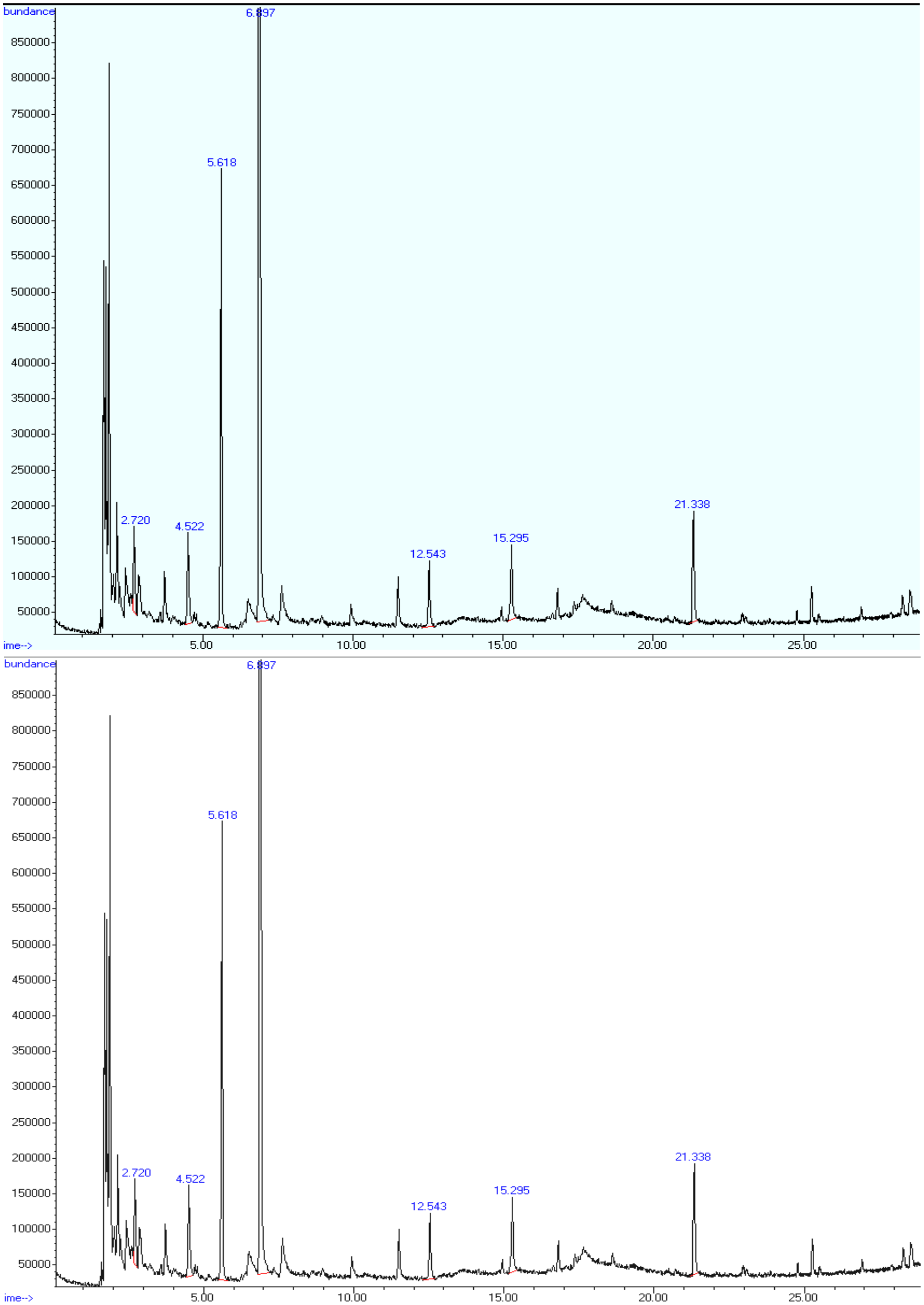
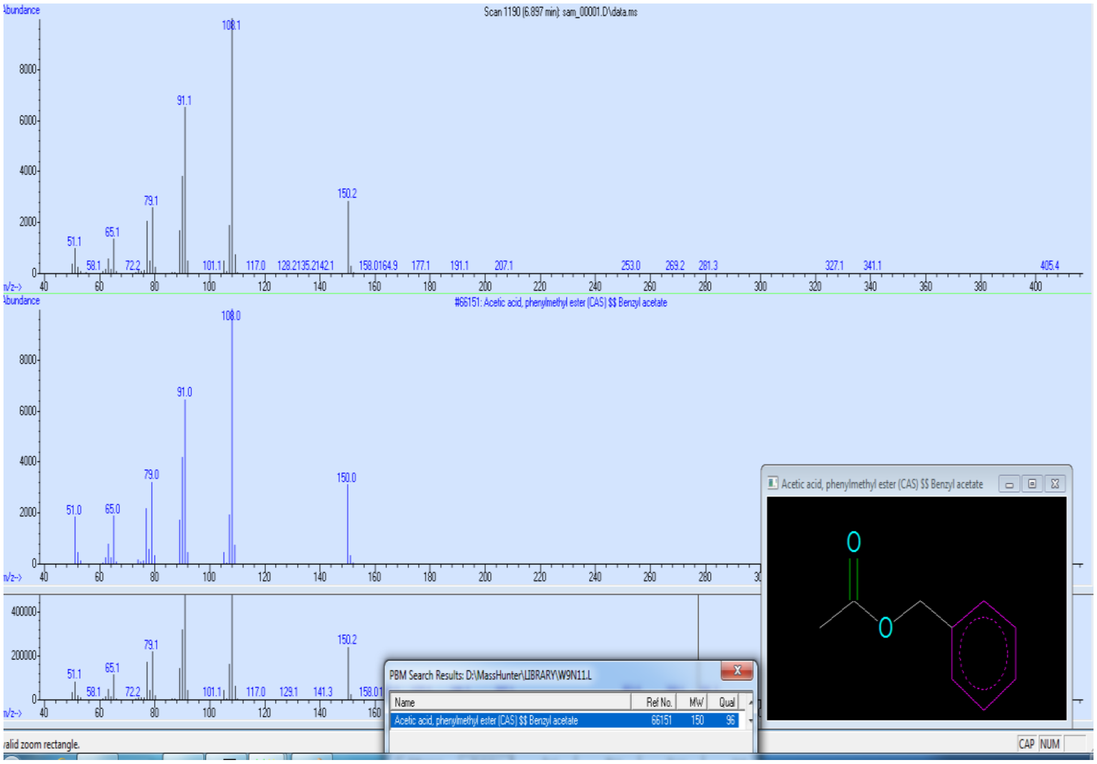


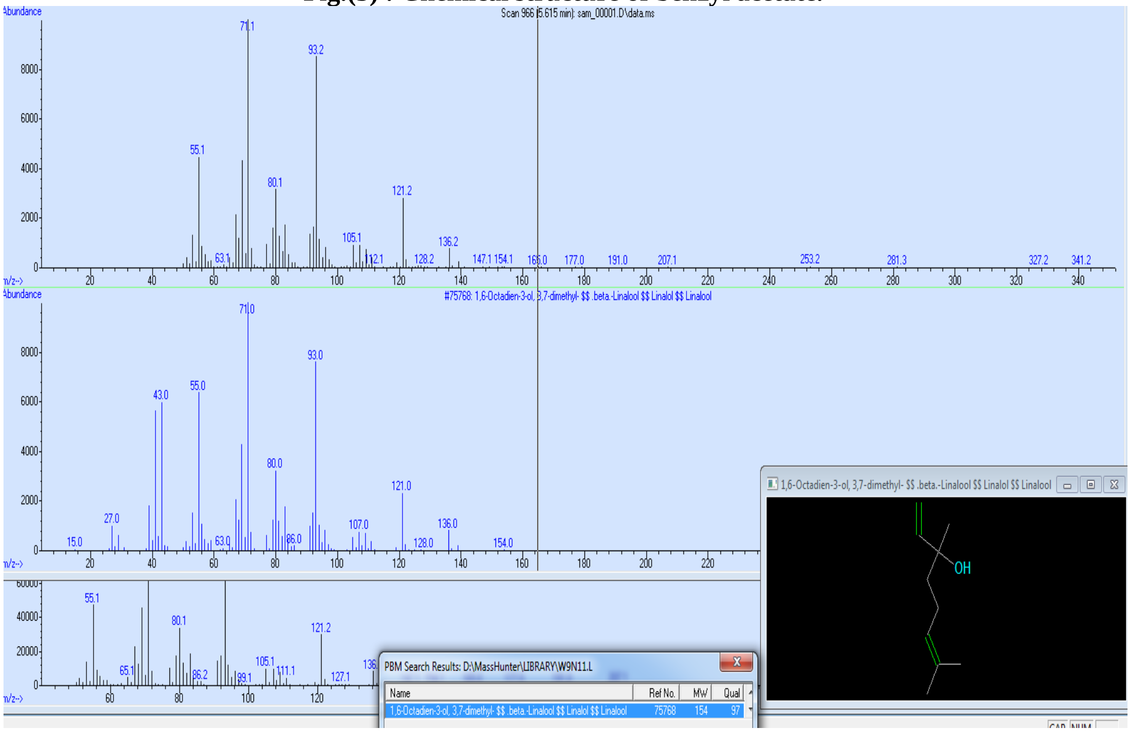
Fig.(2) : Gas chromatography-mass Spectrometry (GC-MS) of the ethanolic extractant



PBM Search Results: D:\MassHunter\LIBRARY\W9N11.L

Name	Ref No.	MW	Qual
Acetic acid, phenylmethyl ester (CAS) $$ Benzyl acetate	66151	150	96

Fig.(3) : Chemical structure of benzyl acetate.



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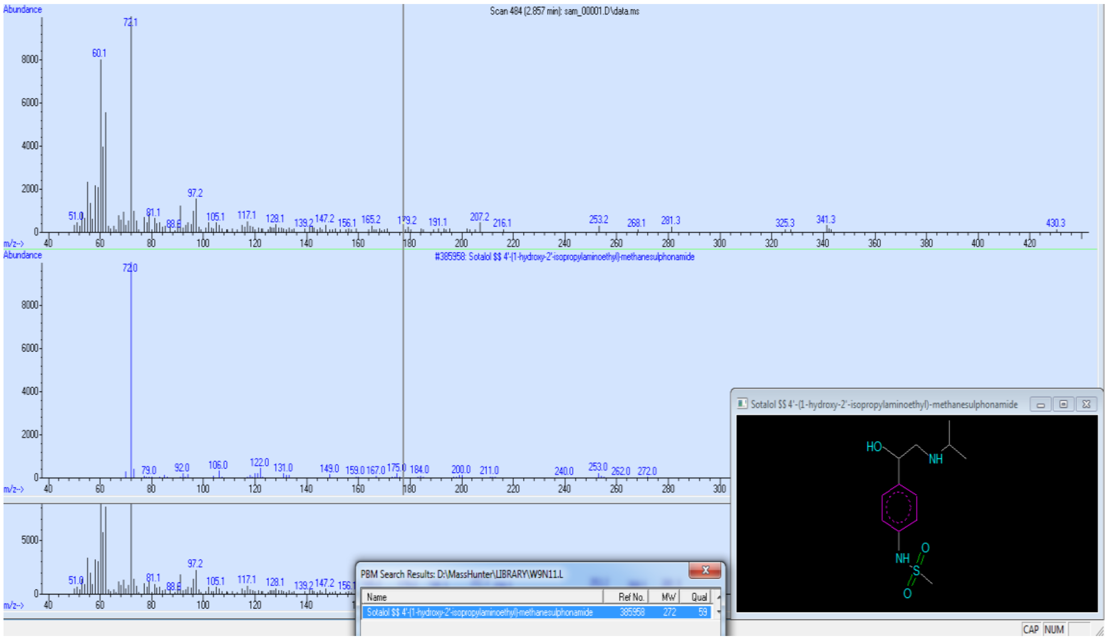
Name	Ref No.	MW	Qual
1,6-Octadien-3-ol, 3,7-dimethyl- $$ .beta.-Linalool $$ Linalol $$ Linalool	75768	154	97

Fig.(4) : Chemical structure of Linalool



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#385958: Sotalol $$ 4'-(1-hydroxy-2'-isopropylaminoethyl)-methanesulphonamide

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Name	Ref No.	MW	Qual
Sotalol $$ 4'-(1-hydroxy-2'-isopropylaminoethyl)-methanesulphonamide	385958	272	59

Sotalol $$ 4'-(1-hydroxy-2'-isopropylaminoethyl)-methanesulphonamide

Fig.(5) : Chemical structure of Sotalol.

3.2. Optimization of the rare earth elements (REEs) extraction.

3.2.1. Effect of diluent type

To study the effect of the diluent type on REEs extraction from the prepared synthetic solution of REEs assaying 200 ppm of by the ethanolic extractant, three different organic diluents were used namely; benzene, kerosene and carbon tetra chloride. The extraction process was performed under the fixed conditions of a pH 1, shaking time of 10 min. in an A/O ratio of 1:1 at room temperature and using ethanolic extractant concentration of 10 vol .% . From the obtained results, it was indicated that carbon tetrachloride was the best diluent in which 50% for REEs extraction was achieved while in the benzene and kerosene diluents only 3% and 1% for REEs extraction were achieved. Thus carbon tetra chloride was chosen as the best diluent in all extraction experiments.

3.2.2. Effect of pH

The effect of pH values of synthetic solution ranging from 0.1 to 5 on REEs extraction by the ethanolic extractant was studied. For this purpose several experiments under the same mentioned conditions 10 vol. % of the ethanolic extractant in carbon tetra chloride, A/O ratio of 1:1 for a shaking time of 10 min. at room temp. were conducted. The results were plotted in Fig.(6). it was observed that the extraction efficiency of REEs decreased from 50% to 2% at the pH values from 1 to 5 respectively, while an increase in the REEs extraction efficiency was achieved by decreasing the pH values of the synthetic solution from 1 to 0.1. This may be due to that at acidic conditions REE_S were present in the sulfate form and the complex between the extractant component and $REEs_2(SO_4)_3$ was decomposed at high pH as the result of neutralization of the sulfate ions. Thus the value of pH 0.1 lead to 82% of REE_S extraction and therefore this is considered as the optimum pH value in the study system.

3.2.3. Effect of solvent concentration

The effect of the ethanolic extractant concentration on REEs extraction efficiency was performed by contacting equal volumes of the REEs synthetic solution and the solvent with concentration ranging from 2 to 20% in CCl_4 at fixed conditions; pH 0.1, contact time 10 min. at room temperature. From the obtained data in Fig.(7), the extraction efficiency of REEs was greatly improved from 50 to 70 % where the ethanolic extractant concentration increased from 2 to 8. At the vol.10% of the ethanolic extractant concentration the REEs extraction achieved about 82%. By increasing the concentration of the ethanolic extractant there was no remarkable extraction efficiency recorded. Thus, in the next work, the ethanolic extractant concentration was fixed at the optimum value of 10% for REEs extraction.

3.2.4. Effect of the A/O phase ratio

The effect of the A/O phase ratio on REEs extraction percentage was studied by doubling and tripling the aqueous phase with respect to the organic phase. The conditions for REEs extraction were fixed at a pH 0.1, shaking time of 10 min. at room temp. and using a 10 vol% of carbon tetrachloride. The obtained results shown in Table (2) revealed an extraction efficiency of REEs attaining, 82% and 80% respectively at the A/O phase ratios of 2/1 and

3/1, in a manner to indicate that 1ml of the ethanolic extractant can extract about 3.24 and 4.8 mg REEs respectively.

Table (2): Effect of A/O phase ratio on REEs extraction efficiency.

A/O phase ratio	REEs extraction efficiency,%
1/1	82
2/1	82
3/1	80

3.2.5. Effect of contact time:

To study the effect of contact time on REE_S extraction varied contact times of 1,2,3,5 and 15 min. were used, while fixing the other experimental conditions at pH of 0.1, A/O ratio of 1:1 at room temp. and 10 vol % of the ethanolic extractant. The obtained results indicated that REEs extraction was achieved where at 3 and 5 min., up to 50% and 70% have been extracted. The results illustrated in Fig.(8) indicated that the REEs extraction was about 82% in the 10 min. this was thus considered as the optimum contact time.

3.2.6. Effect of temperature

Using the previously optimum conditions of pH 0.1, an A/O ratio of 1:1, shaking time of 10 min. and 10 vol. % ethanolic extractant for the studied system and diluted in carbon tetrachloride, a series of experiments was performed to study the effect of temperature in the range from 25 ºC to 70 ºC for REEs extraction. As shown in Fig.(9), it was found that by progressively increasing the temperature an adverse effect on REEs extraction efficiency from 80 down to 20% was observed. This was most probably due to the decomposition of the components of the organic solvent under high temp.

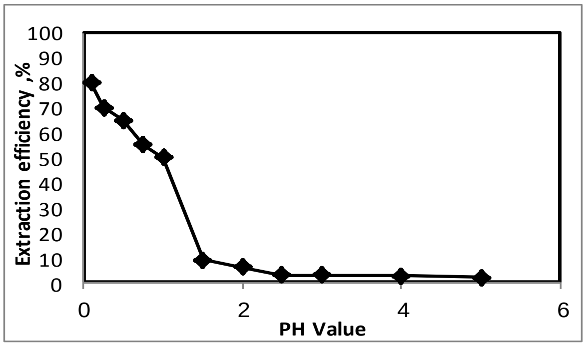


Fig. (6): Effect of pH on REEs extraction efficiency %.

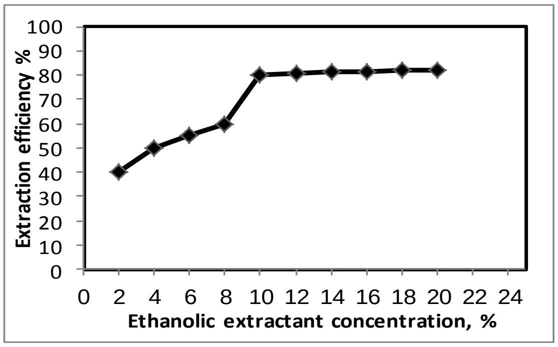


Fig. (7): Effect of ethanolic extractant Concentration on REEs extraction efficiency %.

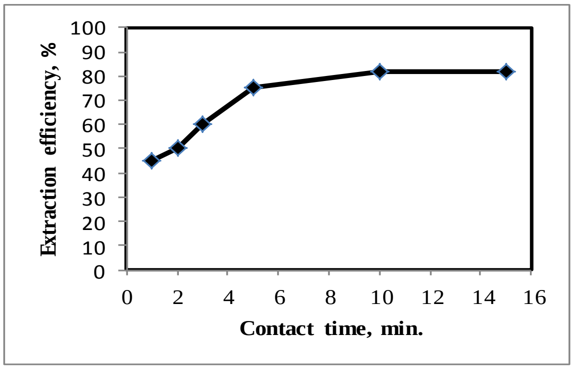


Fig. (8): Effect of contact time on REEs extraction efficiency %.

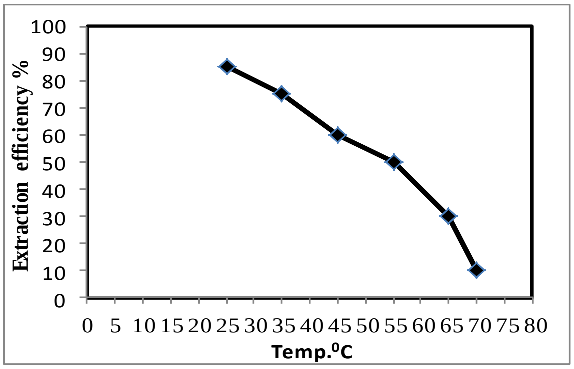


Fig. (9): Effect of temperature on REEs extraction efficiency %.

3.2.7. Effect of interfering metal ions upon REEs extraction efficiency, %.

In order to investigate possible interference of other metal ions in ethanolic exractant in CCl_4 with REEs in their ores a proper solution of (1000 ppm) concentration for each of U, Cu, Ni, Fe, Zr, V, Ba, and La, Ce, and Y as REEs was prepared. To study the effect of latter, 10 ml of the mentioned 9 metal solutions together with 10 ml of a uranium solution assaying also 1000 ppm were mixed in a manner that each of which would assay 100 ppm. The concerned experiments were then performed at the previously optimum extraction conditions for REEs via ethanolic extractant pH 0.1, A/O ratio of 1:1 at room temp. with 10 vol % of the ethanolic extractant in CCl_4 and a shaking time of 10 min. After phase separation, the metal ions and REEs were analyzed and the obtained results have revealed that decreasing the pH value to 0.1 (studied optimum pH for REEs) an increase in the REEs extraction efficiency was achieved and none of the added metal ions were extracted.

Table (3): Effect of pH upon the extraction percent REEs with some interfering metal ions

pH	Extraction %									
	U	Y	Ce	La	V	Fe	Zr	Ba	Ni	Cu
0.1	2.5	80	82	80	17	12	15	14	18	44
0.5	4	60	65	64	15	9	12	9	14	32
1	5	50	55	52	10	7	8	7	8	21
2	18	3	3	3	8	4	5	4	6	11
3	80	2	1	3	1	20	1	2	3	3
4	95	1	1	2	1	2	1	2	3	3

From the above studied the optimum extraction conditions for about 80% of REEs content from sulfate solution via ethanolic extractant Would be summarized as following:

A/O	:	1:1
Contact time	:	10 min.
ethanolic extractant Concentration	:	10 %
Temperature	:	room temp.
pH	:	0.1

3.3. REEs saturation capacity.

To determine the saturation capacity of the ethanolic extractant, a known volume of the extractant was repeatedly contacted with the prepared synthetic REEs solutions under the previously determined optimum conditions using 1g (density of the extracted was measured by density meter which equal to 1) of the ethanolic extractant (10 vol.% in CCl_4). After each contact, REEs were analyzed in the obtained raffinate till almost complete saturation of the extractant. From the results shown in Table (4), it was clearly evident that the saturation capacity of the ethanolic extractant attained about 12 mg /1g of the extractant for REEs.

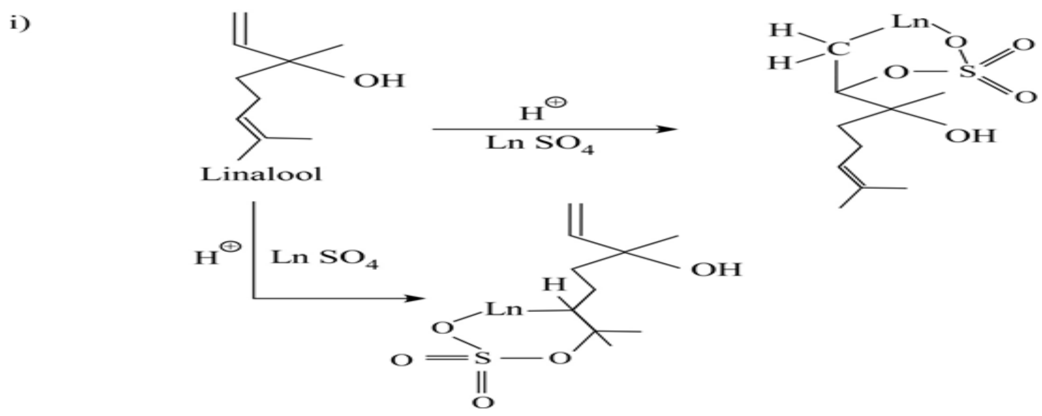
Table (4): REEs saturation capacity of the ethanolic extractant.

Contact number	Loaded amount mg/1g upon ethanolic extractant
1	6
2	3.5
3	1.5
4	0.5
5	0.3
6	Nil
Total	11.8

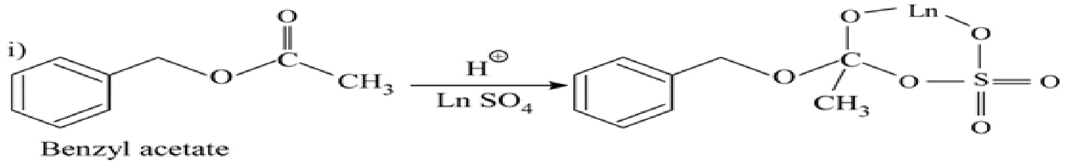
The obtained data support indeed the possible mechanism of rare earth elements species extraction by the HAE, which is believed to be achieved through the OH, C=C and C=O groups of the extractant via; .

Mechanism of REEs complexation

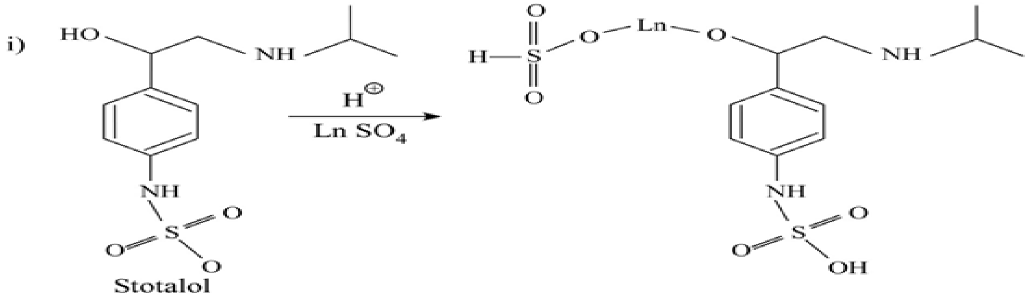
1] Formation of adduct upon double bond



2] 1,2-Nucleophilicaffition with catalized acid medium



3] Formation of alkoside by sulfate



3.4. Physical parameters

3.4.1. Thermodynamic characteristics of rare earth elements (REEs) extraction:

Variations of rare REEs extraction data with temperature for rare REEs extraction from the aqueous phase by used ethanolic extractant was used to calculate the thermodynamic constants including the standard enthalpy (ΔH), and the standard entropy (ΔS) based on Van't Hoff plot using the following formula:

$$\ln K_{\mathrm{d}} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

Where K is the equilibrium constant R = 8.3145 J $\mathrm{mol}^{-1}\mathrm{K}^{-1}$ and T = absolute temperature in Kelvin. ΔH and ΔS were determined from the slope and intercept of ln Kd versus 1/T graph.

Fig. (10) Plots ln K_d versus 1/T, K^{-1} which give a straight line whose slope equals (-ΔH / R) for the extraction of rare earth elements. The ΔH and ΔS values for rare earth elements, in case of ethanolic extractant are − 66.12 kJ/mol and -205.37 J/mol k respectively.as calculated from the slope and intercept using the Van't Hoff equation.

These values of ΔH and ΔS have then been used to obtain the corresponding free energy (ΔG= − 65.91 kJ/mol) at 298°K for ethanolic extractant using the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

The negative value of ΔH indicates that the extraction of REEs in this system is an exothermic process and that the reaction becomes more favorable at room temperature. The negative value of ΔG indicates that the reaction is spontaneous. On the other hand, the observed decrease in the negative values of ΔG with elevated temperature implies that the reaction becomes more favorable at room temperatures.

3.4.2. Kinetic characteristics of rare earth elements (REEs) extraction by ethanolic extractant

In terms of kinetic modeling, the pseudo-first-order and pseudo-second-order equations were used for the mathematical interpretation of the REEs extraction rate from the aqueous phase by ethanolic extractant. The pseudo-first-order equation is represented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Where q_e and q_t are the amounts of metal ions adsorbed at equilibrium and at time t respectively, and k1 is the equilibrium rate constant of the pseudo first-order equation (1/min). On the other hand, the pseudo-second-order kinetic model is represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 is the equilibrium rate constant of pseudo second-order equation. The slope and intercept of the plot t/q_t versus t were thus used to calculate the pseudo second-order rate constants k_2 and q_e.

The pseudo-first -order kinetic model was found to best fit the experimental results of rare earth elements extraction from the aqueous phase by ethanolic extractant in carbon tetrachloride with correlation coefficients very close to unity other than pseudo second-order kinetic model (Figs 11 and 12).

The parameters of the pseudo-first order kinetic model for REEs from the 200 ppm aqueous solution by used ethanolic extractant at 25ºC have been calculated and were found as following Table (5).

Table(5):Pseudo First-order constants of REES extraction by used ethanolic extractant at 25ºC.

Pseudo First-order constants	Result of ethanolic extractant
K_1	0.132
q_e	5.99
R^2	0.94

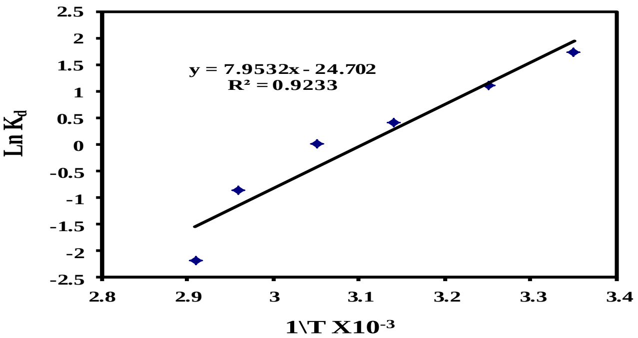


Fig.(10): Plot of $\ln K_d$ against reciprocal temperature for REEs by ethanolic extractant.

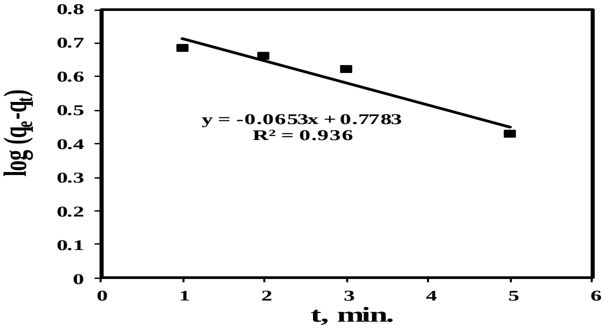


Fig.(11):Plot of $\log(q_e - q_t)$ versus time (t) for kinetic extraction of REEs at 25°C.

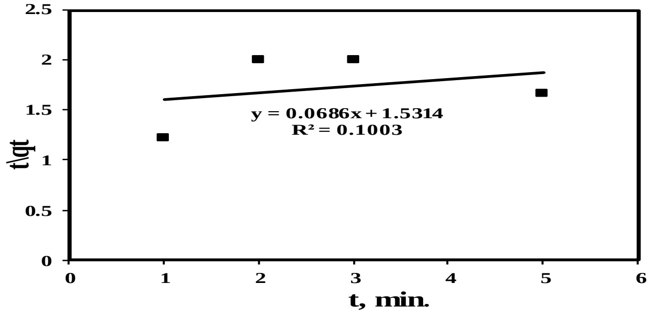


Fig.(12):Plot of t/q_t versus time (t) for kinetic extraction of REEs at 25°C.

3.5. Optimization of the REEs stripping factors loaded upon the ethanolic extractant.

Stripping of REEs was carried out at room temperature by shaking equal volumes of the loaded solvent with a suitable stripping solution for a proper time. Factors influencing the stripping efficiency include stripping agent and its concentration, aqueous to organic phase ratio (A/O), stripping time and temperature.

3.5.1. Effect of the stripping agent type:

Different stripping agents were applied to strip REEs from the loaded 10% the ethanolic extractant in carbon tetrachloride. These included distilled water and 1 M of each mineral acid HCl, H_2SO_4 and HNO_3 as well as 1 M NaCl acidified to the extent of 1M of HCl, H_2SO_4 and HNO_3 .The stripping experiments were carried out at an A/O ratio of 1/1 for 15 min. contact time at room temp. and using a settling time of 5 min. The obtained results presented in Table (6) revealed that NaCl acidified HCl at the mentioned molarity was actually the most efficient stripping agent for REEs from the loaded extractant with 95% efficiency.

Table (6): Effect of stripping agent type on uranium and REES stripping efficiency from the loaded ethanolic extractant.

Stripping agent type	REEs stripping efficiency % for ethanolic extracant
Water	5
(1mole) HNO_3	30
HCl (1mole)	45
H_2SO_4 (1mole)	40
(HNO_3/NaCl) mole of each	59
(NaCl/ HCl) mole of each	95
(NaCl/ H_2SO_4) mole of each	70

It is interesting to mention here, that REEs will stirpped with NaCl/ HCl solution (mole from each).

3.5.2. Effect of molarity NaCl / 1M HCl upon REEs stripping efficiency from the loaded solvent respectively:

The concentration effect of both NaCl and HCl on uranium stripping from the loaded HAE was studied while fixing the other stripping factors; contact time for 15 min., the settling time for 5 min., O/A phase ratio of 3/1 at room temperature. From the obtained results given in Table (6), it was obvious that 1M NaCl / 1M HCl acid has resulted in a 95% uranium stripping efficiency. On the other hand from the obtained results in Table (7), it was shown that 1M NaCl / 1M HCl acid achieved about 95% of REEs stripping efficiency.

Table (7): Effect of NaCl and HCl acid molarity on REEs stripping efficiency from the loaded ethanolic extractant.

Molarity of NaCl /HCl	REEs stripping efficiency % for HAE
HCl (1 mole) / NaCl(1 mole)	95
HCl (0.5 mole) / NaCl(1 mole)	80
HCl (0.25mole) / NaCl(1 mole)	55

3.5.3. Effect of O / A phase ratio:

The effect of the O/A phase ratio on REEs stripping efficiency was studied from 1/1 up to the ratio of 4/1 using 1M NaCl /1M HCl. From the obtained results in Table (8), it was shown that on increasing the O/A phase ratio from 1/1 to 2/1, 90% of REEs stripping was achieved while at the ratio 3/1 95% of REEs stripping was achieved. However, increasing O/A phase ratio to 4/1 the stripping efficiency was decreased to only 70 % thus the O/A phase ratio of 3/1 was the optimum O/A phase ratio for the REEs stripping.

Table (8): Effect of A/O phase ratio on REEs stripping efficiency.

O/A phase ratio	REEs stripping efficiency,%
1/1	90
2/1	90
3/1	95
4/1	70

3.5.4. Effect of contact time:

The effect of contact time on REEs stripping efficiency was studied in the range from 5-20 min. at the previously studied conditions of optimum molarity of NaCl (1 mole) /HCl (1 mole), O /A ratio of 3/1 at room temperature and using a settling time of 5 min. From the data shown in Table (9) it was found that 15 min. as stripping time is the sufficient to achieve 95% of the total REEs.

Table (9): Effect of stripping time upon REEs stripping efficiency for ethanolic extractant.

Stripping time	REEs stripping efficiency,% for ethanolic extractant
5	60
10	75
15	95
20	95

While the REEs-loaded upon ethanolic extractant was subjected to REEs stripping using 1M NaCl /1M HCl under the studied optimum stripping factors. These included:

Stripping agent type	:	1M NaCl /1M HCl
A/O	:	1:3
Contact time	:	15 min.
Temperature	:	room temp

3.6. A Case study: Abu Zeneima ore material (South Eastern Sainai, Egypt) as a case study**.**

According to, the optimum leaching conditions of uranium and REEs from its mineralization at Abu Zeneima ore material (South Eastern Sainai, Egypt) include a H_2SO_4 acid concentration 300 g/L, an agitation time of 4h, a S/L ratio of ½ at 100°C and using an ore grain size of –200 mesh.

Characterization of Abu Zeneima gibbsite ore:

As previously mentioned, the working technological sample was provided from Abu Zeneima gibbsite ore lenses found in the shale beds. Results of the complete chemical analysis of the working sample are shown in Table (10). On the other hand, the gibbsite ore is also characterized by a relatively high CaO and MgO contents reaching about 7 and 3 % respectively. On the other hand ,analysis of the interesting metal values in the working Abu Zeneima technological sample was revealed that besides 560 ppm U, the REEs were found to assay up to 2700 ppm and Zn up to 3650 ppm. It was important to mention herein REEs individual was reported in mentioned Table (11). The latter indicate that, the gibbsite sample has Ce and La assay up to 834 pm and 209 ppm beside Y and Gd about 500 ppm and 460 ppm respectively

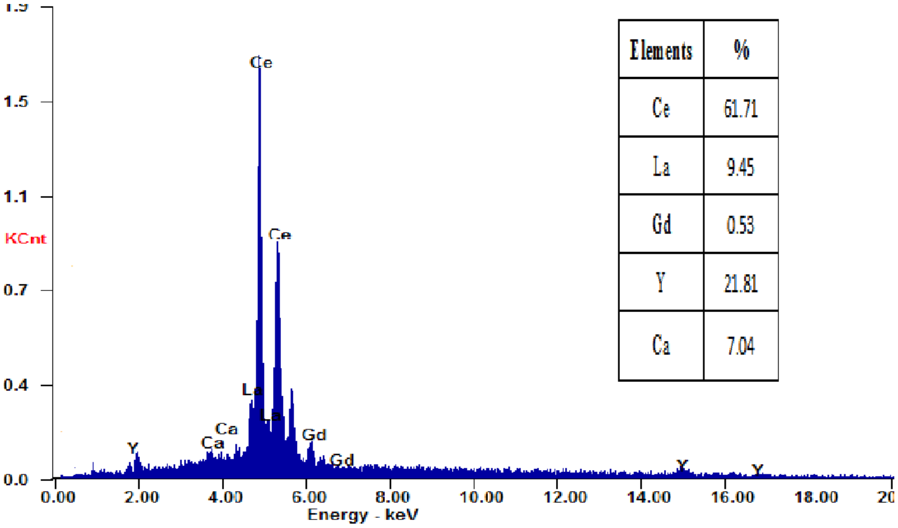
Table (10): Chemical analysis of Abu Zeneima ore material.

Major oxide	**%**	**Traces**	**ppm**	REEs individual	
				Element	**ppm**
SiO_2	11.07	U	560	La	209
TiO_2	0.97	ΣREEs	2700	Ce	834
Al_2O_3	33.43	Zn	3650	Nd	278
Fe_2O_3	8.24	Cr	760	Sm	214
MgO	3.09	V	134	Eu	111
MnO	4.86	Cu	167	Gd	460
Na_2O	2.14	Ni	89	Tb	72
P_2O_5	0.33	Mo	19	Dy	19
CaO	7.25	Cd	45	Ho	0.75
K_2O	2.10			Yb	0.98
L.O.I.*	23.17			Tm	0.67
Total	97.82			Y	500

On the other hand the REEs extraction efficiency of 82% was obtained. The loaded efficiency of each individual REEs was tabulated in Table (11). The REEs-loaded the ethanolic extractant was subjected to REEs stripping using 1M NaCl /1M HCl under the studied optimum stripping factors. These included an O/A ratio of 3/1 at room temperature for 15min. contact time. The obtained strip liquor was then subjected to precipitation using 20% oxalic acid and to precipitate REEs as lanthanides oxalate **(Habashi, 1993).** Therefore, a 20 % oxalic acid solution was used for this purpose after raising the pH value of the striping solution to 3.5. Almost complete precipitation of REEs was attained at pH 1. These conditions represent the optimum conditions for the REEs precipitation. The obtained white REE-oxalate product was filtered and properly washed with distilled water to get rid of any impurities. The latter was subjected to EDX semi-quantitative analysis to identify its individual REEs distribution as shown in Fig. (13).

Table (11): Chemical analysis of individual REEs extraction efficiency .

Element	REEs individual before extraction, ppm	REEs individual remained after extraction, ppm	Extraction efficiency ,%
La	209	26.9	87.13
Ce	834	82.4	90.12
Nd	278	28.4	89.78
Sm	214	167.7	21.65
Eu	111	110.8	0.17
Gd	460	26.5	94.24
Tb	72	71.4	0.79
Dy	19	18.9	0.56
Ho	0.75	0.74	0.45
Yb	0.98	0.97	0.97
Tm	0.67	0.66	0.14
Y	500	65	87



Elements	%
Ce	61.71
La	9.45
Gd	0.53
Y	21.81
Ca	7.04

Fig. (13): EDAX analysis of the produced REEs oxalate

Conclusions

The investigate of the potentiality of plant wastes to extract REEs as means for their recovery was studied. In this regard, using sun flower plant residue extractants (*Helianthus annuus)* as a solvent extraction for rare earth elements (REEs) was the main target of this work. To optimize the REEs extraction by HAE several experiments were conducted to determine the relevant factors affecting the extraction of REEs from a synthetic solution which have actually been achieved about 82% of REEs. These involved 10 vol. of ethanolic extractant, an O/A ratio of 1:1 for a shaking time 10 min. at the pH of 0.1. Under these conditions, the achieved REEs capacity has attained 12mg/g for REEs. REEs stripping from loaded HAE were achieved using 1M NaCl /1M HCl, O/A ratio of 3/1 at room temperature for 15min. contact time and a settling time of 5 min. The obtained strip liquor was then subjected to precipitation using 20% oxalic acid and to precipitate REEs as lanthanides oxalate. The pseudo first order kinetic model was found to best fit the experimental results of REEs extraction by HAE extractant with a correlation coefficient very close to unity. The data on the effect of temperature on REEs extraction by HAE showed that the enthalpy change is −66.12 kJ/mol indicating its exothermic nature.

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