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Extraction of Rare Earth Elements from Industrial Waste Using Natural Clinoptilolite

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ABSTRACT

For extracting of rare earth elements (REE) from the industrial wastes, adsorption process is applied. Natural clinoptilolite was thermally treated and used as an adsorbent for the removal of REE from byproducts residue of phosphoric acid industry (Sample-I) as well as Abu-Rusheid Project (Sample-II) in Egyptian Nuclear Materials Authority. The factors affected the adsorption process were studied such as; effect of time, temperature, agitation speed, and mass/volume (m/v), in addition to sequential chemical treatment during different steps. The results showed that by using thermal clinoptilolite 87% and 91% of REE were removed from the treated solutions of Sample-I, and Sample-II respectively. The stripping of REE from clinoptilolite was carried out using (0.5M) Na_2CO_3 for 30 minutes at room temperature, the stripping percent of rare earth elements was achieved 95.8 % and 87.6 % for clinoptilolite bearing Sample-I & that bearing Sample-II respectively.

Keywords:

Clinoptilolite; Adsorption; phosphogypsum; Abu-Rusheid; Rare earth elements; Stripping

1. INTRODUCTION

Rare earth elements (REE) are the special metals with significant chemical toxicity and radioactivity **[1-3]**. Large quantities of REE emitted from aqueous solutions of natural sediments, mill waste and ammunition have migrated into the environment **[4-6]**. Nowadays, several routes have been developed, such as chemical precipitation-crystallization, ion exchange, solvent extraction, and film separation to deal with waste water containing rare earth elements, however, these routes are not economical **[7-9]**. Adsorption is the process of deposition of molecular species on the surface. The adsorbed molecular species are called adsorbate and the surface on which adsorption occurs is called the adsorbent **[10]**.

Clinoptilolite is a common natural zeolite that have the ideal formula $Na_6Al_6Si_{30}O_{72}\cdot 24H_2O$, though due to interactions with natural ground waters, some of the Na^+ ions will have been replaced by K^+, Mg^{2+} and Ca^{2+} ions **[11-12]**. Clinoptilolite mineral is the most common zeolites in nature and have been found in many areas all around the world, for instance, in Europe, Asia, Africa, Australia and New Zealand, and in many countries of the Americas **[13]**. Clinoptilolite has found wide application in many fields, including agriculture as a slow-release carrier of fertilizers, insecticides, pesticides, antibacterial agents and growth promoters **[14, 15]**, environmental protection, pharmaceuticals **[16]**, petroleum technology **[17]** and of adsorption REE. Clinoptilolite is used in environmental engineering to remove heavy metals, dyes and surfactants from water, and also can be used in production of anti-diarrheal and antiviral drugs, anticancer therapies and drug carriers **[18-21]**.

Phosphogypsum (PG) is an important industrial by-product derived from phosphoric acid and phosphate fertilizer manufacture by dihydrate process which contains appreciable amounts of REE. In this process the phosphate ore is dissolved in concentrated H_2SO_4 to produce phosphoric acid as filtrate and phosphogypsum as a residue. The amount of this by-product exceeds considerably than the mass of the product, because the amount of produced PG ranges from 4.5 to 5.5 tons per ton phosphoric acid in terms of dry matter depending on the nature of the phosphate ore and the methods of production **[22]**. Recently, Nuclear Materials Authority released a complete exploration program in Abu-Rusheid area which characterized by containing numerous minerals , so it can be called poly-mineralization area, such as uranium and thorium minerals, in addition to REE and base metals .

The present work aims to use a natural clinoptilolite as a low cost material in the adsorption of REE from industrial wastes via simple method and to improve the adsorption properties of clinoptilolite by thermal treatment. This can be achieved by studying the ability of natural clinoptilolite to extract rare earth elements from industrial wastes, hydrothermal treatment of natural clinoptilolite for enhancing the extraction percentage, decreasing the time of extraction, and studying the factors affecting the REE adsorption processes such as: type of sample waste, contact time, agitation speed, temperature, REE concentration, the ratio of clinoptilolite to REE solution, and sequential chemical treatment for overall processes. The extraction efficiency will be calculated under optimum conditions for each experiment then will be illustrated diagrammatically. The stripping of REE from clinoptilolite was carried out using suitable stripper.

2. EXPERIMENTAL

2.1. Materials and Apparatus

Natural clinoptilolite sample was sourced from El-Ahuoq area, Taiz governorate, El-Yemen Republic. Two samples in Egyptian Nuclear Materials Authority were studied, the first one was the phosphogypsum waste a byproduct from Phosphoric Acid Project (sample-I), while the second was a byproduct waste (sample-II) received from Lamprophyre area, Abu-Rusheid Project. The HNO_3 and $(NH_4)_2CO_3$ were provided from El-Nasr Chemicals Company, Egypt. The concentrations of major oxides, fluorine, and ∑REE are measured using metertech UV/VIS SP8001 Spectrophotometer, China. Identification of unknown minerals was carried out by X-ray diffraction technique using Philips PW 3710/31 diffractometer with automatic changer PW-1775, (21 positions), Holland. Determination of the trace element was carried out by X-ray fluorescence technique using Philips X' Unique-II spectrometer with automatic sample changer PW 1510, Holland. The IR spectra of the samples were done using FT-IR spectrometer (Bomen, Hartman & Braun, and model MB-157, Canada). The studied samples were analyzed using scanning electron microscopy SEM, JSM–84OA, JEOL, Tokyo, Japan, with the possibility of enlargement by 180.000 times and the resolution of 10 nm.

2.2. Preparation of clinoptilolite

Clinoptilolite was prepared for adsorption process which undergoes washing with hot distilled water then dried at 110°C oven for 60 minutes. The clinoptilolite has been gravimetrically determined, which contains 4.7±0.9 moisture content. The physical properties of natural clinoptilolite were illustrated in **Table 1**.

Table 1: The physical properties of natural clinoptilolite

Bulk (Particle) Density, g/cm^3	**1.85**	**Specific Density, g/cm^3**	**2.37**
Overall Surface Area, m^2/g	**89.4**	**Appearance (Color)**	**Grayish-white**
Porosity %	**27.3**	**Humidity %**	**6.74**
Total Pore Area, m^2/g	**35.6**	**L.O.I %** ***Loss of ignition***	**13.5**
Average Pore Diameter, µm	**0.03**	**Hardness, Moh'no.**	**4.01**
Solubility %	**7.35**	**pH**	**6.83**
Swelling Index	**2.49**	**Grain Size**	**< 6 mm**

Morphologically, the clinoptilolite is a micro-porous arrangement natural zeolite composed of a three-dimensional structure regular of AlO_4 and SiO_4 tetrahedral, which may be associated via a common oxygen atom. Clinoptilolite appears as white, green or purple monoclinic framework silicate crystals [23]. The physical properties of clinoptilolite, such as density and permeability, have no defined unit as they depend on several factors; including its depth in the raw material pile in which the clinoptilolite is placed; the deepest the clinoptilolite in the pile, the greatest its density and the lowest its permeability. The specific gravity varies between 2.3 & 2.6, plus about 25% of the total H_2O content [24].

The chemical alkaline treatment of the natural clinoptilolite was carried out using 0.5N KOH solution in ratio 1:4 solid/solution at 60^{o}C for 90 min. After each experiment the slurry was filtered out and washing till the pH reached to 7.0 then burned at 700^{o}C for 24 hours. Thermal treatment can result in cation migration, thereby influencing its location and pore openings. The change in the surface properties during heating was attributed to the increase in the agglomeration size of clinoptilolite crystals at high temperatures [23]. The heat treatment of the same samples causes an increase in surface area and pore volume. Na^+, Mg^{2+} & Ca^{2+} were counterbalance ions on the clinoptilolite surface and exchanged their sites mainly for K from solution. This could be the reason why KOH was more effective in removing the REE. Constant heat stability with KOH treatment also shows that Si/Al ratio is an important parameter for the heat stability. No change was observed in the structure and thermal stability of clinoptilolite after alkali treatments [25].

2.3. Analytical procedure

In glass beakers, a known amount of clinoptilolite was taken, with the addition of known volume of the studied wastes at room temperature and mixed for a known time. Other processes were performed by using suitable stripper which mixed with clinoptilolite bearing REE from different studied samples. The factors affecting the adsorption and stripping processes (such as contact time, temperature, phase ratio, and sequentional chemical treatment) were optimized.

The total rare earth element in two studied samples was measured spectrophotometrically using Arsenazo-III as indicator **[26]**. The method was described as: To the acidic sample solution (pH ≈ 1), add 1 mL 1% ascorbic acid solution. After few minutes, add 1 mL of the format buffer then 2 mL of arsenazo III solution, and dilute with water to ≈ 20 mL. Adjust the colored solution of pH ≈ 2.6 by (0.1 M) NaOH. Transfer the solution to a 25 mL standard flask, make up to the mark with distilled water, and measure the absorbance at 650 nm against reagent blank solution. A series of standard solutions containing a wide concentrations range from 0.01 to 0.08 ppm was used.

3. RESULTS & DISCUSSION

3.1. Clinoptilolite, Spectroscopic Characterization

The spectroscopic characterization of clinoptilolite samples was carried out using X–ray diffraction, IR spectra, SEM, as well as X-ray fluorescence as follow:

3.1.1. X-Ray Diffraction (XRD)

The results of the XRD spectroscopy evaluation confirmed the pattern of the raw clinoptilolite **(Fig. 1)**. The pattern had crystal form factors that corresponded to the functional peaks of the clinoptilolite. The analyzed model matched the reference code 98-000-2606 and the density of the zeolite was recorded as 2.15 g/cm^3. The discovery describes that the chemical formula of clinoptilolite is as $[Na_{1.66}\ K_{2.56}\ Ca_{1.9}\ (Al_{5.48}\ Si_{30.52}\ O_{72}).19.16H_2O]$. Although they differ in practice, the Si/Al ratio for a similar clinoptilolite formula structure was found to be 5.57. This subset of natural inorganic minerals also suggested a type of monoclinic structure **[13-18, 23]**.

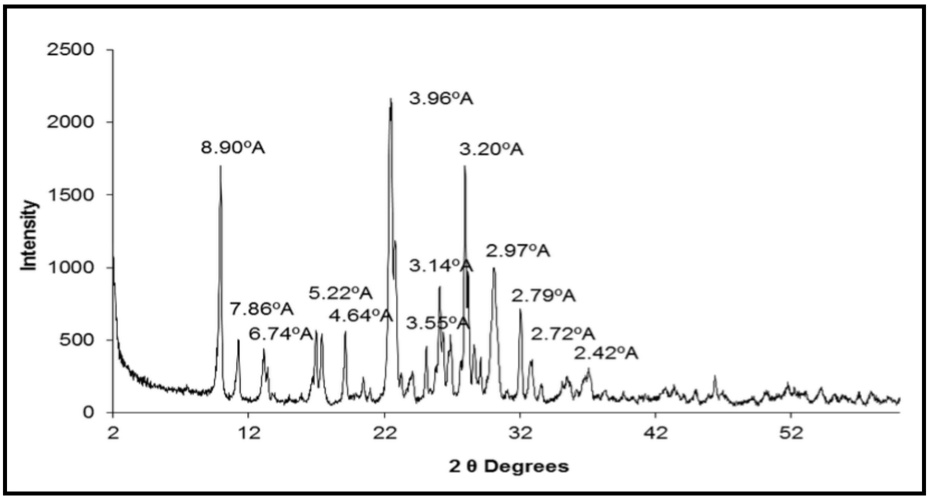

Fig. 1: XRD pattern of the natural clinoptilolite

3.1.2. FT-IR Spectra

Clinoptilolite provide upward push to broader bands in the wave-number region 3400-3260 cm^{-1} which correspond to symmetric and asymmetric stretching vibration of the OH groups **(Fig. 2)**. The shift in wave-numbers with respect to equal vibration found for water vapor (3750 cm^{-1}) offers proof of the presence of hydrogen bonds in the complex water-framework oxygen-cation. The bands of the wave-number 2920 cm^{-1} belonging to overtone harmonic vibration of in plane bending vibration of H-O-H had been found. The medium intensity bands of the bending H-O-H vibration arise in the wave-number region 1630-1640 cm^{-1}. The very strong and broad bands with fine structure or splits of the asymmetric stretching vibration of the cationic bonds appear in the wave-number region 990-1190 cm^{-1}. Owing to comparable force constants of the Al-O and Si-O bonds, the vibrations of these bonds are not distinguishable **[23]**.

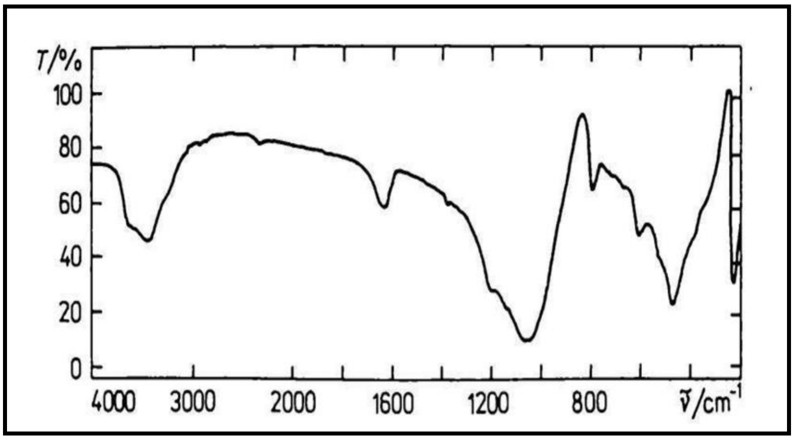

Fig. 2: The FT-IR spectra of the natural clinoptilolite

3.1.3. Scanning Electron Microscopy (SEM)

SEM represents a totally effective morphological investigation device for a definitely prepared mineral sample. The SEM micrograph displays the micro-morphological features of the clinoptilolite material. Aggregates of clinoptilolite are predominantly tabular in shape, with some displaying widths of 3-4µm. Such simplified mineral preparation technique, based on the cutting/polishing of the sample surface, did not permit to visualize the real mineral texture and to evidence the presence of a meso-porosity. Therefore, to proof the mineral texture, clinoptilolite sample was conveniently powdered before SEM observation **(Fig.3)**.

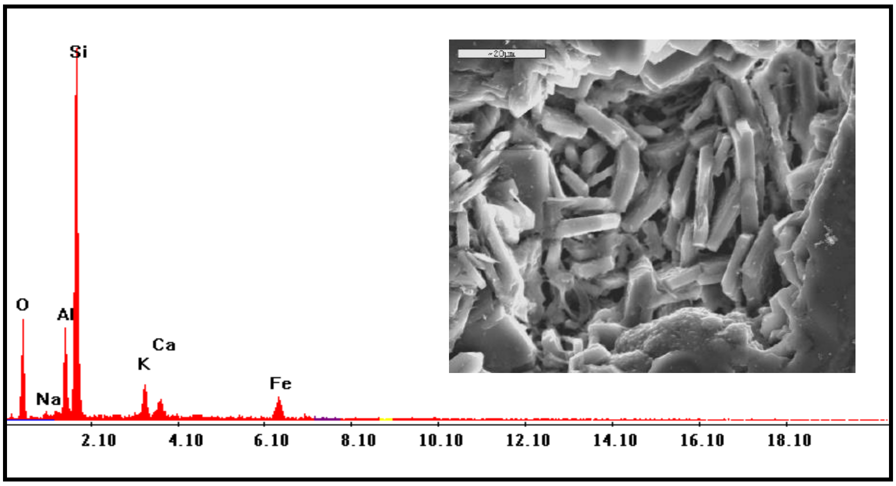

Fig. 3: The SEM & EDX of the natural clinoptilolite

In order to isolate the thinnest fraction of the powder, which corresponds to the most delaminated mineral fraction, the powder was sieved by a fine-mesh grid, then was placed on the surface of an electrically conductive carbon tape, placed on an Al stub for SEM, and after, Au/Pd sputtering, observed by the SEM. As visible, the clinoptilolite particles have a finely-grained polycrystalline structure, much like texture of lamellar type **[16-18, 23]**.

3.2. Preparation of Clinoptilolite

The effect of particles size and chemical standard concentration of REE were the main factors affect the preparation of clinoptilolite to undergo adsorption processes, which can be studied as follows:

3.2.1. Effect of particles size

After drying and grinding using crusher machines, the bulk sample of granular clinoptilolite was carefully quartered into homogeneous smaller samples; these samples were matter of chemical and spectroscopic analyses as well as work's experiments. One kg of the bulk clinoptilolite from both natural and thermal sources was fractionated into five homogeneous fractions with different fractions to show the effect of particle size on the distribution of REE in these samples. The portions were prepared for the spectrophotometric measurement and the enrichment factor (En) was calculated as a ratio of particular REE content in a certain fraction to its content in the bulk clinoptilolite:

$$En = A_n / A$$

Where A_n is the concentration (ppm) of the REE in the given fraction (n), and, A is its concentration (ppm) in the clinoptilolite bulk.

The particle size of clinoptilolite would make it amenable for extraction due to increasing the surface area of the extractant which is exposed to REE in nitrate solution. The effect of particle size of the clinoptilolite was studied using samples having a size varying from < 48, 63, 75, 125, and 250 µm on equal volume of standard rare earth elements (1000 ppm) at room temperature for 30 minutes, the results were shown in **Fig.4**.

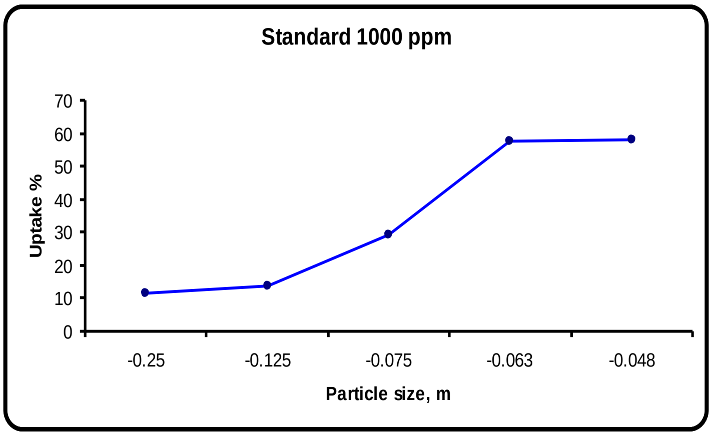

Fig.4: Effect of clinoptilolite particle size on the uptake of REE

The results indicated that the REE extraction efficiency increases by decreasing the particle size. The extraction efficiency increases from 8.5% to 59.2% which corresponding to 915 to 408 ppm standard rare earth elements respectively. This behavior may be due to decrease the surface area of the clinoptilolite as an extractant. So the particle size (< 63µm) of clinoptilolite was more sufficient for extraction of REE with an efficiency of 59.2%. Most rare earth elements particles are enriched in the fines particle sizes of < 63µm, comparable to that found in the bulk of clinoptilolite. The distribution of REE content into the different portion was achieved in which about 28.4% was incorporated into coarse portion that present about 64% of the total sample weight. On the other hand, about 71.6% of REE content was captured into the fine portion (< 75 to 63µm) which was about 36% of the total sample.

3.2.2. Effect of REE standard concentration

The effect of concentration of standard REE on the removal efficiency was experimented using solutions range from 100 to 1000 ppm (50 mL). The different REE standards were agitated for 35 min. at room temperature with different volumes (2-8g) of clinoptilolite (< 63µm). The results were plotted in **Fig.5**.

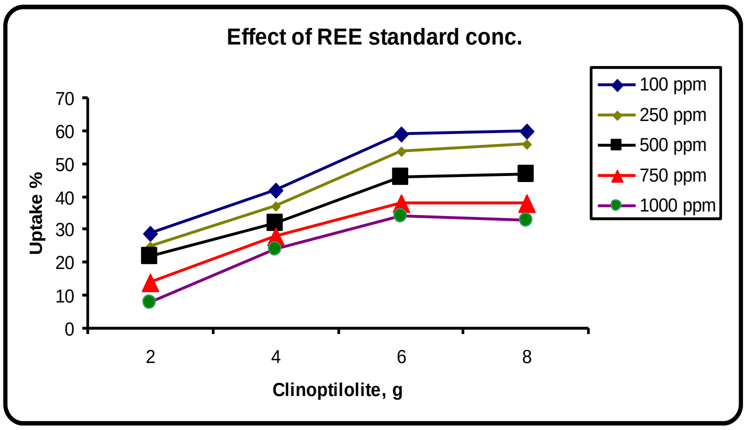

Fig. 5: Effect of standard REE conc. on the uptake percentage

The results indicated that, the ability of clinoptilolite to adsorb rare earth elements decreases with increasing the concentration of the standard from 100 to 1000 ppm. The uptake percentage, for example, becomes 59%, 54, 46%, 38 and 34% under the addition of 6g of the natural clinoptilolite per 50 mL of 100, 250, 500, 750, 1000 ppm standard rare earth elements respectively. The concentration of REE was decreased in the standard solution corresponding to the increase in the uptake percentage of clinoptilolite.

3.3. Preparation of the studied Samples

The byproduct of Abu-Rusheid and phosphoric acid projects were undergone several leaching factors using HNO_3 solutions, as a leachate **[27]**. The nitric acid concentration, agitation time, temperature, and phase ratio have been investigated to determine the optimum leaching parameters which achieve maximum efficiencies for REE with minimum gangue.

3.3.1. Effect of HNO_3 concentration

The effect of HNO_3 amount ranged from 1-8 M on the uptake of REE was studied at room temperature under the addition of 10g solid to 500ml acid for 30 min. **(Fig.6)**. From the obtained data, by increasing the HNO_3 concentration, the dissolution of rare earth elements was enhanced in which the leaching efficiencies become 65.6% at 5M HNO_3 for Sample-I, and 78.9% at 7M nitric acid for Sample-II.

3.3.2. Effect of contact time

The effect of agitation time on the leaching efficiency of rare earth elements was studied to identify the time required for maximum dissolution. Under time ranged from 10-60 minutes with fixed conditions of 10g of each waste per 500 mL of nitric acid (5M and 7M HNO_3 for Sample-I & Sample-II respectively) at room temperature (**Fig.7)**. The illustrated results of the leaching experiments indicated that maximum dissolution for rare earth elements (65.6 & 81.1%) was achieved at 30 & 40 minutes for Sample-I & Sample-II respectively and no appreciable increase in leaching efficiency over these values.

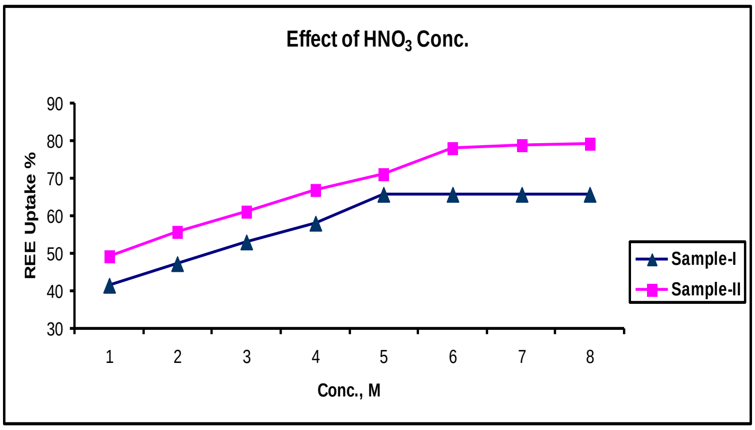

Fig. 6: Effect of HNO_3 conc. on the uptake of REE

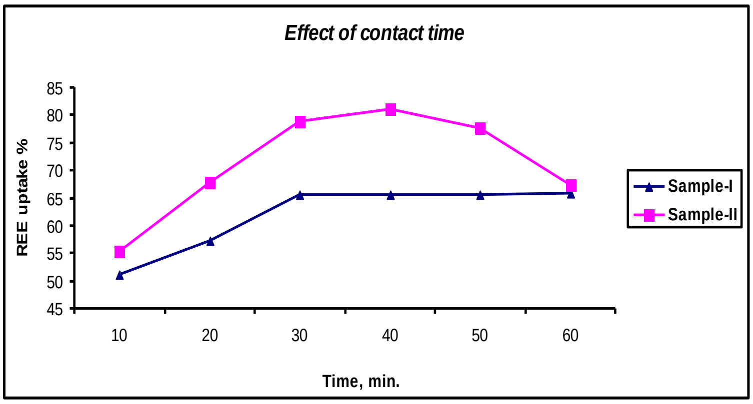

Fig.7: Effect of time on the uptake of REE

3.3.3. Effect of temperature

Effect of temperature on the leaching efficiencies of REE was studied from 25 to 55°C under the addition of 500 ml of 5M and 7M HNO_3 for 30 and 40 min. to 10g of Sample-I & Sample-II respectively. The results were represented in **Fig.8**.

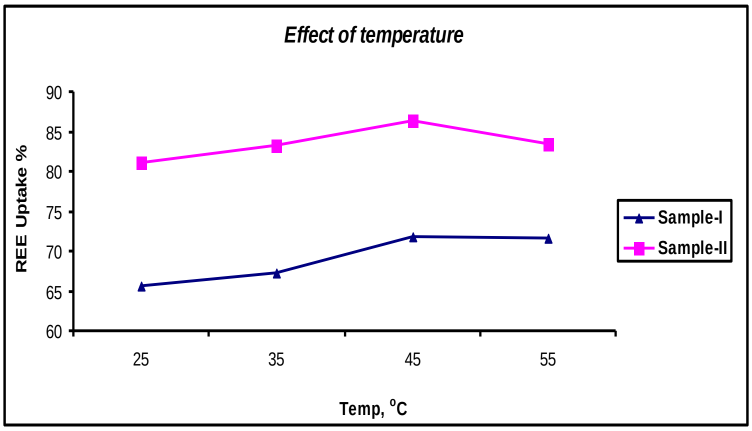

Fig. 8: Effect of temperature on the uptake of REE

The results indicated that the leaching efficiencies of REE were increased with temperature and became 71.8 % and 86.4 % at 45°C for Sample-I & Sample-II respectively. Therefore, it was preferred to perform the leaching processes using HNO_3 at this temperature, which achieved maximum dissolution of REE.

3.3.4. Effect of phase ratio

The effect of solid/liquid ratio from 10-40 g of each solid sample per 500 mL of HNO_3 was studied under the conditions of 5M acid for 30 min. (sample-I) & 7M acid for 40 min. (sample-II) at 45°C. The result of REE leaching efficiency graphically represented in **Fig.9**. From the results, by varying the solid/liquid ratio, REE efficiency was enhanced. Under the addition of 30g of each solid waste, the efficiency equals 84.7 and 93.5% for Sample-I & Sample-II respectively. Therefore, solid /liquid ratio of 30g per 500 ml was the preferable for achieving high REE leaching efficiency.

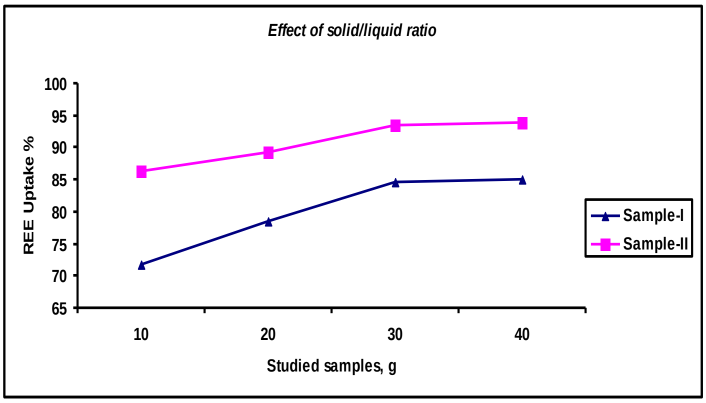

Fig. 9: Effect of phase ratio on the uptake of REE

From the reported data, the optimum conditions for giving high leaching efficiency of REE from the two studied samples was achieved under the conditions of 5M & 7M of HNO_3, 30 & 40 min. contact time, 30g per 500 ml of acid at temperature of 45°C, which leads to 84.7% and 93.5% REE leaching efficiency respectively.

3.4. Adsorption of Rare Earth Elements

REE in the two studied samples under study were undergone adsorption process using natural and thermal clinoptilolite fractionated sample. The factors affect the adsorption process such as; types of rare earth elements waste, contact time, agitation speed, temperature, mass/volume, and sequential chemical treatment were studied:

3.4.1. Type of REE samples

The presence of different impurities in the wastes samples like; Fe, Zr, Zn, Pb, F, other trace or major components, will cause a serious problem for extracting of REE in general way, therefore, the received waste has been treated using HNO_3 under the previous optimum conditions. The 500 mL of samples were agitated with 10g natural & thermal clinoptilolite for 30 min. at room temperature. The data were illustrated in **Tables 2-3**. The results for adsorption of REE from the treated samples using the natural and thermal clinoptilolite were illustrated in **Fig.10.** The obtained results clarified that the adsorption of REE by clinoptilolite depends on the type of impurities in different studied sample.

Table 2: Major constitutes % in the two samples treated by HNO_3

Components	**CaO**	**SO_3**	**SiO_2**	**P_2O_5**	**Fe_2O_3**	**Na_2O**	**K_2O**	**TiO_2**	**H_2O**	**L.O.I**
Sample-I	27.5	33.1	8.73	1.05	5.3	0.07	0.12	0.82	18.1	3.42
Sample-II	1.09	1.12	34.2	0.10	3.70	0.14	1.42	0.31	9.71	7.01

Table 3: Analysis of trace elements (ppm) in the two samples treated by HNO_3

Elements	**Cr**	**Co**	**Cu**	**Cd**	**Zn**	**Zr**	**Pb**	**As**	**V**	**Ba**	**B**	**Be**	**Ni**	**REE**
Sample-I	80	191	135	98	740	298	132	76	241	203	88	123	112	1360
Sample-II	41	77	162	91	837	341	690	112	398	211	254	104	198	1685

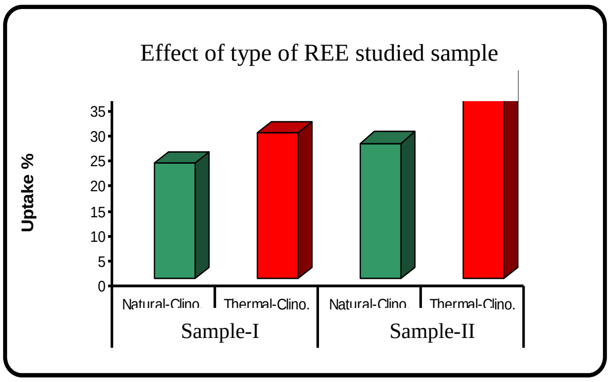

Fig. 10: Effect of type of REE samples on uptake percentage

For the sample-I (by-product Phosphogypsum), the uptake percentage was 25% & 34%, and became 27% & 39% for sample-II (by-product from Abu-Rusheid project, Lamprophyre area) using natural and thermal clinoptilolite respectively. On the other hand, the concentration of REE was decreased in the different studied samples for natural clinoptilolite which indicates that the thermal type have good adsorption capacity.

3.4.2. Effect of time

The effect of agitation time on the uptake of REE from the studied materials was investigated, the contact time ranged from 15-60 minutes was chosen. About 10g of the homogenized (< 63µm) solid clinoptilolite was reacted with 500 mL of the two waste using agitation speeds of 150 rpm at room temperature. From the plotted results **(Fig. 11 a-b)**, it is clear that, the uptake of REE in sample-I was increased to be 30% and 49%, while the maximum value became 32% and 51% for sample-II at 45 minutes using natural and thermal clinoptilolite respectively.

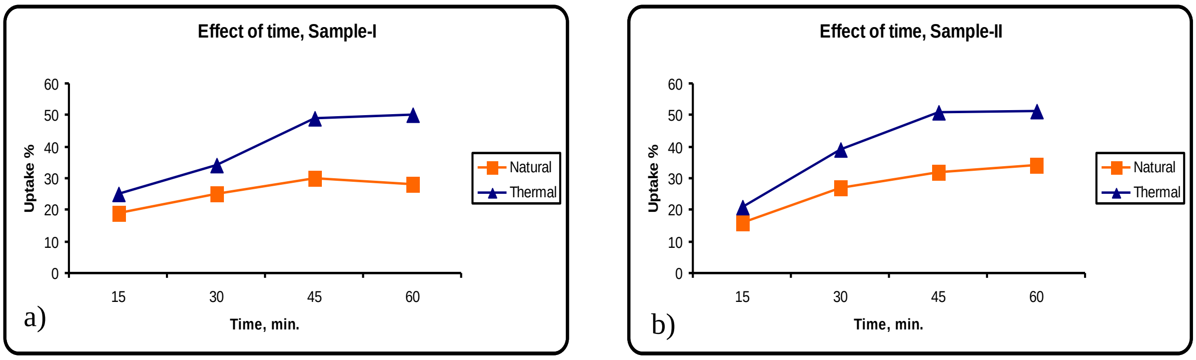

Fig. 11: Effect of time on REE uptake percentage from sample-I & II

3.4.3. Effect of agitation speed

To show the effect of agitation speed on the adsorption of rare earth elements onto the clinoptilolite, six agitations speed were applied, 50, 100, 150, 200, 250, and 300 rpm. Under room temperature 10g of clinoptilolite was agitated for 45 minutes with 500 mL of the two studied wastes, the results obtained were shown in **Fig. 12 (a-b)**.

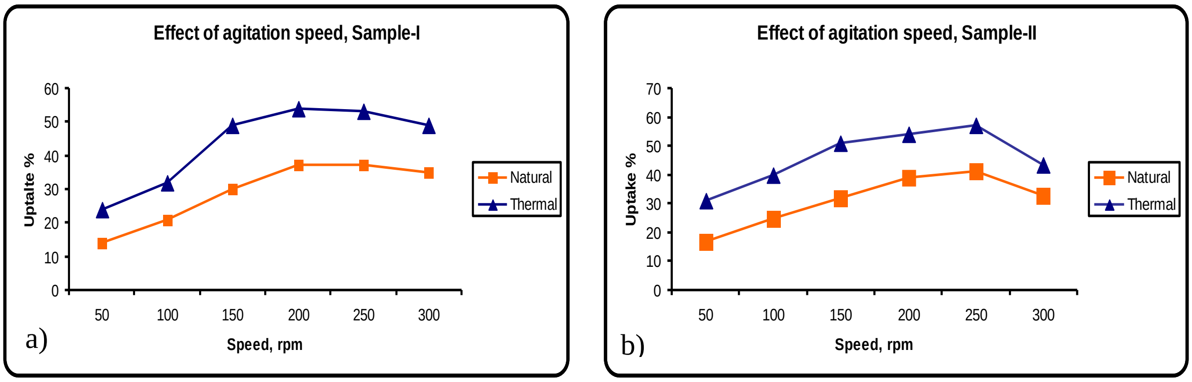

Fig. 12: Effect of agitation speed on REE uptake percentage from sample-I & II

The highest adsorption rate is obtained at 250 rpm for two types of clinoptiolite (natural and thermal), this is due to the formation of small broken particles at 300 rpm, thereby enhancing the desorption process **[3]**. For sample-I, 200 rpm was taken corresponding to uptake of 37.1 & 54.0% of REE using natural & thermal clinoptilolite respectively, while 250 rpm was chosen for sample-II corresponding to adsorb 41.2, 57.3 % of REE using natural & thermal type respectively.

3.4.4. Effect of temperature

To study the effect of temperature on the adsorption process, clinoptilolite samples of 10g (<63µm) were agitated with the 500 ml of the two waste samples for 45 minutes, the temperature was varied between 15°C to 65°C (**Figs. 13a-b)**.

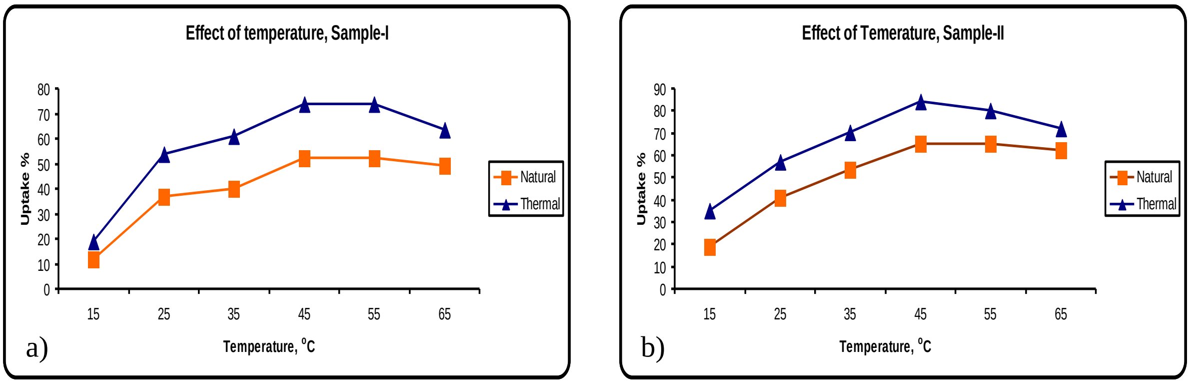

Fig. 13: Effect of temperature on REE uptake percentage from sample-I & II

The results revealed that at 45°C a remarkable increase in the REE uptake percentage for sample-I which achieved 52.1 & 74%, while for sample-II the uptake became 65.3& 84% when using natural & thermal clinoptilolite respectively. After this value the process was restricted by increase viscosity **[23]**.

3.4.5. Effect of mass per volume (M/V)

Different amounts of natural and thermal clinoptilolite ranged from 5-25g were agitated under previous conditions for each sample to study the effect of mass/volume on the adsorption efficiency. The values in **Fig. 14 (a-b)** showed that, by the addition of 20g & 15g of natural & thermal clinoptilolite, the REE uptake percentage became 65 & 87% as well as 76, 91% for sample-I & II respectively. The amount variation of clinoptilolite was occurred depending on the concentration of REE in each sample.

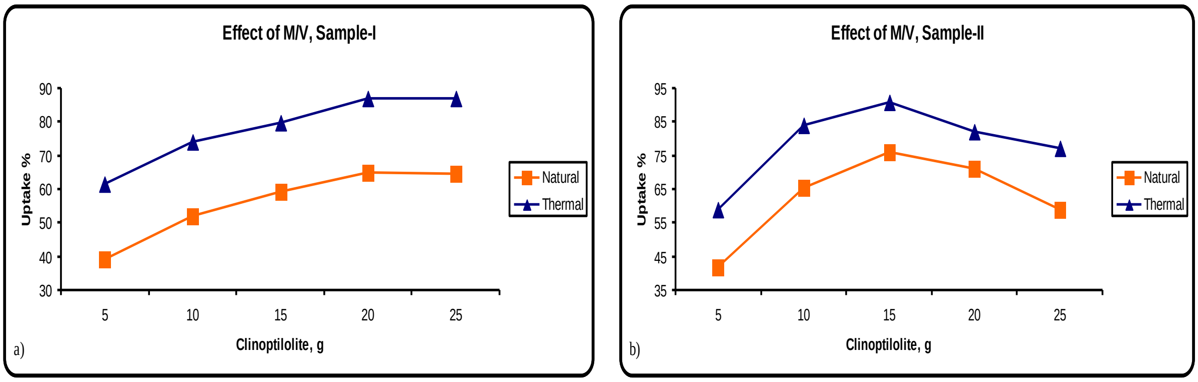

Fig. 14: Effect of mass/volume on REE uptake percentage from sample-I & II

3.4.6. Effect of settling time

The treated solution was kept in a 1L cylinder (W=7cm and H=17cm) and allowed to stand for different periods ranging from 24 (1 day) to 168 (7 days) hours to study the rate of settling of clinoptilolite on the sample-I and sample-II. Using the optimum conditions for rare earth elements adsorption, the process was carried out and the results are plotted in **Fig.15** which indicated that the clinoptilolite for sample-II precipitated after adsorption process required about 120 hours (5 days) for complete formation. On the other hand, the clinoptilolite for sample-I required about 144 hours (6 days) for complete precipitation. The rate of precipitation was slow in case of clinoptilolite for sample-II which need several days to complete crystals formation.

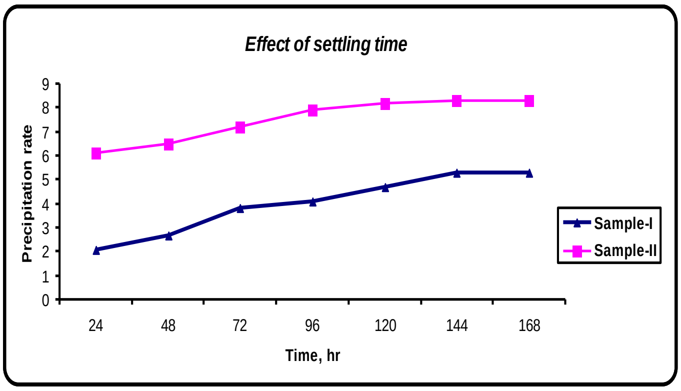

Fig. 15: Effect of settling time on clinoptilolite particles

3.4.7. Estimation of optimum conditions

The optimum conditions for adsorption of REE from the studied samples can be summarized in the following **Table 4**:

Table 4: Estimation of optimum conditions for two wastes

Sample Type	Conditions	Uptake %	
		Natural	Thermal
Sample-I	**45 min.**	**65**	**87**
	200 rpm		
	45 °C		
	20 g M/V		
Sample-II	**45 min.**	**76**	**91**
	250 rpm		
	45 °C		
	15 g M/V		

3.4.8. Sequential chemical treatment

The two wastes of REE were undergone successive adsorption process (3_steps) using natural and thermal clinoptilolite of (< 63µm) particle size under the previous optimum conditions. The results are illustrated diagrammatically in **Fig. 16 (a-b)**.

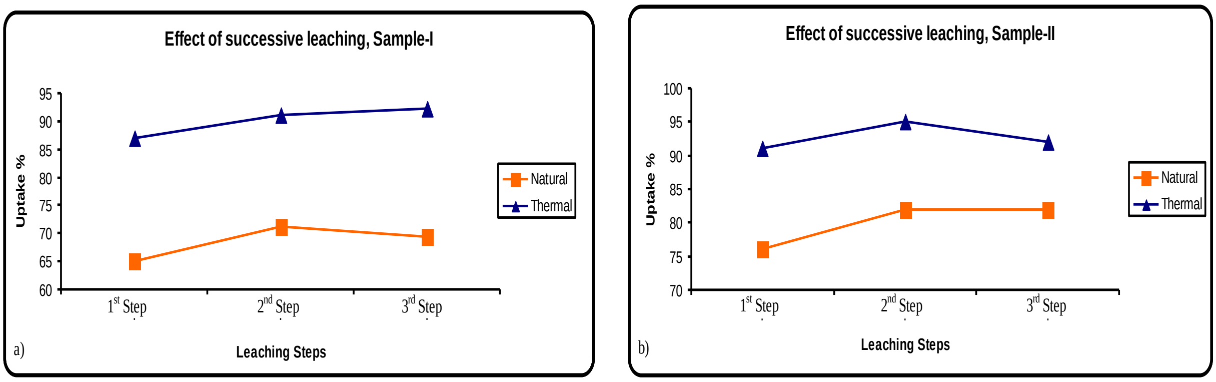

Fig. 16: Effect of successive leaching processes on REE uptake percentage

After two successive leaching processes; about 6 and 4% of REE was removed by using natural & thermal clinoptilolite respectively corresponding to 71.1 & 91% uptake % for Phosphogypsum as well as 82 & 95% for Abu-Rusheid wastes. In the third step there is no applicable removal of REE as the waste was saturated with the fractionated clinoptilolite.

3.4.9. Analysis of the products

After the separation of leaching products via centrifugation, the obtained de-contaminated wastes as well as clinoptilolite were undergone chemical analyses and the results were tabulated in **Tables 5 & 6**.

Table 5: Trace elements (ppm) in the clinoptilolite adsorbed-sample-I & II

Elements	Cr	Co	Cu	Cd	Zn	Rb	V	Ba	Be	Sb	Se	Nb	REE
Sample-I	60	184	43	207	139	69	89	632	85	47	69	190	1170
Sample-II	37	91	16	145	162	75	42	347	101	23	72	212	1508

Table 6: Trace elements (ppm) in the adsorbed REE samples

Elements	Cr	Co	Cu	Zn	Zr	V	Ba	Be	Ni	Sn	Se	REE
Sample-I	78	187	45	219	174	215	189	114	128	141	20	42
Sample-II	46	94	23	642	361	357	161	91	184	17	60	27

From the data in **Tables (5-6)**, the thermal clinoptilolite have a good REE adsorption efficiency from the studied samples. The concentration of rare earth elements was decreased from; 1360 to 42 ppm for sample-I, and from 1685 to 27 ppm for sample-II. On the other hand, the thermal clinoptilolite became rich with an adsorbed amount of REE.

3.5. Stripping Processes

The stripping investigations were carried out to choose the best conditions that can successfully strip the most REE content from clinoptilolite. The effect of types of stripper, shaking time, phase ratio, and stage number were studied as following:

3.5.1. Effect of stripper types

Different types of stripper were used in the stripping investigations such as H_2O, HCl, HNO_3, H_2SO_4, & Na_2CO_3. Under room temperature, the reaction was carried out by mixing 100 mL of each stripper (0.5M) with 5g of pregnant clinoptilolite (adsorbed REE from samples I & II) for 20 minutes. The stripping efficiency was determined as strength of clinoptilolite with extracted REE content (**Fig. 17)**.

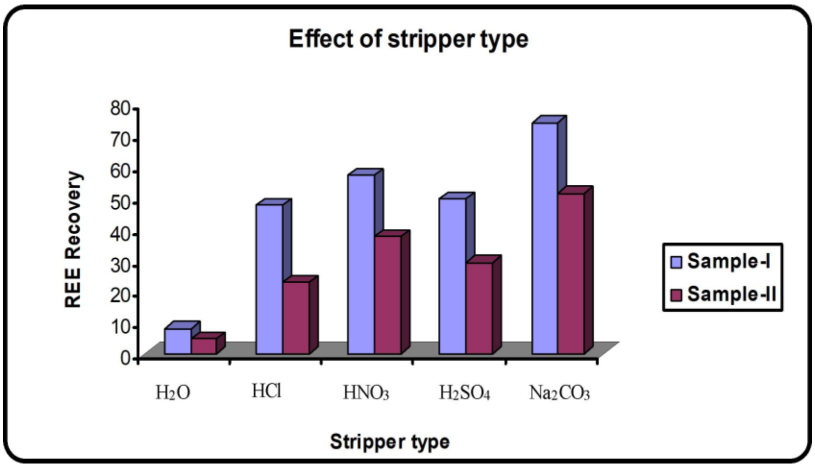

Fig. 17: Effect of stripper type on REE-clinoptilolite-samples

The results showed that the stripping by alkaline solutions was always higher than any acidic solutions. The solution of Na_2CO_3 achieved an elution efficiency of 74.2 and 51.3% for phosphogypsum-clinoptilolite and Abu-Rusheid-clinoptilolite respectively.

3.5.2. Effect of shaking time

The effect of shaking time on stripping process for clinoptilolite bearing REE has been investigated using 100 mL Na_2CO_3 (0.5M) mixed with 5g solid clinoptilolite at room temperature, while the shaking time ranged from 10 to 40 minutes **(Fig.18)**.

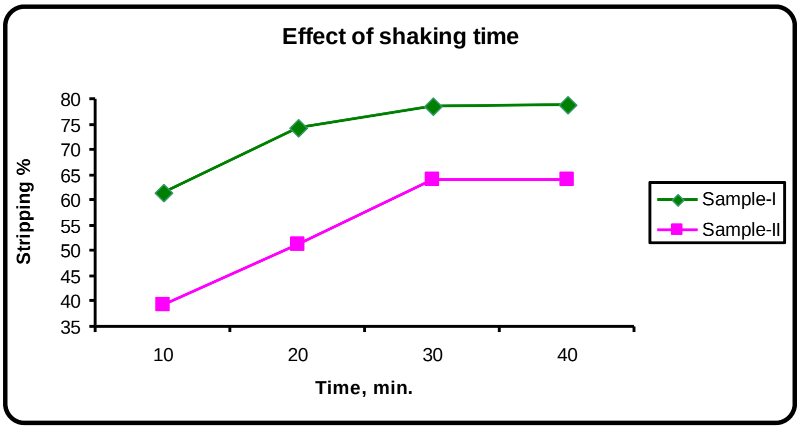

Fig. 18: Effect of shaking time on the stripping process

The results showed that the stripping efficiency increases from 10 to 30 min. then remained more or less constant at 40 minutes. This indicated that the process is rapid, i.e. it is not always a variety controlled process. At time of 30 min., the stripping percentage for Sample-I-clinoptilolite and Sample-II clinoptilolite was 78.6 & 64.1% respectively.

3.5.3. Effect of phase ratio

The effect of solid/aqueous phase ratio on REE stripping from the pregnant clinoptilolite was studied using Na_2CO_3 (0.5M) at room temperature. The shaking time was 30 minutes, while solid/aqueous phase ratio was varied from 1/20 ~ 1/40 (corresponding to 5g/100 mL ~ 5g/ 200 mL).

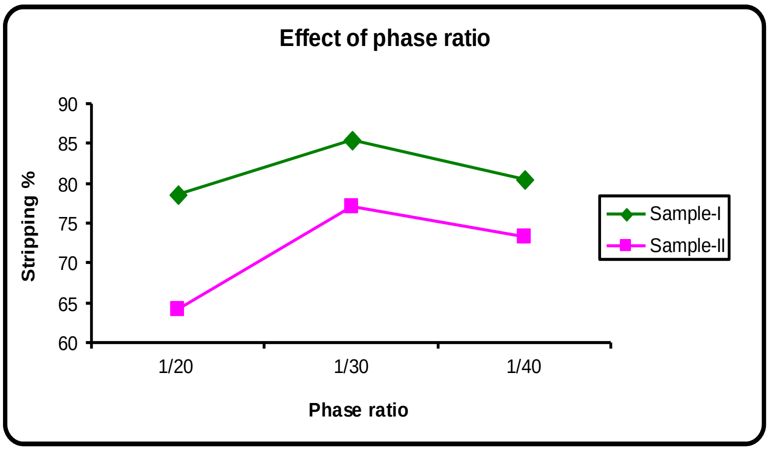

Fig. 19: Effect of liquid/solid ratio on the stripping process

The results (**Fig.19)** indicated that upon increasing aqueous/solid ratio, the stripping efficiency increased to exhibit a maximum at 1/30 ratio (5g/ 150 mL) which achieved 85.4, and 77.1% for clinoptilolite bearing rare earth elements from phosphogypsum and Abu-Rusheid wastes respectively. Further increase in aqueous/solid ratio was associated with a very slight change in stripping percentage. Accordingly, aqueous/solid ratio of 1/30 is recommended as a suitable stripping phase ratio of REE with Na_2CO_3 solution.

3.5.4. Successive stripping steps

The clinoptilolite from adsorption processes was undergone successive leaching steps for stripping of rare earth elements under the previous optimum conditions of room temperature, time, solid/aqueous phase ratio, and concentration of sodium carbonate solution. The results were diagrammatically showed in **Fig. 20**. The results indicated that by increasing the number of recycle steps, the stripping efficiency of rare earth elements from clinoptilolite bearing phosphogypsum and Abu-Rusheid wastes was increased to become 95.8 and 87.6% respectively at the third stripping step, then became constant after that.

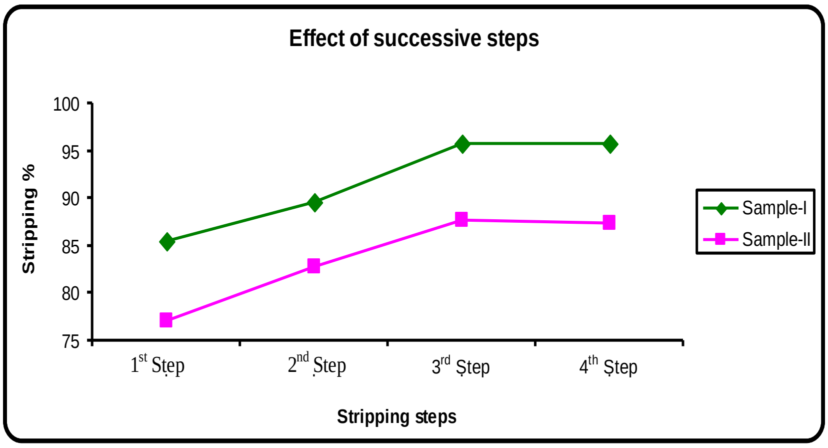

Fig. 20: Effect of stage number on the stripping process

4. CONCLUSIONS

A successful leaching procedure of REE samples, the by-products from processing of phosphoric acid (phosphogypsum) and Abu-Rusheid project (Lamprophyre Area) in Nuclear Materials Authority, Egypt, has been developed in the present work. This was achieved through leaching of REE by using natural clinoptilolite. The corresponding relevant factors were studied and the conclusions can be summarized as follows:

1- By the fractionation of clinoptilolite, the REE removal efficiency exhibited 59.2% for the fraction <63µm particle size. The uptake percentage was decreased from 59.2% to 34% when the concentration of standard REE was increased from 100 to 1000 ppm respectively. The two solid samples were undergone dissolution using HNO_3 under desired conditions to obtain the complete leaching of major REE content.

2- Treatment of the two contaminated wastes using thermal clinoptilolite enhanced the REE uptake percentage and the different conditions for adsorption process were optimized. The results showed that the uptake was 87% when 20g clinoptilolite were agitated (200 rpm) with 500 ml of sample-I at 45°C for 45 min., and became 91% when 15g clinoptilolite was mixed with 500 ml of sample-II at 250 rpm for 45 min. at 45°C.

3- Rare earth elements were stripped from the clinoptilolite using 0.5M Na_2CO_3 under optimum conditions; the stripping percentage achieved 95.8, and 87.6 for sample-I & sample-II by-products respectively. Finally, it is more economical to use optimized natural clinoptilolite in the reduction of REE from waste materials to produce indigenous materials that can be used safely in the many industrial applications.

REFERENCES

1. Zhang, W; Ji, B.: Adsorption of cerium (III) by Zeolites synthesized from Kaolinite after rare earth elements (REE) recovery, Journal of Chemosphere, 2022, 303(1), 253-262. DOI.org/10.1016/j.chemosphere.2022.134941

2. De Souza, A.; Giese, E.: Recovery of rare earth elements from Brazilian ion adsorption clay: A preliminary study, Orbital: the Electronic Journal of Chemistry, 2021, 14 (1), 10-14. DOI: 10.17807/orbital.v14i1.1569

3. Akhmadiyeva, N.; Abdulvailyev, R.; Abikak, Y.; Manapova, A.; Gladyshew, S.; Ruzakhunova, G.; Sukurov, B.: Kaolinite clay as a raw material for erbium extraction, Journal of Heliyon, 2023, 9 (4). DOI: 10.1016/j.heliyon.2023.el4280

4. Patel, K.; Sharma, S.; Maity, J.; Martin-Ramos, P.; Fiket, Ż.; Bhattacharya, P.; Zhu, Y.: Occurrence of uranium, thorium and rare earth elements in the environment: A review, Journal of Frontiers in Environmental Science, 2023, 1-18. DOI:10.3389/fenvs.2022.1058053

5. Costis, S.; Mueller, K.; Coudert, L.; Neculita, C.; Reynier, N.; Blais, J.: Recovery of potential rare earth elements from mining and industrial residues: A review and case studies, Journal of Geochemical Exploration, 2021, 221. DOI:10.1016/j.gexplo.2020.106699

6. Kolawole, T.; Olatunji, O.; Ajibade, O.; Oyelami, C.: Sources and levels of REE contamination of atmospheric dust in Nigeria, Journal of Health and Pollution, 2021, 11 (30), 1-17. DOI:10.5696/2156-9614-11.30.210611

7. Lokshin, E.; Tareeva, O.; Elizarova, I.: Recovery of rare earth elements from the wet process phosphoric acid, Russian Journal of Applied Chemistry, 2013, 86 (5). DOI: 10.1134/S1070427213050017

8. Ndjama, J.; Mafany, G.; Ndondo, R. G.; Belmond, B. E.; Bessa, A. Z.: Rare earth elements in surface waters and sediments of the Mgoua watershed, southwestern Cameroon, Arabian Journal of Geoscience, 2022, 15 (1001), 2-13. DOI:10.1007/s12517-022-10278-0

9. Piarulli, S.; Hansen, B.; Ciesielski, T.; Zocher, A.; Malzahn, A.; Olsvik, P.; Sonne, C.; Nordtug, T.; Jenssen, B.; Booth, A.; Farkas, J.: Sources, distribution and effects of rare earth elements in the marine environment: current knowledge and research gaps, Journal of Environmental Pollution, 2021, 291, 118230. DOI:10.1016/j.envol.2021.118230

10. Markovska, I.; Mihalev, T.; Georgiev, D.: Study on the adsorption properties of natural zeolite type clinoptilolite and synthetic zeolite ‘L’ towards manganese and iron ions, Journal of Oxidation Communications, 2016, 39 (4-II), 3443-3450.

11. Mosai, A.; Chimuka, L.; Cukrowska, E.: Li, K.; The recovery of rare earth elements (REE) from aqueous solutions using natural zeolite and bentonite, Journal of Water Air & Soil Pollution, 2019, 230 (8). DOI:10.1007/s11270-019-4236-4

12. Pabis-Mazgaj, E.; Gawenda, T.; Pichniarczyk, P.; Stempkowska, A.: Mineral composition and structural characterization of the clinoptilolite powders obtained from zeolite-rich Tuffs, Journal of Minerals, 2021, 11 (10), 1030-1051. DOI:10.3390/min11101030

13. Verrswijk, S.; Weckhuysen, B.: Emerging analytical methods to characterize zeolite-based materials, Journal of National Science Review, 2022, 9 (9). nwac047. DOI:10.1093/nsr/nwac047

14. Sadeghi, S.; Albaji, M.; Golabi, M.; Nasab, S.: Using modified clinoptilolite zeolite to remove pollutants and salt from agricultural drainage water in a model drainage system, International Journal of Environmental Research, 2021, 15, 859–873. DOI:10.1007/s41742-021-00359-5

15. Stepova, K.; Fediv, I.; MaŽeikienë, A.; Sarko, J.; Mazeika, J.: Adsorption of ammonium ions and phosphates on natural and modified clinoptilolite: isotherm and breakthrough curve measurements, Journal of Water, 2023, 15 (10), 1933, 1-14. DOI:10.3390/w15101933

16. Cerri, G.; Farina, M.; Brundu, A.; Daković, A.; Giunchedi, P.; Gavini, E.; Rassu, G.: Natural zeolites for pharmaceutical formulations: Preparation and evaluation of a clinoptilolite-based material, Journal of Microporos and Mesoporos Materials, 2016, 223, 58-67. DOI:10.1016/j.micromeso.2015.10.034

17. Kalbuadi, D.; Goenadi, D.; Santi, L.; Nurtjahja, L.: The potential use of natural clinoptilolite zeolite for crude oil spill removal from Sea Water, Journal of Minerals and Materials Characterization and Engineering, 2019, 7 (6): 446-453.
DOI:10.4236/jmmce.2019.76031

18. Soukeur, A.; Szymczyk, A.; Berbar, Y.; Amara, M.: Extraction of rare earth elements from waste products of phosphate industry, Journal of Separation and Purification Technology, 2021, 256, 117857.
DOI: 10.1016/j.seppur.2020.117857

19. Güngör, D.; Özen, S. Development and characterization of clinoptilolite, mordenite, and analcime based geopolymers: A comparative study, Journal of Case Study in Construction Materials, 2021, 15, e00576.
DOI:10.1016/j.cscm.2021.e00576

20. Kalebić, B.; Pavlović, J.; Dikić, J.; Rečnik, A.; Gyergyek, S.; Škoro, N.; Rajić, N.: Use of natural clinoptilolite in the preparation of an efficient adsorbent for ciprofloxacin removal from aqueous media, Journal of Minerals, 2021, 11 (5), 518, 1-22.
DOI: 10.3390/min11050518

21. Costafreda, J.; Martín, D.: New deposit of mordenite–clinoptilolite in the eastern region of Cuba: uses as pozzolans, Journal of Molecules, 2021, 26 (15), 4676, 2-15.
DOI:10.3390/molecules26154676

22. El-Didamony, H.; Gado. H.; Awwad, N.; Fawzy, M. M.; Attallah, M.: Treatment of phosphogypsum waste using suitable organic extractants, Journal of Hazardous Materials, 2013, 244, 596-602.
DOI: 10.1016/j.jhazmat.2012.10.053

23. El Shamy, H.; Khalil, M.; Atrees, M.; El Aoady, M.: Uranium adsorption from its solutions by the natural & treated clinoptilolite, Faculty of Science, Ain Shams University, 2022, 145p.

24. Mansouri, N.; Rikhtegar, N.; Panahi, H.; Atabi, F.; Shahraki, B.: Porosity, characterization and structural properties of natural zeolite Clinoptilolite as a sorbent, Journal of Environment Protection Engineering, 2013, 39 (1), 139.
DOI: 10.5277/EPE130111

25. Baile, P.; Fernández, E.; Vidal, L.; Canals, A.: Zeolites and zeolite-based materials in extraction and microextraction techniques, Journal of Analyst, 2019, 144 (2), 366-387.
DOI:10.1039/c8an01194j

26. Marczenko, Z. Spectrophotometric Determination of Elements, John Wiley and Sons, Inc., Ellis Horwood for publication, New York, 1976, 643p.

27. Mosai, A.; Chimuka L.; Cukrowska, E.; Kotzé, I.; Hlanganani T.: The recovery of rare earth elements from aqueous solutions using natural zeolite and bentonite, Journal of Water, Air & Soil Pollution, 2019, 230, Article No. (188), 1-17.
DOI: 10.1007/S11270-019-4236-4