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LEACHING OF RARE EARTH ELEMENTS FROM PHOSPHATE ROCK USING SULFURIC ACID: PROCESS OPTIMIZATION AND KINETIC STUDIES

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ABSTRACT

Rare earth elements (REEs) are crucial raw materials for 'smart' electronic devices and emerging renewable energy resources. Accordingly, the global attention for the secondary REEs resources such as phosphate rock is increased. Recognizing effective leaching of REEs from phosphate rock is essential from a strategic perspective for addressing the world demand highly growth rate. The present study investigates the leaching of REEs from phosphate rock using sulfuric acid. The impact of the main variables on the leaching performance was examined. Design of experiments (DoE) methodology was applied for optimization the REEs leaching process. The anticipated data declare that about 96.6% leaching percent could be achieved according to the following conditions: 1.5 M sulfuric acid concentration, 30 mL/g as liquid/ solid ratio, 55 °C reaction temperature and stirring time of 1.0 hr. shrinking core model (SCM) was applied to explore the kinetic attitude of REEs leaching process. The exhibited results deduced that leaching process is well depicted using the ash layer diffusion kinetic model. In addition, the activation of energy of REEs leaching process was found to be equal 9.01 kJ/mol.

INTRODUCTION

Rare earth elements (REEs) is a group of elements that identified by the European Union's (EU) experts as a one of the critical materials (Jonsson et al., 2023). The International Union of Pure and Applied Chemistry define the REEs as a group of 17 elements (15 lanthanides, scandium and yttrium (Jowitt et al., 2018). REEs are essential in many technological applications such as magnets, laser equipment, defense systems, and smart-phone cameras; therefore, they are much more prevalent in our day-to-day lives (Liu et al.,

2023). The global demand of REEs are highly increased in the last few years, whereas it increased from about 136,100 tons in 2010 to about 177,660 ton in 2023, with increasing rate roughly by about 3.5% year-on-year (Kumari and Sahu, 2023; Liu et al., 2023).

Powered by the world supply challenges, a great global attention is payed to the secondary REEs resources. Phosphate rock, which is the main source for phosphoric acid and phosphate fertilizers, is one of the main secondary resources for REEs. The average REEs content in phosphate rock is about 0.05% (Ait

Brahim et al., 2022; Wu et al., 2018). REEs take the place of calcium ions in the apatite lattice due to their similarity in the ionic size (Ait Brahim et al., 2022; Wu et al., 2018). Commercial phosphoric acid is mainly produced by wet production process, in which phosphate rock is treated with sulfuric acid to produce liquid phosphoric acid (as a main product) and solid phosphogypsum as a by-product (Liu et al., 2022). During the wet production process, REEs in the phosphate rock is distributed between the two phases, whereas about 20% exist in the liquid phosphoric acid, while about 80% transferred to the phosphogypsum (Battsengel et al., 2018; Lütke et al., 2022; Roshdy et al., 2023). Accordingly, the recovery of REEs from the phosphate rock will be more effective approach than the recovery of REEs from two phases (phosphoric acid and phosphogypsum).

So far, various works were performed for the leaching of REEs from phosphate rock. Of these are the performed leaching for REEs from Phalaborwa ore, South Africa using sulfuric acid, then apply bearing immobilized tridentate amido ligands for the adsorption of REEs from sulfate leachate adsorb (Ogata et al., 2016). Applied the phosphoric acid for the leaching of REEs from Zhijin phosphate rock, China (Li et al., 2021a). Conducted leaching of REEs from Esfordi apatite concentrate, Iran using phosphoric acid (Soltani et al., 2019). Reported that nitric is the most effective among HClO_4 , HCl , and H_3PO_4 for the leaching of REEs from fluorapatite (Stone et al., 2016). Introduced Fanshan phosphate material, China for the phosphoric acid for the leaching of REEs (Wu et al., 2019). Investigated the dissolution of REEs from Abu-Tartur phosphate rock, Egypt (Roshdy et al., 2023).

To the author knowledge, the application of sulfuric acid in the leaching of REEs from phosphate rock is scarce and mainly concerning with its comparison with other mineral acids in the leaching process

(Battsengel et al., 2018; Ogata et al., 2016). So far, the systematic investigation, kinetics and the optimization of the REEs leaching from phosphate rock with sulfuric acid solution are lacked.

In this contribution, the present work investigate the systematic studies for the main variables that affect the REEs leaching from Abu-Tartur phosphate rock, Egypt using sulfuric acid solution. Kinetics of the leaching process is performed to explore the mechanism of the leaching process. In addition, design of experiment methodology is applied for the process assessment, optimization, and establishing an empirical equation for the leaching process.

EXPERIMENTAL

Materials and Reagents

Analytical grade sulfuric (98%) and hydrochloric (37%) acids were supplied from Merck KGaA, Germany and utilized for the preparation of the leaching and stripping reagents respectively. Abu Tartur phosphate rock working sample was supplied from Misr Phosphate Company, Egypt. Mineralogical analysis of the supplied phosphate sample that performed using X-ray powder diffraction (XD1180 model, Schimadzu, Japan) obvious that the sample minerals are mainly Fluorapatite, together with minor existence of quartz, dolomite, and calcite (Fig. 1) (Roshdy et al., 2023). However, the main chemical components were 30.1% P_2O_5 , 44.4% CaO , 2.3% SiO_2 , 0.9% MgO , and 1810 $\text{mg L}^{-1}\Sigma\text{REEs}$ as declared from XRF analysis using X-ray Fluorescence spectroscopy (Axios, sequential WD-XRF spectrometer, PANalytical, UK) (Table 1), (Roshdy et al., 2023).

Leaching Procedures

The leaching experiments were conducted by stirring a certain weight of the phosphate sample (particle size of 150-63 μm) with a proper volume of the sulfate solution

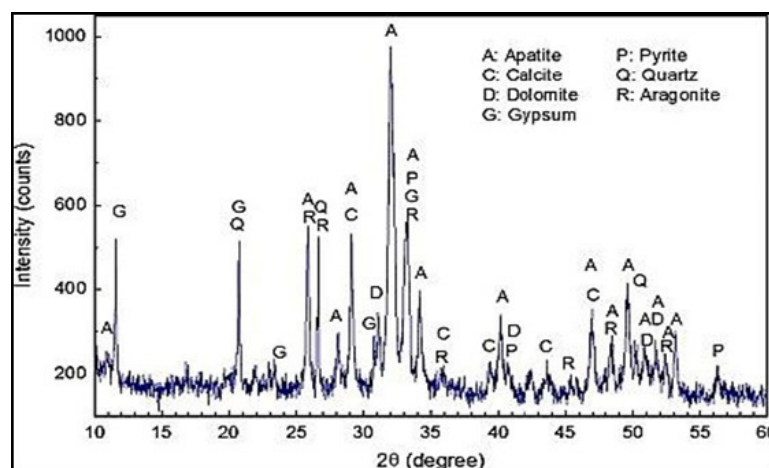


Fig. 1 : XRD pattern of Abu Tartur phosphate rock (Roshdy et al.,2023)

Table 1 : Chemical characterization of Abu Tartur phosphate rock (Roshdy et al., 2023)

Constituent, wt. %			
P₂O₅	30.1	SO₃	1.50
CaO	44.4	MgO	0.90
Fe₂O₃	3.8	Al₂O₃	0.46
F	2.8	Na₂O	0.28
SiO₂	2.3	L.O.I.*	5.1
Constituent, mg/kg			
∑ REEs			1810

using a glass reactor (500 mL) fitted with a mechanical stirrer (DLH model, VELP, Italy) and placed in a thermostatically water bath (TSSWB15 model, Thermo Scientific, USA) to maintain the required reaction temperature with an accuracy of ± 1 °C. a subsequent filtration process for the slurry was performed after the desired stirring time. Shimadzu

UV-Visible spectrophotometer (model UV-160A, Japan) was applied to measure \sum REEs concentration in the aqueous phase using Arsenazo III method (Marczenko and Balcerzak, 2000). The leaching trials were performed in duplicates and the average leaching efficiencies were reported. The analytical precision for the spectrophotometer in terms of the rel-

ative standard deviation of replicate analyses was less than 5%. The leaching efficiency was calculated using the following equation (1):

$$\text{Leaching, \%} = m_L / m_s \times 100 \quad (1)$$

where m_L and m_s are the constituent (i.e. \sum REEs) concentration (g) in the leaching liquor and the working sample respectively.

Design of Experiments, Model Equation and Process Optimization

The design of experiment (DoE) methodology is a combination of statistical and mathematical approaches for experiments designing, modelling, analyzing the effects of variables, and the interactions between these variables (Anderson and McLean, 2018; Zhang et al., 2023). The full factorial design (2^p) is a type of DoE, which is widely applied for process optimization with a minimum number of experiments (Anderson and McLean, 2018; Johnson, 2018; Zhang et al., 2023). According to this methodology, the selected parameters were investigated in three levels (-1, 0, +1). The experimental design was performed and analyzed using the design expert program v10.0 (State Ease, Inc., Minneapolis, MN) software, and was randomly performed for minimizing the systematic error. The first and quadratic polynomial statistical models were represented in equations 2 and 3 and applied to analysis the impact of variables interactions (Johnson, 2018; Nyangi et al., 2021; Zhang et al., 2023). The analysis of variance (ANOVA) was performed, and the determination coefficient (R^2) was applied to explore the significance of the models.

$$y = b_o + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n \sum_{i>j}^n b_{ij} x_i x_j \quad (2)$$

$$y = b_o + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^n \sum_{i>j}^n b_{ij} x_i x_j \quad (3)$$

where: y : Target value: REEs leaching efficiency [%]; x_i : Factors; N : Number of factors: 4; b_o : Ordinate section; b_i , b_{ij} , b_{ij} : Regression parameters of linear, squared, and cross effects.

Leaching Kinetics

The leaching of REEs from Abu-Tartur phosphate rock is a type of heterogeneous non-catalytic reactions, which take place at a solid/liquid boundary layer. Investigating the leaching kinetics is imperative to understand the reaction mechanism and explore the rate controlling step (Ait Brahim et al., 2022; Li et al., 2021a; Roshdy et al., 2023). So far, shrinking core model (SCM) is used to investigate the leaching kinetics (Aly et al., 2013; Nandagopal, 2023). The main concept of the applied models could be existing in the corresponding references. In the present work, set of experiments were performed at different reaction temperatures ($25-50 \pm 1$ °C) for stirring time interval of (0-120 min) to explore the kinetic behavior of REEs leaching from phosphate rock using sulfuric acid. A highly stirring speed was applied during the leaching experiments, so the impact of film diffusion control on the REEs leaching process could be neglected. Hence, equation 4 (for the surface chemical reaction), and equation 5 (for the ash layer diffusion control) could use to express the kinetics of the leaching process (Aly et al., 2013; Nandagopal, 2023).

$$kt = 1 - 3(1 - m_1)^{1/3} \quad (4)$$

$$kt = 1 - 3(1 - m_1)^{2/3} + 2(1 - m_1) \quad (5)$$

where k is the apparent reaction rate constant (min^{-1}), t is the time (min).

RESULTS AND DISCUSSION

Leaching Investigation

Impact of reaction time and temperature

The dependence of REEs leaching from phosphate rock using sulfuric acid on reaction time was investigated by conducting a set of trials at reaction time interval of 15-480 min. The experimental conditions were kept at rock particle size of 150 μm , sulfuric acid concentration of 0.8 M, liquid/ solid ratio of 2.5/ 1, stirring speed 100 rpm, and reaction temperature interval of $25 - 50 \pm 1$ °C. The displayed data on Fig. (2) exhibits a rapidly increment

in the reaction initial stage up to 120 min (equilibrium stage) for all investigated reaction temperature. This performance could be attributed to the availability of free hydrogen ions which dissolve the REEs from the phosphate rock as displayed in equation 6 (Battsengel et al., 2018; Lütke et al., 2022; Roshdy et al., 2023). In addition, the rock small particles support the fast penetration of the sulfuric acid to the particles (Lütke et al., 2022). Prolong the equilibrium time is depicted by a sluggish leaching process which presumably due to the expending most of hydrogen ions in the reaction (Lütke et al., 2022; Walawalkar et al.,

2016), besides the formation of phosphogypsum particles which trap the dissolved REEs ions (Battsengel et al., 2018; Lütke et al., 2022; Ogata et al., 2016). The same behavior mentioned for and the phosphate and REEs leaching of from phosphate ore from China (Anderson and McLean, 2018; Johnson, 2018; Nyangi et al., 2021; Zhang et al., 2023), and the P and REEs leaching from an iron-rich fluorapatite concentrate (Soltani et al., 2019). Further experiments were performed using 120 min reaction temperature.

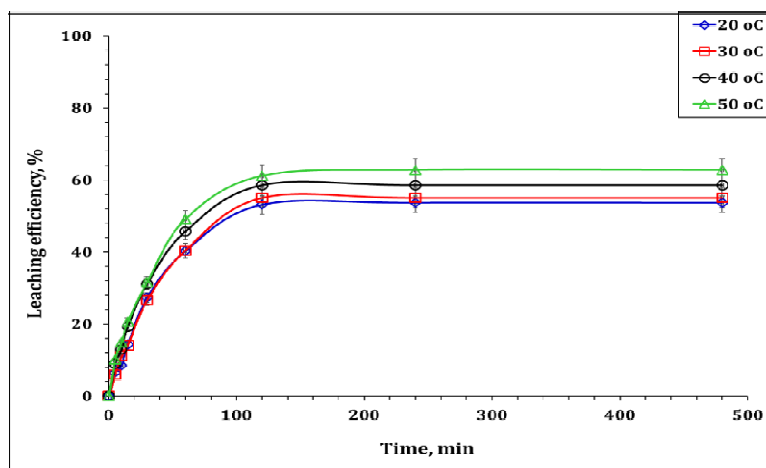
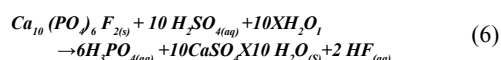


Fig. 2: Effect of reaction time on REEs leaching efficiency (liquid/ solid ratio of 2.5 mL/g; particle size: 150 μm ; 100 rpm; 0.8 M sulfuric acid concentration; 25°C)

Impact of sulfuric acid concentration

Figure 3 deduces the variation of REEs leaching efficiency as a function of sulfuric acid concentration. The leaching conditions were fixed at phosphate rock particle size of 150 μm , reaction time of 120 min; liquid / solid ratio of 2.5 mL/g, stirring speed of 100 rpm; and reaction temperature of 25 °C, while sulfuric acid concentration was in the range

0.4-3.5M. The inquired results illuminated the positive impact of sulfuric acid concentration up to 1.0M on the REEs leaching efficiency, which deem to be due to the increase in the H^+ ions concentration in the solution with the sulfuric acid boosting (Li et al., 2021b; Wu et al., 2019). Prolong acid concentration, is depicted with a dramatically decrease in the leaching efficiency. This performance could

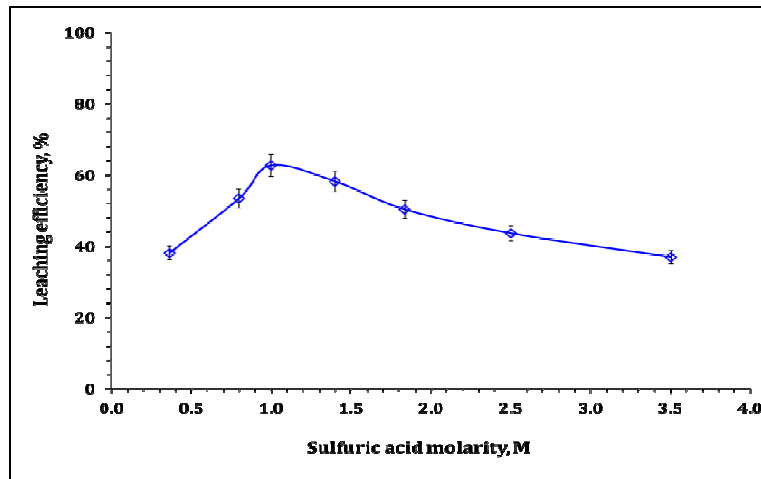


Fig. 3: Effect of sulfuric acid concentration on REEs leaching efficiency (particle size: 150 μm ; liquid/ solid ratio of 2.5 mL/ g; 100 rpm; 120 min; 25°C)

be attributed to the precipitation of REEs as phosphate and fluoride salts (Gupta and Krishnamurthy, 1992; Khawassek et al., 2015). Sulfuric acid concentration of 1.0 M was chosen for further experiments.

Impact of liquid/solid ratio

A set of experiments were carried out to explore the impact of liquid/ solid ratio (bulk density) on the REEs leaching efficiency. The experimental parameters were maintained at reaction time of 120 min, stirring speed of 100 rpm, rock particle size of 150 μm , reaction temperature of 20 °C, and sulfuric acid concentration of 1.0M, while liquid to solid ratio varied from 2.5 to 25 mL/g. As expected, REEs leaching percent boost, as the liquid/ solid ration increase up to 10mL/g (Fig. 4). This performance deem to be owned to the decrease in the bulk density which in turn improves the mobility of the ions in the liquid phase (Soltani et al., 2019; Wu et al., 2019). The same performance were mentioned for the leaching of P and REEs from phosphate using phosphoric acid (Li et al., 2021b; Wu et

al., 2019). Rees leaching efficiency is slightly changed for the liquid/ solid ration extend to 20 mL/ g. The preferred liquid/ solid ratio of 10 g/ L is selected for the further experiments.

Design of experiments, model equation and optimum

The optimization of REEs leaching process was achieved in two steps; (1) performing a factorial experimental design for the most appropriate variables, and (2) statistical optimization for the anticipated data. The following parameters; stirring time, reaction temperature, sulfuric acid concentration, and liquid/solid ratio were considered as the main effective parameters in phosphate rock leaching efficiency. Hence, a factorial experimental design 2^4 with twenty experiments (16 experiments and 4 repetitions at the central point) was carried out. The factorial experiments were carried out at constant phosphate rock particle size (150 μm) and stirring speed (100 rpm) while the investigated levels for other variables were displayed in Table 2. The impact of the main variables and their interaction

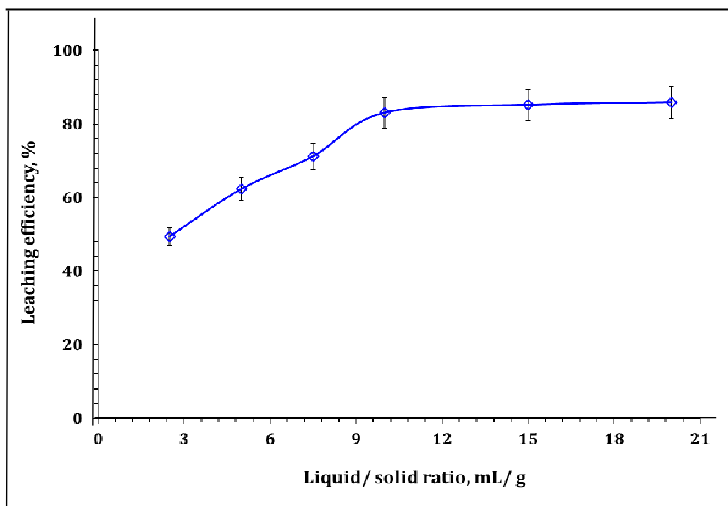


Fig. 4: Effect of liquid/ solid ratio on REEs leaching efficiency (particle size: 150 μm ; sulfuric acid concentration of 1.0 M; 100 rpm; 120 min; 25°C

on the leaching efficiency was displayed in Table 3. The anticipated data declares that the highest REEs leaching efficiency was 96.6% (experiment 15) according to the following conditions: 1.5 M sulfuric acid concentration, 30 mL/ g as liquid/ solid ratio, 55 °C reaction temperature and stirring time of 1.0 hr.

The Pareto chart (Fig. 5) was used to display the impact of the significant variables and interactions on the REEs leaching efficiency. From the Figure, it is obvious that the most positive significant effect is the liquid/ solid ration (D), followed by BC (i.e. the interaction between temperature and acid molarity), and finally BD (i.e. the interaction between temperature and L/ solid ration). On contrary, the leaching efficiency is high negatively influenced with the ABCD (i.e. the interaction between stirring time, temperature, acid molarity, and L/ S ratio), followed by ABC (i.e. the interaction between stirring time, temperature, and acid molarity), then ACD (i.e. the interaction between stirring time, acid molarity, and L/ S ratio), and the interaction between stirring

time and L/ S ration (AD). It is worth noted that the variables of stirring time, acid molarity and temperature have negative impact on the leaching percent. The importance of DoE methodology could be recognized from declaring the Pareto chart, which explore the impact of the main variables as well as the interaction between these variables on the leaching efficiency of REEs.

The impact of the main variables (i.e. stirring time, reaction temperature, sulfuric acid concentration, and liquid/ solid ration) on the REEs leaching percent is displayed on Fig. (5) and compered with the results displayed on Fig.(3) from the O-F-A-T methodology (section 3.1.). The displayed results from O-F-A-T methodology declares that stirring time has positive impact on the REEs leaching percent which is an opposite to the results from the DoE methodology. This performance could be explained to that as the reaction time increases, the crystallization of calcium sulfate (phosphogypsum) improves (Eq. 1) which trap REEs ions in its surface and in

Table 2 : Factors levels of the 2⁴ full factorial design

Factors	Coded variables	Low level (-1)	Middle level (0)	High level (+1)
Stirring time, hrs.	A	1.0	2.0	3.0
Temperature, °C	B	25	40	55
Sulfuric acid molarity, M	C	0.5	1.0	1.5
Liquid/solid ratio, mL/g	D	10	20	30

Table 3 : Design matrix of the 2⁴ full factorial design. The experiments shaded in grey correspond to the replicated center point

Std.	A: Time, hrs.	B: Temp., °C	C: Molarity, M	D: L/S Ratio, mL/ g	Efficiency, %
1	1.0	25	0.5	10	60.1
2	3.0	25	0.5	10	58.2
3	1.0	55	0.5	10	57.8
4	3.0	55	0.5	10	40.6
5	1.0	25	1.5	10	38.9
6	3.0	25	1.5	10	70.3
7	1.0	55	1.5	10	64.2
8	3.0	55	1.5	10	76.8
9	1.0	25	0.5	30	44.1
10	3.0	25	0.5	30	75.7
11	1.0	55	0.5	30	46.0
12	3.0	55	0.5	30	78.3
13	1.0	25	1.5	30	39.7
14	3.0	25	1.5	30	56.0
15	1.0	55	1.5	30	96.6
16	3.0	55	1.5	30	81.4
17	2.0	40	1	20	69.8
18	2.0	40	1	20	72.0
19	2.0	40	1	20	68.4
20	2.0	40	1	20	70.3

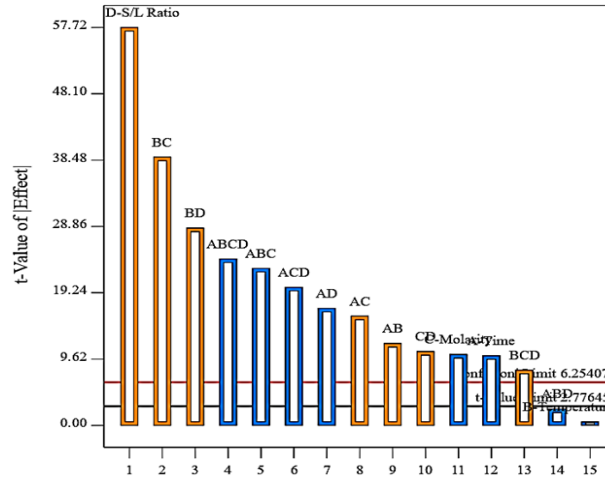


Fig. 5: Pareto Diagram for REEs leaching process

turn decreases the leaching efficiency of REEs (Lütke et al., 2022; Ogata et al., 2016), which reflects the fast kinetic of the REEs leaching reaction. The same observation could be recognized for the impact of sulfuric acid concentration, whereas the O-F-A-T methodology obvious the positive impact of this variable on the REEs leaching percent while the DoE methodology data exhibits the negative impact of this variable on the leaching percent. This attitude seems to be due to the increase of sulfuric acid concentration improves the dissolution of P_2O_5 and other constituent in the phosphate rock such as fluoride which in turn increase the formation of insoluble salts of REEs phosphate and fluoride salts (Gupta and Krishnamurthy, 1992; Khawassek et al., 2015; Soltani et al., 2019). The DoE methodology results demonstrated that the increase in reaction temperature decreases the REEs dissolution percent, which could be owned to the precipitation of REEs phosphate salts as shown in Equation 7 (Cetiner et al., 2005; Roshdy et al., 2023), which is in convers to the observed results from Fig. (2). The negative impact of reaction temperature increment on

REEs solubility in phosphoric acid owned to the precipitation of REE phosphates salts also reported by Liang et al. (Li et al., 2021b), and Wu et al. (Wu et al., 2018).



The positive effect of the liquid/ solid ration on the REEs leaching efficiency could be exhibited from Fig.(5). This performance could be due to the increase in the ions in the liquid phase as the decrease in the solution bulk density (Soltani et al., 2019; Wu et al., 2019).

The most significant parameters and interactions that affecting the leaching of REEs from phosphate rock could be recognized from the analysis of variance (ANOVA). The F-value and p-value were used to determine the influence of each variables and interactions. The anticipated data in Table 4 declares that all variables and interactions are significant of the leaching efficiency (p-value is <0.05) except temperature (B), and the interaction of time, temperature, and molarity (ABC) are not significant. Concerning the software instruc-

Table 4 : Analysis of variance for REEs leaching

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	9417	15	627.8	549.5	0.0001
A-Time	116.64	1	116.64	102.09	0.0021
C-Molarity	121	1	121	105.91	0.002
D-S/L Ratio	3806.89	1	3806.89	3332.07	< 0.0001
AB	161.29	1	161.29	141.17	0.0013
AC	287.3	1	287.3	251.47	0.0005
AD	329.42	1	329.42	288.33	0.0004
BC	1730.56	1	1730.56	1514.71	< 0.0001
BD	936.36	1	936.36	819.57	< 0.0001
CD	131.1	1	131.1	114.75	0.0017
ABC	592.92	1	592.92	518.97	0.0002
ACD	457.96	1	457.96	400.84	0.0003
BCD	73.1	1	73.1	63.98	0.0041
ABCD	665.64	1	665.64	582.62	0.0002
Pure Error	3.43	3	1.14		
Cor Total	10308.87	19			

tions, the linear polynomial model was used to express the REEs leaching using sulfuric acid. Equation 8 exhibits the model of the leaching process after eliminating the insignificant terms.

$$\text{Leaching percent} = +61.54 + 5.62 A + 3.94 C + 3.18 D - 4.06 AB + 0.0188 AC + 2.51 AD + 8.09 BC + 4.68 BD - 0.2437 CD - 2.23 ABC - 7.87 ACD + 1.63 BCD - 1.79 ABCD \dots \dots \dots (8)$$

The predictability of the elaborated model was inquired by performing three experiments within the same experimental conditions (i.e. 1.5 M sulfuric acid concentration, 30 mL/ g as liquid/ solid ratio, 55 °C reaction temperature and stirring time of 1.0 hr.). The displayed data in Table 5 declares that the relative error mean value for the three experiments are <4%, which reflects the predictability of the model.

Leaching Kinetics

The kinetic performance of REEs leaching

process is profoundly dissected by mathematically treated the experimental results using surface chemical reaction (Eq. 4), and ash layer diffusion (Eq. 5) of shrinking core model. The kinetic curves of REEs leaching process were displayed on Figs. (6 & 7) for equations 4 and 5 respectively. The appropriateness of the applied equations was explored from the coordination coefficient (R^2), and the kinetic terms of REEs leaching process was evaluated and displayed in Table 6. The anticipated results declare that, within the investigated temperature interval (25-50 ±1 °C), equation 5 possess the highest R^2 values (0.99) for the leaching process which reflects that the ash layer diffusion is the rate controlling step for REEs and P_2O_5 leaching from phosphate rock using sulfuric acid. It is worth noted that, the leaching rate constants for REEs increase as the reaction temperature increases, which elaborate an endothermic nature for the leaching process.

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Table 5 : Experiment in triplicate to validate REE models

No.	Reaction parameters				REEs yield (%)
	Sulfuric acid concentration (M)	Ratio (mL/ g)	Temperature (°C)	Reaction time (min)	
1	1.0	30	55	120	96.1
2	1.0	30	55	120	95.2
3	1.0	30	55	120	95.9

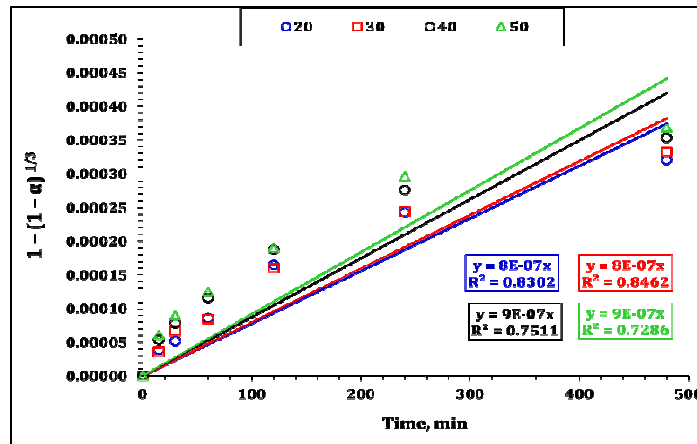


Fig. 6: Effect of temperature on the function $[1 - (1 - \alpha)^{1/3}]$

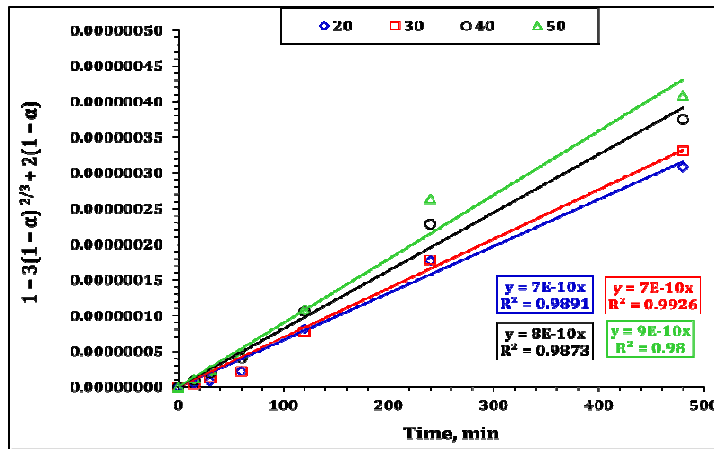


Fig. 7: Effect of temperature on the function $[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)]$

Table 6: The rate constant, K , min^{-1} for REEs at different temperature ranges

Temperature, °C	Rate constant, K , min^{-1}
25	2.71 E-09
30	2.88 E-09
40	3.27 E-09
50	3.58 E-09

Arrhenius equation (Eq 9) was applied to evaluate the leaching activation energy (E_a , J/mol), and figure out the nature of the leaching process (Gupta and Krishnamurthy, 1992; Khawassek et al., 2015; Soltani et al., 2019):

$$k = A \cdot \exp^{-E_a/RT} \dots (9)$$

where k and A are the overall rate constant and the frequency factor respectively (min^{-1}), R (8.314 J/K·mol) is the universal gas constant, and T (K) is the reaction temperature.

Figure 8, which represent the variation of $\ln K$ versus $1000/T$ (Arrhenius plot), was used to evaluate the activation energy for REEs leaching process. The results confirmed that the leaching of REEs from phosphoric acid

is endothermic process whereas the activation energy was found to be equal 9.01 kJ/mol. In addition, $E_a < 40$ kJ/mol which confirming that the leaching process is controlled by ash layer diffusion (Aly et al., 2013; Nandagopal, 2023). The same kinetic performance (ash layer diffusion) was reported for the dissolution of Abu-Tartur phosphate rock using hydrochloric (Aly et al., 2013) and phosphoric (Roshdy et al., 2023) acids, and Guizhou Zhijin phosphate rock using phosphoric acid (Li et al., 2021a).

CONCLUSION

The present work focusing on the efficient

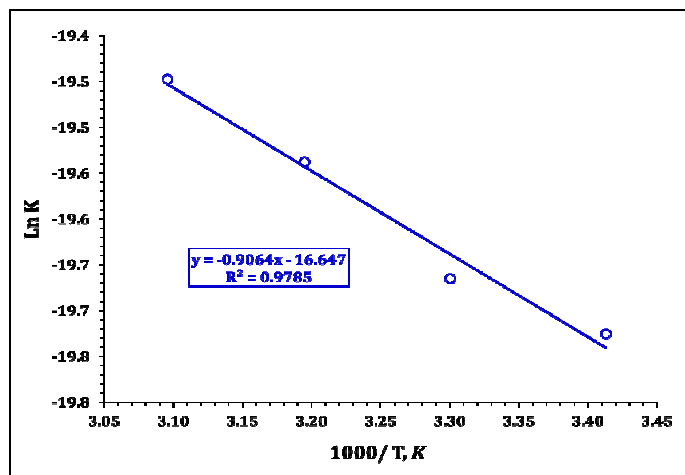


Fig. 8: Arrhenius plot for REEs leaching process

leaching of REEs from phosphate rock using sulfuric acid for addressing the global REEs demand. The influence of leaching time, sulfuric acid concentration, liquid/ solid ratio, and reaction temperature on the REEs leaching percent was conducted. The full factorial design (2^4) was performed for process screening and optimization. The deduced results obvious that 1.5 M sulfuric acid concentration, 30 mL/ g as liquid/ solid ratio, 55 °C reaction temperature and stirring time of 1.0 hr, could be used for achieving REEs leaching percent of about 96.6%. Kinetic analysis of the experimental data using shrinking core model displayed that the ash layer diffusion kinetic mechanism is controlling the leaching process. In addition, the endothermic nature of the leaching process could be recognized from the attained activation energy (9.01 kJ/ mol).

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دراسة اذابة حامض الكبريتيك للعناصر الارضية من صخور فوسفات ابوظطور باستخدام تصميم التجارب لتحسين معاملات الاذابة

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العناصر الأرضية النادرة (REEs) هي مواد خام هامة جدا في مجال تصنيع الأجهزة الإلكترونية «الذكية» ومصادر الطاقة المتجددة الناشئة. وبناء على ذلك، يزداد الاهتمام العالمي بمصادر العناصر الأرضية النادرة الثانوية مثل صخور الفوسفات. ويعتبر استخلاص العناصر الأرضية من صخور الفوسفات امرا فعالا و ضرورياً من المنظور الاستراتيجي لزيادة معدل النمو المرتفع للطلب العالمي. تتم الدراسة الحالية على عمل دراسة استخلاص العناصر الارضية النادرة من صخور الفوسفات باستخدام حامض الكبريتيك لذلك تم دراسة تأثير العوامل الرئيسية على عملية الاستخلاص من بين هذه العوامل تم تطبيق منهجية تصميم التجارب Design of experiments (DoE) لتحسين عملية استخلاص العناصر الأرضية النادرة و اشارت البيانات المتوقعة إلى أنه يمكن تحقيق حوالي ٩٦,٦٪ من نسبة الاستخلاص وفقاً للشروط التالية: تركيز حمض الكبريتيك ١,٥ مولار، ٣٠ مل/جم كنسبة سائل/صلب، درجة حرارة التفاعل ٥٥ درجة مئوية وزمن التقليل ١,٥ ساعة تم تطبيق نموذج تقلص النواة (SCM) shrinking core model لتعيين الموقف الحركي لعملية استخلاص العناصر الأرضية النادرة. وقد اوضحت النتائج المعروضة أن عملية الترشيح تم تصويرها بشكل جيد باستخدام النموذج الحركي لانتشار طبقة الرماد. بالإضافة إلى ذلك، وجد أن طاقة التنشيط لعملية ترشيح العناصر الأرضية النادرة يساوي ٩,٠١ كيلوجول/مول.