



# Maximizing the exploitation of phosphogypsum wastes using soaking technique with citric acid, recovering rare-earth and residual phosphate contents

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**Abstract:** Phosphogypsum (PG), the main by-product of phosphoric acid production industries, is considered one of the most important secondary sources of rare earth elements (REEs). The current study focuses on the recovery of REEs content and the residual phosphate content existing in the PG with preserving on the  $\text{CaSO}_4$  skeleton to be used in other various applications. These attainments are carried out using citric acid leaching process via soaking technique. Several dissolution parameters for REEs using citric acid were studied, including soaking time, soaking temperature, citric acid concentration, solid-to-liquid ratio, and recycling of the citrate leaching solutions in the further REEs dissolution experiments. The best-operating conditions were 14 d of soaking time, 7.5% citric acid concentration, and the solid-to-liquid ratio of 1/5 at ambient temperature. About 79.57% dissolution efficiency of REEs was achieved using the optimal conditions. Applying four soaking stages by mixing different fresh PG samples with the same citrate solution sequentially, cumulative dissolution efficiency for REEs was found to be 64.7% under optimal soaking conditions. REEs were recovered using Dowex 50X8 resin from citrate solutions with 96% extraction efficiency. Dissolution kinetics proved the pseudo-first-order nature, reversible reactions, and two activation energies for all REEs.

**Key words:** phosphogypsum; rare earths; citric acid; dissolution; soaking; Dowex 50X8; pre-concentration

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## 1 Introduction

Rare earth elements (REEs) and their derivatives are among the most important materials in modern technology [1–4]. In recent years, new efforts have been started to mitigate the supply risk for REEs through technospheric mining of secondary REE-containing resources [5–6]. Recycling of REEs from end-of-life items and recovery from stocks of landfilled industrial process residues are two examples of technospheric mining

[7–9]. Process residues, unlike end-of-life products, contain relatively low quantities of REEs but have a large volume. Therefore, the total amounts of REEs locked in them are very large and they can become a significant source for these elements. Phosphogypsum (PG), a result of phosphoric acid manufacture via sulphuric acid digestion of phosphate rock, is one of the most important REE-containing wastes, which contains trace amounts of many other elements including REEs [10]. Currently, for every tonne of phosphoric acid

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produced, approximately 2.3 tonnes of PG are created [11–12]. Global estimated world production of PG is 100–280 million tonnes annually [13] that are stored in the form of stacks [14]. The concentration of REEs in PG is 0.04%–1.57% (w/w) depending on the type and source of the rock [15–16]. This means that PG can potentially be used as a secondary source for REEs. Hence, fundamental and practical investigation of an efficient leaching process to recover REEs from PG is of high interest [17].

A few studies have been undertaken globally to look into the recovery of REEs from PG. JAROSÍŃKI et al [18] developed a recovery process for REEs by leaching with dilute sulfuric acid followed by solvent extraction with nonyl-phenyl phosphoric acid in kerosene. PRESTON et al [19–20] developed a process to recover REEs from South African phosphate rock, using nitric acid instead of sulfuric acid and adding calcium nitrate and ammonium nitrate. LOKSHIN et al [21] studied the use of sulfuric acid (3 mol/L) with a solid-to-liquid (S/L) ratio of 1/4 with a residence time of 3 h. The recovery efficiency of REEs was about 30%–45%. They also investigated the use of sulfuric acid (3.6 mol/L) and sodium salt (0.4–1.2 g/L) to recover REEs [22]. A mixture of sulfuric and nitric acids with 3.2 to 1.2 ratios was found to provide 70% to 80% recovery efficiency for REEs [23]. Using HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, AL-THYABAT et al [24] extracted REEs from phosphoric acid sludge and PG, with leaching efficiencies of 58% and 49%, respectively. WALAWALKAR et al [17] investigated microwave treating processes for PG under optimal operating conditions of 80 °C, 1.5 mol/L hydrochloric acid concentration, S/L of 1/8 and 20 min. In addition to aqueous leaching methods, a few studies that used organic solvents (such as tri-butyl phosphate (TBP) and tri octyl phosphine oxide (TOPO) in kerosene) as leaching agents were performed to extract REEs content directly from PG [25–26]. Industrially, these trials were too complex and expensive when tested on a pilot scale.

The use of strong mineral acids such as HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> may negatively affect the environment. Because of their simpler handling, lower acidities, and considerably easier

degradability, organic acids or significantly more diluted mineral acids [27] may have an advantage in this regard [28]. Citric acid is an organic acid that comprises three carboxylic groups, with  $pK_{a1}=3.13$ ,  $pK_{a2}=4.76$  and  $pK_{a3}=6.40$  hydrogen dissociation constants at 25 °C [29]. Metal ion displacement with hydronium ions and the formation of soluble metal-ligand complexes by metal chelation are two proposed mechanisms for citric acid dissolution [30]. On the other hand, the strong mineral acids would destroy the chemical structure of the PG by highly dissolving calcium content which is considered the main component of PG, which will affect the reusing of the treated PG in many several civilized fields [31–36].

The main objective of this work was to investigate the hydrometallurgical dissolution of REEs from PG using the soaking technique with citric acid. Firstly, identification was carried out on the chemical composition, morphology, REEs distribution and crystal structure, of the PG sample using various microscopy and spectroscopy techniques, including aqua-regia digestion, followed by ICP-OES, SEM-EDAX, XRD, and XRF analysis. Secondly, batch experiments were performed using citric acid to determine the optimal operating conditions, namely; the soaking time, soaking temperature, citric acid concentration, solid-to-liquid ratio, and recycling of the citrate solutions in the further REEs dissolution experiments. Thermodynamics and kinetics of the REEs dissolution processes were studied. Finally, recovery of the phosphate content existing in PG sample was also investigated.

## 2 Experimental

### 2.1 Materials and characterization

All used reagents and acids were in analytical grade. Double distilled water (DDW) was used throughout this work. Phosphogypsum samples were collected from the phosphoric acid purification pilot plant, Anshas site, Nuclear Materials Authority, Egypt. The wetted samples as shown in Figure 1 were firstly dried overnight in an oven at 313 K. The dried PG was subjected to complete instrumental analysis using energy dispersive X-ray analysis spectroscopy (SEM-EDAX), and XRD.



**Figure 1** Wetted PG obtained from Anshas site

REEs concentration in the PG under study was determined by complete dissolution of a representative PG sample. This was carried out using reflux digestion with aqua regia at 493 K. 0.5 g of dried PG sample was mixed with a strong acid mixture (3:1 of HCl:HNO<sub>3</sub>). The sample was digested for 3 to 4 h. Then dilute HNO<sub>3</sub> acid was used to prepare the digested sample. The filtrate was cooled and characterized by inductively coupled plasma optical emission spectrometer (ICP-OES) with RF current 1200 W and nebulizer gas pressure 36 L/min. Calcium content was determined using complexometric titration against EDTA [37] and phosphorous content was determined spectrophotometrically at 420 nm using ammonium molybdate and ammonium vanadate additives [38].

## 2.2 Soaking experiments

The dried PG was subjected to dissolution study using citric acid. Several dissolution parameters were studied to determine the optimal

conditions at which the maximum dissolution efficiencies for REEs were achieved. Soaking time, soaking temperature, citric acid concentration (CA conc.), solid-to-liquid ratio S/L, and recycling of the citrate solutions in the further REEs dissolution experiments were summarized in Table 1. At each experiment, 10 g from the dried PG was mixed with a definite concentration citrate solution and specific S/L ratio under ambient temperature. The slurry was agitated for one hour using a hot plate magnetic stirrer and then left for different periods. During the soaking time, every day, the mixture was agitated for 15 min and allowed to rest. After regular soaking intervals, the slurry was agitated for the last hour at higher temperature, settled, and subjected to analysis for its REEs content.

At the end of the experiment, the clear filtrate was completely dried then dissolved in diluted with 20% nitric acid and stored in sealed plastic test tubes at room temperature. These samples were analyzed using ICP-OES to determine the concentration of REEs in the leached solution. Calcium and phosphorous content were determined as previously mentioned. Reproducibility tests showed that the experimentally measured data were accurate to within  $\pm 5\%$ .

## 2.3 Rare earths recovery experiments

Rare earths were firstly separated from the citrate leach liquors using Dowex 50X8 strong cation exchange resin. The citrate feed solution pH was firstly adjusted using 50% sodium hydroxide solutions. The aqueous feed solution and the activated resin were agitated together and then the loaded resin was scrubbed before the elution process.

Hydrochloric acid as an eluate was the

**Table 1** Studied REEs soaking experiments from PG

Soaking parameter	Variable condition	Fixed condition
Soaking time/d	1, 7, 14 and 21	5, 10% CA, 1/5 S/L, 293 K soaking temperature, 313 K last hour temperature
Citric acid concentration/%	5.0, 7.5, 10.0, 15.0 and 20.0	14 d, 1/5 S/L, 293 K soaking temperature, 313 K last hour temperature
Solid/liquid ratio	1/2.5, 1/5, 1/7.5, 1/10 and 1/12.5	14 d, 7.5% CA, 293 K soaking temperature, 313 K last hour temperature
Last hour temperature/K	293, 313, 333 and 353	14 d, 7.5% CA, 1/5 S/L, 293 K soaking temperature
Recycling of dissolution experiments	1st, 2nd, 3rd and 4th	14 d, 7.5% CA, 1/5 S/L, 293 K soaking temperature, 313 and 353 K last hour temperature

confidant choice at which the elution process for rare earths would carry out from the loaded resin [6]. The rare earths content was precipitated from the eluate solution using oxalic acid addition. The rare earth's oxalate precipitate was decanted, washed, ignited, and analyzed using EDAX to identify the purity of the rare earths produced cake.

The phosphorous content existing in PG has been recovered from the citrate raffinate solutions after the recovery of REEs. These considerable contents were attributed to a mixture from remaining phosphoric acid and un-leached part from phosphate rocks. The phosphate content was precipitated as sodium salts and analyzed using XRD and EDAX to determine their constituents.

### 3 Results and discussion

#### 3.1 PG characterization results

The XRD analysis of the PG sample revealed three main solid phases: gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), and hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ). No REEs solid phase was detected by XRD, given their low concentrations. The XRD pattern is presented in Figure 2.

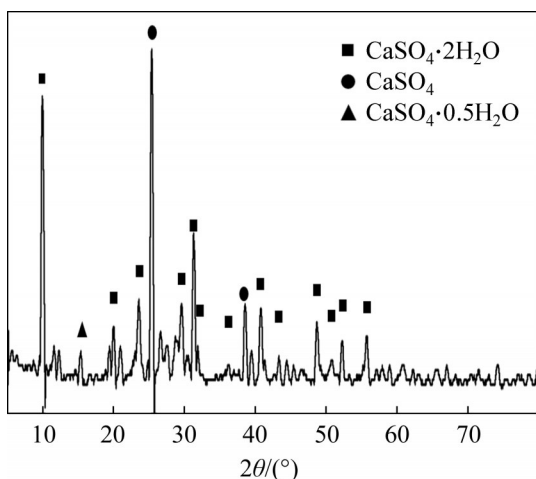


Figure 2 XRD pattern for dried PG

The SEM analysis was performed to observe the overall morphology of the PG sample. The cross-section of the powder particles was also analyzed to gain additional information on the distribution of REEs inside the PG particles. As expected, the EDAX analysis of the cross-section images identified Ca, S, P, and O as the main elements

within the particles. In addition, regions of REEs (La and Ce) were identified within the particles as

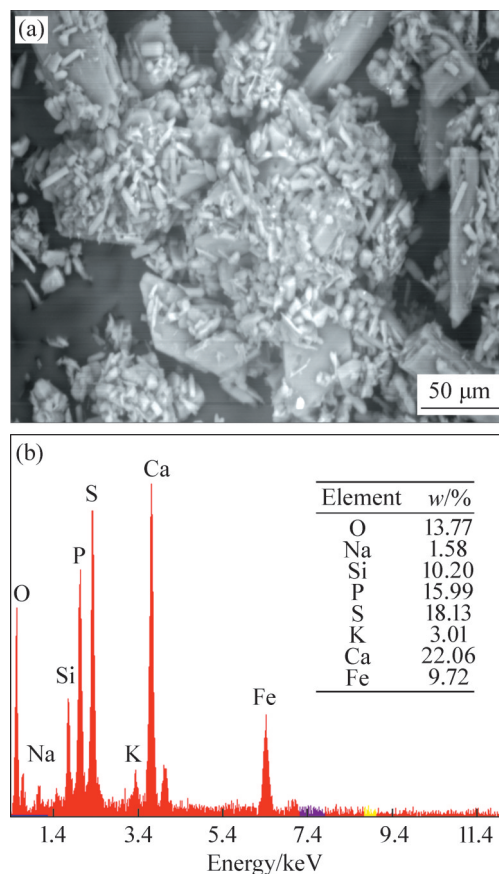


Figure 3 SEM image (a) and EDAX spectrum (b) of dried PG

shown in Figure 3.

Elemental analysis for the dried PG to determine the major and minor oxides constituents was carried out using XRF instrumental technique as shown in Table 2. The XRF results matched with the EDAX-chart and it was also noticed that the major constituents were P, S, Ca, Fe and Si respectively. Y and Ce were also detected as minor constituents in the XRF analysis. After aqua regia digestion, the composition of the as-received PG sample in terms of REEs was evaluated by ICP-OES. For this purpose, three PG samples were taken from three different batches, and from each batch,

Table 2 XRF-analysis for the dried PG wt%

Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>
3.03	0.36	1.32	6.72	31.40	29.62	0.91	15.06	0.08
V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	Rb <sub>2</sub> O	SrO	Y <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	F
0.02	0.02	0.07	9.22	0.03	0.20	0.01	0.05	1.90

three samples were characterized. Table 3 presents the average concentration of REEs in the PG sample. The total content of REEs in the digested solution was 214.2 mg/L. As can be seen, La, Ce, Nd, Gd, Er, Yb, and Y have higher concentrations than the other REEs; hence, we focused on these seven elements because of their higher concentration.

**Table 3** ICP analysis for the REEs content in the dried PG mg/L

La	Ce	Nd	Gd	Dy	Er	Yb	Lu	Y
35.35	31.13	62.50	4.15	0.38	7.09	2.94	0.98	68.00

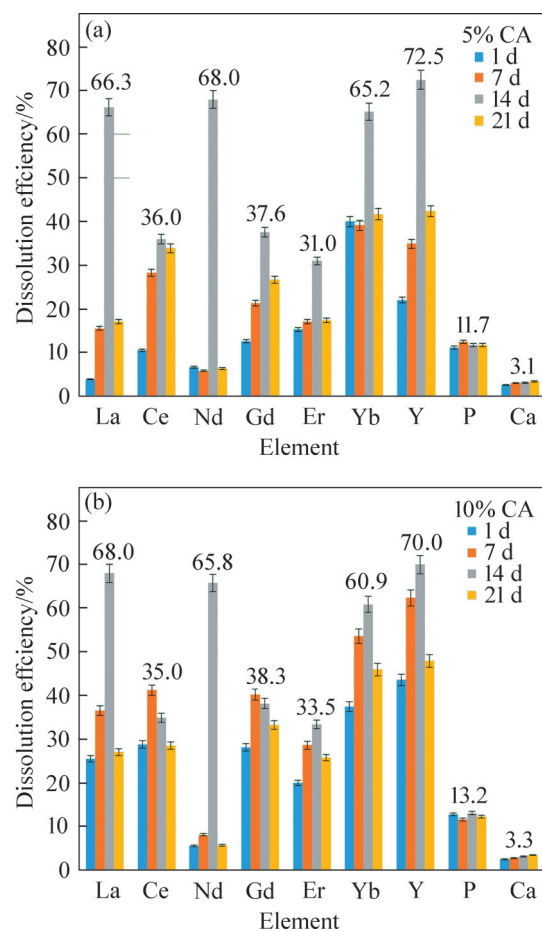
### 3.2 Soaking parameters results

#### 3.2.1 Soaking time

The use of citric acid was a unique choice according to the low dissolution efficiency for the calcium content presented in the PG compared with the use of the other mineral acids. The dissolution of high content of calcium could be affected on the reusing of treated PG in many several civilized fields as agriculture, road paving, and building [39–40]. Determining the equilibrium time of the dissolution reaction, in which the forward and reverse reactions of a system proceed at equal rates, was performed through studying a wide range of soaking times ranging from 1 d to 21 d. These experiments were carried out under fixed conditions, namely 5% and 10% CA concentration, 1/5 S/L ratio, 293 K soaking temperature, and 313 K for the last agitation hour.

From the results presented in Figure 4, it was noticed that the dissolution efficiencies of REEs were increased sharply by prolonging the soaking time from 1 d to 14 d. By prolonging the time over 14 d, a sharp reduction in the REEs dissolution was noticed. So, 14 d was the optimal soaking time at which the maximum dissolution efficiencies were performed. The soaking time was studied using 5% and 10% different CA concentrations. Using the two concentrations, the optimal soaking times were 14 d but the 5% was favored according to the enhancement in the dissolution efficiencies of REEs than the other concentration.

As a result of the presence of citric acid dissolved in a complicated aqueous medium with phosphogypsum, which contained a mixture of



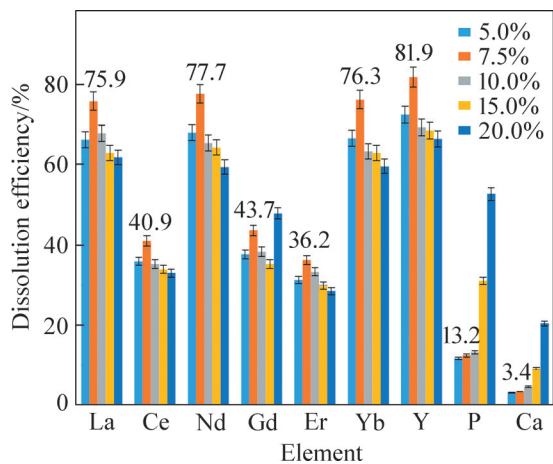
**Figure 4** Effect of soaking time on the dissolution of REEs: (a) 5% citric acid; (b) 10% citric acid

phosphoric acid residues, high content of organic compounds, and other contaminations. This aqueous mixture allowed the bacterial activity in the mixture to increase, which caused the breaking down of the existing organic acids. Over time, citric acid begins to partially decompose into carbon dioxide and water, and accordingly, there was a constriction in acid concentration as a result of continuous decomposition with time. On the other side, this sharp drop in the dissolution efficiency was attributed to the possibility of re-adsorption of these REEs through the PG surface, which was considered a good sorbent material for rare earth elements [41].

#### 3.2.2 Citric acid concentration

Generally, the acid concentration played an important role in the dissolution process. In our study, a range of citric acid concentrations from 5% to 20% was tested to determine the optimal CA at which the maximum dissolution efficiency of REEs

occurred. These experiments were conducted under conditions of 14 d soaking time, 1/5.0 S/L ratio, 293 K soaking temperature, and 313 K for the last



**Figure 5** The effect of citric acid concentration on the dissolution of REEs

agitation hour. The results are plotted in Figure 5.

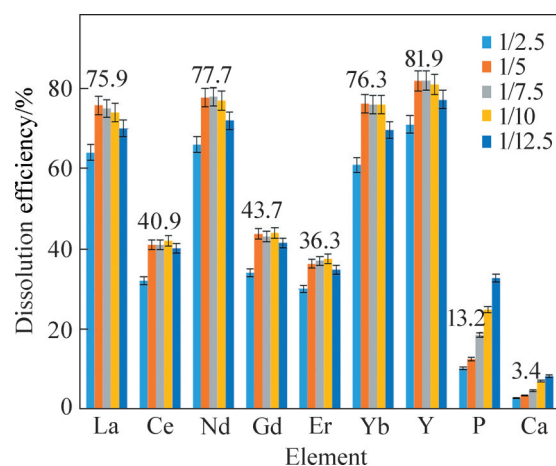
By increasing the CA concentration from 5% to 7.5%, the REEs dissolution efficiencies were enhanced. These dissolution enhancements of REEs were followed by a significant and continuous decrease in the REEs leachability with the increase in acid percentage from 7.5% to 20% CA. This might be attributed to the increase of the citric acid concentration causing depression in the dissolution mechanism which depends on the bacterial activity. Bacterial activity and media fermentation are largely dependent on the pH of the medium [42 – 43], which changes as the quantity of acid increases, resulting in a decrease in bacterial activity [44]. It also noticed that the low dissolution efficiency of Ca was obtained using 7.5% CA than using high CA concentrations. So, 7.5% CA concentration was considered the appropriate choice for the next studied factors.

Previously, several microorganisms were isolated from PG samples, including gram-positive bacteria BRM15, BRM19, and BRM20, as well as gram-negative bacteria BRM16, BRM17, and BRM18 [45]. These bacterial colonies showed a solubilization halo resulting from their ability to solubilize CaHPO<sub>4</sub> present in the medium [46]. The bacterial activity has the ability to remove not only sulfate but also heavy metals from PG [47]. So, the bacterial activity and the fermentation process of the PG must be controlled using a proper pH to

facilitate the liberation of REEs. As a result, the bacterial activity and the citric acid activity were considered the main parameters that controlled the REEs dissolution from PG sediments.

### 3.2.3 Solid-to-liquid ratio

Several soaking experiments using solid-to-liquid ratios ranging from 1/2.5 to 1/12.5 S/L were performed to determine the optimal S/L ratio causing maximum dissolution efficiencies of REEs. The maximum dissolution efficiencies of REEs were obtained using 1/5.0, 1/7.5 and 1/10.0 S/L ratios with small variations (Figure 6). These experiments were carried out under fixed conditions, namely, 14 d soaking time, 7.5% CA, 293 K soaking temperature, and 313 K for the last agitation hour. From the figure shown, it was clear that the use of very high or very low ratios of acidic solutions (1/12.5 or 1/2.5) was undesirable, because a lower percentage (1/2.5) means lower acid concentration and therefore lower REE solubility. On the other side, when the ratio of the acidic solution was raised above the required limit (1/12.5), the percentage of acid increased, and then the bacterial activity and the decomposition processes were weakened, as mentioned earlier in the effect of acid concentration. The other S/L ratios caused a reduction in the REEs dissolution. Low dissolution efficiency of Ca was attained using 1/5 S/L ratio compared with using the other ratios. So, economically, the 1/5 S/L ratio was the more appropriate ratio which caused the maximum REEs dissolution with using a minimum acid consumption. This was paired with the minimum dissolution of calcium content.

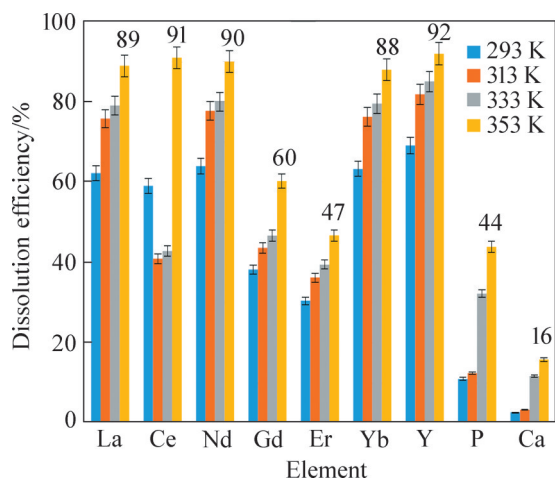


**Figure 6** The effect of solid-to-liquid ratio on the dissolution of REEs

### 3.2.4 Last hour temperature

The use of long period of time in the rare earth dissolution processes by soaking technique at room temperature was economically preferable as the costs raised significantly with elevating the temperatures over room temperature. This was clearly perceived with the scarcity of rare earth proportions in the original PG. Therefore, during the current study, all the different soaking experiments for PG were performed at room temperature for the entire soaking period except for the last hour only. So, to study the effect of temperature on the REEs dissolution efficiency, different temperatures for the last agitating hour were studied ranging from 293 to 353 K and the slurry was then decanted, filtered, and finally analyzed to determine the REEs dissolution efficiency. This was performed under constant conditions of 14 d soaking time, 7.5% CA, 1/5.0 S/L ratio, and 293 K soaking temperature.

From results represented in Figure 7, considerable enhancements in the REEs dissolution efficiency were acquired from rising the temperatures of the last agitation hour from 293 to 353 K. These enhancements in the REEs dissolution were attributed to the positive effect gained from external support (raising the dissolution temperature) which enhanced the dissolution kinetics. On the other side, the dissolution of phosphorus and calcium elements was sharply increased by rising the last agitation temperatures from 293 to 353 K. For P and Ca, the increases in dissolution efficiency ranged from 11% to 44% and



**Figure 7** The effect of last agitation hour temperature on the dissolution of REEs

2.7% to 16 %, respectively. The noticeable increase in phosphorous dissolution had a positive effect, whose recovery will be studied later in this paper. On the other hand, increasing the dissolution of calcium had a negative effect on the subsequent REEs recovery experiments which caused complications in the direct precipitation processes for REEs with oxalic acid. Nevertheless, 353 K was considered the most appropriate temperature for the last agitation hour.

### 3.2.5 Recycling of soaking experiments

The recycling of the soaking feed solutions played a very important role in acid and water consumption during the soaking processes. On the other hand, high REEs concentrations were obtained using the recycling steps, which were considered a positive factor in the next REEs recovery steps. Four soaking contacts were performed using the same aqueous feed solution with four fresh dried PG samples, each separately. After each contact, the slurry was filtered and the feed solution was mixed with the next fresh PG sample using the optimal soaking condition, namely 14 d soaking time, 7.5% CA, and 293 K soaking temperature, and 313 and 353 K for the last agitation hour.

From Figure 8, it was noticed that there was a high variation between the first contact and the rest recycled contacts in the dissolution of some REEs, namely La, Gd and Y. On the other side, small dissolution variations were obtained for the other elements as Ce, Nd, Er, and Yb. The cumulative dissolution efficiencies for REEs using 313 K for the last agitation hour were accepted and there was a small variation in the dissolution of all elements except Ce. So, four contacts using the same citrate feed solution could be used. This resulted in a feed solution of high REEs content with low consumption in the acid and water during the soaking processes.

During the recycling processes at ambient temperature, small variations in the calcium and potassium dissolution efficiencies were obtained; this was considered a positive sign. By performing the cumulative experiments using 353 K for the last agitation hour, considerable enhancements in the dissolution efficiencies for all elements were noticed.

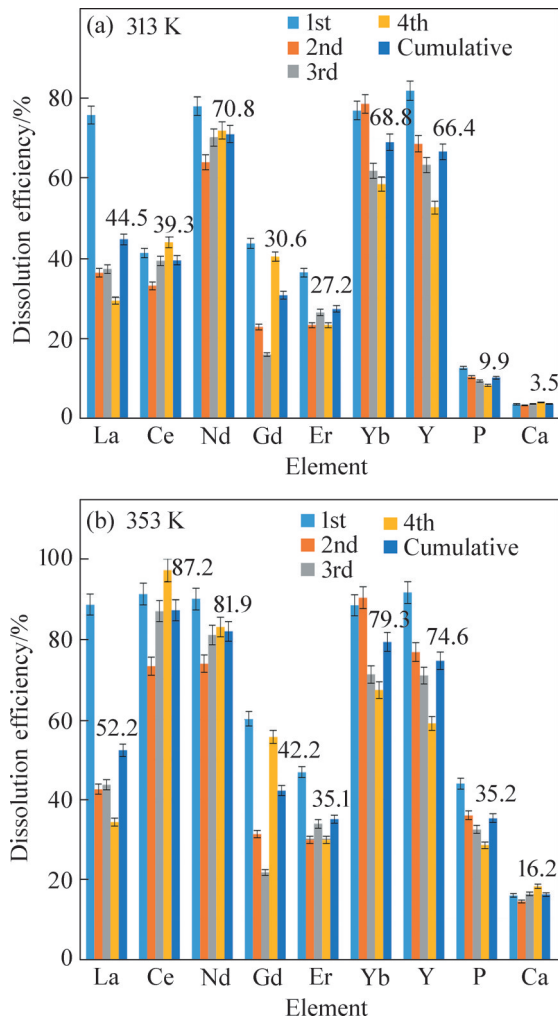


Figure 8 Recycling effect of soaking experiments at 313 K (a) and 353 K (b) last hour temperature

### 3.3 Dissolution kinetics

#### 3.3.1 General equation including Arrhenius model

Several models were investigated in order to explain the chemical reaction to determine the order of the dissolution reaction. The general equation was plotted as following:

$$f(x) = a \exp(bx) + c \exp(dx) \quad (1)$$

where  $a$  and  $c$  are constants;  $b$  and  $d$  are analogies to forward and backward rate constants and vice versa. The equilibrium constant  $K$  of this work can be approximated as follows:  $K = b/d$  or  $=d/b$  as the sign of them (means formation/deformation directions)

For isothermal systems ( $T = 25\text{ }^\circ\text{C}$  or  $298\text{ K}$ ), Gibbs free energies were calculated as follows:

$$\Delta G = -RT \ln K \quad (2)$$

where  $R = 8.314$  is the gas constant and  $T$  is the thermodynamic temperature.

And from Arrhenius relation Eq. (3) [48], we have:

$$K = A_r \exp(E/(RT)) \quad (3)$$

where  $A_r$  was the Arrhenius constant and  $E$  was the activation energy for the reaction.

By introducing Eq. (3) into Eq. (1), for the parallel or reversible reaction:

$$f(t) = a C_0 \exp(-t A_{r1} \exp(E_1/(RT))) + (C_0 - a) \exp(-t A_{r2} \exp(E_2/(RT))) \quad (4)$$

where  $A_{r1}$ ,  $A_{r2}$ ,  $E_1$  and  $E_2$  are Arrhenius constants and activation energy for the two parallel or reversible reactions;  $C_0$  is the original concentration of REEs in the PG.

By applying the general equation including Arrhenius model Eq. (4) using the results of dissolution processes at several times for all studied REEs, the experimental results were graphed using MATLAB program in 2D curves as shown in Figure 9. The Gibbs free energies, the activation energies, and the correlation coefficient for the dissolution reactions for REEs are listed in Table 4.

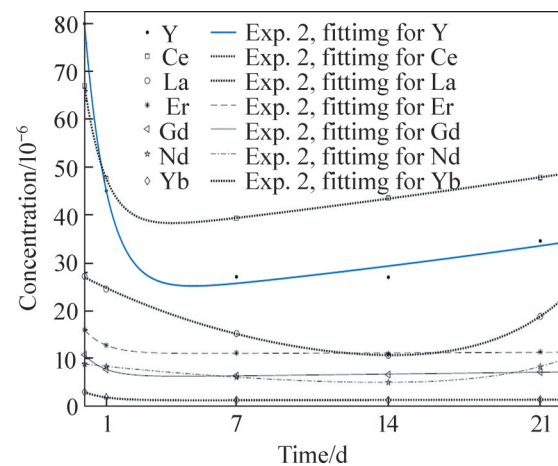


Figure 9 General equation including Arrhenius model parameters for REEs dissolution processes

Table 4 General equation including Arrhenius model parameters for REEs dissolution processes

REE	$\Delta G/(kJ \cdot mol^{-1})$	$E_1/(kJ \cdot mol^{-1})$	$E_2/(kJ \cdot mol^{-1})$	$R^2$
Y	-9.67	0.76	11.14	0.999
Ce	-10.60	0.64	12.45	0.999
La	-2.48	4.14	2.04	0.999
Er	-16.21	0.61	10.08	0.996
Gd	-12.09	17.91	0.32	0.999
Nd	-3.62	4.75	0.85	0.999
Yb	-12.73	0.81	10.47	0.998



From the obtained results, the dissolution reactions of all REEs using citric acid were matched well with the studied model; high correlation coefficients  $R^2$  were obtained for all dissolution processes as shown in Table 4. It was also indicated that the rare earths dissolution process was carried out through two reactions with two variable activation energies, one of which had a very high value over the other.

### 3.3.2 Uptake general model

The uptake general model Eq. (8) was derived as follows [49]:

The pseudo- $n$ th-order rate equation (Eq. (5)) can be derived as follows for any pseudo order [50]:

$$dq/dt=k(q_e-q_t)^n \tag{5}$$

where  $q_e$ ,  $q_t$  and  $n$  are the dissolved element concentrations at equilibrium  $t$ , their concentration at any time and order of reaction, respectively

By separation and integration, we obtain:

$$q_t=q_e-(q_e^{(1-n)}+(k(n-1)t))^{(1-n)} \tag{6}$$

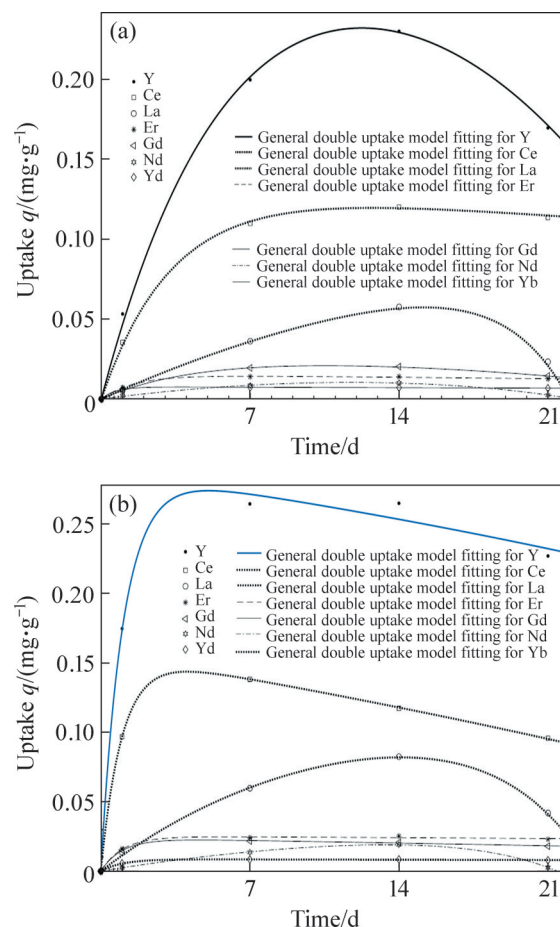
By introducing Arrhenius relation Eq. (3) into Eq. (6) and rearrange, we obtain;

$$(q_e-q_t)^{(1-n)}+q_e^{(1-n)}=(n-1)tA_i \exp(\Delta E/(RT)) \tag{7}$$

$$q_e=q_e - [q_e^{(1-n)}+((n-1)tA_i \exp(\Delta E/(RT)))]^{(1-n)} \tag{8}$$

Using the dissolution results of REEs from PG with citric acid of 5% and 10% concentrations, uptake general model was represented in 2D curves using MATLAB program as shown in Figure 10.

The calculated correlation coefficients were closer to unity for the pseudo-first-order kinetic model. The Gibbs free energy,  $\Delta G$ , presented in Table 5, gave information about the type of REEs dissolution processes using the citric acid. The negative value of free energy of digestion  $\Delta G$



**Figure 10** Uptake general model curves using 5% (a) and 10% (b) citric acid

confirmed the feasibility and spontaneous nature of dissolution processes for all REEs. The dissolution reactions for all REEs were carried out through two reactions. Each reaction has a reaction rate constant ( $K$ ) and reaction order ( $n$ ). The calculated reaction orders for dissolution reactions of all REEs were closer to one. The reaction order results agreed with the previous model results. The acid dissolution natures for all REEs were performed through two reactions. The obtained data featured in 2D

**Table 5** Uptake general model parameters for REEs dissolution processes

Parameter	Y		Ce		La		Er		Gd		Nd		Yb	
	10% CA	5% CA	10% CA	5% CA	10% CA	5% CA	10% CA	5% CA	10% CA	5% CA	10% CA	5% CA	10% CA	5% CA
$\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$	-9.7	—	-10.6	—	-2.5	—	-12.1	—	-12.1	—	-3.7	—	-12.7	—
$K_1/\text{d}^{-1}$	0.95	0.154	-0.01	0.30	0.09	0.05	1.05	0.66	1.05	0.66	0.06	0.05	-0.01	1.53
$K_2/\text{d}^{-1}$	-0.02	-0.07	1.01	-0.01	-0.24	-0.33	-0.01	-0.01	-0.01	-0.01	-0.24	-0.10	1.03	-0.01
$n_1$	0.999	0.999	0.992	1.006	0.990	1.002	1.012	0.995	1.012	0.995	0.98	0.96	1.002	1.002
$n_2$	1.002	0.999	1.002	0.990	1.013	1.012	0.999	1.003	0.999	1.003	1.028	1.046	1.004	1.001
$R^2$	0.996	0.998	0.999	0.999	0.999	0.999	0.998	0.997	0.998	0.997	0.999	0.998	0.997	0.999

(Figure 10) showed that the process could be approximated more satisfactorily by the uptake general model as the predominant mechanism. The reversible or parallel reactions were determined from the sign of the reaction rate constants for the two reactions. When they have the same signal, the two reactions were parallel, while having an opposite signal indicates the reversibility of the reactions. In our study, the opposite signal showed the reversible nature of our dissolution reaction for all REEs.

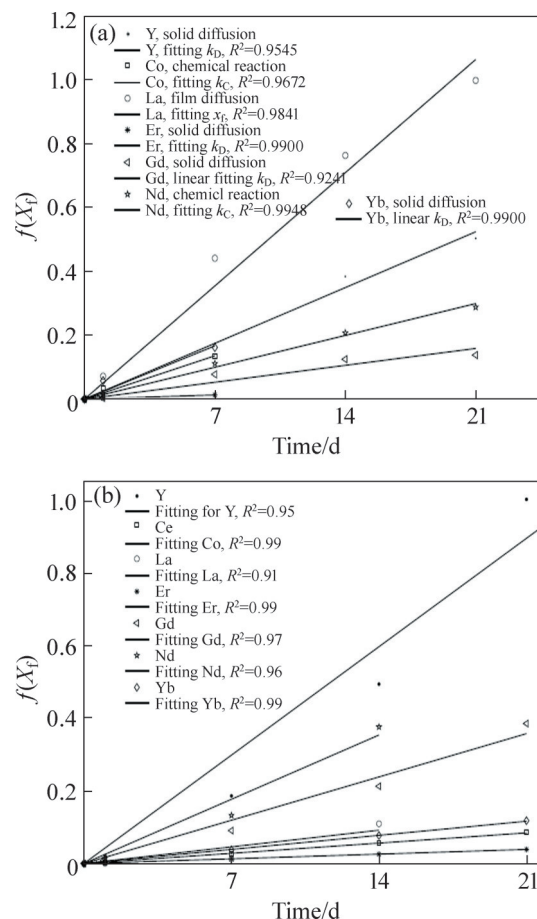
### 3.3.3 Shrinking core model

The mechanism proposed by the shrinking core model assumes the particles as uniform non-porous grains. Initially, the reaction occurs in the grain surface and then the reaction zone moves into the solid leaving a product layer behind. The total radius of the particle remains constant, while the radius of the unreacted core and the layer of products vary over time as a function of conversion. The approximate solution of the shrinking core model applied in this work was a combination of the resistances that can simultaneously occur in a particle under reaction: acid diffusion in the layer surrounding the particle, acid diffusion through the product layer around the unreacted core, and chemical reaction on the unreacted core surface. The graphical simulation that relates the conversion as a function of time ( $t$ ) for a spherical particle is given by Eq. (9) [50]:

$$t = (1/K_p)X + (1/k_D)[1 - 3(1-X)^{2/3} + 2(1-X)] + (1/k_C)[1 - (1-X)^{1/3}] \tag{9}$$

where  $K_p$ ,  $k_D$  and  $k_C$  represent the resistances to the external mass transfer, product layer diffusion, and chemical reaction, respectively, and  $X$  is fractional conversion.

The experimental findings were graphed using the MATLAB program by applying the generalized shrinking core model Eq. (9) to the dissolution process several times for REEs, as shown in Figure 11. The overall uptake model is divided into two parts: forward and backward reaction. Correlation coefficient  $R^2$  for all dissolution reactions experiments using citric acids for the forward and backward reactions of REEs elements



**Figure 11** Approximation of shrinking core models curves for forward-reactions (a) and backward-reactions (b)

was closer to unity. All of the backward reactions for REE elements were film diffusion-controlled whether for the detected time or the plateau. On the other side, the forward reactions for Y, Er, Gd and Yb were solid diffusion, for Nd and Ce were chemical, and finally for La was film diffusion.

### 3.4 Dissolution thermodynamic

Variable dissolution results using different temperatures (ranging from 298 to 353 K) were studied to determine the thermodynamic parameters of the REEs dissolution by soaking with a citric acid medium. The non-linear floatotherm including van't Hoff equation model was implicated to determine these parameters. A floatotherm term was suggested as a result of temperature varying and the Langmuir model was the started idea.

From the two equations (Langmuir equation and van't Hoff equation), a suggested Floatotherm

van't Hoff equation was derived as following [50]:

$$f(C, T) = Q_m \frac{(\exp(-\Delta H/(RT) + \Delta S/R))C^n}{(1 + (\exp(-\Delta H/(RT) + \Delta S/R))C)^m} \quad (10)$$

where practically,  $n$  and  $m$  tend to unity. The suggested model can be represented in 3D using MATLAB as shown in Figure 12.

The Gibbs free energy,  $\Delta G$ , is calculated from the following equation [43]:

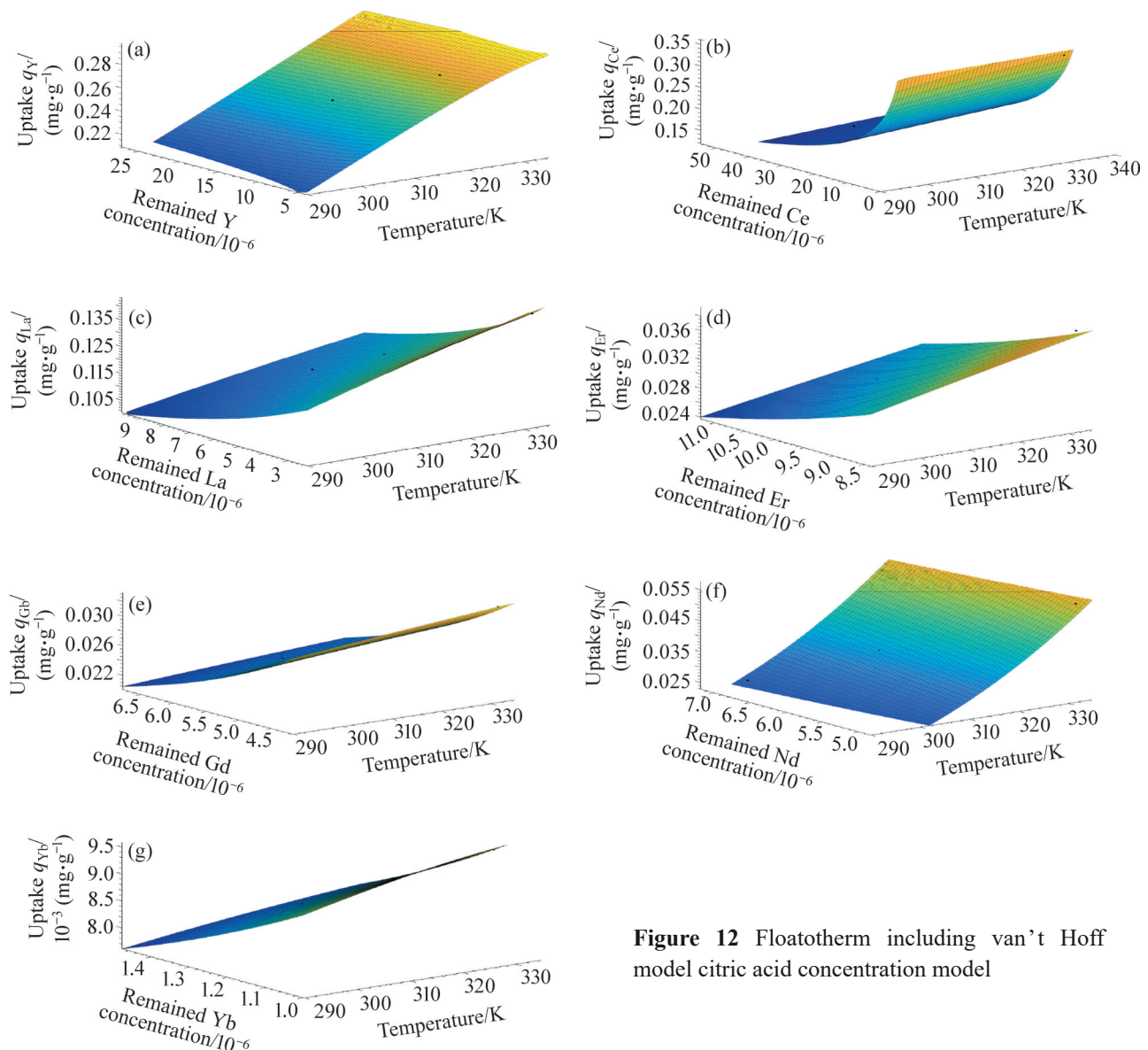
$$\Delta G = \Delta H - T\Delta S \quad (11)$$

The thermodynamic dissolution parameters; enthalpy, entropy, Gibbs free energy, and the correlation coefficient for REEs using soaking with citrate are plotted in Table 6.  $K_d$  ( $\Delta H$ ),  $\Delta S$ ,  $T$ , and  $R$  are the distribution coefficient, the enthalpy, the entropy, the thermodynamic temperature, and the

gas constant, respectively. The positive value of  $\Delta H$  confirmed the endothermic nature of dissolution reactions for all REEs except Y which has exothermic nature. The negative value of free energy of digestion  $\Delta G$  confirmed the feasibility and spontaneous nature of dissolution processes for all REEs at all temperatures. These results matched well with the previous uptake model results. Thus, the adsorption process was found to be endothermic and spontaneous.  $\Delta S$  had a positive value in most dissolution experiments, indicating an increase in the randomness at the solid/solution interface during the attack of citric acid on the ore particles.

### 3.5 REEs recovery results

A series of adsorption experiments for total



**Figure 12** Floatotherm including van't Hoff model citric acid concentration model

**Table 6** Thermodynamics parameters for REEs dissolution processes

Parameter	$\Delta H/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	$\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$				$R^2$
			298 K	313 K	333 K	353 K	
Y	-57.63	-161.20	-9.56	-7.18	-5.57	-3.95	0.997
Ce	22.96	112.60	-10.59	-12.284	-13.410	-14.536	0.999
La	11.02	45.32	-2.48	-3.16	-3.62	-4.07	0.995
Er	24.89	137.93	-16.21	-18.28	-19.66	-21.04	0.987
Gd	13.64	86.37	-12.10	-13.39	-14.25	-15.12	0.996
Nd	23.01	65.078	-3.617	-2.641	-1.989	-1.339	0.998
Yb	5.57	24.02	-12.73	-13.09	-13.33	-13.57	0.997

REEs were performed using strong cationic ion exchange resin, namely Dowex 50X8, from the citrate feed solutions of 214 mg REEs/L concentration. The feed solution pH was varied from 1.0 to 2.2 using sodium hydroxide solution (50%). The optimal pH was 1.4 at which 96% of REEs was recovered from the citrate solutions. These extraction experiments were performed under fixed conditions of 75 min contact time between the two phases, 1/250 resin/feed solution ratio, and stirring the two phase with 200 r/min stirring rate in a conical flask at ambient temperature. A saturated resin was gained after applying the optimal adsorption conditions [6].

The adsorption of REEs onto the studied resin was performed to beneficiate the REEs concentration and prepare a semi-purified rare-earths precipitate, which was considered the main target of this paper. This resin was previously studied and achieved a successful adsorption of REEs from mineralizations leaching solutions containing different undesirable gangues. A physisorption mechanism was proved for the adsorption of REEs with a strongly acidic cation exchange resin, Dowex 50X8.

The REEs content was eluted from the loaded resin using a diluted hydrochloric acid solution. The elution conditions were 4.0 mol/L hydrochloric acid, 120 min contact time, 1/6 eluate/resin ratio, and stirring speed 250 r/min at ambient temperature. Therefore, the elution efficiency for rare earths from the saturated resin under these conditions reached 92% as shown in Table 7. According to the findings of this investigation, Dowex 50X8 resin was successful in extracting and pre-concentrating total rare earths from citrate feed solutions containing approximately 214 mg REEs/L. Stripping chloride

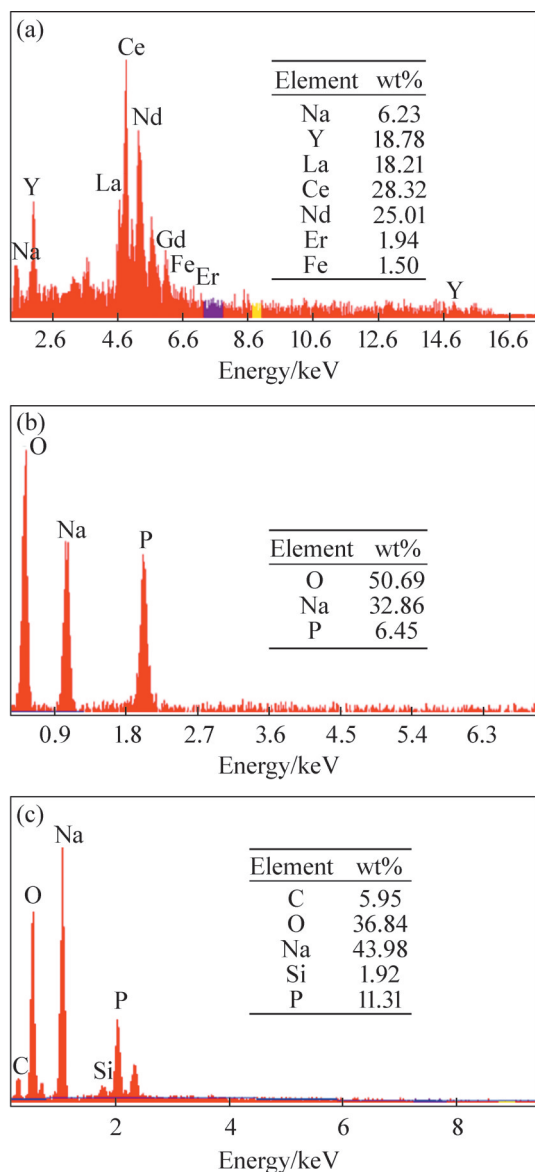
solutions of 7651 mg/L were gained through the stripping stage of the saturated resin. This means a successful pre-concentration process for the content of rare earths was done with a pre-concentration factor (PF) of about 36. The total rare earth components were precipitated using oxalic acid at pH 1.0 from the appropriately collected eluate fraction. The precipitated cake was decanted, filtered, washed with 1% oxalic acid, ignited at 1000 °C, and finally analyzed against its constituents using EDAX-technique to identify the final cake constituencies. The analytical results indicated in Figure 13 proved the presence of considerable contents of rare earths in the presence of minor undesirable gangues.

### 3.6 Sodium phosphate and sodium citrates recovery results

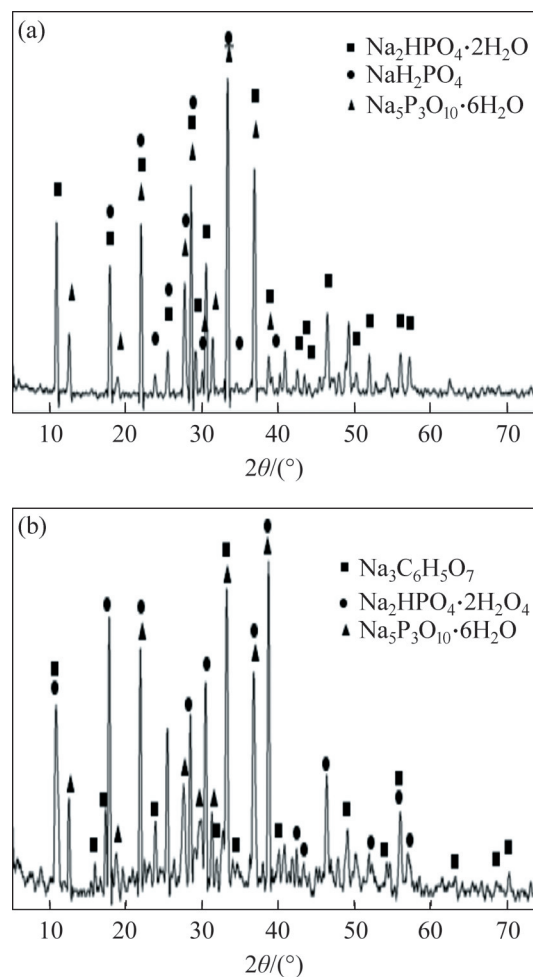
Considerable amounts from citrate and phosphates were remained in the raffinate solutions after REEs recovery using Dowex 50X8 resin. To enhance the economics of the REEs recovery from the PG using the soaking technique, several steps were carried out to recovery both citrate and phosphate contents. The raffinate solutions after REEs recovery were precipitated using a sodium hydroxide solution of 50% at pH 7.0. A slurry solution was produced and filtered, and then a final filtered solution was obtained. The filtered solution was condensed by heating on a hot plate until reaching to the half-volume. After resting the condensed solution for 24 h at ambient temperature, white crystalline powders were formed, decanted, separated, and washed with ethanol. The washed precipitates were dried at 110 °C and finally identified with XRD and EDAX analysis. After removing these first precipitates, the remained

**Table 7** ICP analysis for the REEs content in the eluate

Element	La	Ce	Nd	Gd	Dy	Er	Yb	Lu	Y
Concentration/(mg·L <sup>-1</sup> )	1295.83	1128.91	2266.90	152.45	73.79	257.30	106.47	35.87	2333.89

**Figure 13** EDAX-charts for the pre-concentrate REEs oxide cake (a), the sodium phosphate (b), and the sodium citrate and phosphates precipitate (c)

solutions were collected and exposed to complete drying to remove all water content. A second white precipitate was obtained, dried at 110 °C, and instrumentally characterized using XRD and EDAX analysis. From Figures 13(b) and (c), the main elements presented in the EDAX-chart for the two precipitates were Na, P, and O for the first precipitate and Na, C, and O for the second respectively. On the other side, Figure 14 displays the XRD-charts for the two white precipitates,

**Figure 14** XRD patterns for the sodium phosphate (a), and the sodium citrate and phosphates precipitate (b)

which prove the sodium phosphates and sodium citrates precipitates formation, respectively. The sodium phosphates XRD-chart revealed a presence of mixture from Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>·6H<sub>2</sub>O salts. As well, the XRD-chart for sodium citrates proved the presence of the high content from sodium citrates Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> and sodium phosphates salts.

So, these steps were succeeded in the recovery of most phosphates and citrate content as sodium salts from the raffinate solution after the REEs recovery steps. These salts have much important utilization. Therefore, these by-products enhanced the economics of REEs recovery process using soaking with citrate.

## 4 Conclusions

In the present work, the process of recovery of rare earth elements (REEs, mainly Ce, La, Gd, Nd, Er, Yb, and Y) from PG (main by-product of phosphoric acid production) was investigated. It can be concluded that there was low concentrations of REEs located inside the crystalline forms of the PG and were not adsorbed on the surface. Citric acid was succeeded in the dissolution of large portions of REEs content in the PG with mild dissolution for calcium content. Optimal dissolution conditions for REEs using the soaking technique were 14 d soaking time, 7.5% CA, 1/5.0 solid-to-liquid ratio, 293 K soaking temperature, and 353 K for the last agitation hour. By applying these conditions, about 79.57% dissolution efficiency for total REEs was gained after four dissolution stages using the same citric acid solution and four different portions from the dried PG. Using three kinetic models (general equation including Arrhenius model, uptake general model, and shrinking core model), the dissolution processes for all REEs were performed through two reversible reactions with different activation energies. All the backward dissolution processes were carried out through film diffusion control while the forward dissolution reactions were mixed from solid diffusion, chemical, and film diffusion. The thermodynamics calculations showed the endothermic nature of the dissolution process for all REEs except Y. REEs recovery from the citrate feed solutions was accomplished using Dowex 50X8 resin under optimal adsorption conditions. The diluted hydrochloric acid was used as an eluent for REEs from the loaded resin. Sodium phosphate and sodium citrates precipitates were recovered from the raffinate solution after precipitation with sodium hydroxide solution. These products enhanced the economics of the REEs recovery processes using the citrate soaking technique.

## Contributors

Ahmed Atef ELIWA and Amal Essam MUBARK provided the concept and edited the draft of manuscript. Nasr Abelaziz ABDELFATTAH conducted the literature review. Ebrahim Abd El GAWAD analyzed the calculated results using MATLAB program. Ahmed Atef ELIWA and Amal

Essam MUBARK replied to reviewers' comments and revised the final version.

## Conflict of interest

The authors declare that they have no conflict of interest.

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## 中文导读

### 利用柠檬酸浸泡技术最大化利用磷石膏废弃物回收稀土和残留磷酸盐

**摘要：**磷石膏(PG)是磷酸生产工业的主要副产物，被认为是稀土元素(REEs)最重要的二次来源之一。本研究重点是回收PG中存在的REEs和残留的磷酸盐的同时，保留CaSO<sub>4</sub>，以用于其他各种应用。这些成果是采用柠檬酸浸出工艺实现的。研究了几个参数对柠檬酸浸出回收稀土的影响，包括浸泡时间、浸泡温度、柠檬酸浓度、固液比以及柠檬酸浸出溶液在进一步的稀土溶解实验中的循环利用。最佳操作条件为室温浸泡时间14 d，柠檬酸浓度为7.5%，固液比为1/5。优化条件下稀土的溶解效率为79.57%。将不同的新鲜PG样品与相同的柠檬酸溶液依次混合浸泡4个阶段，在最佳浸泡条件下，稀土的累积溶解效率为64.7%。采用Dowex 50X8树脂从柠檬酸溶液中回收稀土，萃取效率为96%。溶解动力学证明了稀土的伪一级性质、溶解过程为可逆反应，存在两个活化能。

**关键词：**磷石膏；稀土；柠檬酸；溶解；浸泡；Dowex 50X8；预浓缩