



ISSN 1110-0451



(E S N S A)

Sorption and separation of Er and Y from phosphoric acid using commercial cation exchange resin; Amberlite IR-120

E.M. Abu Elgoud, H.A. Madbouly*, Z.H. Ismail

Hot Laboratories Center, Egyptian Atomic Energy Authority, 13759, Egypt

ARTICLE INFO

Article history:

Received: 1st Mar. 2023

Accepted: 7th May 2023

Available online: 25th July 2023

Keywords:

Amberlite IR-120;

Erbium;

Yttrium;

Sorption;

Phosphoric acid;

Separation

ABSTRACT

Rare earth elements (REE) are found in low amounts (hundreds of ppm) in phosphoric acid solutions. Due to the strong acidity and complex nature of phosphoric acid, the development of a particularly cost-effective method for the selective recovery and separation of REEs is necessary. Extraction of REEs with commercial chelating ion exchange resins may be considered a promising alternative to the traditional but costly and pollutant solvent extraction technique. In this work, the possibility of extracting erbium(III) and yttrium(III) from phosphoric acid using a commercial cation exchange resin (Amberlite IR-120) has been investigated. In a batch system, several factors such as acid concentration, contact time, initial metal ion concentration, V/m ratio, and temperature that may affect the sorption of these metal ions were separately examined. The changes in standard thermodynamic quantities were calculated, and the outcomes indicated that the sorption of both studied metal ions is endothermic, spontaneous, and connected with an increase in the randomness of the system. During the full concentration range under study, the adsorption adhered to the Langmuir isotherm model. Desorption with 1.0 mol/L citric acid followed by 1.0 mol/L sodium sulfate (1.0 mol/L) allowed separation of Er(III) and Y(III) and recovery with 79.0% and 65.9%, respectively.

INTRODUCTION

The major raw material for the production of phosphoric acid is the phosphorite ores found in phosphate rocks. The majority of phosphorite deposits across the world include REEs because calcium ions are isomorphically substituted by rare-earth ions in the lattice of phosphorite ores [1, 2]. According to the ore's origin, phosphate ores can contain varying amounts of rare earth elements (REEs), and they are often regarded as a secondary source of REEs [3, 4]. Most of the phosphoric acid produced by the wet method is turned into phosphate fertilizers [5]. Aydina et al. [6] demonstrate that the majority of the REEs present in the phosphoric acid phase finally end up in the phosphate fertilizer. Phosphate fertilizer that contains REEs may cause long-term soil pollution. However, as valuable elements, REEs are used extensively across a wide range of industries and are in high demand.

Due to China's restrictions on the export of rare earth (REEs), both the supply and cost of rare earth around the

world have had significant variations over the past few years [5]. To assure a supply for their domestic requirements, many developed countries have started to support and encourage further rare earth prospecting. Recovering rare earth from phosphate rock has drawn increasing interest in recent years in an effort to boost rare earth supply and enhance the quality of phosphoric products [7]. To increase rare-earth availability of rare-earths and enhance the quality of phosphoric products, more and more attention has been paid to recovering rare earths from phosphate rock in recent years. To increase rare-earth availability and enhance the quality of phosphoric products, rare-earth recovery from phosphate rock has received more and more attention in recent years [7].

The rare earth elements, erbium, and yttrium are used in numerous applications and innovative technologies. The composition of phosphors that emit blue, red, and green wavelengths includes yttrium oxide [8]. Yttrium is

important in our lives because it is utilized in a variety of applications, including the manufacture of hydrogen storage cells, high-performance magnets, rechargeable batteries, computer and laptop memories, nuclear reactors, electronic filters, fiber optic laser cables, LCD, electrodes catalysts, and plasma screens [9, 10]. Furthermore, yttrium can be utilized in the pigment, fertilizer, and medical imaging industries. Yttrium is commonly employed as an additive in alloys. This makes aluminum and magnesium alloys harder. It's also utilized as a catalyst in the polymerization of ethene and the creation of microwave filters for radar. Yttrium-90 has some medical applications, including the treatment of some diseases, such as liver cancer [10]. The main applications of erbium include the pink-colored Er^{+3} ions, which have optical fluorescence characteristics that are particularly useful in several laser applications [9]. Glasses or crystals that have been doped with erbium can serve as an optical amplification medium [9]. It is also utilized as a neutron-absorbing control. It is often used as a photographic filter and, due to its tenacity, it can be utilized as a metallurgical additive. Erbium is extensively utilized in YAG lasers for aesthetic laser operations [11]. The solvent extraction method, which uses some of the organophosphate compounds, has been used to commercially extract REEs from wet process phosphoric acid (WPPA) [12]. Ion exchange [13], membrane separation [14, 15], extraction chromatography [16, 17], and bioaccumulation [18, 19] are some of the other studied techniques for recovering REEs from phosphoric acid. In fact, solid ion exchangers have gained popularity for REEs recovery from WPPA due to their potential advantages over other methods. This is almost entirely attributable to the fact that this method is relatively less expensive and is less affected by temperature and acid concentration. Additionally, there would be no need for a pretreatment because the acid would not be contaminated with an organic solvent.

In concentrated phosphoric acid, resins may suffer from chemical degradation and swelling therefore the selection of suitable resin for the drastic condition of phosphoric acid is of very importance. Moreover, most of the literature concerns other acidic media (hydrochloric, sulfuric, nitric) and cannot be directly applied to such an acidic medium containing strong complexing phosphates. Despite these possible

limitations, a number of commercially available resins have promising properties with low prices, making REE sorption a potentially attractive alternative. This alternative has indeed been examined by a number of authors. Hérès et al [20] published a study on the recovery of REEs from 4.0 mol/L phosphoric acid solutions using a variety of chelating resins with phosphonic or phosphinic groups; Tulsion CH-93, Purolite S940, Amberlite IRC-747, Lewatit TP-260, Lewatit VP OC 1026, Monophos and Diphonix. The obtained extraction yields ranged from 20 to 60% with low separation efficiency. It has been demonstrated that the aminomethyl phosphonic resin Purosorb 140 macropore sulphocationite cation-exchanger provides an effective sorption/elution behavior when used in a small column for extractions of REEs from phosphoric acid solutions [21]. Sorption of La, Fe, and Al from phosphoric acid was studied by Konkova et al [22] with macroporous sulfocationites resins (MTC1600 and KU-2-8). They reported that the MTC1600 resin is a better sorbent for lanthanum and the sorption process is dependent on the ionic form of the resin (H^+ , NH_4^+ , and Na^+). Reddy and Kumar [23] studied the use of (Tulsion CH-96, a macroporous bi-functional phosphinic acid resin; T-PAR, a phosphoric acid resin; and Tulsion CH-93, an amino phosphonic acid resin) to extract REE from highly concentrated phosphoric acid but they exhibit a low yield of extraction (<20%) when the phosphoric acid concentration is 5.0 mol/L or more. In our previous studies, the strongly acidic cation exchange resin (SQS-6) was used to evaluate the sorption of Ce(IV), Pr(III), Er(III), and Y(III), La(III) and Nd(III) from the phosphoric acid medium in the range of 4–10 M [2, 24]. The experimental sorption capacities were found to be 5.23 mg/g, 13.8 mg/g, 12.7 mg/g, 12.58 mg/g, 8.82 mg/g, and 3.78 mg/g for Ce (IV), La (III), Nd (III), Pr(III), Y(III), and Er(III), respectively.

In that context, the focus of the current work has been concerned with the investigation of the sorption and separation of Er(III) and Y(III) as examples of REEs from concentrated phosphoric acid solutions using Amberlite IR-120, a commercially available highly acidic cationic exchanger. Amberlite IR-120 (Am-IR120) has been selected because it has extreme chemical stability in concentrated phosphoric acid, comparatively low price, and has a sulfonic group that has good selectivity toward REEs.

EXPERIMENTAL

Materials and Chemicals

The commercial ion exchange resin Amberlite IR-120 (Am-IR120) was produced by the manufacturer Rohm and Hass Co. (USA). It is a macroporous, strongly acidic, sulfonated polystyrene cation exchanger. The H⁺ form of the Am-IR120 has a moisture content of around 55% and 8% S-DVB with a mesh size of 16-50. The resin operates in the pH range of 0-14 with a maximum operating temperature of 150 °C. On a wetted bed volume basis, the resin has an exchange capacity of 1.9 meq/mL.

The stock solutions of Er(III) and Y(III) (1.0 g/L) were generated by dissolving a known quantity of the metal oxide (Aldrich) in a small amount of concentrated nitric acid. They were then evaporated until they were almost dry, washed several times, and then added double-distilled water was added up to the mark to get it to the desired concentration. To simulate the removal process of Er(III) and Y(III) in wet-process phosphoric acid, the desired required metal concentrations for the test solutions were obtained by diluting a known volume of stock solution with concentrated phosphoric acid. The remaining chemicals used are all of the analytical grades.

Sorption and desorption procedures

Unless otherwise stated, batch sorption tests were carried out by stirring 0.05 g of Am-IR120 resin with 5.0 mL of a 100 mg/L metal ion contained in 4.0 M phosphoric acid solution at 25°C in a thermostated shaker bath (G.F.L. 1083, Germany). The resin was removed from the solution by centrifugation at 5500±5 rpm for 5 minutes in order to prevent the development of colloidal suspension. For the purpose of calculating the metal ion concentration before (C_o) and after (C_e) sorption, a known volume was separated from the solution phase before and after equilibration (30.0 min). The Arsenazo III technique was used to measure the concentration of Er(III) and Y(III) ions in the various samples at pH 3.5 in a format buffer solution at a wavelength of 650 nm [23] using Shimadzu, UV-visible spectrophotometer model UV-160, Japan.

The following equation was used to get the Am-IR120 capacity, q_o (mg/g):

$$q_o = (C_o - C_e) \left(\frac{V}{m} \right) \quad [\text{mg/g}] \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentrations of metal ions in the solution (mol L⁻¹), V

is the volume of solution (L), and m is the weight of the resin (g). According to the following equation; the distribution coefficient (K_d) is calculated:

$$K_d = \left(\frac{C_o - C_e}{C_e} \right) \left(\frac{V}{m} \right) \quad (2)$$

$$K_d = \left(\frac{q_e}{C_e} \right) \quad (3)$$

Where V is the volume (L) and m is the weight (g) of the resin, C_o and C_e are the initial and equilibrium concentrations (mg/L) of metal ions, respectively.

The desorption of Er(III) and Y(III) loaded on the Am-IR120 resin was examined using different eluates such as (HNO₃, HCl, H₂SO₄, Sodium acetate, Sodium carbonate, Citric acid, Ammonium carbonate, Sodium sulfate). For this purpose, the loaded Am-IR120 resin, which has a maximum capacity of both Er(III) and Y(III), is allowed to dry in the air. In a ratio of 5/1 eluate to resin, an exact weight of the loaded resin was mixed with an eluting agent and shaken for 120 min at 25 °C. Then the Am-IR120 was separated from the solution by centrifugation and the metal concentration is determined in the eluting solution. The desorption efficiency DE (%) was determined using the following:

$$DE = \frac{C}{C_o} \times 100 \quad (4)$$

Where C (mg L⁻¹) is the concentration of metal ions after desorption and C_o (mg L⁻¹) is the concentration of metal ions within the resin.

RESULTS AND DISCUSSION

1- Factors affecting the adsorption of metal ions

1.1 Effect of phosphoric acid concentrations

To determine the influence of varying phosphoric acid concentrations on the adsorption ability of Am-IR120 toward Er(III) and Y(III), the acid concentration is changing between 3.0 and 7.0 mol/L. As displayed in Fig. (1), the adsorption of both studied metal ions decreases from ~80% to ~ 8% as H₃PO₄ concentration increases from 3.0 to 7.0 mol/L. This decrease may be attributed to the ability of Er and Y to generate complexes with phosphate ions at high concentrations of H₃PO₄ [26,27]. The separation of studied metal ions is shown to be preferable at 4.0 mol/L, so it will be used for the remainder of the experiments.

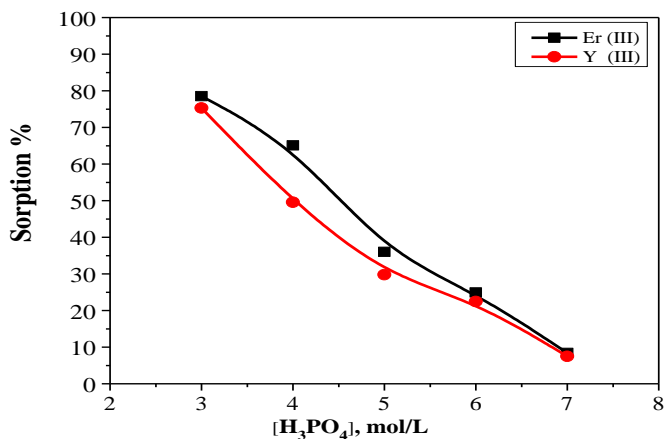


Fig. (1): Effect of phosphoric acid concentration on the sorption of 100 mg/L of Er(III) and Y(III) with Am-IR120 at 0.05 L/g (V/m), 30 min (shaking time), and 25°C.

1.2 Contact time

In the time range of 1.0 to 90.0 min, the effect of contact time on the sorption of Er(III) and Y(III) (100 mg/L each) onto Am-IR120 from 4.0 mol/L phosphoric acid was examined. The results illustrated in Fig. 2 indicated that the uptake percent increases with time until it reaches a plateau at 30 min for Er(III) and 60 min for Y(III), with a sorption percent of ~ 65 % and 55%, respectively. Consequently, from a separation point of view, an equilibrium contact time of 30 minutes will be used for all subsequent studies.

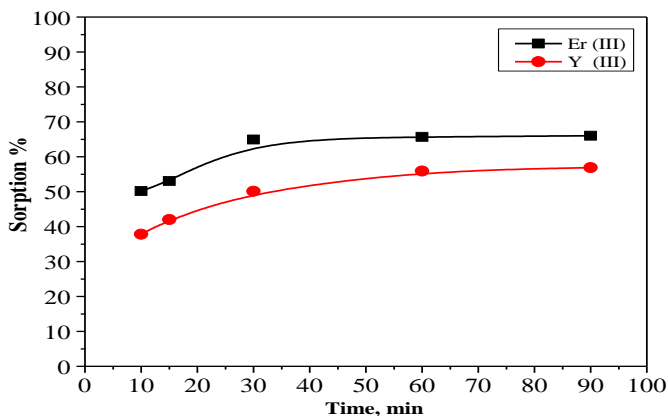


Fig. (2): Effect of contact time on the sorption of 100 mg/L of Er(III) and Y(III) with Am-IR120 from 4.0 mol/L phosphoric acid at 0.05 L/g (V/m) and 25°C.

1.3 Initial metal concentration

The effect of varying the concentration of the metal ions under investigation on the adsorption efficiency of Am-IR120 resin was examined within the range of 50 to 400 mg/L. According to the results obtained (Fig. 3), metal uptake increased with increasing initial metal ion

concentration up to 250 mg/L for Er(III) and 300 mg/L for Y(III). After which metal ions uptake remained constant at 3.51 and 2.64 mg/g for Er(III) and Y(III), respectively, which is considered as the maximum loading capacity of Er(III) and Y(III) onto Am-IR120.

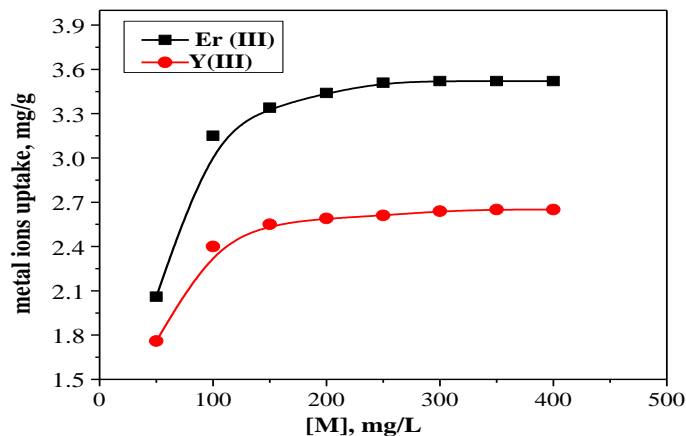


Fig. (3): Effect of initial metal ion concentration on the sorption of Er(III) and Y(III) with Am-IR120 from 4.0 mol/L phosphoric acid at 0.05 L/g (V/m), 30 min (shaking time) and 25°C.

1.4 V/m ratio

To examine the adsorption capability of the resin, the effect of varying resin weight to solution volume ratio (V/m, L/g) on the sorption of Er(III) and Y(III) was investigated from 4.0 mol/L phosphoric acid in the range from 0.02– 0.10 L/g. The obtained results are given in Fig. 4 where it is clear that the uptake of Er(III) was enhanced by decreasing the v/m ratio up to 0.035 after which it reached a constant value of 3.51 mg/g. The uptake of Y(III) increases more gradually than Er(III), with a constant uptake value of 2.64 mg/g at 0.025. Therefore a v/m ratio of 0.10 L/g is better suited for separation feasibility.

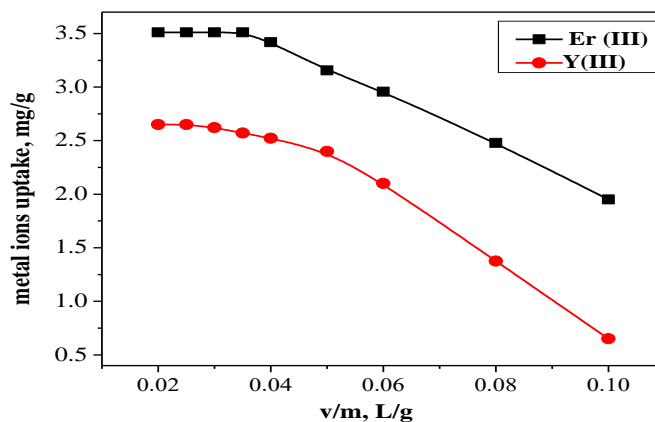


Fig. (4): Effect of V/m ratio on the sorption of 100 mg/L of Er(III) and Y(III) with Am-IR120 from 4.0 mol/L phosphoric acid, 30 min (shaking time) and 25°C.

1.5 Effect of temperature

At various temperatures between 25 and 70 °C, the effect of temperature on the sorption of Er(III) and Y(III) with Am-IR120 was studied from 4.0 mol/L phosphoric acid. As observed, the sorption of these metal ions increases with the temperature reaching almost quantitative adsorption at 70 °C (Fig. 5). Consequently, for the separation of the studied elements 25 °C is more suitable.

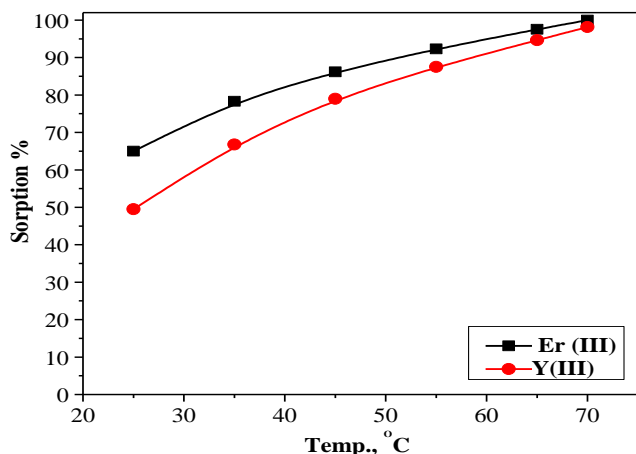


Fig. (5): Effect of temperature on the sorption of 100 mg/L of Er(III) and Y(III) with Am-IR120 from 4.0 mol/L phosphoric acid at 0.05 L/g (V/m) and 30 min (shaking time).

2- Thermodynamic of the adsorption process

For sorption of Er(III) and Y(III) on Am-IR120, the standard thermodynamic parameters which include ΔG° (free energy change), ΔH° (enthalpy change) and ΔS° (entropy change), were calculated from the following relationships:

$$\Delta G^\circ = -RT \ln K^{\circ d}, \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

$$-RT \ln K^{\circ d} = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

$$\ln (q_e / C_e) = (\Delta S^\circ / R) + (-\Delta H^\circ / R) 1/T \quad (8)$$

Where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), C is a constant and T is the absolute temperature. The distribution ratio (K_d) for calculating ΔG° must be a dimensionless parameter, so ΔG° was calculated according to the method reported by XUEYONG and XIN [28].

A straight line with a slope of $(-\Delta H^\circ/R)$ is produced by plotting $\ln K_d$ against $1/T$, as illustrated in Fig. 6.

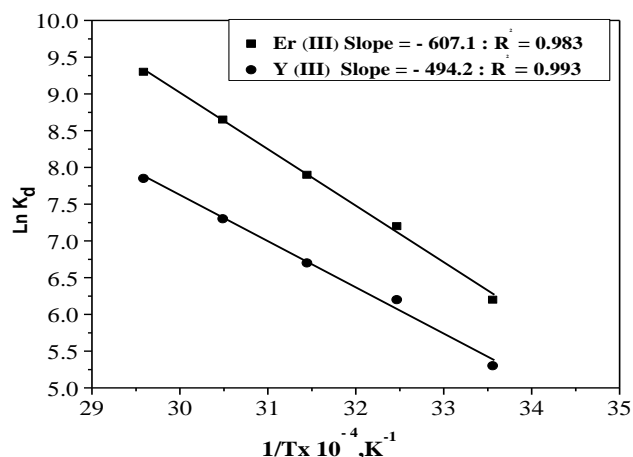


Fig. (6): Relation between ($\ln K_d$) and ($1/T$) for the sorption of Er(III) and Y(III) from phosphate medium onto Am-IR120 resin.

Table 1 shows the values of ΔG° , ΔH° , and ΔS° derived from the aforementioned formulae. Negative ΔG° values for both studied metals indicated that the sorption processes are feasible and spontaneous. The endothermic nature of the sorption process of Er(III) and Y(III) is indicated by the positive values of ΔH° whilst the increase in the system's randomness is demonstrated by positive values of ΔS° .

Table (1): Thermodynamic parameters for the sorption of Er(III) and Y(III) with Am-IR120 from 4.0 mol/L phosphoric acid.

Thermodynamic parameter	Er(III)	Y(III)
Enthalpy change (ΔH°), kJ mole ⁻¹	5.05	4.11
Free energy change (ΔG°), kJ mole ⁻¹	-61.26	-50.57
Entropy change (ΔS°), J mole ⁻¹ K ⁻¹	222.52	183.48

3- Sorption isotherm

The most popular mathematical models used for the description of the adsorption process are the Freundlich and Langmuir isotherms.

3.1. Freundlich isotherm model

This model is expressed as:

$$q_e = K_f C_e^{1/n} \quad [\text{m/g}] \quad (9)$$

This expression can be linearized to give [29]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad [\text{m/g}] \quad (10)$$

The graph in Figure 7(a) shows the relationship between $\log q_e$ (mg/g) and $\log C_e$ (mg/L). The adsorption intensities (n) and capacities (K_f) for Er (III) and Y (III)

were calculated based on the slope and intercept of the plots in Fig. (7a) and shown in Table 2. For both metal ions under study, the Freundlich isotherm slope is smaller than 1, with values of $1 > (1/n) > 0$. This indicates that the various metal ions studied have favorable adsorption on the Am-IR120. However, this model does not support the experimental capacity for the examined metal ions as the model's K_f values produced are significantly lower than the experimental values (Table 2). therefore supporting the reported experimental capacity for various metal ions. Therefore, even though its data support the linearity of the experimental results with large values of R^2 , the Freundlich model does not fully explain the experimental results for these elements.

3.2. Langmuir isotherm model

According to the following equation, the monolayer adsorption capacity, Q_0 (mg/g), was determined [30]:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0} \right) b + \left(\frac{1}{Q_0} \right) C_e \quad [\text{g/L}] \quad (11)$$

Figure 7(b) shows the C_e/q_e plot against C_e for Er (III) and Y (III) sorption. The monolayer adsorption capacity

Q_0 (mg/g) and Langmuir constant (b) of the metal ions that were studied were determined from the slope and intercept of the plot and are shown in Table 2.

The equilibrium parameter, RL , is a dimensionless constant that represents one of the essential characteristics of the Langmuir isotherm model. It is provided by the formula below.

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

Where b is a constant obtained from the above equation.

Table 2 displays RL values that were calculated using the Langmuir model. Am-IR120 exhibited high favorable sorption of Er (III) and Y (III) at all studied concentrations as indicated by the RL values which were determined to be <1.0 and >0 .

Also, it was found that the experimentally determined sorption capacities for the investigated elements were comparable to the estimated sorption capacities obtained using the Langmuir model, as shown in Table 2. This supports the Langmuir model's validity as a theoretical explanation for the observed sorption data.

Table (2): Langmuir and Freundlich parameters for sorption of Er (III) and Y (III) onto Am-IR120.

Metal ions	Freundlich Parameters			Langmuir parameters			
	K_f (mg/g)	n	R^2	Q_0 , (mg/g)	b , (ml/mg)	R_L	R^2
Er (III)	1.51	5.71	0.83	3.48	0.201	0.047	0.999
Y (III)	1.23	6.58	0.88	2.67	0.15	0.063	0.999

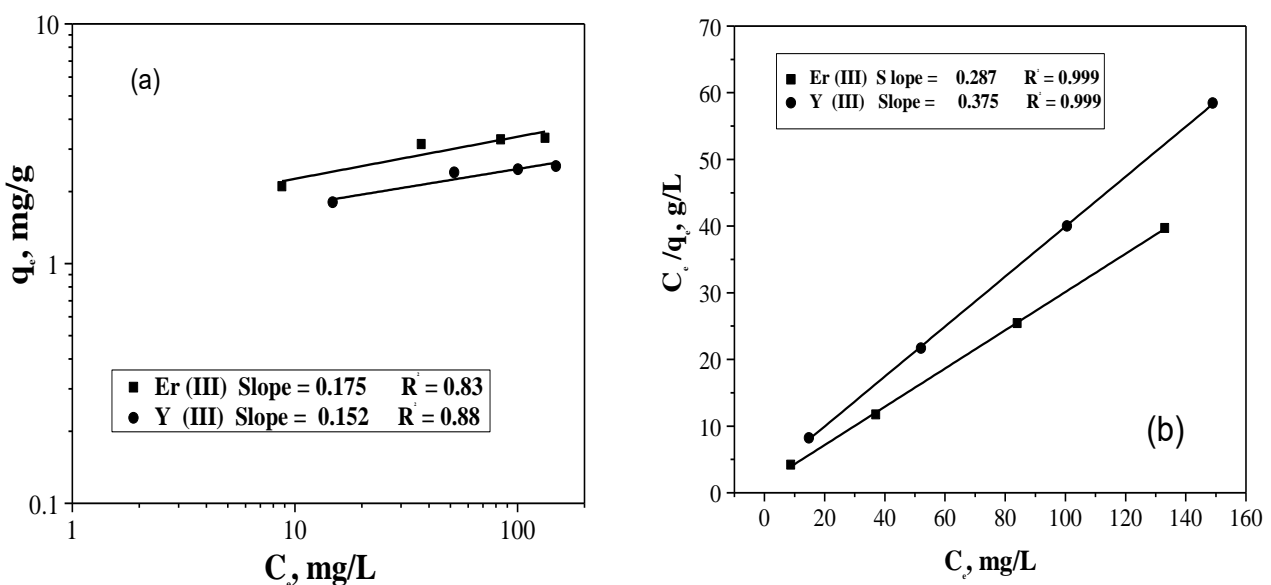


Fig. (7): Freundlich (a) and Langmuir (b) isotherms for the sorption of Er (III) and Y (III) onto Am-IR120 resin at 25°C.

4- Desorption of metal ions

Desorption of the adsorbed metal ions is very important for the recovery of adsorbed elements, the ability to separate elements, and the possibility of reusing the adsorbents. The desorption of Er (III) and Y (III) from the loaded Am-IR120 resin was tested. For this aim, a number of reagents were attempted at varying concentrations, including HNO₃, HCl, H₂SO₄, sodium acetate, sodium carbonate, citric acid, ammonium carbonate, and sodium sulfate. It can be seen from Table 3 that desorption with HNO₃, HCl, sodium acetate and sodium carbonate was ineffective. For Er(III) 1.0 mol/L of citric acid and H₂SO₄ are the most effective eluting agents. While 1.0 mol/L sodium sulfate is the best one for Y(III). 1.0 mol/L citric acid is good from a separating perspective.

For recovery and separation of Er (III) and Y (III) from the saturated Am-IR120, the desorption was carried out in two steps: the first one with 1.0 mol/L citric acid followed by desorption of the same resin with 1.0 mol/L Sodium sulfate in the second step, Table 4. As can be seen the overall elution of Er(III) with 1.0 mol/L citric in 3-stages was about 79%. While 65.9% elution of Y(III) was achieved with 1.0 mol/L Sodium sulfate in three stages.

Table (3): Desorption of Er (III) and Y (III) from loaded Am-IR120resin.

Eluting agent	Desorption efficiency, (DE %)	
	Er (III)	Y (III)
HNO ₃ (mol/L)		
1.0	0	0
HCl (mol/L)		
1.0	4.0	0
H ₂ SO ₄ (mol/L)		
1.0	29.9	8.3
Sodium acetate (mol/L)		
1.0	0	0
Sodium carbonate (mol/L)		
1.0	0	0
Citric acid (mol/L)		
1.0 (pH=3.0)	48.3	3.0
0.5	27.9	13.1
0.1	19.3	17.7
Ammonium carbonate (mol/L)		
1.0	3.6	0
Sodium sulfate (mol/L)		
1.0	16.1	35.9
0.5	11.1	21.0
0.1	5.9	15.3

Table (4): Recovery and separation of Er (III) and Y (III) from loaded Am-IR120 resin.

	Desorption efficiency, (DE %)			
	First step Citric acid (1.0 mol/L)			
	Stage-I	Stage-II	Stage-III	Total
Er (III)	48.3	20.0	10.7	79.0
Y (III)	3.0	1.7	0.7	5.4
Second step Sodium sulfate (1.0 mol/L)				
Er (III)	3.4	2.1	1.0	6.5
Y (III)	35.9	18.3	11.7	65.9

CONCLUSION

The sorption of Y(III) and Er(III) from 4.0 mol/L phosphoric acid using a cheap commercially available strongly acidic cation exchanger (Amberlite IR-120) has been performed. It was concluded that the sorption of metal ions decreases with increasing H_3PO_4 concentration and increases as the V/m ratio decreases. The thermodynamic results demonstrated that the sorption process is an endothermic and spontaneous process and the positive value of ΔS° shows an increase in the randomness of the system. The equilibrium sorption isotherms for Y(III), and Er(III) sorption fitted with the Langmuir model. The separation of Er(III) and Y(III) was achieved by desorption of loaded Am-IR120 with 1.0 mol/L citric acid followed by 1.0 mol/L sodium sulfate. Compared to other adsorbents used in the extraction and separation of REEs from phosphoric acid like SQS-6 [24], Amberlite IR-120 showed high efficiency in the separation of Y(III), and Er(III) besides its lower price and availability.

ACKNOWLEDGMENTS

This research is funded by the Egyptian Atomic Energy Authority and did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

- [1] Jarvis, I., Burnett, W. C., Nathan, Y., Almbaydin, F. S. M., Attia, A. K. M., Castro, L. N., & Zanin, Y. N. (1994). Phosphorite geochemistry: state-of-the-art and environmental concerns. *Eclogae Geologicae Helvetiae*, 87(3), 643-700.
- [2] Abu Elgoud, E. M., Ismail, Z. H., Ahmad, M. I., El-Nadi, Y. A., Abdelwahab, S. M., & Aly, H. F. (2019). Sorption of Lanthanum (III) and Neodymium (III) from Concentrated Phosphoric Acid by Strongly Acidic Cation Exchange Resin (SQS-6). *Russian journal of applied chemistry*, 92, 1581-1592.
- [3] Gupta, C.K., and Krishnamurthy, M.N., *Extractive Metallurgy of Rare-Earths*, London: CRC Press, 2005.
- [4] Emsbo, P., McLaughlin, P. I., Breit, G. N., du Bray, E. A., & Koenig, A. E. (2015). Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis?. *Gondwana Research*, 27(2), 776-785..
- [5] Liang, H., Zhang, P., Jin, Z., & DePaoli, D. (2017). Rare-earth leaching from Florida phosphate rock in wet-process phosphoric acid production. *Minerals & Metallurgical Processing*, 34, 146-153.
- [6] Aydin, I., Aydin, F., Saydut, A., Bakirdere, E. G., & Hamamci, C. (2010). Hazardous metal geochemistry of sedimentary phosphate rock used for fertilizer (Mazıdag, SE Anatolia, Turkey). *Microchemical Journal*, 96(2), 247-251.
- [7] Zhang, P. (2014). Comprehensive recovery and sustainable development of phosphate resources. *Procedia Engineering*, 83, 37-51.
- [8] Zulkipli, N. F., Muhammad, A. R., Batumalay, M., Rosol, A. H., Altuncu, A., Durak, F. E., & Harun, S. W. (2022, July). Yttrium Oxide (Y_2O_3) as a Pulse Initiator in a Mode-Locking Erbium-Doped Fiber Laser. In *Photonics* (Vol. 9, No. 7, p. 486).
- [9] Voncken, J. H. L., & Voncken, J. H. L. (2016). Applications of the rare earths. The rare earth elements: an introduction, 89-106.
- [10] Sakr, A. K., Cheira, M. F., Hassanin, M. A., Mira, H. I., Mohamed, S. A., Khandaker, M. U., & Hanfi, M. Y. (2021). Adsorption of yttrium ions on 3-amino-5-hydroxypyrazole impregnated bleaching clay, a novel sorbent material. *Applied Sciences*, 11(21), 10320.
- [11] Awwad, N. S., Gad, H. M. H., Ahmad, M. I., & Aly, H. F. (2010). Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk. *Colloids and Surfaces B: Biointerfaces*, 81(2), 593-599.
- [12] Fattah, N. A. A. A. (2016). Potentiality of alcoholic purification of Abu-Zaabal impure phosphoric acid for selective ion exchange recovery of uranium. *J Chem Eng Process Technol*, 7, 1-9.
- [13] Crock, J. G., Lichte, F. E., & Wildeman, T. R. (1984). The group separation of the rare-earth elements and yttrium from geologic materials by cation-exchange chromatography. *Chemical Geology*, 45(1-2), 149-163.
- [14] Kopyrin, A. A., Afonin, M. A., Fomichev, A. A., & Bakharev, M. S. (2008). Simulation of nonequilibrium extraction of rare-earth elements with liquid membranes: I. Generalized mathematical model. *Radiochemistry*, 50, 281-285.

- [15] Chitra, K. R., Gaikwad, A. G., Surender, G. D., & Damodaran, A. D. (1997). Studies on ion transport of some rare earth elements through solvating extractants immobilised on supported liquid membrane. *Journal of membrane science*, 125(2), 257-268.
- [16] González, C. H., Cabezas, A. J. Q., & Díaz, M. F. (2005). Preconcentration and determination of rare-earth elements in iron-rich water samples by extraction chromatography and plasma source mass spectrometry (ICP-MS). *Talanta*, 68(1), 47-53.
- [17] Ignatova, S. N., Maryutina, T. A., Spivakov, B. Y., & Karandashev, V. K. (2001). Group separation of trace rare-earth elements by countercurrent chromatography for their determination in high-purity calcium chloride. *Fresenius' journal of analytical chemistry*, 370, 1109-1113.
- [18] Tsuruta, T. (2007). Accumulation of rare earth elements in various microorganisms. *Journal of Rare Earths*, 25(5), 526-532.
- [19] Chua, H. (1998). Bio-accumulation of environmental residues of rare earth elements in aquatic flora *Eichhornia crassipes* (Mart.) Solms in Guangdong Province of China. *Science of the total environment*, 214(1-3), 79-85.
- [20] Hérès, X., Blet, V., Di Natale, P., Ouattou, A., Mazouz, H., Dhiba, D., & Cuer, F. (2018). Selective extraction of rare earth elements from phosphoric acid by ion exchange resins. *Metals*, 8(9), 682.
- [21] Zhazira, B., Bagdaulet, K., Nina, L., & Kaisar, K. (2021). Sorption Extraction of Rare Earth Metals from Wet-Process Phosphoric Acid. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 83(1), 140-152.
- [22] Konkova, T. V., Quynh, T. N., & Papkova, M. V. (2018). Sorption of rare earth metals, iron and aluminum from phosphoric acid by sulfocationites. *Tsvetnye Metally*, 9, 54.
- [23] Reddy, B. R., & Kumar, J. R. (2016). Rare earths extraction, separation, and recovery from phosphoric acid media. *Solvent Extraction and Ion Exchange*, 34(3), 226-240.
- [24] Abu Elgoud, E. M., Ismail, Z. H., Ahmad, M. I., El-Nadi, Y. A., Abdelwahab, S. M., & Aly, H. F. (2022). Solid-Liquid Extraction of Rare Earth Elements Ce (IV), Pr (III), Er (III), and Y (III) from Concentrated Phosphoric Acid Solutions Using Strongly Acidic Cation Exchange Resin (SQS-6). *Russian Journal of Applied Chemistry*, 95(4), 602-615.
- [25] Marczenko, Z., "Spectrophotometric Determination of Elements", 1976, Ellis Horwood Ltd., Poland.
- [26] Radhika, S., Nagaraju, V., Kumar, B. N., Kantam, M. L., & Reddy, B. R. (2012). Solid-liquid extraction of Gd (III) and separation possibilities of rare earths from phosphoric acid solutions using Tulsion CH-93 and Tulsion CH-90 resins. *Journal of Rare Earths*, 30(12), 1270-1275.
- [27] Kumar, B. N., Radhika, S., & Reddy, B. R. (2010). Solid-liquid extraction of heavy rare-earths from phosphoric acid solutions using Tulsion CH-96 and T-PAR resins. *Chemical Engineering Journal*, 160(1), 138-144.
- [28] Zhou, X., & Zhou, X. I. N. (2014). The unit problem in the thermodynamic calculation of adsorption using the Langmuir equation. *Chemical Engineering Communications*, 201(11), 1459-1467.
- [29] Freundlich, H., *Colloid and Capillary Chemistry*, London: Methuen and Co. Ltd., 1926.
- [30] Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9), 1361-1403.