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Removal of lanthanum and gadolinium from nitrate medium using Aliquat-336 impregnated onto Amberlite XAD-4

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Abstract

Aliquat-336 in benzene was supported on Amberlite XAD-4 crosslinked polystyrene resin. The use of XAD-4 impregnated with Aliquat-336 resin for removal of lanthanum(III) and gadolinium(III) from nitrate medium was carried out using batch technique. Various parameters affecting the uptake of these metal ions such as contact time, metal ion concentrations, *V/m* and pH value were separately studied. Effect of temperature on the equilibrium distribution values has been studied to evaluate the changes in standard thermodynamic quantities. A comparison of kinetic models applied to the adsorption rate data was evaluated for Lagergren first order, the pseudo second order and Morris–Weber kinetic models. From the results, both pseudo second order and intraparticle diffusion models were found to best correlate the experimental rate data. The capacity of the impregnated resin for both lanthanum(III) and gadolinium(III) was found to be 4.73 and 4.44 mg/g. From the results, impregnation of Aliquat-336 onto Amberlite XAD-4 provides an efficient impregnated resin for the removal of lanthanum(III) and gadolinium(III) from 0.1 M nitrate aqueous solution.

Keywords: Removal; Lanthanides; Nitrate medium; Impregnation; XAD-4; Aliquat-336

1. Introduction

The increase in industrial activities and nuclear applications over the past decades has contributed significantly to the development of metal recovery and separation techniques. Solvent impregnated resin (SIR) has been shown to an effective media for recovery and selective separation of metal ions from aqueous solutions [1–3]. Development of impregnated resins is considered as a link between solvent extraction and ion exchange technologies and plays an important role in separation science [4]. Impregnated resins are characterized by selectivity of dissolved extractants with operational simplicity of solid ion exchange equipment. Also, SIR are easily prepared and the wide choice of reagents of desired selectivity is available. The macroporous (macroreticular) polymeric resins, are the most suitable to incorporate large amounts of extractants due to the high specific area, high mechanical strength and rather low solvent swelling during the impregnation process. They are also, characterized by their organophilic nature owing to their hydrophobic surface and macroporous structure [5].

Lanthanide elements have gained a great attention owing to their unique properties and wide range of applications. These elements and their compounds have found a variety of applications especially in metallurgy, ceramic industry and nuclear fuel control [6,7]. For example, gadolinium oxide, one of its largest uses in nuclear power reactors is as shielding and fluxing devices [8]. Lanthanum(III) and gadolinium(III) are considered as fission products, they may be leaked to the environment and cause risks. So they are considered as hazardous materials. The sorption of lanthanum(III), neodymium(III), terbium(III), thorium(IV) and uranium(VI) on Amberlite XAD-4 resin loaded with bicine ligands was investigated [9]. The authors found that the trace amount of these metal ions were quantitatively retained on the resin and recovered by eluting with 1 M hydrochloric acid. Various studies on the synthesis, characterization and sorption properties of polymeric materials have been published. The sorption behavior and mechanism of a novel chelate resin, imino-diacetic acid resin (IDAAR), for Yb(III) has been investigated in HAc-NaAc medium. The sorption capacity of this resin towards Yb(III) is 187 mg/g resin at 298 K [10]. A new chelating

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agent bis[(*O*-carbomethoxy)phenoxy]ethylamine has been synthesized using a facile microwave induced process. This ligand was appended onto a crosslinked polystyrene resin XAD-4 and adsorption properties of La(III), Nd(III) and Sm(III) towards this resin were studied [11]. El-Dessouky and Borai [12] studied the extraction chromatography of thorium ion by solid phase impregnated resins containing bi-functional organic extractant. They found that the impregnated resin containing CYANEX-301 and 15C5 can be utilized for selective separation and preconcentration of thorim ion from nitrate medium in the presence of several interfering ions.

In previous work [13] recovery and selective separation of Cu(II) and Cd(II) from nitrate solution by XAD-7 which was loaded with CYANEX-301 in chloroform was studied through batch and column techniques. From the results it was found that this impregnated resin is efficient for recovery and separation of both Cu(II) and Cd(II). Extension to this field, this work is directed to assess the possible use of solvent impregnated resin, XAD-4 impregnated with Aliquat-336 in benzene, for removal of lanthanum(III) and gadolinium(III) from nitrate medium. The parameters affecting the adsorption properties of these metals as contact time, initial metal concentrations, pH, *V/m* and temperature were investigated.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were of analytical grade. Lanthanum and gadolinium oxides were of Fluka products. Sodium nitrate was from BDH and Arsenazo (III) was supplied by Merck. Aliquat-336 (tri-*n*-octylmethylammonium chloride) was obtained from Merck. Amberlite XAD-4 resin was obtained from Rohm and Hass Co., USA. Amberlite XAD-4 was kept in contact with chloroform–water solution to remove preservative and residual monomers species. The resin was then filtered, dried at room temperature for 24 h and kept in a desiccator for further usage.

2.2. Impregnation process

The impregnation process was carried out by dry method which is the most widely used [14]. The impregnation solution was 50 ml of 5% Aliquat-336 in benzene. The sorbent was prepared by mixing 25 g of purified support with 50 ml of the extractant solution. The resulting slurry is gently stirred for 2 h and benzene was then removed by evaporation at ambient room temperature ($25 \pm 1\,^{\circ}C$), then the resin was dried at 70 °C.

2.3. Procedure

Lanthanum and gadolinium solutions were prepared by dissolution of certain weights of their oxides in nitric acid, heated to dryness, washed several times with double distilled water and dissolved in 0.1 M sodium nitrate to obtain solutions containing 1.0 g/l for each metal. Lanthanum and gadolinium concentrations were determined spectrophotometrically by measuring their maximum absorbance at 652 nm by Arsenazo (III) method [15] using Shimadzu double beam recording spectrophotometer model 160A.

Batch sorption experiments were performed by shaking 0.05 g of the impregnated resin with 5 ml of the metal solution in a thermostated shaker bath adjusted at $25 \pm 1\,^{\circ}C$. The pH of each solution was adjusted to values ranging from 1.5 to 6.5 with dilute solutions of ammonium hydroxide and nitric acid. The amount of metal uptake was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of metal retained in the resin q_e (mg/g) was calculated using the relation:

$$q_e = C_o - C_e \times \frac{V}{M} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mg/L) of metal ions in solution, respectively, V is the volume of solution (l) and M is the weight (g) of the adsorbent.

The distribution coefficient (K_d) of metal ions between the aqueous phase and the resin phase is calculated from the relation:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{M} \quad (2)$$

3. Results and discussion

The factors affecting the adsorption of both lanthanum(III) and gadolinium(III) by Aliquat-336/Amberlite XAD-4 impregnated resin studied in this work are: the contact time, the hydrogen ion concentration, *V/m* ratio, metal ion concentration in the aqueous phase and temperature. Untreated XAD-4 and liquid–liquid extraction were tested to compare them with the impregnated resin. The results are shown in Table 1, whereas the impregnation of XAD-4 with Aliquat-336 in benzene enhanced the removal percent of both lanthanum(III) and gadolinium(III).

3.1. Contact time

The adsorption kinetic of lanthanum(III) and gadolinium(III) on XAD-4 impregnated by Aliquat-336 resin were studied as a function of contact time in the range 1.0–60 min. As shown in Fig. 1, the adsorption of metal ions increased with time and attained equilibrium after 30 and 15 min for both lanthanum(III) and gadolinium(III), respectively. The kinetic data indicates that there is no significant change in the distribution ratio after this time up to 60 min.

Table 1
Removal percent of lanthanum(III) and gadolinium(III) by different techniques

Metal ions	Solvent extraction	Removal percent	
		Ion exchange (XAD-4)	Impregnated XAD-4
La(III)	10.2	42.4	94.6
Gd(III)	8.7	34.3	88.8

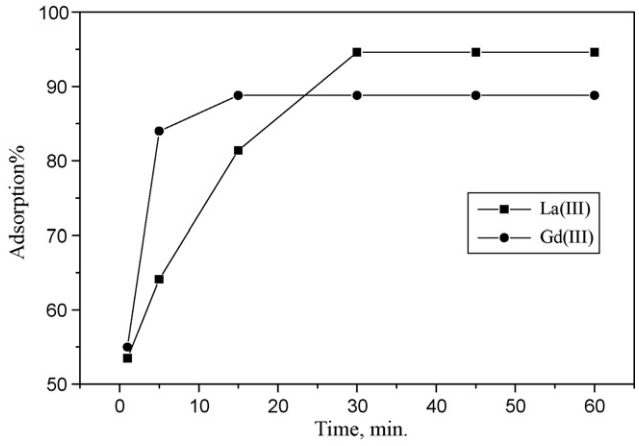

Fig. 1. Effect of contact time on the adsorption of La(III) and Gd(III) onto Aliquat-336 impregnated XAD-4 resin.

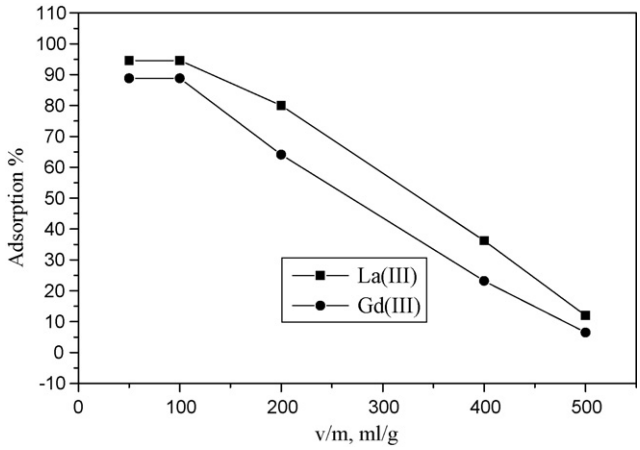

Fig. 3. Effect of *V/m* ratio on the adsorption of La(III) and Gd(III) on Aliquat-336 impregnated XAD-4 resin.

3.2. Effect of pH

The adsorption of lanthanum(III) and gadolinium(III) onto the impregnated resin from nitrate medium and *V/m* ratio 100 was studied in the pH range from 1.5 to 6.5 and the results obtained are shown in Fig. 2. From the figure it was observed that the adsorption of lanthanum(III) and gadolinium(III) on the resin is low in acidic solutions and it increases by increasing the pH. The maximum adsorption were attained at pH 5.5 and 6.5 for gadolinium(III) and lanthanum(III), respectively. The chemical formula for Aliquat-336 is $CH_3N[(CH_2)_7CH_3]_3Cl^-$, it contains a chlorine molecule which may exist as a negative chloride ion. Lanthanum(III) and gadolinium(III) ions would have to diffuse across a surface liquid film, they diffuse through the resin particle and finally react with the Aliquat-336 extractant in the SIR. The chloride species form complexes with metal ions to neutralize their charges and simultaneously sorbed onto XAD-4 to satisfy the stable coordination number 8. At low pH values, hydrogen ions found in the acidic solution compete the metal ions so, the adsorption of the metal ions is low and by increasing pH value the adsorption increases.

3.3. Effect of V/m ratio

The influence of the *V/m* ratio on the adsorption of lanthanum(III) and gadolinium(III) was studied at constant temperature ($25 \pm 1\,^{\circ}C$). In this respect different ratios (ml/g) were taken from 25 to 500 to evaluate the optimum solution volume per resin weight that could be used for a high adsorption capacity. Fig. 3 represent the relation between *V/m* (ml/g) and adsorption percent of both lanthanum(III) and gadolinium(III). It is noted from the results that the adsorption percent of both lanthanum(III) and gadolinium(III) increases as *V/m* decreases from 500 to 100 ml/g and then remains constant with further decrease of *V/m* up to 25 ml/g. Thus, the optimum *V/m* ratio was kept at 100 ml/g during all experiments.

3.4. Effect of metal ions concentration

The adsorption percent of lanthanum(III) and gadolinium(III) from nitrate solution containing metal ion concentration in the range 50–1000 ppm at pH value 5.5 is shown in Fig. 4. The results show that the maximum adsorption of both lanthanum(III) and gadolinium(III) is obtained at concentration of

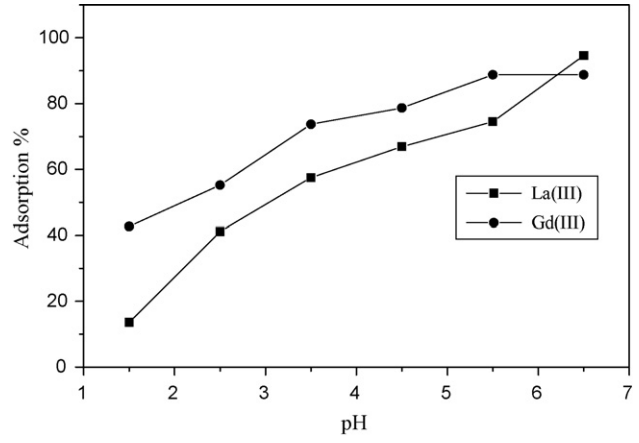

Fig. 2. Effect of pH on the adsorption of La(III) and Gd(III) onto Aliquat-336 impregnated XAD-4 resin.

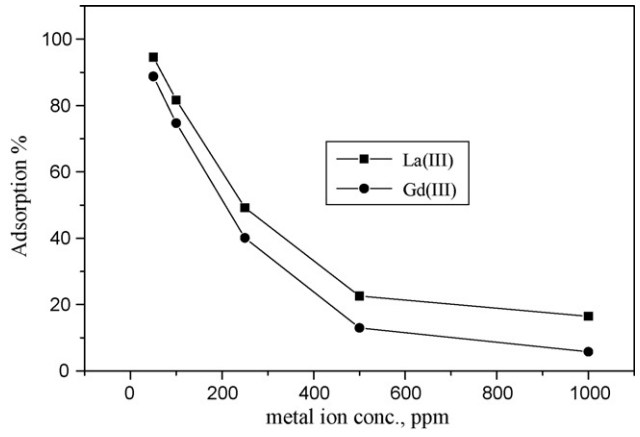

Fig. 4. Effect of metal ion concentration on the adsorption of La(III) and Gd(III) onto Aliquat-336 impregnated XAD-4 resin.

50 ppm and a gradual decrease in the adsorption was observed with the increase in the concentration of both metal ions. The loading capacity of the resin for both lanthanum(III) and gadolinium(III) were calculated by Eq. (1). The maximum loading capacity of XAD-4 impregnated by Aliquat-336 for lanthanum(III) and gadolinium(III) were found to be 4.73 and 4.44 mg/g, respectively.

3.5. Effect of temperature

The effect of temperature on the adsorption of lanthanum(III) and gadolinium(III) from nitrate solution by impregnated resin Aliquat-336/XAD-4 at pH 5.5, *V/m* ratio 100 ml/g and concentration of metal ions 50 ppm is studied. From the results it is clear that increasing the temperature from 25 to 65 °C leads to decrease in the adsorption of the two elements.

The van't Hoff equation [16] given below, can be used to calculate the enthalpy changes associated with the adsorption process of these metal ions.

$$\log K_d = \frac{\Delta H^\circ}{2.303R} \times \frac{1}{T} + C \quad (3)$$

where R is the universal gas constant, K_d the distribution coefficient, T is the absolute temperature and C is a constant.

The plots of K_d vs. $1/T$ for the adsorption of lanthanum(III) and gadolinium(III) ions are shown in Fig. 5. A straight line was observed, from which ΔH° (the enthalpy variation) can be deduced according to the following equation:

$$\Delta H^\circ = -2.303R \times \text{Slope} \quad (4)$$

where R is the universal gas constant. The free energy variation, ΔG° was also calculated based on the logarithmic value of the distribution ratio ($\log K_d$) at 25 °C.

$$\Delta G^\circ = -2.303RT \log K_d \quad (5)$$

where T is the absolute temperature. The entropy variation, ΔS^0 was obtained from ΔG^0 and ΔH^0 as follows:

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

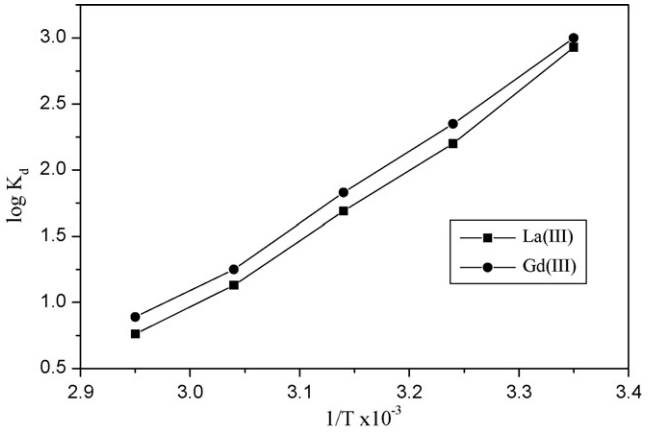

Fig. 5. Variation between $\log K_d$ with $1/T$ for the sorption of La(III) and Gd(III) ions from nitrate medium onto Aliquat-336 impregnated XAD-4.

Table 2
Thermodynamic parameters for the adsorption of lanthanum(III) and gadolinium(III) from nitrate medium by Aliquat-336/XAD-4

Metal ions	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)	ΔS^0 (J/mol K)
La(III)	−102.6	−16.71	−260.8
Gd(III)	−94.2	−16.48	−286.2

The thermodynamic parameters of the sorption of lanthanum(III) and gadolinium(III) were calculated and given in Table 2. The negative values of ΔH° indicate the exothermic character of the solid phase extraction and sorption process, but the negative value of ΔG° indicates the spontaneous nature of both lanthanum(III) and gadolinium(III) sorption. The negative ΔS° value suggests that the system exhibit random behavior.

As recommended [17] an ion exchange process is classified as film-diffusion controlled when $E_a < 16.7$ kJ/mol, particle-diffusion controlled when E_a below 42 kJ/mol and reaction controlled when E_a is equal to 50.2 kJ/mol. Calculation of the activation energy of the impregnated resin containing XAD-4 loaded with Aliquat-336 from the slope of the straight line obtained by applying Arrhenius equation shows that E_a values are equal to 31.7 and 38.2 kJ/mol for gadolinium and lanthanum, respectively, which confirmed that the reaction is mainly particle diffusion controlled.

3.6. Sorption isotherm

The experimental results obtained for the adsorption of lanthanum(III) and gadolinium(III) on Aliquat-336 impregnated onto XAD-4 resin at room temperature 25 ± 1 °C under the optimum conditions of contact time (30 min) and *V/m* ratio of 100 were found to obey Freundlich adsorption isotherm. The Freundlich equation written as follows:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where K_f and n are the Freundlich constants, which represent the adsorption capacity and the intensity of adsorption, respectively. The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of adsorbent (q_e) and the concentration of the metal in solution at equilibrium (C_e). Fig. 6 shows the plot of $\log q_e$ (mg/g) vs. $\log C_e$ (mg/l), the linear form of the plot indicating the applicability of the classical adsorption isotherm to this system. The fitting of the data of Freundlich isotherm suggests that, the sorption process is not restricted to one specific class of sites and assumes surface heterogeneity [18]. The adsorption capacities (K_f) and the adsorption intensities (n) for lanthanum(III) and gadolinium(III) ions are calculated from the intercept and the slope of the plots and are listed in Table 3. The slope of Freundlich isotherm for both metal ions is less than 1, n values show favorable adsorption of metal on Aliquat-336/XAD-4 resin. The sorption capacity values which was calculated using relation (1) is different from that obtained from Freundlich isotherm (Table 3). This difference is due to that K_f is the relative adsorption capacity indicative to the selectivity order of the investigated metal ions. Higher values for K_f indicate higher affinity for lanthanum(III) and gadolin-

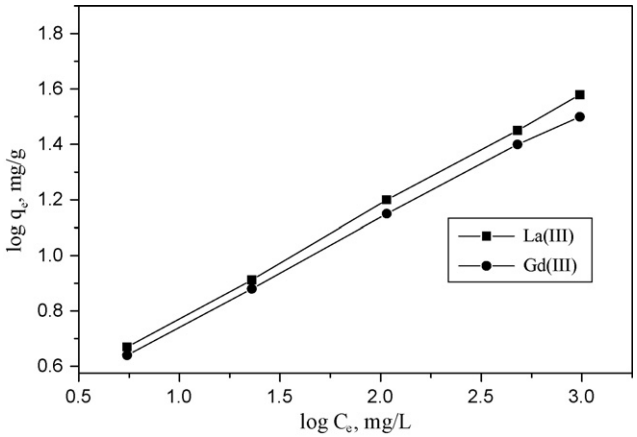

Fig. 6. Freundlich isotherm for the sorption of La(III) and Gd(III) onto Aliquat-336 impregnated XAD-4 resin.

Table 3
Parameters of Freundlich isotherm for sorption of lanthanum(III) and gadolinium(III) ions onto Aliquat-336/XAD-4 resin

Metal ions	Parameters of Freundlich model			Apparent capacity (experimental)
	K_f (mg/g)	n	R^2	q_e (mg/g)
La(III)	3.29	3.09	0.998	4.73
Gd(III)	2.29	2.63	0.999	4.44

ium(III). The apparent capacity (q_e) is a quantitative value for the capacity power for the Aliquat-336/XAD-4 resin and follows the same order.

The distribution of each metal ion between the solid–liquid interface at equilibrium has been applied to Langmuir isotherm model. The Langmuir isotherm equation could be written as:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^\circ b}\right) + \left(\frac{1}{Q^\circ}\right) C_e \quad \text{(linear form)} \tag{8}$$

where q_e is the amount of solute sorbed per unit weight of adsorbent (mg/g). C_e is the equilibrium concentration of the solute in the bulk solution (mg/L). Q° is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption ($b \propto e^{-\Delta G/RT}$).

The Langmuir isotherm for sorption of lanthanum(III) and gadolinium(III) ions on the impregnated resin are presented in Fig. 7. The straight line obtained from the sorption isotherm indicates that sorption of both ions fit with Langmuir isotherm. Table 4, illustrate the calculated Langmuir parameters for sorption of lanthanum(III) and gadolinium(III), and the correlation coefficient values (R^2) for both ions. The monolayer sorption

Table 4
Langmuir parameters for sorption of lanthanum(III) and gadolinium(III) ions from nitrate medium onto Aliquat-336/XAD-4 resin

Metal ion	Parameters for Langmuir model		
	Q° (mg/g)	b (L/g)	R^2
La(III)	11.49	0.089	0.9999
Gd(III)	15.87	0.092	0.9999

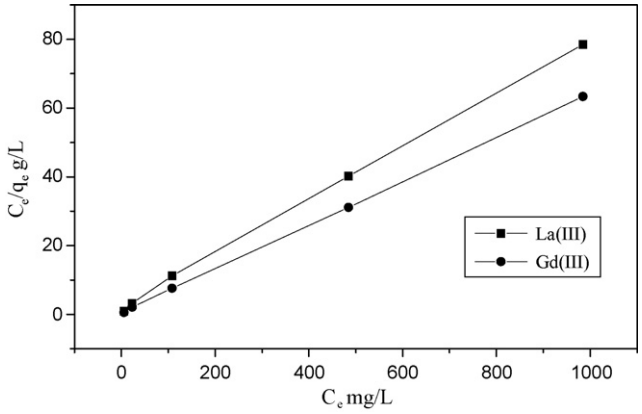

Fig. 7. Langmuir isotherm for sorption of La(III) and Gd(III) onto impregnated XAD-4 by Aliquat-336.

capacity (Q°) for lanthanum(III) and gadolinium(III) ions was found to be 11.49 and 15.87, respectively.

Although the Freundlich and Langmuir constants K_f and Q° have different meanings, they lead to the same conclusion about the correlation of the experimental data of the sorption model. The basic difference between K_f and Q° is that Langmuir isotherm assumes sorption-free energy independent of both the surface coverage and the formation of monolayer whereas the solid surface reaches saturation. While, the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate. In conclusion, Q° is the monolayer sorption capacity, while K_f is the relative sorption capacity or sorption power [19].

3.7. Kinetic modeling

Most sorption processes take place by a multistep mechanism comprising (i) diffusion across the liquid film surrounding the solid particles, (ii) diffusion within the particle itself assuming a pore diffusion mechanism and (iii) physical or chemical adsorption at active sites [20].

The transient behavior of the batch sorption process of each studies metal ion at different temperatures was analyzed using Lagergren first order kinetics model and the pseudo second order model [21,22]. The Legergren first order model was given by the equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{9}$$

where q_e and q_t are the concentrations of ion in the adsorbent at equilibrium and at time t, respectively, (mg/g) and k_1 is the pseudo first order rate constant (min^{-1}).

Plots of $\log(q_e - q_t)$ vs. t for both metal ions are shown in Fig. 8. Approximately, linear fits were observed for the two ions, during the first 30 min of shaking time, the first order rate constants K_{ad} were evaluated from the slope of linear plots obtained and found to be 0.078 and 0.274 min^{-1} for lanthanum(III) and gadolinium(III), respectively. The low correlation coefficients of 0.96 and 0.91 for lanthanum and gadolinium, respectively, confirm that it is not appropriate to use Lagergren kinetic model to predict the sorption kinetics of the studied ions onto Aliquat-336 impregnated XAD-4.

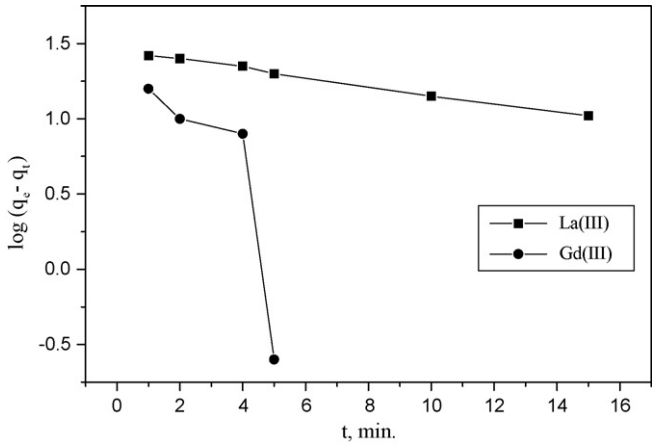

Fig. 8. Lagergren plots for the adsorption of La(III) and Gd(III) ions from nitrate medium onto Aliquat-336 impregnated XAD-4.

The kinetic data were further analyzed using the pseudo second order model; the linear form of this model is as follows [21]:

$$\frac{t}{q_e} = \frac{1}{h} + \frac{1}{q_e}t \tag{10}$$

where the initial sorption rate h (mg/g min) is given by $h = k_2 q_e^2$ and k_2 is the rate constant of pseudo second order equation (g/mg min).

The plots of t/q_t vs. t for both lanthanum(III) and gadolinium(III) ions sorption at 25 °C are presented in Fig. 9. The relations are linear and the values of the correlation coefficients (R^2), suggest a strong relationship between the parameters and explain that the process of sorption of each ion follows pseudo second order kinetics. The correlation coefficients, as shown in Table 5, has an extremely high value and the theoretical q_e values agree with the experimental ones. These results suggesting that the pseudo second order sorption mechanism is predominant and the over all rate of each ion controlled by the chemisorption process [21].

Other simplified model is also tested, at intensive stirring of the sorptive system, the intraparticle diffusion of the solute

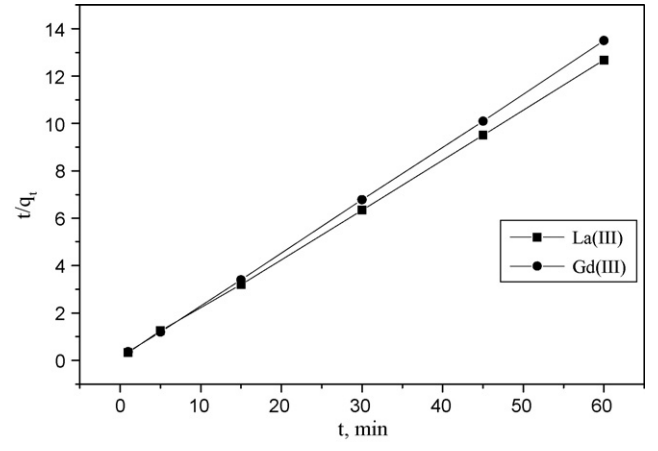

Fig. 9. Pseudo second order plots for the removal of La(III) and Gd(III) ions from nitrate solution by Aliquat-336/XAD-4.

Table 5
The calculated parameters of the pseudo second order kinetic model for the sorption of lanthanum(III) and gadolinium(III) ions onto Aliquat-336/XAD-4

Metal ions	q_e (mg/g)	h (mg/g min)	k_2 (g/mg min)	R^2
La(III)	4.9	2.58	0.1	0.999
Gd(III)	4.48	11.1	0.55	0.9999

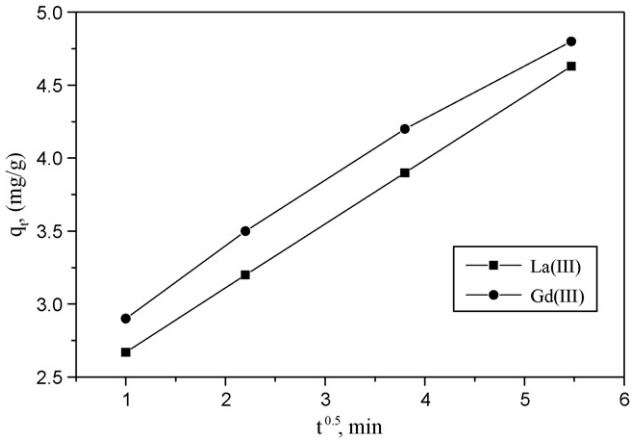

Fig. 10. Morris–Weber plots for the adsorption of La(III) and Gd(III) ions from nitrate solution onto Aliquat-336 impregnated XAD-4 resin.

sorbed from the solution into the sorbent pores could be a limiting step. In this study intraparticle diffusion (Morris–Weber) model [23,24] was used, the Morris–Weber equation is written as:

$$q_t = K_{ad}\sqrt{t} \tag{11}$$

where K_{ad} is the rate constant of intraparticle transport (mg/g min$^{0.5}$).

According to this model, plotting a graph of q_t vs. $\sqrt{t}$, should be linear if intraparticle diffusion is involved in the adsorption process. If these lines pass through the origin the intraparticle diffusion is the rate controlling step. Furthermore, such plots may also demonstrate a multilinearity [25]. As shown in Fig. 10, it indicated that the intraparticle diffusion was not the controlling step because it did not pass through the origin. The Morris–Weber relationship holds well for both lanthanum(III) and gadolinium(III) where the correlation coefficients (R^2) found to be 1.0 and 0.999. The values of K_{ad} were calculated from the slope of the linear plots obtained and found to be 0.43 and 0.42 for lanthanum(III) and gadolinium(III), respectively.

4. Conclusions

The application of Aliquat-336 loaded on XAD-4 for the sorption of lanthanum and gadolinium ions from aqueous nitrate solutions has been demonstrated in batch technique. The sorption of the investigated metal ions increases by increasing the contact time and decreasing by increasing *V*/*m* ratio and metal ion concentration. The sorption process is exothermic in nature. The equilibrium isotherms for sorption of the investigated metal ions have been modeled successfully using the Freundlich isotherm. Kinetic rate data have been tested for dif-

ferent kinetic model expressions and the data were successfully modeled using pseudo second order and Morris–Weber models. The numerical values of E_a obtained are <42 kJ/mol, indicating a diffusion-controlled process. From the results, impregnation of aliquat-336 onto Amberlite XAD-4 provides an efficient impregnated resin for the removal of lanthanum(III) and gadolinium(III) from 0.1 M nitrate aqueous solution.

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