La (III) Separation by Tri Octyl Phosphine Oxide (Cyanex 921) Based on Amberlite Xad-4 Chelating Resin

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Abstract
The novel core–shell type polymeric supports with accessible phosphorus groups were synthesised in the search for new reactive materials designed for the synthesis of functional resins. Amberlite XAD-4 adsorbent was impregnated with tri octyl phosphine oxides (Cyanex 921), which were then polymerized in the polymer carrier structure. The syntheses were evaluated by capturing FT-IR spectra, SEM micrographs, and analysing the sorption process. Batch studies were conducted to study the influence of some factors like pH, contact time, the metal ions concentration, and temperature on sorption efficiency of La (III) ions. The results showed that the optimum conditions were at pH equal to 0.5 and an equilibrium contact time of 30 min. According to the results of the sorption data analysis, the pseudo-second-order and Langmuir models were better fitted than the other estimated models. The sorption capacity of La (III) ions into impregnated resin as adsorbent martial was 54.25 mg g⁻¹. The results revealed that the used adsorbent has been used successfully as a promising material for the elimination and recovery of La ions from the aqueous solutions. The impregnated resin exhibits a high chemical stability, reusability and fast equilibration. Further, the above procedure has been successfully employed for the application of real sample.

Keywords Impregnation · Sorption · Lanthanum (III) · Amberlite XAD-4 · Cyanex 921 · Preconcentration

1 Introduction
Separation of REEs is a difficult task in metallurgy extraction. Because of the chemical similarity of REEs, the separation process necessitates a number of treatments, including the hydrometallurgy method. The extraction of REEs from ores is a complex and time-consuming process that includes beneficiation, decomposition of the mineral concentrate to extract REEs, and chemical processing that includes impurity removal and separation of individual REEs to produce a purified saleable product. The hydrometallurgical method consists of several processes, including (i) baking or cracking the REEs concentrate; (ii) leaching, neutralisation, and precipitation methods; and (iii) separation and purification processes that include solvent extraction and ion exchange [1].

The recovery of rare earth elements (REEs) from monazite mineral has been studied in our laboratory using a combination of pyrometallurgy and hydrometallurgy techniques, with acid leaching being one of the required steps [2–4].

Lanthanum is one of the most abundant rare earth elements, and its unique physical and chemical properties have piqued the interest of scientists. Lanthanum represents about 30% of the total amount of REEs used. It is one of the commonly utilized metals for making super alloys, catalysts, special ceramics, and condensers. Furthermore, the recovery of lanthanum is largely unexplored. As a result, it is critical to develop low-cost technologies for its removal and recovery [5].

Polystyrene (S) and divinyl benzene (DVB) copolymers are the most commonly used supports for the preparation of ion-exchange resins. A first step in the preparation of such materials is the copolymerization of styrene (S) and divinyl benzene (DVB) to form a crosslinked suspension copolymer, S/DVB. The method yields a material with transverse, extremely durable covalent bonds, resulting in polymeric beads that are resistant to any chemical environment [6].
Solvent impregnated resins (SIRs) have been demonstrated to be effective sorbents for the selective recovery of metal ions from aqueous solutions; however, commercial resin applications are limited to a few examples. The sorption equilibria of a diverse group of transition metals, metalloids, lanthanides, and actinides are studied in the case of synthetic SIRs typically prepared by the wet impregnation process [7].

Amberlite XAD (styrene-divinyl benzene copolymer) resins, as the copolymer backbone for the immobilisation of chelating ligands, have some physical advantages over other resins, such as porosity, uniform pore size distribution, high surface area, and chemical stability toward acids, bases, and oxidising agents. Adsorption of chelating ligands onto these supports or covalent coupling of the chelating moiety has been used to create polymeric chelating resins that are versatile, durable, have good loading capacity towards metals, have enhanced hydrophilicity, and can be used under a variety of conditions. As a result, the reaction of Amberlite XAD resin with appropriate chelating agents is widely used for separation and preconcentration [8].

EI-Sofany studied removal of La (III) and Gd (III) by using XAD-4 resin impregnated with Aliquat-336. The impregnated resin's capacity for lanthanum (III) and gadolinium(III) was found to be 4.73 and 4.44 mg g⁻¹, respectively [9].

Chelating agents that have been used in the modification of Amberlite XAD 4 thus far have been briefly reproduced in this review to preconcentration of toxic heavy metals and REEs [10].

Ferric ions were efficiently removed from HCl solutions using Amberlite XAD-7 resin impregnated with trioctylphosphine oxide (Cyanex 921). At intermediary extractant loading (in the range 300–450 mg Cyanex 921 g⁻¹) [11].

This paper aims to lanthanum separation through adsorption on a functionalized material with phosphorus groups. The functionalization material was used to improve its sorbent properties. Kinetic, thermodynamic, and equilibrium studies have been done in order to determine the conditions of the lanthanum adsorption process.

Lanthanum was chosen for this study due to its presence in groundwater, rivers, estuaries, soil, and air, in various concentrations, leads to environmental problems and its more importance in the future technology.

2 Experimental

2.1 Materials and Reagents

All other materials were of analytical grade and used without further purification. Cyanex 921 (1% in kerosene) purchased from Merck (Darmstadt, Germany). Standard and stock solutions were prepared using double distilled water. On the other hand, Amberlite XAD-4 (styrene divinyl benzene Copolymer) with 750 m² g⁻¹ surface area, 50 Å pore diameter and 20–50 mesh bead size was procured from Rohm and Hass Co., USA. Washing with methanol, water, HNO₃ with 1 mol L⁻¹, water, NaOH with 1 mol L⁻¹ and water, respectively to remove inorganic and organic contaminants. Lanthanum Oxide from Alfa Aesar, USA with 99.99% purity. High-purity reagents from Sigma-Aldrich, Merck and Fluka were used in the preparations of all standard solutions. For pH adjustment, 0.01 M H₂SO₄ and 1 M NaOH solutions were used. The chemical structure of Amberlite XAD-4 and Cyanex 921 was giving in Fig. 1.

2.2 Impregnation Process

Recently, impregnated resins have been widely studied for the recovery of rare earths. The impregnated resin technology could overcome the subsequent problems of using solvent extraction such as emulsion formation, extractant loss, and many complicated cycles. The impregnation process was carried out by dry method which is the most widely used [12]. 0.5 g of dry Amberlite XAD-4 resin was placed in 0.025 L of kerosene containing 0.2 mmol cyanex921 with stirring for 12 h. Separated the resin by filtration through a filter paper then was washed with double distilled water to remove the excess of solvent. An air-dried resin was produced after drying at 70 °C. Using the gravimetrically method to determine ligand content in the impregnated solution by weighing the dry ligand residue after removing the resin and evaporation of the solution. The impregnated resin amount was calculated from the material balance to be 0.523 gm.

Fig. 1 The Amberlite XAD-4 and Cyanex 921 chemical structure, which are used in this study
2.3 Batch Experiments for the Adsorption of Lanthanum Ions

The estimation of the appropriate pH value for the adsorption of lanthanum ions on the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger was carried out in a typical metal ion adsorption experiment: A 0.02 g of impregnated resin was immersed in a 0.01 L solution containing 250 mg L\(^{-1}\) lanthanum ion concentrations adjusted at pH values ranging from 0 to 4 and shacked using an orbital shaker in a temperature-controlled water bath at 25 °C for 1 h at a constant agitation speed of 300 rpm. After equilibration, the mixture was filtered, and the lanthanum-ion-containing filtrate was analyzed for adsorption. Following the estimation of the appropriate pH value for the adsorption process, other experiments, such as the effect of contact time, lanthanum ions concentration, solution temperatures are carried out. A simple mechanism of adsorption for the targeted metal ion was shown in Fig. 2 with La\(^{+3}\) ions reactions with the impregnated resin.

Impregnated resin dosage was conducted according to the estimated pH value. In general, the adsorption capacity (mg L\(^{-1}\)) and sorption efficiency percent of lanthanum-ion-impregnated resin were calculated using Eqs. (1) and (2) [13, 14]:

\[
q_e = \frac{(C_i - C_e) V}{m}
\]  

(1)

\[
R\% = \frac{(C_i - C_e) \times 100}{C_i}
\]  

(2)

where \(q_e\) is the lanthanum ion uptake (mg g\(^{-1}\)), \(V\) is the solution volume (L), \(m\) is the mass of the impregnated resin (g), and \(C_i\) and \(C_e\) are the initial and equilibrium lanthanum ion concentrations (mg L\(^{-1}\)). The effect of co-existing cations on the sorption of lanthanum ions onto the adsorbent was investigated. Lanthanum had an initial concentration of 250 ppm, while the competing ions had a concentration of 100 ppm. Following the dissolution of competing ions in solutions containing lanthanum ions, sorption experiments were carried out in the same manner as described in the sorption experiment.

![Simple representation for the resin mechanistic adsorption of solute from aqueous solutions and La\(^{+3}\) ions reaction with the impregnated resin](image)

Fig. 2 Simple representation for the resin mechanistic adsorption of solute from aqueous solutions and La\(^{+3}\) ions reaction with the impregnated resin
2.4 Methods and Analysis

UV–vis spectrophotometer (UV-1 601 model Shimadzu) was used to determine La(III) in the form La(III)–arsenazo(III) complex at 650 nm using Arsenazo III as an indicator. The surface morphology of Amberlite XAD-4 impregnated cyanan 921 resin was studied by scanning electron microscope model JEOL-JSM-5600LV and by Fourier Transform Infrared (FTIR) spectra which were performed in KBr discs using Nexeus–Nicolite model 640-MSA. FTIR, Thermo Electronics Co. (USA). An atomic absorption model G.B.C.A.A was employed for measuring trace elements in sulfate leach liquor. X-ray diffraction (XRD) analyses were done with a Philips X-ray generator model PW 3710 = 31. Batch experiments were done in an isothermal circulator (Lindberg Blue,USA) at 300 rpm. The pH measurements were carried out Ino LabWTW model digital pH-meter.

3 Results and Discussion

3.1 Fabrication and Characterization of the Impregnated Resin

3.1.1 FTIR Spectroscopy and X-Ray Diffraction

Figures 3 and 4 illustrate the FTIR and the X-Ray diffraction diagrams for (a) Amberlite XAD-4, (b) impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger, (c and d) impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with La+3 ions in the standard solution and with the acidic leach liquor of monazite mineral. The obtained FTIR spectra show the following bands: ymax  (cm−1) 3433 (O–H groups) 2923 (C–H, –CH2), 1381(C–H bend in plane), 1029(C–O, C–C, CH2 rock). The band of the P=O group shifts from 1172 cm−1 for impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger to 1157 and 1165 cm−1 for impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with La+3 ions in the standard solution and with the acidic leach liquor of monazite mineral. The observed lower uptake values for lanthanum ions in the impregnated resin with lanthanum ions at 20 of 24.1°C. It can be said that the high intensity peak belongs to impregnated resin with acidic leach liquor of monazite was found at 24°. The other diffraction peaks of functionalized resin were found at 29.2°, 35°, 42.6°, 50° and 57.6°. This XRD pattern proved the successful synthesis of impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger.

3.1.2 Scanning Electron Microscope (SEM)

The SEM image of the Amberlite XAD-4 and the prepared impregnated resin was illustrated in Fig. 5a and b. Microphotographs of sorbent show a cylindrical shape form of the impregnated Amberlite with a porous structure, according to the SEM image. The sorbent spheres have a thickness of about 1 m and a surface covered with 50–100 mm pores diameter. Lanthanum-loaded sorbent SEM revealed that a cluster forms of lanthanum on the walls spheres, as demonstrated by SEM in Fig. 5c. Results show the presence of lanthanum after adsorption onto impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger. The SEM picture on Fig. 5d shows the adsorption of lanthanum in sulfate leach liquor of monazite mineral. The EDEX of the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with standard La+3 ions, and with sulfate leach liquor of monazite mineral was illustrated in Fig. 6a and b.

3.2 Batch Experiments of Lanthanum Ions Adsorption on the Impregnated Resin

3.2.1 pH Effect

One of the main factors which controlling the adsorption process of the La+3 ions through impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger is the pH effect. The pH dependency of the extraction process can be explained by the competition between H+ and La3+ ions on the impregnated resin. Figure 7 shows the effect of pH, in the range of 0.0–4.0, with a fixed weight of the impregnated ion-exchanger (20 mg) and 0.01 L solution volume of 250 mg L−1 La+3 ions at 25 °C for 1 h contact time. The adsorption of La+3 ions depends on the lanthanum speciation/surface charge in solution at specific pH values. The sorption begins at pH 0 and increase till pH 1 then decrease till pH 4. The complete sorption for lanthanum ions is in the region of pH 0.0–1; this is due to an increase in the concentration of H+, a small size with a high mobility. As a result, at active sites on the adsorbent, H+ competes fiercely with lanthanum. Increases the pH of the solution to reflect the gradual decrease in lanthanum adsorption efficiency. It could be attributed to the presence of fewer competing hydrogen ions. The observed lower uptake values for lanthanum ions...
Fig. 3 FT-IR spectra of a Amberlite XAD-4, b impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger, c impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with standard La$^{3+}$ ions, d impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with acidic monazite leach liquor.
at higher pHs is due to the hydrolysis of La\(^{3+}\) and formation of La(OH)\(_3\) species.

### 3.2.2 Effect of the Adsorbent Dose

The effect of impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger dose on the adsorption of lanthanum ions was studied at an ambient temperature of 25 °C with 30 min contact time. As obtained in Fig. 8, it was noted that the lanthanum recovery percentage increases with increasing the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger dose. The impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger could remove nearly 95% of lanthanum ions with a dose of 100 mg, which could be explained by the availability of surface area and thus adsorption sites. The removal efficiency percent of lanthanum ion from aqueous solution at pH = 0.5 was significantly influenced by adsorbent dose. The amount removed from solution increased significantly from 17.68% (by 10 mg) to 95% (by 100 mg) of the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger. However, the adsorption efficiency varied slightly at impregnated ion-exchanger dose greater than 100 mg. At low impregnated ion-exchanger doses, all types of sites are completely exposed, and surface adsorption is saturated faster, resulting in a higher qe value at equilibrium. Furthermore, the adsorption distribution coefficient (K\(d\), L g\(^{-1}\)) calculated as (K\(d\) = C\(_s\)/C\(_L\)) [15] can explain the binding ability of impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger towards lanthanum ions. The term C\(_s\) refers to the concentration of La\(^{3+}\) ions adsorbed on the impregnated particles (mg g\(^{-1}\)), while C\(_L\) refers to the concentration of La\(^{3+}\) ions in aqueous solution (mg L\(^{-1}\)). Figure 8 shows that the K\(d\) increases as the adsorbent dose increases, indicating
Fig. 5  SEM images for  

- **a** Amberlite XAD-4,  
- **b** impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger,  
- **c** impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with standard La\(^{3+}\) ions,  
- **d** impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with sulfate leach liquor of monazite mineral.

Fig. 6  EDEX for  

- **a** impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with standard La\(^{3+}\) ions,  
- **b** impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with sulfate leach liquor of monazite mineral.
that the adsorbent surface is heterogeneous. In the case of a homogeneous surface, the $K_d$ values remain constant as the adsorbent concentrations increase at the optimal pH value.

### 3.2.3 Contact Time Effect

The variation of contact time is one of the most important parameters in determining an adsorbent's adsorption potential. Lanthanum ion adsorption on impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger was studied for 1–60 min at 25 °C and pH 0.5. The uptake of lanthanum ions represents 31.16 percent of the uptake capacity at the plateau within 15 min, and equilibrium was reached within 30 min from a synthetic water sample containing 250 mg L$^{-1}$ of lanthanum ions. The adsorption/time data in Fig. 9a was fitted with a pseudo-second-order model in an attempt to describe the adsorption kinetics. In this model, all adsorption steps, including external diffusion, internal diffusion, and adsorption, are combined in Eq. (3) [16]:
\[ \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \]  

(3)

\( k_2 \) denotes the overall pseudo-second-order rate constant (g mg\(^{-1}\) min). The plot of \( t/q_t \) versus \( t \) in Fig. 9b produced a straight line with a slope and an intercept from which the \( q_e \) and \( k_2 \) were calculated. Clearly, there was a satisfactory agreement between the calculated and experimental values of \( q_e \). This implies that the adsorption process follows pseudo-second-order kinetics and is dependent on the concentration of both surface active sites and lanthanum ions. The adsorption/time data were treated according to the intraparticle diffusion Equation to demonstrate the effect of intraparticle diffusion on the rate of adsorption (4) [17]:

\[ q_t = x + k_i t^{0.5} \]  

(4)

where \( K_i \) (mmol g\(^{-1}\) min\(^{0.5}\)) is the intraparticle diffusion rate constant and \( x \) is the intercept that is proportional to the thickness of the boundary layer. As shown in Fig. 9c, the plots are distinguished by two major stages, one of which passes through the origin and the other does not. This indicates that both intraparticle diffusion and the boundary layer influence the rate of adsorption.

### 3.2.4 Effect of Initial Concentration of Lanthanum Ions

The effect of initial lanthanum ion concentrations on uptake was investigated by varying the initial concentrations \( \text{La}^{+3} \) at optimum pH value 0.5 for 30 min, resulting in maximum uptake capacities of 14, 25.5, 38.95, 43.11, and 43.01 mg g\(^{-1}\) at 25, 40, 50, 60, and 70 °C, respectively. The adsorption capacity of the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger was evaluated using different isotherms models such as the Langmuir and Freundlich models in order to better understand the adsorption capacity. The Langmuir isotherm assumes that adsorption takes place at homogeneous adsorption sites on the sorbent and that intermolecular forces decrease rapidly as one moves away from the adsorption surface. Equation (5) can be used to express the Langmuir model shown in (Fig. 10a) [18]:

\[ \frac{C_e}{q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}} \]  

(5)

where \( C_e \) is the equilibrium concentration of lanthanum ions in solutions (mg L\(^{-1}\)), \( q_e \) is the amount adsorbed on impregnated resin at \( C_e \) (mg g\(^{-1}\)), \( Q_{\text{max}} \) is the maximum adsorption capacity (mg g\(^{-1}\)), and \( K_L \) is the Langmuir binding constant related to adsorption energy (L mg\(^{-1}\)). The Freundlich isotherm model, which can be applied to multilayer adsorption based on the assumption that energetic surface heterogeneity, is the earliest known relationship describing non-ideal and reversible adsorption. The Freundlich isotherm model shown in (Fig. 10b) is described by nonlinear and linear equations, which can be written as Eqs. (6) and (7) [19]:

\[ q_e = K_F C_e^{1/n} \]  

(6)

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(7)

\( K_F \) and \( n \) are the Freundlich constants for adsorption capacity and intensity, respectively. \( K_L \), \( Q_{\text{max}} \), \( K_F \), and \( n \) values were obtained. The maximum Langmuir adsorption capacities (Qmax) obtained were in good agreement with the

![Fig. 10](image-url) **Fig. 10** a Langmuir plot, b linear Freundlich plot of the adsorption of lanthanum ions on impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger at different temperatures
experimental ones, and the values of $R^2$, a measure of goodness of fit, confirm that the Langmuir model represents the experimental data better than the Freundlich model. However, the linear approach yielded higher $R^2$ values for the Freundlich isotherm parameters than the non-linear least-squares approach. Furthermore, as shown in Fig. 10, when these models are compared, Langmuir isotherm models have a higher correlation of determination than Freundlich models. This demonstrates the homogeneity of active sites on an Amberlite XAD-4 adsorbent impregnated with a Cyanex 921 ion-exchanger surface. For the actual La$^{3+}$ ion concentrations in solution, calculations were performed to determine the predicted amount of lanthanum as a function of the weight of impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger. This means that the required impregnated resin weight for any concentration range could theoretically be calculated prior to the adsorption process. The weight of impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger required to intake La$^{3+}$ ions at concentrations ranging from 50 to 1000 mg L$^{-1}$ in one litter of La$^{3+}$ solutions was calculated to be 54.25 mg g$^{-1}$. The impregnated resin demonstrated significant adsorption efficiency, comparable to that of previously prepared organic adsorbents such as oxides and phosphates (Table 1) [20–26].

### 3.2.5 Effect of Coexisting Competing Ions

To investigate the effect of coexisting competing ions, separately, mono-valent potassium, sodium ions, and divalent calcium, magnesium ions and tri-valent aluminum, iron ions and tetra-valent silica and thorium ions were chosen as competing ions to investigate the effect of coexisting ions on the adsorption capability of the impregnated resin. In details, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Si$^{4+}$ and Th$^{4+}$ were mixed with 250 ppm of La$^{3+}$ aqueous solution, with their final concentration at 250 ppm. Static adsorption experiments were performed by immersing 0.02 g of impregnated resin in 0.01 L of the mixed solution and stirring the system for 30 min at pH 0.5. The concentration of lanthanum ions was determined again by a UV spectrometer and ICP instrument. As illustrated in the Fig. 11. The percentage of lanthanum uptake on impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger decreased slightly in the presence of competing ions. In terms of exerted effect, the metal ions are ranked as follows: Si$^{4+}$ > Th$^{4+}$ > Fe$^{3+}$ > Al$^{3+}$ > Ca$^{2+}$ > Mg$^{2+}$ > Na$^+$ > K$^+$. This could be because the lanthanum adsorbing sites in the impregnated resin are better suited to the uptake of Si$^{4+}$ and Th$^{4+}$ ions than K$^+$ and Ca$^{2+}$ uptake.

### 3.3 Thermodynamics Studies of Lanthanum Ions Adsorption on the Impregnated Resin

For evaluation of the temperature effect on adsorption of La$^{3+}$ ions using synthesized impregnated resin, the adsorption process was carried out in a series of batch experiments at temperatures ranging from 25 to 70 degrees Celsius. The following were the other parameters: At 25 °C for 30 min, a 0.01 L solution volume of 250 mg L$^{-1}$ La$^{3+}$ ions was contacted with 0.02 g of adsorbent resin. As seen in Fig. 12, adsorption capacity increases with increasing temperature till reach maximum uptake capacity of 46.91 mg g$^{-1}$ at 60 and 70 °C observed in capacity at which indicate that, temperature has an effect on adsorption process of La(III) ions on the impregnated prepared resin.

### Table 1 Adsorption capacities of La$^{3+}$ ions on various inorganic absorbents are compared

| Adsorbent                                           | Uptake, mg g$^{-1}$ | References |
|-----------------------------------------------------|---------------------|------------|
| Aliquat-336 Chelating with Amberlite XAD-4 resin     | 4.73 mg g$^{-1}$ for La$^{3+}$ | [20]       |
| Monoaza dibenzo 18-crown-6-ether Chelating with Amberlite XAD-4 resin | 9.17 mg g$^{-1}$ for La$^{3+}$ | [21]       |
| carboxylated cellulose filter with TEMPO-mediated oxidation system | 33.7 mg g$^{-1}$ for La$^{3+}$ | [22]       |
| Amberlite XAD-4-resin functionalized with bicine ligands | 0.35 mmol g$^{-1}$ for La$^{3+}$ | [23]       |
| Cysteine-functionalized chitosan magnetic nano-based particles | 17 mg g$^{-1}$ for La$^{3+}$ pH 6 | [24]       |
| Platanus orientalis leaf                             | 29 mg g$^{-1}$ for La$^{3+}$ pH 4 | [25]       |
| Magnetic alginate beads                              | 1.8 mmol g$^{-1}$ for La$^{3+}$ pH 5 | [26]       |
| Amberlite XAD-4 adsorbent with Cyanex 921           | 54.25 mg g$^{-1}$ for La$^{3+}$ pH 0.5 | This study |

Fig. 11 The competing ions effect on lanthanum uptake onto impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger
The following thermodynamic equations could be used to calculate the change in enthalpy ($\Delta H^\circ$), entropy ($\Delta S^\circ$), and standard free energy ($\Delta G^\circ$) [27]:

$$\Delta G^\circ = \Delta H^\circ + T \Delta S^\circ$$

(8)

where $\Delta H^\circ$ is the adsorption enthalpy, $\Delta S^\circ$ is the entropy change, and $T$ is the temperature (K). $\Delta H^\circ$ and $\Delta S^\circ$ can be calculated from the slope and intercept of Van’t Hoff’s equation.

$$\log K_d = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$

(9)

where, $R$ is gas constant (8.314 J mol$^{-1}$ K), $T$ is absolute temperature in Kelvin (K). $K_d$ is (obtained from Eq. 9 at different temperatures and Fig. 13).

Table 2 shows the values of thermodynamic parameters. The presence of a positive value for $\Delta H^\circ$ indicates that lanthanum adsorption on the impregnated resin is endothermic. The negative $\Delta G$ values indicate that lanthanum ion adsorption on the impregnated resin is feasible and spontaneous. Furthermore, the interactions’ Gibbs free energy shows that the processes are favorable for the formation of an electrostatic interaction between La ions and impregnated resin. Moreover, the positive value of $\Delta S$ indicates that the randomness increases at the solid/liquid interface during the adsorption onto the studied resin.

### 3.4 Regeneration

Metal ion extraction should be economical if the materials used have high reproducibility, performance, recyclability, and durability. The effective elution of the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 cation exchanger was found feasible using HNO$_3$ (1 M), HCl (1 M) and CH$_3$COOH (1 M). 1 M nitric acid gives high percent recovery of lanthanum equal 82.3 than of HCl and CH$_3$COOH which equal 78.5 and 69.33 respectively as shown in Fig. 14a. Repeat the experiments with different concentrations of HCl and HNO$_3$ (0.5, 1 and 2 M) to produce the more effective eluting agent. From Fig. 14b, it was found that 2 M HCl gives the highest recovery equal 95.4 than that of other concentrations and that of nitric acid which are equals 63.9 and 78.5 for 0.5 and 1 M HCl and equals 79.6, 82.3 and 66.55 for 0.5, 1 and 2 M HNO$_3$ respectively. The impregnated resin was kept up to six cycles of regeneration and reuse before a slight decrease in efficiency was noticed. This minor change in impregnated resin efficiency is most likely caused by stripping agent treatment during the recycling process. The sensitivity, specificity, and reusability of the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 cation exchanger, as well as its ease of use, give it potential not only for lanthanum remediation but also for lanthanum extraction from natural ores.

### 3.5 Applicability Evaluation

As the traditional industrial method, monazite mineral digested by 98% sulfuric acid in hydrothermal autoclaves [28]. It was done on a 100 g monazite sample with 90 ml concentrated H$_2$SO$_4$. Approximately 85% of the sample was
dissolved, yielding 1 L of leach liquor via dilution with distilled water, with the remaining 15% remaining as a residue that was filtered. The efficiency of adsorption of the resin for lanthanum ions was determined using monazite sulfate leach liquor, which is considered the cheapest process for monazite opening. Complete analysis for the hydrous cake was carried out which contains $\text{UO}_2^{2+}$; $\text{La}^{3+}$; $\text{Ce}^{3+}$; $\text{Pr}^{3+}$; $\text{Nd}^{3+}$; $\text{Sm}^{3+}$; $\text{Gd}^{3+}$; $\text{Th}^{4+}$ with 0.491, 18, 31.79, 7.43, 15.41, 5.06, 4.67, 1.273%. The lanthanum sorption was performed using 1 L of acidic monazite leach liquor in contact with 1 gm impregnated resin for 30 min at room temperature and a pH of 0.5. After equilibration, the solution was filtered and the lanthanum concentration was determined. The total sorption capacity of lanthanum from sulfate media was confirmed using SEM as shown in Figs. 5d and 6b. It was found that the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger in sulfate media adsorbed lanthanum with 94.13% with the addition of Ce.

### 4 Conclusions

In this study, we described the adsorption of lanthanum ions on the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger. The impregnated resin had a large surface area and large pore sizes, allowing it to easily trap lanthanum ions from aqueous solutions. The pH of the solution played an important role in the adsorption of lanthanum ions on the impregnated Amberlite XAD-4 adsorbent with Cyanex 921 ion-exchanger with an optimum pH at 0.5. The elution was carried out by 2 M HCl with 95.4 lanthanum recovery percent. The adsorption isotherm was well fitted by Langmuir and Freundlich isotherm models and the calculated maximum adsorption capacity was 54.25 mg g$^{-1}$ at 25 °C. Moreover, the capture-and-release process of the impregnated resin for lanthanum ions has an efficiency of up to 94.13% in real samples (acidic leach liquor of monazite).

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**Declarations**

**Conflict of interest** The authors have not disclosed any competing interests.

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