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Lanthanum (III) Removal onto Lewatit TP 214 Resin in Nitrate Medium: Kinetic and Thermodynamic Study

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Abstract: *This study aims to investigate lanthanum(III) removal onto Lewatit TP 214 resin containing thiourea group in polystyrene- divinylbenzene matrix, in batch process. The effects of parameters such as the concentration, pH level, contact time, ionic strength and temperature were investigated. The results showed remarkable affinity of resin towards lanthanium(III) cations. The maximum uptake values of Ln(III) was 38.46 mg/g. Percentage removal increases with increasing initial pH solution, lanthanium(III) cations removal was better in initial pH values of 5.20, at room temperature. The uptake kinetic for lanthanium(III) onto Lewatit TP 214 was best described by the pseudo second order model. The Langmuir isotherm fit well obtained equilibrium data compared to the Freundlich isotherm. The thermodynamic data for lanthanium(III) cations sorption onto Lewatit 214 resin, indicate that the process endothermic (ΔH = + 5.72 KJ.mol^{-1}). In addition, the thermodynamic study showed also negative ΔG values, indicating that the sorption process of lanthanium(III) is spontaneous.*

Keywords: *lanthanum (III) removal, Lewatit TP 214 resin, kinetics, thermodynamics.*

I. Introduction

Rare earth elements (RE) have gained considerable attention due to their unique properties and a guide range of applications [1, 2]. Recovery of lanthanides is interesting due to its high market prices along with various industrial applications. Different methods have been proposed for separation and preconcentration of lanthanides, such as co-precipitation, solvent extraction, liquid-liquid extraction, etc [3, 4]. Solvent extraction is the most common methodologie for the preconcentration and separation of lanthanides from various matrices. Solvent extraction are not economically attractive and it have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites, which may create health and environmental problems [5]. Solid-phase extraction (SPE) is the most common technique used for metal pre-concentration in aqueous phase. It is simpler to operate and easier to separate. Various adsorbents including chelating resins and ion exchange resins are used in extraction of metal ions [6, 7]. Lewatit TP 214 is a monospherical, macroporous chelating resin with thiourea groups, having a high affinity for metal cations (Fig.01). The objective of this research is to carry out a sorption of lanthanum(III) ions from aqueous solutions, using resin Lewatit TP 214. The effects of analytical parameters, such as adsorption kinetic, isotherm study and temperature were investigated.

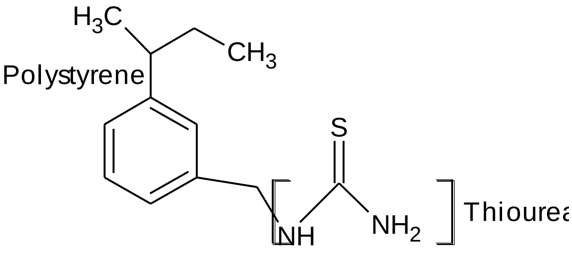

Fig.01: Lewatit TP 214 resin

II. Experimental

2.1. Reagents

Lewatit TP 214 (from Bayer) is a chelating ion-exchange resin having thiourea as functional groups in a styrene matrix. Their physical properties and specifications as reported by the suppliers are shown in Table 1.All solutions were prepared from analytical grade chemicals and distilled water. A stock solution of 1.0.10^{-2} mol L^{-1} of $La(NO_3)_3 \cdot 6H_2O$ (from Fluka) was prepared by dissolving 4.3302 g in 1L of distilled water. The diluted solutions of lanthanum ions were prepared by appropriate dilution of the stock solutions. Hydrochloride acid (37%) and Sodium hydroxyde were purchased from Merck. Ethanol, sodium chloride, sodium nitrate, Sodium sulphate and Arsenazo(III) were provided from Fluka.

Table.1: General description and properties of Lewatit TP 214

Description	Lewatit TP 214
Producer	Bayer, Germany
Functional group	Thiourea
Matrix	Cross linked polystyrene
Structure	Macro porous
Physical form and appearance	Mat beige spheres
pH range	0-10
Thermal stability	80 °C
Bead size	0,55 (± 0,05) mm
Water retention	50-56%
Total exchange capacity	1,2 meq/cm^3
Additional information	High mechanical and osmotic resistance

2.2. Apparatus

The sorption of La(III) on resins was studied by the batch process. A shaker (Haier model) was used for adsorption experiments except for temperature effect where a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. Visible spectra were measured using Perkin-Elmer-Lambda 800 UV-Vis spectrophotometer. pH measurements for all solutions were taken on a potentiometer Consort C831 with combined glass electrode.

2.3. Sorption Studies

The sorption of lanthanum(III) ions onto Lewatit TP 214 beads have been investigated in solid phase extraction from aqueous media in a batch system. 0.100 g of chelating resin was added to 5 mL of Ln(III) solutions in a glass flask (25 mL), and the mixture was shaken at appropriate time. The aqueous phases were separated from the chelating resin by classical filtration and its equilibrium pH values measured. Ln(III) ions concentrations in the aqueous phase were determined, before and after sorption, spectrophotometrically using Arzenazo III at pH=2 [8]. The absorbance of Arzenazo III-lanthanum(III) complex was measured at $\lambda_{max} = 652$ nm. The effect of the pH values of the aqueous solution on Ln(III) removal was studied by varying pH in the range 1.4 to 6.5, pH was adjusted by adding necessary moieties of HCl 0.01 M. The kinetic studies for lanthanum(III) removals were carried out with an initial ion concentration, respectively of $1.0.10^{-3}$ mol.L^{-1} and $2.0.10^{-3}$ mol.L^{-1} at room temperature. The effect of contact time on Ln(III) sorption onto Lewatit TP 214 was studied until 120 min. Whereas other parameters like sorbent dosage, shaking speed and pH remained constant.

The percent Ln(III) removal, (%) was determined as follows:

$$\text{Removal}\,(\%) = \frac{C_0 - C_t}{C_0}.100\% \qquad (1)$$

The amount of Ln(III) uptakes at time t, q_t (mg.g^{-1}), was calculated by Eq. 2:

$$q_t = \frac{C_0 - C_t}{W}.V \qquad (2)$$

where C_0, C_t and C_e are the initial, time and equilibrium Ln(III) ion concentration (mol.L^{-1}), respectively. V (L) is the volume of the solution, and W is the mass of the Lewatit TP 214 resin used (g).

III. Results And Discussion

3.1. Effect of initial pH

The pH value plays an important role in the sorption studies onto chelating resins, because the pH of the solution can influence the aqueous chemistry of lanthanum and the properties of functional groups of resin. Effect of solution pH on the Ln(III) removal ions from the aqueous solution using Lewatit TP 214 was investigated in the pH range of 1.4 to 6.5 using respectively, 5 mL of $1.0.10^{-3}$ mol.L^{-1} and $2.0.10^{-3}$ mol.L^{-1} Ln(III) ions solutions and 0.100 g of chelating resin. (Fig. 2) shows that Ln(III) percent removal increase with increasing pH solution and a maximum values were reached, (62.8% and 47.4 %, respectively for $1.0.10^{-3}$ mol.L^{-1} and $2.0.10^{-3}$ mol.L^{-1} Ln(III) ions solutions) at an initial pH near 5.1. This is due to the favourable conditions for the complex formation of lanthanum with functional groups of resin in this pH region, at low pH values, the decrease of the percent may be attributed to the partial protonation of the active groups (thiourea) and the competition of H^+ with Ln(III) onto sorption sites of Lewatit TP 214 resin. So the following sorption studies will carried out at pH = 5.1.

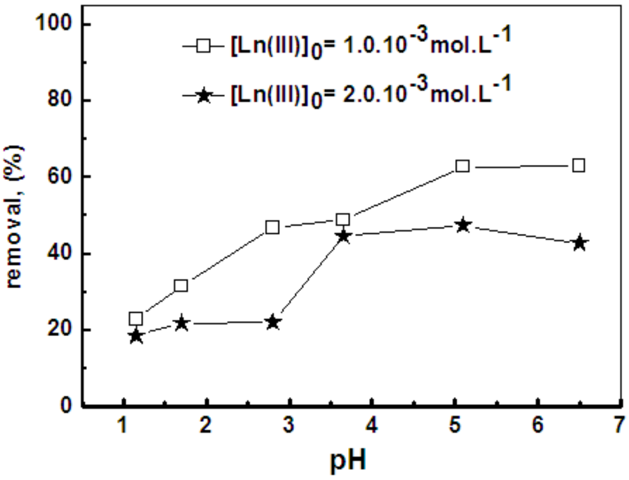

Fig.2: Effect of initial pH for Ln(III) ions removals (%) onto Lewatit TP 214 resin: W_{resin} =0.100 g; V = 5 mL and Ø = 250 rpm.

3.2. Effect Of Contact Time

Early studies on metal sorption by resin, shows that the contact time is an important parameter affecting the sorption process. Fig.3 shows that the kinetic was fast at the initial step of sorption process up to 30 min and then the sorption rate became slow until equilibrium was reached after only 60 min. For the initial lanthanum concentrations mentioned above, extraction yield observed were 63% and 47%, respectively for $1.0.10^{-3}$ $mol.L^{-1}$ and $2.0.10^{-3}$ $mol.L^{-1}$ initial Ln(III) concentrations. In the first step, the binding sites of chelating resin exposed at the surface was higher, so the sorption kinetic was fast, and after the available surface sites were difficult to be occupied [9]. Therefore, in all next experiments, contact time of 60 min was applied.

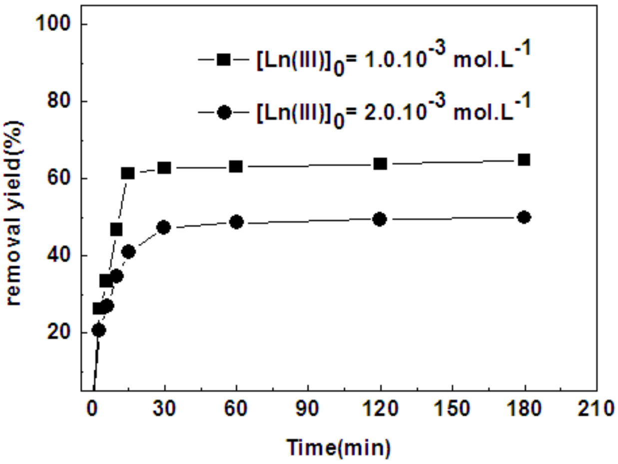

Fig.3: Effect of contact time for Ln(III) sorption onto Lewatit TP 214 resin : W_{resin} = 0.100 g; V = 5 mL, pH = 5.1 and Ø = 250 rpm.

3.3. Sorption Kinetics

In order to analyse the sorption kinetic of Ln(III) ions onto Lewatit TP 214 resin, the pseudo first-order [10] and pseudo second-order [11] kinetic models were applied to experimental data.

1- The linear form of the pseudo-first-order rate equation by Lagergren is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \qquad (3)$$

where q_e and q_t are the amounts of sorbed Ln(III) onto chelating resin at equilibrium and at time t, respectively ($mg.g^{-1}$), and k_1 is the first-order sorption rate constant (min^{-1}).

2- The linear form of the pseudo-second order rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_e is the sorption capacity calculated by the pseudo-second-order kinetic model (mg.g^{-1}), and k_2 is the pseudo-second-order sorption rate constant (g.mg^{-1}.min^{-1}). The correlation coefficients for the pseudo-first-order equation obtained at the studied concentrations are 0,927 and 0,988 and the theoretical q_e values calculated from the first-second-order equation are not in agreement of the experimental data (Table. 2), suggesting that this sorption system is not a pseudo-first-order reaction. High correlation coefficients are obtained ($R \geq 0,991$) when employing the pseudo-second-order model and the calculating equilibrium sorption capacity is close to the experimental data. This indicates that the pseudo-second-order model is more adequate to predict the sorption kinetic for Ln(III) ions onto Lewatit TP 214 resin.

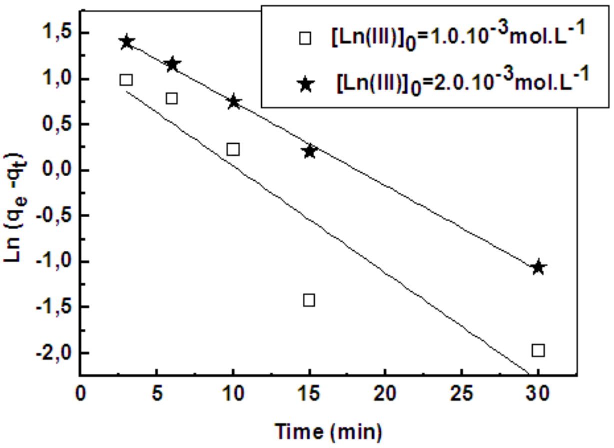

Fig.4: Plot of pseudo first-order for Ln(III) ions sorption onto Lewatit TP 214 resin: W_{resin} = 0.100 g; V_{sol} = 5 mL, pH = 5.1; Ø = 250 rpm.

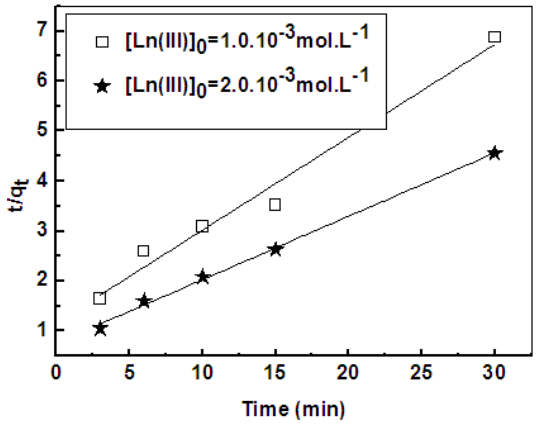

Fig.5: Plot of pseudo second-order for Ln(III) ions sorption onto Lewatit TP 208 resin: W_{resin} = 0.100 g; V_{sol} = 5 mL, pH = 5.1; Ø = 250 rpm.

Table.2: Kinetic modelling of Ln(III) ions sorption onto Lewatit TP 214 resin

Models	Parameters	$[Ln(III)]_0=1.10^{-3}$mol.L^{-1}	$[Ln(III)]_0=2.10^{-3}$mol.L^{-1}
First-order rate model	q (cal.)	3.73	5.33
	q (exp.)	4.50	6.93
	k_1(min^{-1})	0.117	0.092
	R	0.927	0.988
Pseudo-second-order rate model	q (cal.)	5.38	7.87
	q (exp.)	4.50	6.93
	k_2(g.mg^{-1}.min^{-1})	0.029	0.021
	R	0.991	0.999

3.4. Effect Of Initial Ln(III) Ions Concentration

In order to study the effect of initial Ln(III) ions concentration onto sorption capacity using Lewatit TP 214 chelating resin, several experiments were also undertaken by varying initial Ln(III) ions concentration from the range 1.10^{-3} mol.L^{-1} to 1.10^{-2} mol.L^{-1}, with fixed mass resins (0.100 g). The results obtained are shown in Fig.6. It has be seen that sorption capacity increases with increasing initial Ln(III) ions concentration onto chelating resin. The maximum sorption capacity was 38.46 mg/g (Table.3). This result indicates that Lewatit TP

214 resin is an effective sorbent in treatment of diluted lanthanum solutions in batch process. For comparison, this sorption capacity is also considerably higher than those of some other sorbent materials reported in literature: Biosorption of lanthanum and cerium from aqueous solutions by Platanus orientalis leaf powder ($q_{max} = 28.65$mg/g) [12], Removal of lanthanum and gadolinium from nitrate medium using Aliquat-336 impregnated onto Amberlite XAD-4($q_{max} = 04.73$mg/g) [13], La(III) uptake by multiwalled carbon nanotube modified with tannic acid($q_{max} = 05.35$mg/g) [14].

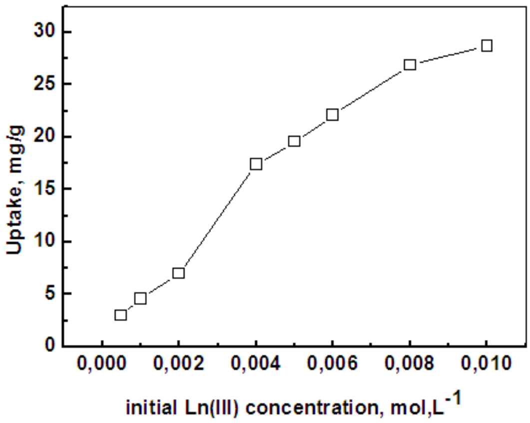

Fig.6: Effect of initial Ln(III) ions concentration on the sorption capacity onto Lewatit TP 214 resin; $W_{resin} = 0.100$ g; V = 5 mL, pH ≈ 5.1 and Ø = 250 rpm.

3.5. Adsorption Isotherm

For interpretation of the adsorption data, Langmuir and Freundlich isotherm models were used [15] (Eq.5 and Eq.6).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (5)$$

$$\mathrm{Ln}q_e = \mathrm{Ln}K_F + \frac{1}{n}\mathrm{Ln}C_e \qquad (6)$$

where C_e is the equilibrium concentration of lanthanum (III) (mol.L^{-1}), q_e the amount of Ln(III) ions sorbed on the chelating resin (mg/g), k_L the Langmuir adsorption constant (L/mol), q_{max} is the maximum amount of Ln(III) ions that can be sorbed by the resin, k_F is the Freundlich adsorption constant and n is a constant which indicate the capacity and intensity of the adsorption, respectively. For the two studied systems, the Langmuir (C_e/q_e versus C_e) plot was found to be linear (Fig.7) for the sorption of Ln(III) ions onto Lewatit TP 214 resin. The correlation coefficients were extremely as high (R = 0.996). The essential feature of the Langmuir equation can be given in terms of a dimensionless separation factor, R_L, defined as (Eq. 7) [16]:

$$R_L = \frac{1}{1 + K_L . C_0} \qquad (7)$$

Where C_0, is the highest initial Lanthanum concentration. The value of R_L indicates the shape of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [16]. In this work, the value of R_L obtained is 0.163. So we suggested monolayer adsorption of Ln(III) ions onto Lewatit TP 214 resin.

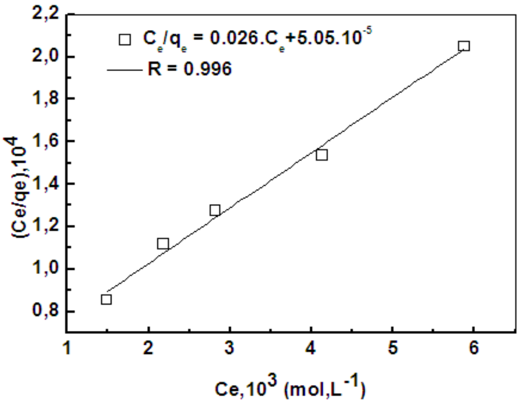

Fig.7: Langmuir isotherm for Ln(III) ions sorption onto Lewatit TP 214 resin: $W_{resin} = 0.100$ g; $V_{sol} = 5$ mL, pH ≈ 5.1; Ø = 250 rpm

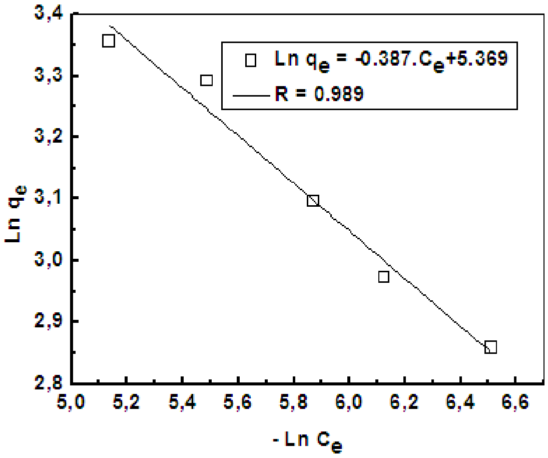

Fig.8: Freundlich isotherm for Ln(III) ions sorption onto Lewatit TP 214 resin: W_{resin} = 0.100 g; V_{sol} = 5 mL, pH ≈ 5.1; Ø = 250 rpm

Table.3: Adsorption isotherm models for Ln(III) ions sorption onto Lewatit TP 214 resin.

Langmuir isotherm		
K_L	q_m	R
514.87	38.46 mg/g	0.996
Freundlich isotherm		
K_F	n	R
214.65	2.58	0.989

3.6. Effect Of Ionic Strength

The effect of ionic strength on Ln(III) ions adsorption depends on a number of factors, including: (1) intrinsic nature of adsorbent surface; (2) chemical properties of adsorbate cation; (3) anions and cations in background electrolyte; (4) pH value of the aqueous solution; and (6) background electrolyte concentration [17]. As the sulphates, chlorides and nitrates of alkali ions (Na^+) frequently accompany cadmium ions in industrial solutions, it is worthwhile to know if they affect the sorption process efficiency. The influence of ionic strength onto Ln(III) sorption was studied at varying concentrations of NaCl, $NaNO_3$ andNa_2SO_4, in aqueous solution, from 0.5 to 2.0 mol.L^{-1}. The influence of the concentration of those salts is shown in figure 9. At $NaNO_3$ and Na_2SO_4 concentrations between 0 and 2.0 mol.L^{-1} there is a negative trend on increasing electrolytes concentrations. The decrease in the sorption of Ln(III) may be due to the formation of more stable metal sulphate or nitrate – complexes, which were non-extractable by the grafted resin. [18,19]. There is no significant effect on Ln(III) sorption in the presence of NaCl as electrolyte.

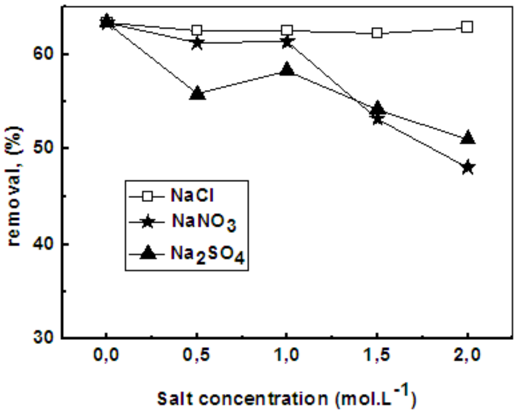

Fig. 9: Effect of ionic strength with different electrolytes on Ln(III) ions sorption onto Lewatit TP 214 resin: W_{resin} = 0.100 g; V_{sol} = 5 mL, pH ≈ 5.1; Ø = 250 rpm;$[Ln(III)]_0$ = 1.0 10^{-3} mol.L^{-1}.

3.7. Thermodynamic Study

The Gibbs free energy change, ΔG_0 is the fundamental criterion of spontaneity. The apparent thermodynamic parameters ΔH and ΔS for the sorption process were calculated from the slopes and intercepts of the linear variation of ($\ln K_d$) vs. (1/T) by eq. 8.

$$\mathrm{Ln}K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (8)$$

where, R is the gas constant, 8.314 $J.mol^{-1}.K^{-1}$ and T is the absolute temperature in Kelvin. The free energy (ΔG) for the sorption was calculated by eq. 9:

$$\Delta G = \Delta H - T\Delta S \qquad (9)$$

Further, the thermodynamic equilibrium constant, K_d (eq. 10), obtained from the distribution constant was used to compute the apparent thermodynamic parameters [20].

$$K_d = \frac{(C_0 - C_e)V}{C_e m} \qquad (10)$$

The calculated apparent thermodynamic parameters for Ln(III) ions sorption onto Lewatit TP 214 resin are summarized in Table 4. The negative values of ΔG are due to the fact that sorption process is spontaneous with high affinity of Ln(III) ions to chelating resin. The positive value of ΔH confirms the endothermic nature of sorption process. The positive value of ΔS reflected affinity of adsorbent towards Ln(III) ions and confirms the increased randomness at solid–solution interface during sorption [21].

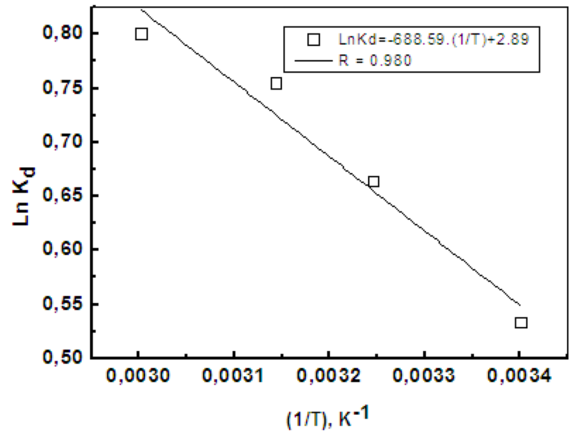

Fig. 10: Variation of Ln K_d with (1/T) for Ln(III) ions sorption onto Lewatit TP 214 resin: $W_{resin} = 0.100$ g; $V_{sol} = 5$ mL, pH = 5.1; Ø = 250 rpm, $[Ln(III)]_0 = 1.0.10^{-3}$ $mol.L^{-1}$

Table 4: Thermodynamics parameters for Ln(III) ions sorption process onto Lewatit TP 214 resin

	ΔH, (kJ/mol)	ΔS, (J/mol.K)	ΔG (kJ/mol)			
Temperature (K)	-	-	294	308	318	333
Values	+ 5.72	+ 24.03	- 1.30	- 1.70	- 1.99	- 2.21

IV. Conclusion

In this study, the sorption capacities of La(III) onto Lewatit TP 214 were studied by batch tests conducted under various experimental conditions such as contact time, pH, initial La(III) content and temperature. Based on the results, the following conclusions are summarized
as below:

1. The sorption of La(III) onto Lewatit TP 214 achieves equilibration most quickly (15 min). The kinetic sorption of La(III) onto this chelating resin follows the pseudo-second order model.
2. The equilibrium batch experiment data demonstrate that Lewatit TP 214 resin is an effective sorbent for the removal of La(III) from aqueous solution with the maximum sorption capacity of 38.46, under the given experimental conditions.
3. The sorption of La(III) on the resins is strongly dependent on pH and lanthanum content. The adsorption process follows Langmuir isotherm, suggesting monolayer adsorption of Ln(III) ions onto Lewatit TP 214 resin.
4. The percentage removal decreases in the presence of $NaNO_3$ and Na_2SO_4 as electrolytes salts.
5. The calculated thermodynamic parameters showed the feasibility, endothermic and spontaneous nature of the sorption of La(III) onto Lewatit TP 214 resin.
6. The results obtained in this study make Lewatit TP 214 resin as promising candidates for sorption, immobilization and pre-concentration of lanthanum ions from nitrate medium.

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