

Studies on the feasibility of using a novel phosphonate resin for the separation of U(VI), La(III) and Pr(III) from aqueous solutions

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Abstract In view to separate La(III), Pr(III) and U(VI) ions, from aqueous solutions, batch experiments are carried out for the sorption and desorption of these ions onto and from a novel functionalized resin. The sorption capacities varied from 1.06 to 47.30 mg/g and increased in the following order La(III), Pr(III) and U(VI), while yields desorption ranged from 73.0 to 94.3% and increased in the following order Pr(III), La(III) and U(VI). Considering the largest difference in sorption capacity and desorption yield of these three elements, at different operates conditions, this material can be potential candidate for the separation of U(VI), Pr(III) and La(III) ions from nuclear and other industrial wastewater.

Keywords Uranium(VI) · Lanthanum(III) · Praseodymium(III) · Ion exchange · Sorption · Phosphonate resin

Introduction

The separation of uranium (actinide) from its associated elements, such as lanthanum and praseodymium (lanthanides), is desired in view of its increased demand in nuclear industries. The conventional methods for the

separation of lanthanides and actinides include adsorption, chemical precipitation, membrane filtration, coagulation and flocculation, electrochemical treatment, and solvent extraction [1–9]. However, most of these methods suffer from technical, economic and health problems related to low selectivity, long time of extraction, and large quantity of hazardous materials used. Sorption by functionalized resin provides an environmentally and economically favorable method for removing and separation of soluble lanthanides and actinides from sources such as nuclear and other industrial wastewater [10, 11].

An especially interesting family of materials used for the separation of uranium, lanthanum and praseodymium are those containing phosphate and amino groups [12–14]. These groups can both chelate cationic and adsorb anionic metal species through electrostatic interactions or hydrogen bonding [15, 16]. In this context, phosphonated polyethylenimine resin arises as an attractive material possessing a large number of secondary amine, ternary amine and phosphonate groups.

This study was performed to develop an effective and practical sorbent suitable for removal and isolation of actinides and lanthanides. We have grafted a polyethylenimine methylene phosphonic acid group on a Merifield resin to obtain a new ions exchange resin. The reaction was performed in distilled water under classic heat. This reaction conducts to a highly functionalized polymer possessing phosphonic acid and amine moieties as chelating groups. This resin, in sodium form, was applied as a new sorption material for uranium(VI), lanthanum(III) and praseodymium(III) ions, from nitrate medium, and in batch process. The effects, on sorption process, of some analytical parameters such as shaking speed, time contact, aqueous pH, initial concentration of U(VI), La(III) and Pr(III), temperature and salts addition were studied in

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detail, while for resin regeneration, three different acids at variables concentrations were tested.

Experimental

Reagents

All solutions were prepared from analytical grade chemicals and distilled water. Commercially Merrifield resin (Chloromethyl styrene–divinylbenzene copolymer, S-3% DVB) and phosphorus acid (H_3PO_3) were purchased from Rohm and Haas Company. Polyethylenimine (Lupasol® G20) is commercially available from BASF with ratio of primary:secondary:tertiary amines (1:0.91:0.64) with an average molecular weight (M_w) of 1300. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Arsenazo III and hydrochloric acid (37%) was provided from Sigma-Aldrich. Nitric acid (70%), sodium hydroxide ($\geq 97.0\%$, pellets), potassium chloride, thiocyanate, and cyanide (KCl, KSCN, KCN) and sodium chloride, nitrate, sulphate and dithionite (NaCl , NaNO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_4$) were purchased from Merck. A stock solutions of 1×10^{-2} mol/L of $\text{UO}_2(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$ were prepared by dissolving 5.0213, 4.3301 and 4.3501 g respectively in 1 L of distilled water. The diluted solutions of uranyl, lanthanum and praseodymium ions were prepared by appropriate dilution of the stock solutions. The initials pH of the sample solutions were adjusted in the desired range by adding dilutes HNO_3 or NaOH solutions.

Apparatus

A FT-IR (Perkin-Elmer 684 IR spectrophotometer) was used for the confirmation of the presence of phosphoanated polyethylenimine on Merrifield resin. FT-IR spectra were obtained with KBr pellets and the spectrum was taken from 4000 to 400 cm^{-1} . All pH measurements were performed with a WTW 3310 Set 2 digital pH meter. The sorption of uranium(VI), lanthanum(III) and Praseodymium(III) on functionalized resin was studied by batch technique. A shaker (Haier model) was used for sorption experiments except for temperature effect where a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. Specord® 210 Plus model analytic Jena UV–Vis spectrophotometer was used to determine U(VI), La(III) and Pr(III) as M^{n+} –Arsenazo III complex in aqueous phase [17–19].

Sorption studies

In aqueous phase, the uranium(VI), lanthanum(III) and praseodymium(III) concentration was determined

spectrophotometrically with Arsenazo III. In a test tube, which contained 2 mL of ammonium acetate/HCl buffer (pH 3.3), were added 100 μL of U(VI), La(III) or Pr(III) solutions to be analyzed and 100 μL of Arsenazo III solution (10^{-3} mol/L). Arsenazo III reacts with U(VI), La(III) and Pr(III) to form a blue complexes which can be estimated at $\lambda_{\text{max}} = 651, 660$ and 578 nm respectively [17–19].

The general method of sorption, used for this study, is described as follows: 0.05 g (w) of polyethylenimine methylene sodium phosphonate grafted Merrifield resin (PEIPR-Na) was equilibrated with 5 mL (V) of metal ions solution of known concentration in a stoppered Pyrex glass flask at an ambient temperature ($22 \pm 1 \text{ }^\circ\text{C}$) in a shaker for predetermined time. The resin was separated by filtration and the filtrate was analyzed by UV–Vis spectrophotometer in presence of Arsenazo III for metal ions content [17–19]. The sorption of U(VI), La(III) and Pr(III) ions on the resin at three different temperatures 22, 27 and $35 \text{ }^\circ\text{C}$ was investigated. For temperature effect, a magnetic stirrer was used and stirring speed was 1000 round per minute to maintain resin particles in suspension. All data reported are based on the average of three replicate measurements.

The percentage of metal ions that is sorbed on the resin (Removal yield) was determined by comparing its concentrations before and after sorption (Eq. 1).

$$\text{Removal yield}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The amount of metal uptakes at time t , q_t (mg/g), was calculated by Eq. (2):

$$q_t(\text{mg/g}) = \frac{(C_i - C_t)}{w} \times V \quad (2)$$

The distribution coefficient (D) of the metal ions between the aqueous solution and the solid resin is also calculated from Eq. (3):

$$D(\text{mL/g}) = \frac{[\text{M}]_{\text{resin}}}{[\text{M}]_{\text{aq}}} = \frac{(C_i - C_e)}{w} \times \frac{V}{C_e} \quad (3)$$

where $[\text{M}]_{\text{resin}}$ and $[\text{M}]_{\text{aq}}$ is La(III), Pr(III) or U(VI) ions concentration in resin phase (mg/g) and in aqueous solution (mol/L) respectively. C_i , C_t and C_e are respectively the initial, time t and equilibrium La(III), Pr(III) or U(VI) concentration (g/L). V is the volume of the solution (5 mL). w is the mass of the functionalized resin used (0.05 g).

Desorption studies

Desorption of U(VI), La(III) and Pr(III) was performed by mixing 1.000 g of loaded resin with U(VI), La(III) or Pr(III) with 5.0 mL of acid solutions (HCl, HNO_3 and

H₂SO₄) at known concentration, and shaken at 310 rpm for 4 h at ambient temperature (22 ± 1 °C). The final U(VI), La(III) and Pr(III) concentrations in the aqueous phase were analyzed by UV–Vis spectrophotometer. All data reported are based on the average of three replicate measurements.

Results and discussion

Ion exchange resin synthesis

Polyethylenimine methylene phosphonic acid grafted Merrifield resin (PEIPR) was originally designed for removing of metal ions, taking advantage of high affinity of phosphate for metals [20]. In order to use this polymer in SPE technique, we prepared a polystyrene–divinyl benzene resin that contained a maximum of polyethylenimine methylene phosphonic group. This fully phosphonated resin (PEIPR) was prepared in two steps (Fig. 1). In first step, after washing with absolute ethanol, the vacuum dried Merrifield resin 3% was reacted with polyethylenimine Lupasol® G20. The reaction mixture was refluxed in toluene for 24 h. The polyethylenimine grafted polystyrene resin beads obtained were purified from the excess of reactants by washing repeatedly with water and ethanol. In the second step, the polyethylenimine grafted polystyrene resin beads was functionalized by phosphonic acid group using the Moedritzer–Irani reaction [21], a mixture of polyethyleneimine grafted polystyrene resin, phosphorous acid, hydrochloric acid–

water (1:1) solution and formaldehyde aqueous solution was vigorously stirred and refluxed for 24 h in toluene. The resulting polymer was filtered and washed repeatedly with distilled water and ethanol. Preliminary sorption tests show that PEIPR beads (in acidic form) are not a good extractant for La(III), Pr(III) and U(VI). Similar results were observed with other phosphate resins [22]. The presence of H⁺ saturates the active sites (heteroatoms: O and N) on the resin and gives it a positive charge which prevents the approach of the cations to be extracted. For this reason, the resin (PEIPR) was treated, several times, with a solution of 1 M sodium hydroxide in order to replace the H⁺ on phosphonic acid group by Na⁺ (Fig. 1). The resulting sodium phosphate polymer (PEIPR-Na) was filtered and washed repeatedly with distilled water and dried in vacuum.

Ion exchange resin characterisation

The presence of amine, on the polyethylenimine (PEI) grafted resin, was confirmed by the presence of absorption at 2910 and 1602 cm⁻¹ (NH). The presence of phosphonic acid on PEIPR was confirmed by the appearance of absorption at 1110 cm⁻¹ (P=O), 1030 (P–O), 2372 and at 2340 cm⁻¹ (P–OH) with the disappearance of NH₂ band at 2910 cm⁻¹ [23–25].

The experimental CHNP analysis data (%) of the PEIPR (in acidic form) was: C: 57.44; H: 6.339; N: 7.00; P: 4.95. This analysis confirm the presence of the two groups, polyethylenimine and phosphonic acid, onto the Merrifield resin.

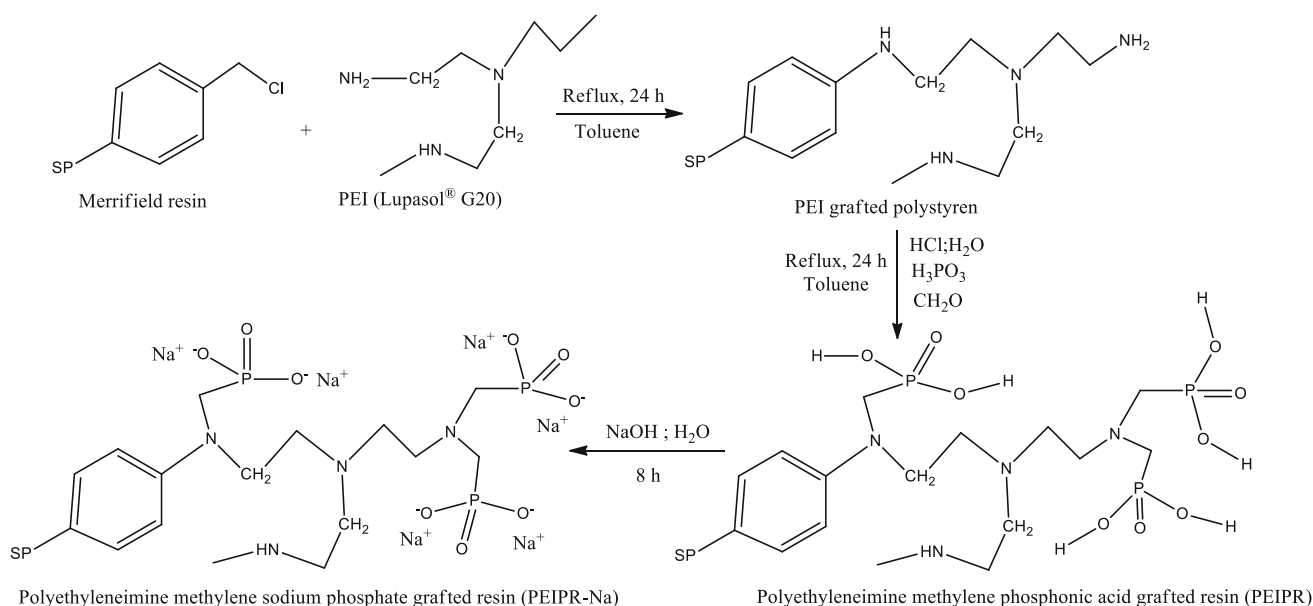


Fig. 1 Schematic illustration of the synthesis process of PEIPR-Na from Merrifield resin and polyethylenimine Lupasol® G20

Uranium(VI), Lanthanum(III) and praseodymium(III) sorption

Effect of shaking speed

The shaking speed (θ) showed a medium effect on U(VI) sorption, yield sorption increases from 94.4 to 97.1% when θ increases from 0 to 310 round per minute (rpm) (Fig. 2).

Shaking speed effect was more important with La(III) and Pr(III) ions. La(III) and Pr(III) ions recovery were respectively only 17.9 and 30.8% without shaking but at shaking speed near 310 rpm, yield recovery becomes 44.3 and 58.6% respectively (Fig. 2). The effect of increasing agitation is to decrease the film resistance to mass transfer surrounding the sodium phosphonate resin beads (PEIPR-Na), which would be beneficial to the U(VI), La(III) and Pr(III) ions sorption onto the resin. Therefore, a shaking speed of 310 rpm was maintained for the subsequent experiments to ensure the invariance of this parameter.

Effect of time contact

The equilibrium sorption time of La(III), Pr(III) and U(VI) on investigated resin (PEIPR-Na) was studied. As shown in Fig. 3, the period of 30 min can be considered as the optimum time for La(III) sorption, while for Pr(III) and U(VI), 250 min is necessary to attain the equilibrium states. Also, high sorption rate and capacity were observed towards U(VI) ions than Pr(III) and La(III). The sorption capacities of PEIPR-Na reached in this study were 1.0, 6.2 and 18.2 mg of La(III), Pr(III) and U(VI) respectively per one gram of resin. Therefore, a time contact of 250 min

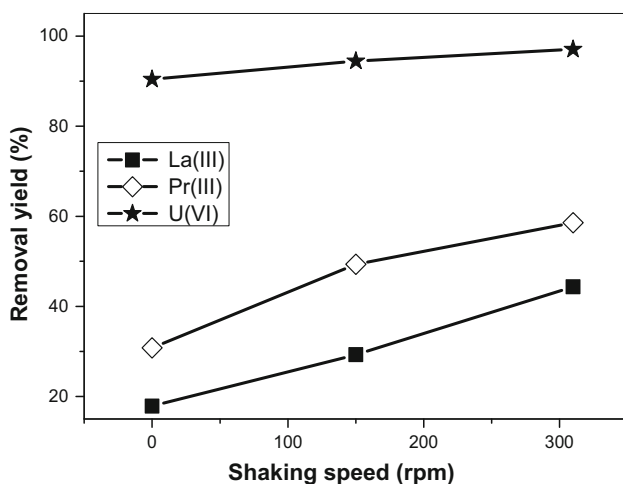


Fig. 2 Removal yield of La(III), Pr(III) and U(VI) by PEIPR-Na as a function of shaking speed, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $V = 5.0$ mL, $w = 0.05$ g, $t = 4$ h and $T = 22 \pm 1$ °C

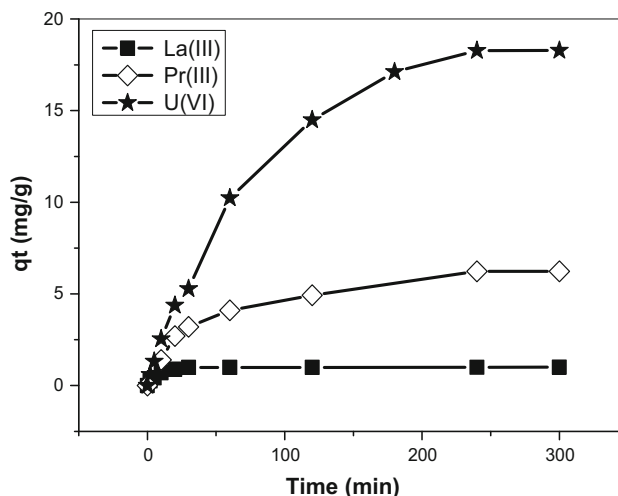


Fig. 3 Removal of La(III), Pr(III) and U(VI) by PEIPR-Na as a function of time, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $V = 5.0$ mL, $w = 0.05$ g, $\theta = 310$ rpm and $T = 22 \pm 1$ °C

was maintained for the subsequent experiments to ensure the invariance of this parameter. Contact times, required to reach maximum sorption on PEIPR-Na, were lower than those of many sorbents cited in literature [1, 2, 20, 26].

The results of the contact time studies on sorption of La(III), Pr(III) and U(VI) on PEIPR-Na resin (Fig. 3) are further analyzed using the standard kinetic models, like the Lagergren first order equation and pseudo-second order type, to understand the rate controlling step in the sorption process [26]. The linearized integrated form of the first-order rate equation for the boundary conditions $t = 0$ and $t = t$ is given as (Eq. 4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e is the amount of La(III), Pr(III) and U(VI) sorbed (mg/g) on the functionalized resin at equilibrium and k_1 is the rate constant of first order adsorption (1/min). Similarly, the relation for linearized integrated form of pseudo-second order kinetic model is given in Eq. (5).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

The units of k_2 in the pseudo-second order model is g/mg min [26]. The correlation constant (r) computed from the trend line drawn from data of Fig. 3 were 0.834, 0.969 and 0.969 for first order and 0.959, 0.996 and 0.999 for the pseudo-second order kinetic model for La(III), Pr(III) and U(VI) sorption respectively (Table 1). The value of correlation constant clearly indicates that the sorption of La(III), Pr(III) and U(VI) species on PEIPR-Na resin follow the pseudo-second order kinetics better than the first order model implying that the rate-controlling step in the exchange process is the chemisorptive forces between the

Table 1 Kinetic model parameters for La(III), Pr(III) and U(VI) sorption by PEIPR-Na

Metal/Model	Lagergren (first order)	Pseudo-second order
La(III)	$K_1 = 0.02413$ $r = 0.834$	$K_2 = 0.016611$ $r = 0.959$
Pr(III)	$K_1 = 0.01347$ $r = 0.969$	$K_2 = 4.669 \times 10^{-4}$ $r = 0.996$
U(VI)	$K_1 = 0.70617$ $r = 0.969$	$K_2 = 0.26495$ $r = 0.999$

metal nitrate ions in the solution phase and the active sites (N, O and P) on the resin [27].

Effect of pH

The pH value is one of the most important factors that affected the metal ions sorption process from aqueous systems by using batch method. The pH of solution controls the surface charge of the sorbent and ionization of the sorbate in solution. The influence of pH on the sorption of La(III), Pr(III) and U(VI), from nitrate solution, was investigated in the range of 0.7–6.8 as is shown in Fig. 4. The results indicate that sorption capacities are lowest at low pH (pH < 2). Highest sorption capacities are observed at pH > 4.3 for La(III) (≈ 1 mg/g), pH near 4.2 for Pr(III) (≈ 6 mg/g) and pH between 2.9 and 5.7 for U(VI) (≈ 19 mg/g). Similar pH intervals were obtained with other sorbent in La(III), Pr(III) and U(VI) sorption [1, 6, 28].

Uptake of La(III), Pr(III) and U(VI) ions at slightly acidic conditions may be explained to proceed via complex

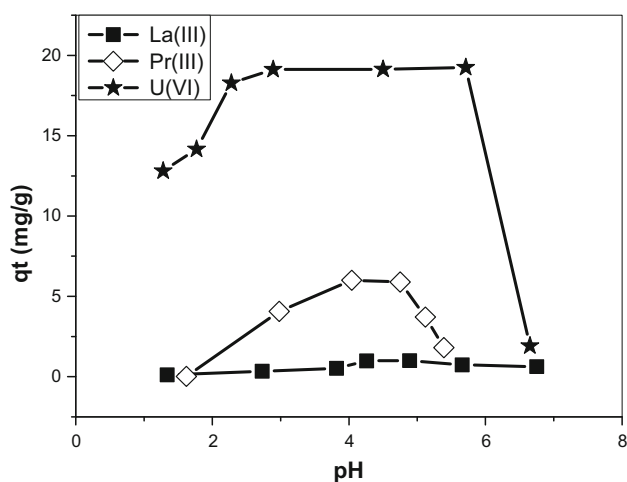
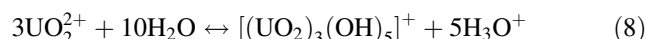
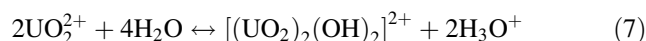


Fig. 4 Removal of La(III), Pr(III) and U(VI) by PEIPR-Na as a function of pH, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $w = 0.05$ g, $V = 5$ mL, $\theta = 310$ rpm and $T = 22 \pm 1$ °C

formation between these ions and the active sites on the resin. This sorption trend can likely be ascribed to the effect of competitive binding between La(III), Pr(III) or U(VI) and hydrogen ions for the binding sites on the surface of the resins. The low sorption capacity at low pH is due to the competition between the excess of H_3O^+ ions in the medium and positively charged cationic species (mainly presented as $[Ln(H_2O)_n]^{3+}$ and UO_2^{2+} present in solution, where Ln = La(III) or Pr(III) [1, 29].

The literature shows that the pKa value of phosphonic acid is about 2 and 5 [30]. Thus, slightly acidic conditions favoured sorption of La(III), Pr(III) and U(VI) ions onto functionalized resin as shown by earlier researchers [1, 6, 31]. This is due to the presence of negatively charged functional groups (phosphonate) on the resin in a slightly acidic medium, more negative sites are becoming available for the sorption of La(III), Pr(III) and U(VI), which leads to the uptake increases. At higher pH, La(III), Pr(III) and U(VI) uptake decrease because ions lead to more stable hydroxides complexes in aqueous phase like $[Ln(OH)_2]^+$, $[Ln(OH)]^{2+}$, $[Ln(OH)_4]^-$, $Ln(OH)_3$, $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, and $[(UO_2)_3(OH)_5]^+$. For example, formation of hydroxocomplexes of U(VI) could be explained by the following equilibriums (Eqs. 6, 7 and 8) [32–34].



Temperature dependence of sorption

Temperature affects directly the removal yield of La(III), Pr(III) and U(VI) ions onto functionalized resin. In the present investigation the sorption experiments were performed at three different temperatures 22, 27 and 35 °C. It was found that the removal yields of La(III), Pr(III) and U(VI) ions increased from 13.7, 49.2 and 41.0% to 49.2, 60.6 and 81.8% respectively with increasing temperature from 22 to 35 °C (Fig. 5). This result is expected; at higher temperature, ions are moving faster, which retards specific or electrostatic interactions that become weaker. The ions become smaller because solvation is reduced. The breaking of bonds on the resin surface and increase in the diffusion rate of La(III), Pr(III) and U(VI) ions across the external boundary layer and in the internal pores of the sorbent. The NH , N and $-P(O)(O^-Na^+)_2$ groups of PEIPR-Na are partially protonated at low temperatures but deprotonation degrees increase at high temperature resulting in an increase metal sorption capacities [35–37].

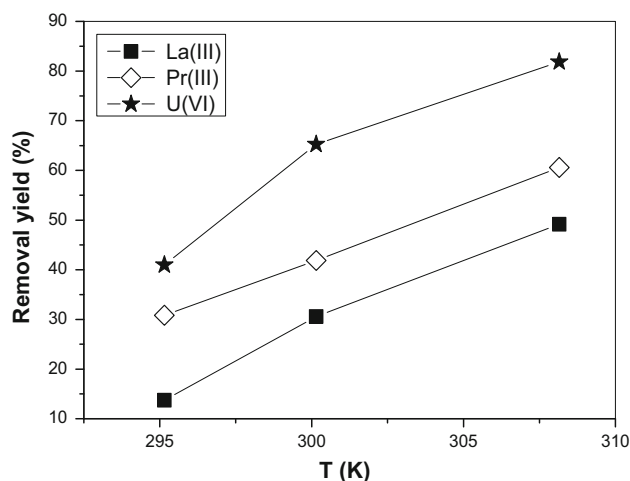


Fig. 5 Yield removal of La(III), Pr(III) and U(VI) by PEIPR-Na as a function of temperature, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $w = 0.05$ g, $V = 5.0$ mL and $\theta = 310$ rpm

Thermodynamic parameters

Assuming that the activity coefficients are unity at low concentrations, thermodynamic parameters (ΔG° , ΔH° and ΔS°) were calculated using Eq. (3) and the following relations (Eqs. 9, 10 and 11) [38]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$$\Delta G^\circ = -RT \ln D \quad (10)$$

$$\ln D = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (11)$$

where R is the universal gas constant (8.314 J/K mol), T is the absolute temperature (K), ΔG° , ΔH° and ΔS° are changes in standard free energy, standard enthalpy, and standard entropy, respectively. ΔH° and ΔS° were obtained from the linear plot of $\ln D$ versus $1/T$ (Fig. 6) and presented in Table 2.

The positive values of ΔS° reflect the big affinity of PEIPR-Na resin for La(III), Pr(III) and U(VI) and suggests increased randomness at the solid-solution interface during sorption. The positive values of ΔH° show endothermic nature of sorption process. The Gibbs free enthalpy change ΔG° was less than 0 indicating that the adsorption process was spontaneous. On the other hand, the observed decrease in the negative values of ΔG° with elevated temperature indicates that the adsorption is more favorable at higher temperatures (see Table 1) [39–41].

Effect of initial metal concentration

The sorption equilibrium of metals ions between aqueous solution and the resin can be described by a sorption isotherm. The sorption experiments were performed using

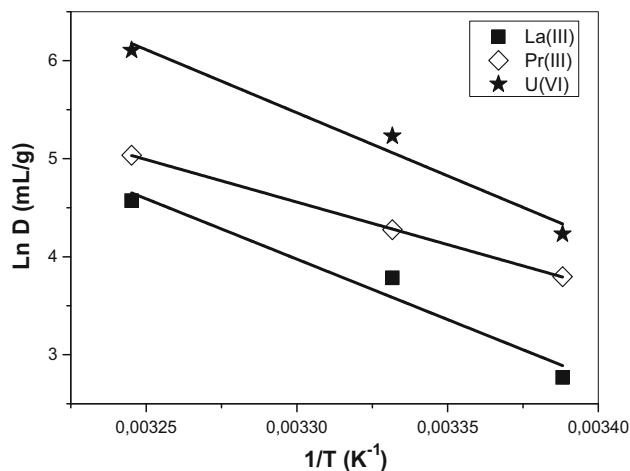


Fig. 6 $\ln D$ of La(III), Pr(III) and U(VI) removal by PEIPR-Na as a function of $1/T$, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $w = 0.05$ g, $V = 5$ mL and $\theta = 310$ rpm

Table 2 Thermodynamic parameters for the sorption of La(III), Pr(III) and U(VI) on PEIPR-Na

Ion	ΔH° (kJ/mol)	ΔS° (J/mol K)	T (K)		
			295.15	300.15	308.15
			ΔG° (kJ/mol)		
La(III)	+102.41	+371.02	-7.09	-8.95	-11.91
Pr(III)	+72.09	+275.79	-9.31	-10.69	-12.89
U(VI)	+106.98	+398.51	-10.64	-12.63	-15.82

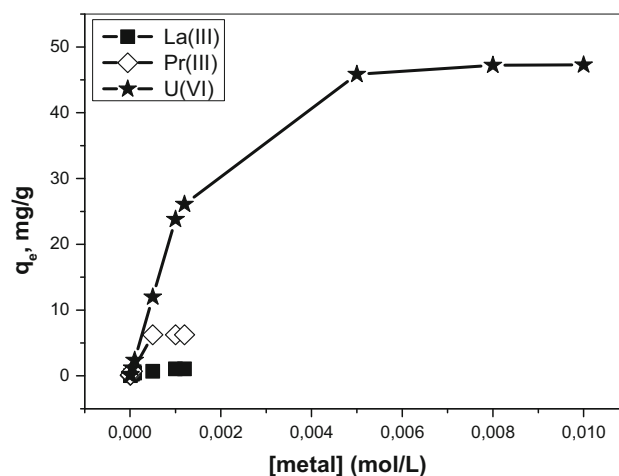


Fig. 7 Sorption isotherm of La(III), Pr(III) and U(VI) on PEIPR-Na as a function of initial La(III), Pr(III) and U(VI) concentrations, $V = 5$ mL, $w = 0.05$ g, $\theta = 310$ rpm, $T = 22 \pm 1$ °C

different initial concentrations of La(III), Pr(III) and U(VI) at 22 ± 1 °C. La(III), Pr(III) and U(VI) sorption isotherms on functionalized resin are presented in Fig. 7 as a function of the initial concentration of metals ions in the aqueous medium. The amounts of La(III), Pr(III) and U(VI) sorbed

per unit mass of the resin increased with the initial metals concentrations as expected, to reach the plateau values that represent saturation of the active groups which are available for interaction with La(III), Pr(III) and U(VI). In other terms, to obtain the maximum sorption capacities for the interested metal ions, the initial concentration were increased from 1.0×10^{-5} to 1.2×10^{-3} mol/L for La(III), from 5.0×10^{-6} to 1.2×10^{-3} mol/L for Pr(III) and from 5.0×10^{-6} to 1.0×10^{-2} mol/L for U(VI). For both metals, resin were saturated at relatively low concentrations (1.0×10^{-3} mol/L with La(III), 0.5×10^{-3} mol/L with Pr(III)) and 5.0×10^{-3} mol/L with U(VI) indicating strong binding for these metal ions. Experimental sorption capacities ($q_m(\text{exp.})$) are 1.06, 6.23 and 47.30 mg/g resin for La(III), Pr(III) and U(VI), respectively. Pr(III) and U(VI) are quantitatively removed at a metal concentration equal or less than 0.5×10^{-4} and 0.1×10^{-4} mol/L, respectively, this behavior indicates that PEIPR-Na resin is very effective in Pr(III) and U(VI) sorption from dilute solutions unlike La(III), even at a concentration equal to 0.5×10^{-4} mol/L the sorption is not complete. The curves show that the uranyl ions are more extracted than lanthanum and praseodymium, in the considered concentration range.

The sorption data were applied to models to understand the sorption mechanism. The Langmuir and Freundlich models are expressed as Eqs. (12) and (13), respectively [38]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{12}$$

$$\text{Ln}q_e = \text{Ln}K_F + \frac{1}{n}\text{Ln}C_e \tag{13}$$

where q_m (mg/g) is the maximum specific uptake corresponding to the site saturation, q_e (mg/g) and C_e (mg/L) are the amount of sorbed metal on the modified resin and the concentration of metal in the solution at equilibrium time, respectively.

The K_L (L/mg) and K_F are the Langmuir and Freundlich sorption isotherm model coefficient. The K_L is the constant related to the free energy of adsorption and represents the affinity between the metal and functionalized resin, and the K_F is the constant indicative of the relative adsorption capacity of the absorbent (mg/g), respectively. The magnitude of $1/n$ gives a measure of favorability of adsorption and the value of $1/n$ less than 1 represent a favorable sorption. The isotherm parameters calculated from the fitting are given in Table 3.

It is concluded from the higher correlation coefficients ($r = 1$ and 0.999 respectively) that the Langmuir equation fits the data better than the Freundlich model for both Pr(III) and U(VI) sorption from which the theoretical maximum sorption capacities (q_m) are very close to the

Table 3 Isotherm model parameters for La(III), Pr(III) and U(VI) sorption by PEIPR-Na

Metal/model	Langmuir	Freundlich
La(III)	$K_L = 0.041$	$K_F = 0.15$
	$q_m = 1.21$	$1/n = 0.391$
	$r = 0.983$	$r = 0.992$
Pr(III)	$K_L = 23.91$	$K_F = 6.23$
	$q_m = 6.24$	$1/n = 1.642 \times 10^{-4}$
	$r = 1$	$r = 0.835$
U(VI)	$K_L = 0.042$	$K_F = 16.81$
	$q_m = 47.87$	$1/n = 0.143$
	$r = 0.999$	$r = 0.988$

experimental values (see Table 2). The Langmuir model indicates that the sorbed Pr(III) and U(VI) is uniformly distributed in a monolayer coverage of the surface of the sorbent [38]. While for La(III), the Freundlich equation fits the data better than the Langmuir model ($r = 0.992$) indicating a multilayer adsorption nature of this metal ions on PEIPR-Na resin [38]. For the study the value of $1/n = 0.391$ exhibits the same trend of a beneficial sorption (Table 3). It is noteworthy that this resins shows significantly similar or higher sorption capacities, towards La(III), Pr(III) and U(VI) as compared with other sorbents as seen in Table 4.

Effect of salts addition

Hydrometallurgical and nuclear effluents often contain a considerable amount of ions especially sodium, potassium, nitrate, sulphate and others which affect the affinity between the sorbent and the sorbate. Therefore, investigation of the ions effect on the La(III), Pr(III) and U(VI) sorption onto PEIPR-Na sorbent is important. To investigate the effect, different sodium and/or potassium salts (chloride, nitrate, cyanide, thiocyanate, sulfate and dithionite) are added in the aqueous phase at the same concentration (1.0 mol/L). La(III), Pr(III) and U(VI) concentrations were fixed at 0.5×10^{-3} mol/L.

Figure 8 shows the La(III), Pr(III) and U(VI) sorption efficiency with various salts in aqueous solutions. From this figure, we note that both La(III), Pr(III) and U(VI) sorption efficiency increased with addition of KCl, NaNO₃, NaCl and KSCN and decreased when we add Na₂SO₄, KCN and Na₂S₂O₄ salts in the aqueous solution.

Generally, this phenomenon might be attributed to the following reasons. One is that the formation of nonextractable anionic La(III), Pr(III) and U(VI) species at higher free anionic concentrations (NO₃⁻, Cl⁻, SCN⁻, CN⁻ SO₄²⁻ and S₂O₄²⁻). The other is that ionic strength of

Table 4 A comparison of the present method with other solid phase sorption and separation chromatographic method for the sorption of La(III), Pr(III) and U(VI)

Element	Sorbent	Sorption capacity (mg/g)	Reference
La(III)	PEIPR-Na	1.06	This work
	XAD-4/Aliquat 336	4.73	[13]
	silica SBA-15/tungstophosphate	11.60	[38]
	SnO ₂ -TiO ₂ nanocomposites	4.96	[42]
	Granitic biotite	2.09	[43]
Pr(III)	PEIPR-Na	6.23	This work
	Silica gel/diglycol amic acid	12.72	[44]
	Clinoptilolite-containing tuff	17.75	[29]
	SBA-15/aurintricarboxylic acid	2.00	[45]
	DMDOHEMA impregnated resin	0.11	[46]
	TODGA impregnated resin	0.06	[46]
	U(VI)	PEIPR-Na	47.30
U(VI)	XAD-2/Tiron	7.70	[13]
	XAD-4/Succinic acid	12.33	[13]
	XAD-2/Cyanex 272	39.98	[13]
	XAD-2/Pyrogallol	6.71	[47]
	XAD-4/o-Vaniline semicarbazone	2.89	[47]
	XAD-4/quinoline-8-ol	2.74	[47]

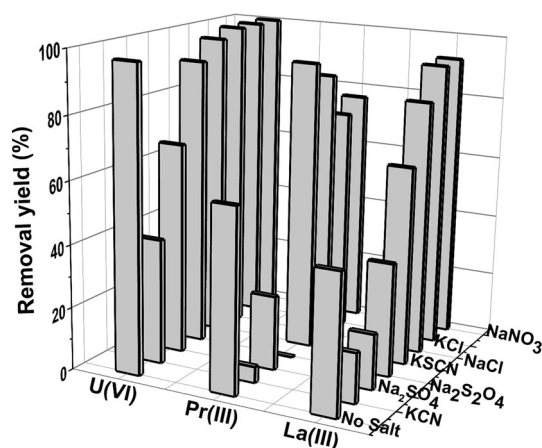


Fig. 8 Sodium and potassium salts addition effect on La(III), Pr(III) and U(VI) sorption by PEIPR-Na, [Salt] = 1.0 mol/L, $w = 0.05$ g, $V = 5.0$ mL, $[La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $\theta = 310$ rpm, $T = 22 \pm 1$ °C

solution can influence the activities coefficients of La(III), Pr(III) and U(VI) which limits their transfer to the sorbent.

The order of the increases effect is given as:

$KCl < NaNO_3 < NaCl < KSCN$ for Pr(III),
 $KSCN < NaCl < KCl < NaNO_3$ for La(III) and
 $KSCN < NaCl = KCl = NaNO_3$ for U(VI), while the
order of the decreases effect is given as: $Na_2SO_4 <$
 $KCN < Na_2S_2O_4$ for Pr(III), $Na_2S_2O_4 < Na_2SO_4 < KCN$
for La(III) and $Na_2S_2O_4 < Na_2SO_4 < KCN$ for U(VI).

It's important to note that: (i) Addition of $Na_2S_2O_4$, in aqueous solution, prevents Pr(III) sorption (Removal

yield = 0%), (ii) Addition of NaCl, KCl and $NaNO_3$ in aqueous solution makes U(VI) sorption quantitative (Removal yield = 100%).

Effect of salts concentration

From precedent figure (Fig. 8), it can be seen that $NaNO_3$ have most positive effect on the sorption process of La(III) and U(VI), while KSCN makes the same effect on Pr(III) sorption. Therefore, investigation of the $NaNO_3$ and KSCN salts concentration as a criterion of the ionic strengths on the La(III), U(VI) and Pr(III) sorption onto PEIPR-Na is important. Figure 9 shows respectively the effect of sodium nitrate and potassium thiocyanate concentrations on the removal yield of La(III), U(VI) and Pr(III), onto synthesised resin at the initials La(III), U(VI) and Pr(III) concentrations of 0.5×10^{-3} mol/L. As it can be seen from this figure, increasing salts concentration from 0 to 1.0 mol/L has positive effect on the sorption percentage of both La(III), U(VI) and Pr(III) ions, whereas, at salts concentration between 1.0 and 2.0 mol/L, the removal yield sorption does not change significantly for both ions.

Uranium(VI), lanthanum(III) and praseodymium(III) desorption

Effect of eluent nature

Desorption is crucial to reuse functionalized resin and it will decrease the process cost. Figure 4 has actually

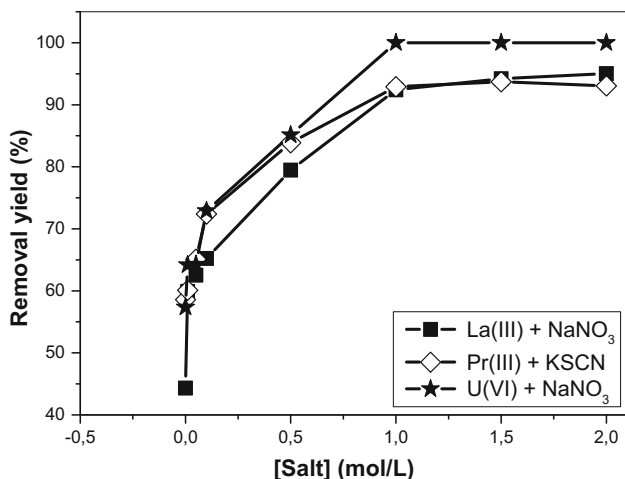


Fig. 9 Effect of NaNO₃ and KSCN salts concentration on La(III), Pr(III) and U(VI) sorption on PEIPR-Na resin, $w = 0.05$ g; $V = 5.0$ mL, $[La(III)] = [La(III)]_i = [Pr(III)]_i = [U(VI)]_i = 0.5 \times 10^{-3}$ mol/L, $\theta = 310$ rpm, $T = 22 \pm 1$ °C

illustrated that low La(III) Pr(III) and U(VI) sorption was observed at low pH values; a matter which implies that desorption from the loaded PEIPR-Na would occur with changing the nature of acid and increasing her concentration [12, 26]. For this purpose, three mineral acids, HCl, HNO₃ and H₂SO₄, at the same concentration (1.0 mol/L), were examined as eventual eluents by batch method in one cycle and at room temperature using 5 mL acid volume for 0.05 g loaded PEIPR-Na. Results are summarised in Fig. 10. From this figure, we can note that:

- The stripping percentage of La(III) using sulphuric acid, at 1.0 mol/L was very good (87.5%),
- The stripping percentage of Pr(III) using both hydrochloric, sulphuric and nitric acids, at 1.0 mol/L, was medium and do not exceed 65% with HCl solution,

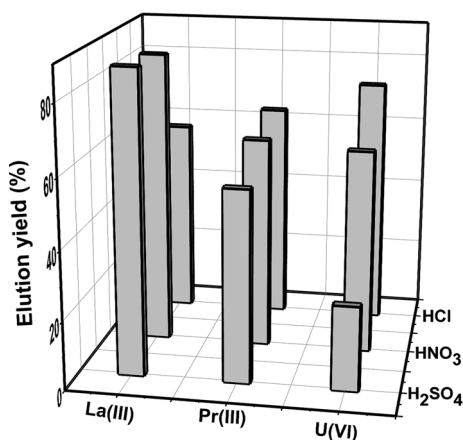


Fig. 10 Effect of eluent nature on La(III), Pr(III) and U(VI) elution, $w = 0.05$ g, $v = 5.0$ mL, $[Acid] = 1.0$ mol/L, $t = 4$ h, $\theta = 310$ rpm, $T = 22 \pm 1$ °C

- HCl solution (1 M) was the better eluent of U(VI) from PEIPR-Na resin (73.1%),
- The order of the increases in the stripping percentage of La(III), Pr(III) and U(VI) are given as: Hydrochloric acid (57.8%) < nitric acid (85.6%) sulphuric acid < (87.5%) for La(III), sulphuric acid (55.6%) < nitric acid (61.9%) < hydrochloric acid (64.2%) for Pr(III) and sulphuric acid (24.5%) < nitric acid (59.9%) < hydrochloric acid (73.1%) for U(VI).

Thus, H₂SO₄ solution was selected as eluent for La(III) and HCl for Pr(III) and U(VI) in order to study the optimum eluent concentrations.

Effect of eluent concentration on U(VI), La(III) and Pr(III) elution

The recovery of La(III), Pr(III) and U(VI) from loaded PEIPR-Na was studied using, respectively, different concentrations of sulphuric (for La(III)) and hydrochloric acids (for Pr(III) and U(VI)) in one cycle and in the range 0.01–5.0 mol/L. The results obtained are presented in Fig. 11. From this figure we note that recovery of both La(III), Pr(III) and U(VI) increased with increasing acid concentration and reached 94.3% at a concentration of 5.0 mol/L using H₂SO₄ for La(III). For Pr(III) and U(VI), elution yields reached 72.5 and 84.3% respectively using HCl 5.0 mol/L. Analyzing the results obtained, it can be observed that for the recovery of lanthanum ions a 2 M H₂SO₄ solution can be used and for the recovery of praseodymium and uranyl ions from the same sorbent it is appropriate to use a solution of 2 mol/LHCl.

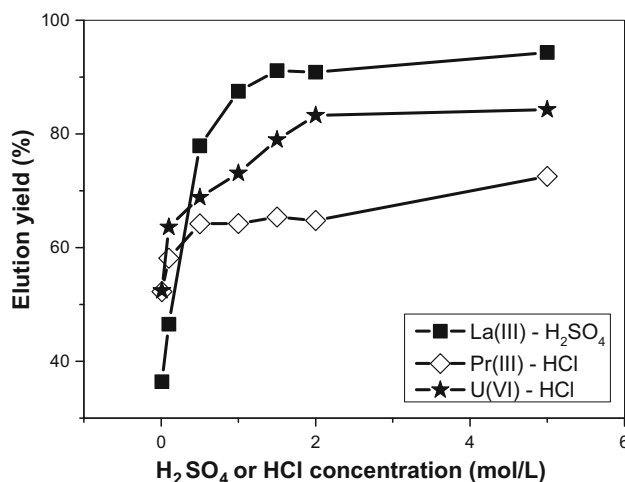


Fig. 11 Effect of leachant concentration on La(III), Pr(III) and U(VI) elution, $w = 0.05$ g, $v = 5.0$ mL, $t = 4$ h, $\theta = 310$ rpm, $T = 22 \pm 1$ °C

Conclusions

In this study, the sorption capacities of La(III), Pr(III) and U(VI) on a novel polyethylenimine sodium phosphonate resin (PEIPR-Na) were studied by batch tests conducted under various experimental conditions such as shaking speed, contact time, pH, initial La(III), Pr(III) and U(VI) content, temperature and presence of another salt in aqueous solution. Based on the results, the following conclusions are summarized as below:

- The sorption of the investigated metal ions increases by increasing the shaking speed and contact time.
- The equilibrium batch experiment data demonstrate that PEIPR-Na is most selective towards U(VI) than Pr(III) and La(III). The maximum sorption capacities were 47.30 mg g^{-1} for U(VI), 6.23 mg/g for Pr(III) and only 1.06 mg/g for La(III) under the given experimental conditions.
- The sorption of La(III), Pr(III) and U(VI) on the resin is strongly dependent on pH medium. Sorption of both La(III), Pr(III) and U(VI) are low in more acidic medium.
- The calculated thermodynamic parameters showed the feasibility, endothermic and spontaneous nature of the sorption of both La(III), Pr(III) and U(VI) ions.
- La(III), Pr(III) and U(VI) sorption efficiency increased with addition of KCl, NaNO_3 , NaCl, and KSCN and decreased when we add Na_2SO_4 , KCN and $\text{Na}_2\text{S}_2\text{O}_4$ salts in the aqueous solution. Presence of $\text{Na}_2\text{S}_2\text{O}_4$ in aqueous solution, prevents Pr(III) sorption (Removal yield = 0%) while presence of KCl, NaNO_3 and NaCl makes uranyl sorption quantitative (100%). This enables the possibility of separation of Pr(III) from aqueous solutions containing La(III) and U(VI).
- The results of La(III), Pr(III) and U(VI) ions desorption reported that: (i) At low acid concentration ($\leq 0.1 \text{ mol/L}$) Pr(III) and U(VI) were most desorbed ($\geq 58.0\%$) while desorption of La(III) do not exceed 47.0% . (ii) At high acid concentration ($\geq 0.5 \text{ mol/L}$), results were inversed, and La(III) and U(VI) were most desorbed (94.3% for La(III) and 84.3% for U(VI)) while desorption of Pr(III) do not exceed 72.5% . This enables the possibility of separation of La(III), Pr(III) and U(VI) from aqueous solutions.
- Quantitative sorption of Pr(III) and U(VI), from dilute solutions (concentration $\leq 10^{-5} \text{ mol/L}$), suggests the possible application of the resin in the pre-concentration of minor Pr(III) and U(VI) from environmental/laboratory waste samples.
- The results obtained in this study make PEIPR-Na as promising candidate for sorption, immobilization and

pre-concentration of U(VI) ions from large volume of solutions containing La(III) and Pr(III).

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