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A new sorbent for europium nitrate extraction: phosphonic acid grafted on polystyrene resin

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Abstract A new chelating polymeric sorbent has been developed using polystyrene resin grafted with phosphonic acid. After characterization by FTIR and elementary analysis, the new resin has been investigated in liquid–solid extraction of europium(III). The results indicated that phosphonic resin could adsorb Eu(III) ion effectively from aqueous solution. The adsorption was strongly dependent on pH of the medium with enhanced adsorption as the pH value of 6.5. The influence of other analytical parameters including contact time, amount of resin, metal ion concentration, and ionic strength were investigated. The maximum uptake capacity of Eu(III) ions was 122.6 mg/g grafted resin at ambient temperature, at an initial pH value of 6.50. The overall adsorption process was best described by pseudo first-order kinetic. When Freundlich and Langmuir isotherms were tested, the latter had a better fit with the experimental data. Furthermore, Eu(III) could be eluted by using 1.0 mol/L H₂SO₄ solution and the grafted resin could be regenerated and reused.

Keywords Solid phase extraction · Ion exchange resin · Europium(III) · Supported phosphonic acid

Introduction

One of the important processes in the management of nuclear wastes is the intra- and inter-group separation of lanthanides and actinides. For this goal, it is pertinent to search for new extraction system in addition to using familiar ones.

The most used methods for separation and pre-concentration of lanthanides include solvent extraction [1], ion exchange [2], adsorption [3], flotation [4], precipitation [5], co-precipitation [6], membrane dialysis [7], Cloud point extraction [8] and chromatographic extraction [9]. Most of these methods suffer from technical, economic and health problems related to selectivity, long time of extraction and large quantity of hazardous materials used.

One of the promising methods is the use of solid phase extraction by functionalized resins that have suitable functional groups capable of interaction with metal ions. The use of solid phase extraction have been proved to be more advantageous in view of their total insolubility in aqueous phase, low rate of physical degradation, high sorption capacity for metal ions, low organic solvent inventory and good flexibility in working conditions [10]. The organic extractant can be grafted to an inert polymeric support like polystyrene, and recently extraction of europium(III) ions from aqueous solutions was carried out using chelating resin with imino diacetate group (Tulsion CH-90 resin) [11], Amberlyst A-15 [12], resin containing bis(2,4,4-trimethylpentyl)dithiophosphinic [13], dipicolinic derivative coordination cages in styrene-based polymeric material [14], Amberlite XAD-7HP resin containing 1 wt% of the Kläui ligand [15], octyl(phenyl)-*N,N'*-diisobutyl carbamoylmethylphosphine oxide and polyacrylonitrile [16], phosphinic acid polystyrene resin [17] and di-(2-ethyl-hexyl) phosphoric acid (HDEHP)-Levextrel resin [18].

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In the present work, we described the new synthesis and characterization of polystyrene resin grafted with phosphonic acid. This resin was applied as a new sorption material for europium(III) extraction in batch process. The effects of analytical parameters, adsorption kinetic, isotherm studies and desorption process were investigated.

Experimental

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer ATR spectrometer. A Bruker Advance 400 spectrometer was used for ^{13}C and ^{31}P MAS NMR analysis. Visible spectra were measured using Perkin-Elmer-Lambda 800 UV-Vis spectrophotometer. pH measurements were taken on a potentiometer Consort C831. Elemental analyses were carried out on a Thermoquest CHP analyzer.

Reagents

Chloromethyl styrene-divinylbenzene copolymer (S-3% DVB) was precursor of Amberlite resin, gifted by Rohm and Haas Company. Triethylphosphite, hydrobromic acid, dichloromethane and acetone were provided from Fluka. Europium carbonate dehydrates (99.99%), sodium nitrate, sodium acetate, ethylenediaminetetraacetic acid (EDTA), ammonium carbonate, sodium chloride, and Arsenazo(III) were obtained from Merck. Hydrochloride acid (36%) and nitric acid (65%) were purchased from Reidel-de-Haen.

Stock solution (1.0 M) of europium(III) nitrate was prepared by dissolving her carbonate dehydrates in chemically pure HNO_3 . Solutions of lower concentrations were prepared by the dilution of stock solution.

Synthesis of polystyrene resin anchored with phosphonic acid

The new sorbent, the phosphonic acid grafted polystyrene resin beads, was synthesized using the Arbuzov reaction [19] (Fig. 1). In first step, after washing with acetone, the vacuum dried Merrifield resin 3% (20.34 g) was reacted with 35 mL of triethylphosphite (excess). The reaction mixture was refluxed for 4 h. The phosphonate grafted polystyrene resin beads obtained were purified from the

excess of reactants by washing repeatedly with water and acetone. The resin beads were dried under vacuum (14.26 g). In the second step, a bromide hydrogen acid (33 mL) was added on the phosphonate grafted polystyrene resin beads (10.00 g), and vigorously stirred under reflux for 3 h. The resulting polymer was filtered and washed repeatedly with distilled water and dichloromethane, and dried in vacuum (8.62 g).

The originality of this synthesis is to use HBr acid [19] instead of HCl acid in phosphonate ester hydrolysis [20]. Indeed, after hydrolysis by HCl, a mixture of phosphonate ester and phosphonic acid resin is produced with a reaction time of 15 h (partial hydrolysis); this explains the lower retention capacities of this grafted styrene-divinylbenzene for metal cations [20]. The hydrolysis by HBr is total, after only 3 h all phosphonate is converted to acidic form [19], for this reason the retention capacities are higher. As a result, these resins have attracted the most attention because they may be easily produced in a wide variety of compositions.

Characterization studies

The structure and purity of the final complexing agent were identified and characterized by MAS NMR of ^{31}P and ^{13}C spectroscopy, FTIR measurement and elemental microanalysis. The MAS NMR spectra showed the expected signals due to the polystyrene skeleton and phosphonic units as matched to the proposed structure (Fig. 1).

^{31}P MAS NMR: 17.8 ppm, ^{13}C MAS: 36.4 ppm ($\text{CH}_2\text{-P}$), 127.75, 130.1, 137.1, and 138.5 ppm.

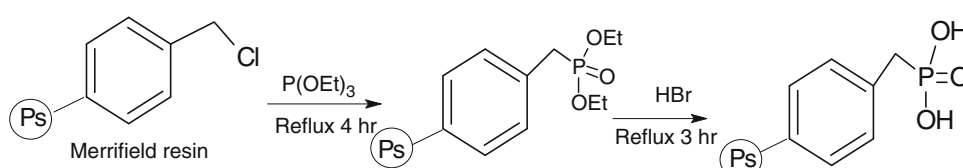
The presence of phosphonic acid was confirmed by the appearance of absorption at $3,000\text{--}2,850\text{ cm}^{-1}$ (OH), $1,124\text{ cm}^{-1}$ (P=O), $1,037\text{ cm}^{-1}$ ($\nu_{\text{as}}\text{ P-OH}$), 941 cm^{-1} ($\nu_{\text{s}}\text{ P-OH}$) and by the disappearance of P-OEt band at $1,023\text{ cm}^{-1}$ [21].

The experimental CHP analysis data (%) of phosphonic acid grafted polystyrene resin is: C, 85.31; H, 9.34; P, 2.35.

Adsorption technique

Batch technique was applied to investigate the different parametric effects on the sorption process. Where a certain weight 0.030 g (m) of the grafted resin was mixed with a certain volume 4 mL (V) of Eu(III) aqueous solutions and equilibrated by shaking in a shaker with speed 250 round

Fig. 1 Scheme for synthesis of phosphonic acid grafted polystyrene resin beads



per minute (rpm) at room temperature. The ratio of m/V was kept constant for all the experiments. The solutions were separated after a certain time and the concentrations of Eu(III) in the aqueous phase were determined, before and after extraction spectrophotometrically with Arzenazo(III) at pH 2.80 [22, 23]. The absorbance of Arzenazo(III)–eu(III) complex was measured at 654 nm. The extraction yield (%) was determined using the following equation (Eq. 1):

$$\text{Extraction yield (\%)} = \left(\frac{C_0 - C_e}{C_0} \right) 100\% \quad (1)$$

where C_0 and C_e , denote the initial and equilibrium concentrations of Eu(III) in the aqueous phase (mol L^{-1}).

Kinetic and sorption isotherms

The kinetic behavior of Eu(III) ions on grafted resin was followed up by application of batch technique. Sorption isotherms for Eu(III) was determined over the concentration range of 9.30×10^{-2} – 25 mmol L^{-1} . The amount of ions sorbed by phosphonic resin, q_t (mg/g), was calculated by the following relationship (Eq. 2).

$$q_t (\text{mg/g}) = (C_0 - C_t) \cdot V \cdot \frac{M}{m} \quad (2)$$

where C_t is the final concentrations at certain time t of the ions in the liquid phase (mol L^{-1}), V is the volume of the aqueous phase (4 mL), m is the weight of grafted resin (0.030 g) and M ($151.96 \text{ g mol}^{-1}$) is the atomic weight of europium.

Results and discussion

Effect of pH

Changes in pH of the medium are one of the most important factors affecting the concentration and metal recovery procedure, which is related to the formation of soluble metal complexes and subsequently their stabilities in aqueous solutions. It is well known that surface charge of adsorbent can be modified by charging the pH of the solution and the chemical species in the solution depends on this parameter [24]. In order to optimize the pH for maximum removal, experiments were conducted in the pH range 1.24–7.21 at ambient temperature, 4 h equilibration time, and 1.0 mmol L^{-1} metal ion concentration. Figure 2 shows the influence of pH in sorption process of europium by modified resin. The data reveals maximum values of Eu(III) around pH 6.5. As can be seen from Fig. 2 the sorption decreases quickly with decreasing pH values. The reason for low adsorption capacity in high acidic media is:

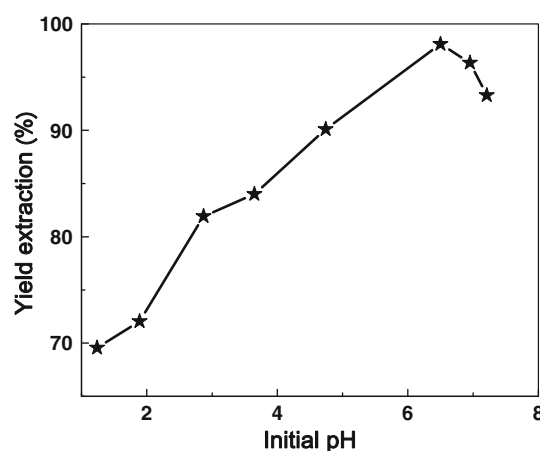
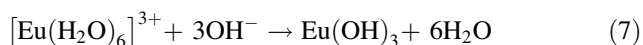
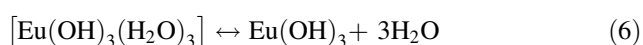
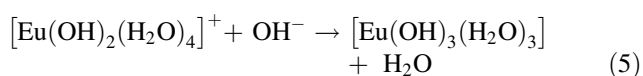
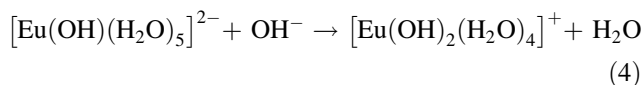
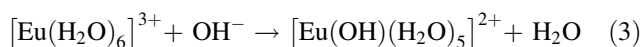


Fig. 2 Effect of initial pH of the aqueous solution on the retention of europium(III) on functionalized resin. $C_0 = 1.0 \text{ mmol L}^{-1}$, $m = 0.030 \text{ g}$, $V = 4 \text{ mL}$, contact time = 4 h

(i) the competition between the excess of H^+ ions in the medium and positively charged cationic species present in solution, (ii) higher acid concentrations suppress hydrolysis of the europium ions, (iii) as pH is increased there is a decrease of positive surface charge, which results in lower coulombic repulsion of the adsorbing metal ions, (iv) formation of soluble metal hydroxide ($\text{Eu}(\text{OH})_3$) and subsequently her stability in aqueous solutions. Consequently the number of moles of Eu(III) removal may decrease at low pH [25]. The observed reduction in the level of metal ion removal from solution by the sorbent indicates that the interaction between the Eu(III) ions and the sorbent is an ion exchange process. The following equations for metal ions as a function of pH were expected [25] (Eqs. 3–7).



Contact time

The rate of loading of Eu(III) onto the grafted polystyrene resin was determined for two concentrations of Eu(III) 1.0 and 0.5 mmol L^{-1} , by shaking 4 mL of Eu(III) with 0.030 g of resin in an Erlenmeyer flasks at ambient temperature for 5, 10, 20, 40, 80, 90, 120, 180, and 300 min. Figure 3 shows that the initial concentration of Eu(III) has

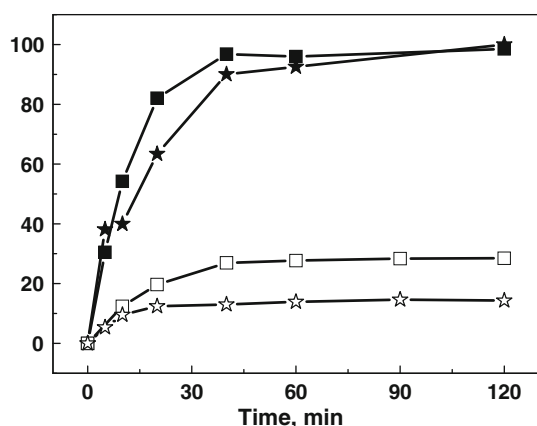


Fig. 3 Effect of agitation time on the sorption of Eu(III) on polymer from aqueous Eu(III) solutions at: $C_0 = 0.5 \text{ mmol L}^{-1}$: Filled square Percent Eu(III) removal (%), open star Uptake (q), mg.g^{-1} , $C_0 = 1.0 \text{ mmol L}^{-1}$: filled star Percent Eu(III) removal (%), open square Uptake (q), mg.g^{-1} ; $V = 4 \text{ mL}$; $m = 0.030 \text{ g}$; shaking rate = 250 rpm; Initial pH = 6.5

a slight effect on the rate of adsorption. For all the adsorption experiments, the amount of europium ions adsorbed onto the grafted resin increased quickly with time and then slowly reached equilibrium after 120 min. The equilibrium time in which the polymer attains 50% saturation with Eu(III) (half time $t_{1/2}$) is <20 min. The amounts of europium metal ions adsorbed at equilibrium (q_e) at $[\text{Eu(III)}] = 0.5$ and 1.0 mmol L^{-1} , respectively, are 14.3 and 28.4 mg g^{-1} .

Rate of kinetics adsorption

The kinetics of Eu(III) adsorption on grafted resin follows the first-order rate expression given by Lagergren (Eq. 8) [26].

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t \quad (8)$$

where q_t and q_e are the amounts of Eu(III) adsorbed (mg g^{-1}) at time, t (min) and equilibrium time (120 min), respectively and K_{ads} the rate constant of adsorption. Linear plots of $\log(q_e - q)$ versus t (Fig. 4) shows the applicability of the above equation for grafted resin. The correlation coefficients of linear plot obtained for Lagergren plot is 0.995, for 0.5 mmol L^{-1} of Eu(III) solution. The K_{ads} calculated from the slope of Fig. 4 is 0.06637 min^{-1} .

Sorption capacity

The retention capacity of functionalized resin was determined by equilibrating 0.030 g of the resin with 4 mL of europium(III) ion solutions at different concentrations (9.30×10^{-2} – 25 mmol L^{-1}), under optimum pH. The

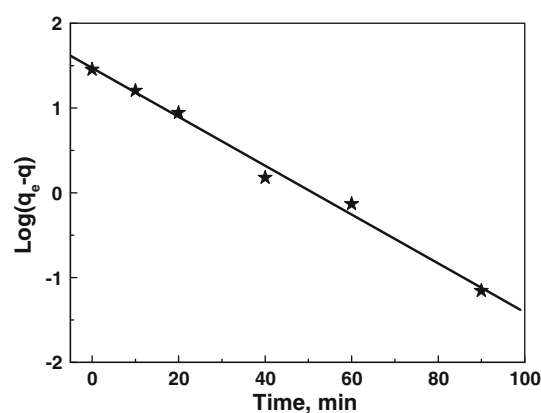


Fig. 4 Lagergren plot for the adsorption of Eu(III). $m = 0.030 \text{ g}$, $V = 4 \text{ mL}$, initial pH = 6.5, $C_0 = 1.0 \text{ mmol L}^{-1}$

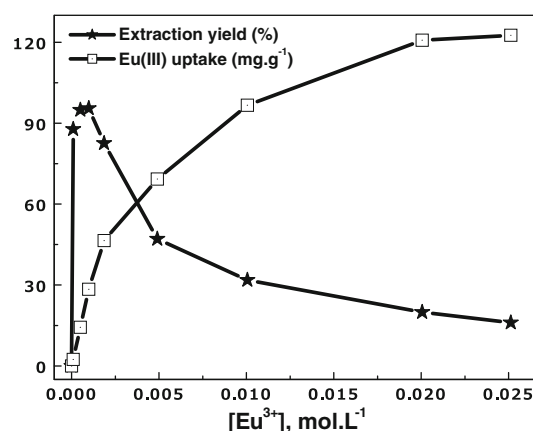


Fig. 5 Effect of initial concentration of Eu(III) on the retention and the extraction yield. $m = 0.030 \text{ g}$, $V = 4 \text{ mL}$, equilibrium time 120 min, pH = 6.5

experimental capacity obtained is 122.5 mg g^{-1} of polymer (Fig. 5).

As seen from Table 1, this capacity is in most cases much higher than solid phase extractants reported in literature so far.

Adsorption isotherm

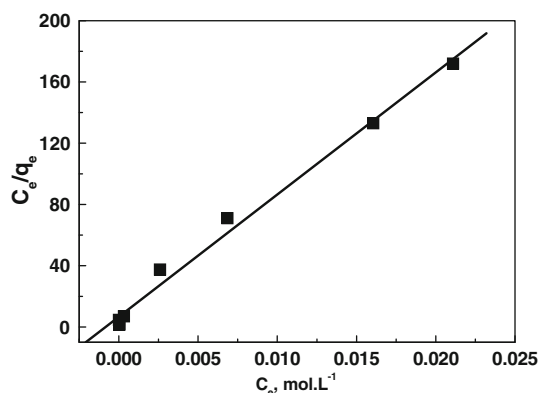
The adsorbed amounts of Eu(III) on resin have been determined as a function of the metal concentration in the supernatant at the equilibrium state and ambient temperature. The Langmuir treatment (Eq. 9) [25] is based on the assumption that (i) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, (ii) the energy of adsorption is constant and (iii) there is no transmigration of adsorbate in the plane of the surface.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (9)$$

Table 1 Comparison of sorption capacities of phosphonic acid grafted polystyrene resin beads with solid phase extractants

Solid phase extractant	Sorption capacity (mg/g)	Metal ion	Reference
Phosphonic acid grafted on polystyrene resin	122.5	Eu(III)	This work
Tulsion CH-90 resin	47.11	Eu(III)	[11]
Silica doped with acyl-hydroxypyrazole	2.12	Eu(III)	[27]
Crab shell particles	52.4	Eu(III)	[28]
EGIB sorbent	57.74	Eu(III)	[29]
Phosphoric acid activated silico-antimonate crystals	0.8	Eu(III)	[30]
Chitosan derivatives	29.47	Eu(III)	[31]
D113 cation exchange resin	290.9	Eu(III)	[32]
Lewatit TP 260 resin	58.33	U(VI)	[33]
Polyethyleniminephenylphosphonamidic acid	39.66	U(VI)	[34]
Ethylenediamino tris(methylenephosphonic) acid grafted on polystyrene resin	41.76	U(VI)	[26]
Succinic acid, Amberlite XAD-4	12.33	U(VI)	[35]
Polyethyleneiminemethylene phosphonic acid	85.69	Cu ²⁺	[36]
Phosphonate ester/phosphonic acid grafted styrene-divinylbenzene	8.46 (pH = 1)	Cu ²⁺	[20]
	7.17 (pH = 1)	Ca ²⁺	
	19.0 (pH = 7)	Ni ²⁺	

where C_e is the equilibrium concentration (mg L^{-1}), q_e the amount adsorbed at equilibrium and q_m and K_L are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e versus C_e shows that adsorption obeys Langmuir adsorption model (Fig. 6). The correlation coefficient for the linear regression fits of the Langmuir plot was found to be 0.995. q_m and K_L determined from the Langmuir plot were found to be 125.3 mg g^{-1} and $1.98 \times 10^{-9} \text{ L mol}^{-1}$, respectively. We note that capacity of sorption deducted after Langmuir model application is similar to this calculated experimentally (122.5 mg g^{-1}). The correlation coefficient for the Langmuir plot was found to be 0.995 indicating a better fit of the experimental data compared to Freundlich plot.

**Fig. 6** Langmuir plot for the adsorption of Eu(III). $m = 0.030 \text{ g}$, $V = 4 \text{ mL}$, initial pH = 6.5, equilibrium time 120 min

The Freundlich equation was also applied to the adsorption. The Freundlich equation is basically empirical but is often useful as a means of data description [26]. It generally agrees quite well compared to Langmuir equation and experimental data over a moderate range of adsorbate concentrations. The linearized Freundlich isotherm is represented by Eq. 11:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e. \quad (11)$$

A plot of $\log(q_e)$ versus $\log C_e$ (figure not shown) is linear and the constants K_F and n were found to be 723.15 mg g^{-1} and 2.51 respectively. The correlation coefficient for the linear regression fits of the Freundlich plot was found to be 0.904.

Diffusion study

The adsorption of europium(III) on the grafted resin from europium nitrate solutions at two different initial metal concentrations was studied as a function of time at ambient temperature. The adsorption onto ion exchange resin must be considered as a liquid–solid phase reaction which includes several steps [37]:

(i) The diffusion of ions from the solution to the resin surface, (ii) The diffusion of ions within the solid resin, (iii) The chemical reaction between ions and functional groups of the resin.

The adsorption of the metal is governed by the slowest of these processes. The kinetic models and the rate equations for the above three cases have been established. The

exchange of ions can be described by the Nernst–Planck equations which apply to counter diffusion of two species in an almost homogeneous media [37]:

If the liquid film diffusion controls the rate of exchange, the following relation can be used (Eq. 12):

$$-\ln(1 - F) = kt \quad (12)$$

If the cases of diffusion of ions in the resin phase controlling process, the equation used is (Eq. 13):

$$-\ln(1 - F^2) = kt \quad (13)$$

In both Eqs. 12 and 13, k is the kinetic coefficient or rate constant. K is defined by expression 14:

$$K = \frac{D_r \pi^2}{r_0^2} \quad (14)$$

where D_r is the diffusion coefficient in the resin phase and r_0 is the average radius of resin particle. Thus, the values of the adsorption rate constant and of the diffusion coefficient in the resin phase calculated from the slope of the straight lines (Fig. 7) are summarized in Table 2.

After testing both mathematical models proposed for homogeneous diffusion in the adsorption of Eu(III) onto the resin, this is best fitted when the metal uptake is particle diffusion controlled (Table 3).

When the adsorption of metal ion involves mass transfer accompanied by chemical reaction the process can be explained by the moving boundary model [38]. This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core and that advances

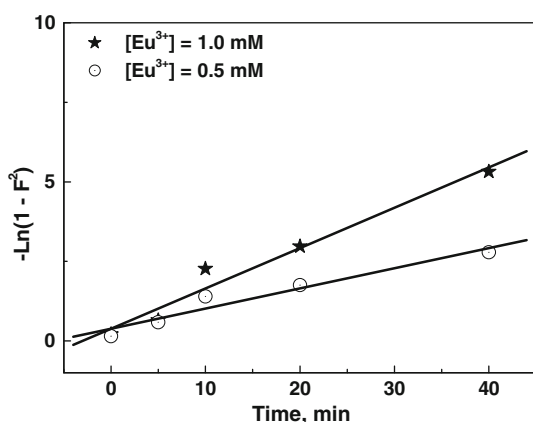


Fig. 7 Plot of Eq. 13 for Eu(III) adsorption on grafted resin

Table 2 Kinetic parameters of Eu(III) adsorption on grafted Resin

Parameter	0.5 mmol L ⁻¹	1.0 mmol L ⁻¹
K (min ⁻¹)	0.06326	0.12673
$D_r \times 9 \cdot 10^6$ (cm ² min ⁻¹)	1.6	3.2

Table 3 The regression equations and regression coefficients (r^2 in parentheses)

Eu(III) (mmol L ⁻¹)	Eq. 12	Eq. 13	Eq. 15
0.5	$y = -0.05994 t$ (0.936)	$y = 0.06326 t$ (0.971)	$y = 0.02526 t$ (0.991)
1.0	$y = -0.09432 t$ (0.955)	$y = 0.12673 t$ (0.983)	$y = 0.03514 t$ (0.985)

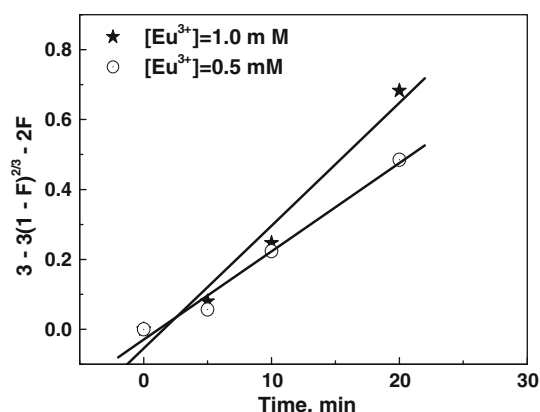


Fig. 8 Plot of moving boundary particle diffusion model for the Eu(III) adsorption on grafted resin

from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by:

$$3 - 3(1 - F)^{\frac{2}{3}} - 2F = kt. \quad (15)$$

The graphical correlation in Fig. 8 of Eq. 15 shows that the moving boundary particle diffusion model fits only the initial adsorption on the grafted resin. The linear regression analysis of functions Eq. 15 is also given in Table 3.

Effect of electrolytes on Eu(III) extraction

As the nitrates and alkali ion frequently accompany lanthanides in industrial solutions, it is worthwhile to know if they affect the extraction process efficiency. Therefore, the influence of the anion of the inorganic salt used to control the ionic strength and that of the concentration of the nitrate ion was considered [39]. The influence on the extraction of Eu(III) was studied at varying concentrations (0.04–1.70 mol L⁻¹) of NaNO₃. The influence of the concentration of sodium nitrate is shown in Fig. 9.

- Higher extraction percentage is observed with increasing nitrate ion concentration [0.04–0.17 mol L⁻¹]. Yield extraction increase from 81.33 to 82.28%, in keeping with the participation of nitrate anions in the extracted complexes.

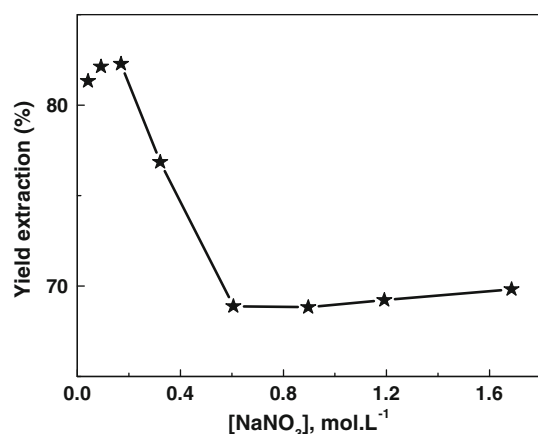


Fig. 9 Effect of NaNO_3 salt concentration on the extraction of Eu(III) with grafted resin. $m = 0.030$ g, $V = 4$ mL, equilibrium time 120 min, $C_0 = 1.0$ mmol L^{-1}

- b) Thereafter, at NaNO_3 concentration between 0.17 and 0.60 mol L^{-1} there is a negative trend on increasing electrolyte concentration, yield extraction decreases from 82.28 to 68.89%. The decrease in the extraction of Eu(III) may be due to the formation of more stable metal nitrate-complexes [39], $[\text{Eu}(\text{NO}_3)]^{2+}$, which was non-extractable by the grafted resin.
- c) The variation of the nitrate salt concentration from 0.60 to 1.70 mol L^{-1} , is found to have no detectable effect on extraction yield (near 69%).

Elution studies

In order to investigate the elution behavior of Eu(III) from the loaded resin, elution experiments were conducted with using various eluting agents and in which the acidity of the eluant and contact time were increased.

Selection of eluant

The optimum eluant for quantitative Eu(III) recovery were studied by equilibrating 0.030 g of resin beads with 4 mL of Eu(III) solution (0.5 mmol L^{-1}) in optimum conditions of pH and shaking time. Batch experiments on quantitative desorption of the sorbed metal ions was tested using various eluting agents (HCl , H_2SO_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NaCl , Na_2CO_3 and Na_2SO_4) at 0.1 mol L^{-1} as shown in Fig. 10. It was found that the higher recovery (75%) was obtained using H_2SO_4 0.1 mol L^{-1} . For the other eluants, it was found that only a small proportion of the europium was stripped from the resin, this indicated that the eluants ions only weakly compete with europium. As a result, H_2SO_4 was chosen for elution procedure.

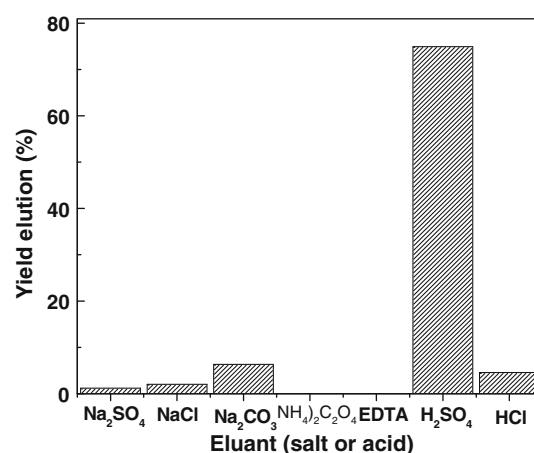


Fig. 10 Optimum eluants for quantitative recovery of Eu(III) . Masse of loaded resin: 0.03 g, contact time = 2 h, V : 4 mL, eluant concentration = 0.1 mol L^{-1}

Effect of the contact time on elution

Aliquots of about 0.030 g of loaded grafted resin (from the experiment at pH 6.5 with 0.030 g resin and 4 mL of 0.5 mmol L^{-1} Eu(III) solution) were bottle-rolled with 4 mL of H_2SO_4 0.1 mol L^{-1} at different time contacts (5–90 min). The percentage desorption is plotted against time in Fig. 11. A curve leading to equilibrium desorption of europium(III) from the grafted resin was obtained. With an increase in contact time from 5 to 60 min, the percentage europium desorption increased from 60.5% to 75%. Subsequent increase in contact time had no effect on europium desorption. Thus, 60 min was the optimum contact time to reach the maximum of desorption.

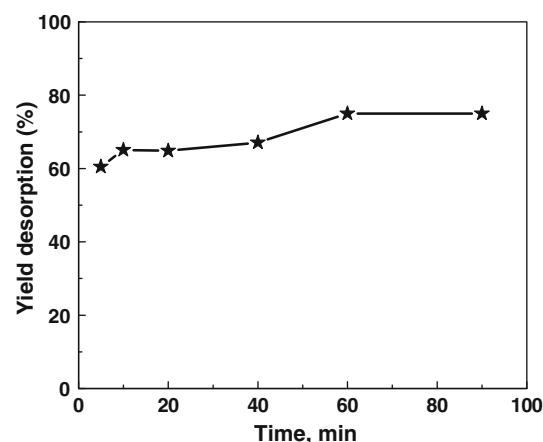


Fig. 11 Effect of contact time on the desorption of Eu(III) loaded on grafted resin. Masse of loaded resin: 0.030 g, H_2SO_4 volume: 4 mL, $[\text{H}_2\text{SO}_4] = 0.1$ mol L^{-1}

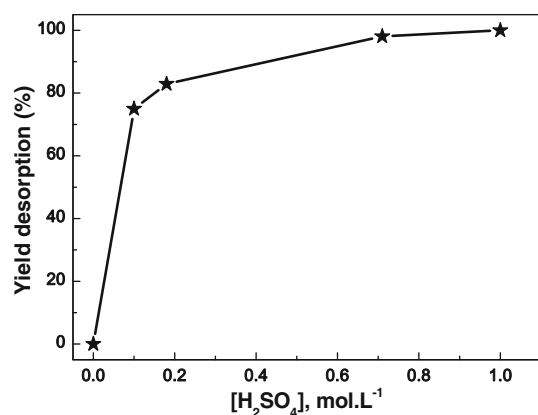


Fig. 12 Effect of H₂SO₄ concentration on the desorption of Eu(III) loaded on grafted resin. Loaded resin quantity: 0.030 g, Acid volume: 4 mL, contact time: 60 min

Effect of the sulphuric acid concentration on elution

Adsorption and elution processes depend on the solution pH. Therefore, elution is possible by controlling the pH/acid concentration of the solution. Elution of europium from loaded grafted resin was carried out using sulphuric acid at different concentrations (0.0–1.5 mol L⁻¹). The contact time was maintained at 60 min. The results in Fig. 12 show that percentage elution increased with increasing acid concentration and a sulphuric acid concentration of 1.0 mol L⁻¹ was found suitable to elute all the Eu(III) from the grafted resin.

Conclusion

A new sorbent the phosphonic acid grafted on polystyrene resin was synthesized using the Arbuzov reaction and used as support material for Eu(III) sorption, in batch process. The extraction efficiency was determined as a function of various parameters such as time, pH, europium concentration, and electrolytes effect. The experimental capacity obtained is 122.5 mg g⁻¹. The kinetics of Eu(III) adsorption on grafted resin follows the first order rate expression given by Lagergren. The equilibrium isotherm for sorption of the investigated metal ions has been modeled successfully using the Langmuir isotherm. The Eu(III) uptake is best explained by a particle diffusion controlled process, whereas the moving boundary model only fits the initial adsorption on the phosphonic resin.

Close to 100% elution of europium(III) can be achieved with H₂SO₄ 1.0 mol L⁻¹ after 60 min of shaking.

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References

1. Ali A, Rehmann H, Anwar J, Saeed MM (2010) Effect of solvent on the extraction of lanthanides with picrolonic acid. *Radiochim Acta* 98(12):801–805
2. Turanov AN, Karandashev VK, Sharova EV, Artyushin OI, Odinets IL (2010) Extraction of Lanthanides(III) from HClO₄ solutions with bis(diphenylphosphorylmethylcarbamoyl)alkanes. *Solvent Extr Ion Exch* 28(5):579–595
3. Tan X, Fang M, Wang X (2010) Sorption speciation of lanthanides/actinides on minerals by TRLFS, EXAFS and DFT studies: a review. *Molecules* 15(11):8431–8468
4. Chirkst DE, Lobacheva OL, Berlinskii IV, Sulimova MI (2009) The thermodynamic properties of hydroxo compounds and the mechanism of ion flotation for cerium, europium, and yttrium. *Russ J Phys Chem A* 83(12):2022–2027
5. Lokshin EP, Tareeva OA (2010) Recovery of lanthanides from extraction phosphoric acid produced by the dihydrate process. *Russ J Appl Chem* 83(6):951–957
6. Kulyukhin SA, Konovalova NA, Rumer IA (2010) Co-precipitation of 137Cs and 85, 90Sr radionuclides from aqueous solutions with the solid phases of CsBPh4 and [M(18-crown-6)]BPh4 (M = Na⁺, Cs⁺). *Radiochemistry* 52(1):49–55
7. Arous O, Amara M, Kerdjoudj H (2010) Selective transport of metal ions using polymer inclusion membranes containing crown ethers and cryptands. *AJSE-Engineering* 35(2A):79–93
8. Ohashi A, Hashimoto T, Imura H, Ohashi K (2007) Cloud point extraction equilibrium of lanthanum(III), europium(III) and lutetium(III) using di(2-ethylhexyl)phosphoric acid and Triton X-100. *Talanta* 73:893–898
9. Riahi F, Bagherzadeh M (2010) Separation of some lanthanide (III) ions by using 18-crowns-6 derivatives from acidic solution. *J Appl Sci* 10:1781–1786
10. Abderrahim O, Didi MA, Moreau B, Villemin D (2006) A new sorbent for selective separation of metal: polyethylenimine methylenephosphonic acid. *Solvent Extr Ion Exch* 24:943–955
11. Dutta S, Mohapatra PK, Dhekane GD, Das AK, Manchanda VK (2008) Solid phase extraction of europium and uranium using Tulsion CH-90 resin. *Desalination* 232(1–3):216–224
12. Achuthan PV, Jangida BL, Sundaresan M (1990) Ion exchange separation of Eu(III), Th(IV), U(VI) and Pu(IV) ions on Amberlyst A-15 in non-aqueous solutions. *J Radioanal Nucl Chem* 141(1):171–178
13. Bhattacharyya A, Mohapatra PK, Manchanda VK (2006) Separation of Am³⁺ and Eu³⁺ using an extraction chromatographic resin containing bis(2,4,4-trimethylpentyl)dithiophosphinic acid as the stationary phase. *J Chromatogr A* 1123(1):26–30
14. Froidevaux P, Happel S, Chauvin AS (2006) Ion-imprinted polymer concept for selective extraction of ⁹⁰Y and ¹⁵²Eu for medical applications and nuclear power plant monitoring. *Chimia* 60(4):203–206
15. Levitskaia TG, Sinkov SI, Lumetta GJ (2008) Actinide binding by Kläui ligands: redox speciation and sorption on an extraction chromatography resin. *Radiochim Acta* 96(12):805–815
16. Kameník J, Šebesta F (2006) Study of europium and selected actinides uptake on composite material CMPO-PAN. *Czech J Phys* 56(1):493–500
17. Mohandas J, Kumar T, Rajan SK, Velmurugan S, Narasimhan SV (2008) Introduction of bifunctionality into the phosphonic acid ion-exchange resin for enhancing metal ion complexation. *Desalination* 232:3–10
18. Yang XJ (1994) Extractive chromatographic separation and inductively coupled plasma atomic emission spectrometric determination of trace impurities in high purity europium oxide. *Talanta* 41(11):1807–1813

19. Villemin D, Moreau B, Kaid M, Didi MA (2010) Rapid one-pot synthesis of alkane- α,ω -diylbisphosphonic acids from dihalogenoalkanes under microwave irradiation. *Phosphorus Sulphur* 185:1583–1586
20. Popa A, Davidescu C-M, Negrea P, Ilia G (2008) Synthesis and characterization of phosphonate ester/phosphonic acid grafted styrene-divinylbenzene copolymer microbeads and their utility in adsorption of divalent metal ions in aqueous solutions. *Ind Eng Chem Res* 47:2010–2017
21. Zenobi MC, Luengo CV, Avena MJ, Rueda EH (2008) An ATR-FTIR study of different phosphonic acids in aqueous solution. *Spectrochim Acta A* 70:270–276
22. Yaftian MR, Hassanzadeh L, Eshraghi ME, Matt D (2003) Solvent extraction of thorium (IV) and europium (III) ions by diphenyl-N,N-dimethylcarbamoymethylphosphine oxide from aqueous nitrate media. *Sep Purif Technol* 31:261–268
23. Marczenko Z (ed) (1993) Separation and spectrophotometric determination of elements. Wiley, New York
24. Villaescusa I, Martinez M, Miralles N (2000) Heavy metal uptake from aqueous solution by cork and yohimbe bark wastes. *J Chem Technol Biotechnol* 75:812–816
25. Guerra LD, Viana RR, Airolidi C (2010) Use of raw and chemically modified hectorites as adsorbents for Th(IV), U(VI) and Eu(III) uptake from aqueous solutions. *Desalination* 260:161–171
26. Kadous A, Didi MA, Villemin D (2010) A new sorbent for uranium extraction: ethylenediamino tris(methylenephosphonic) acid grafted on polystyrene resin. *J Radioanal Nucl Chem* 284: 431–438
27. Bou-Maroun E, Goetz-Grandmont GJ, Boos A (2006) Sorption of europium(III) and copper(II) by a mesostructured silica doped with acyl-hydroxypyrazole derivatives extraction, kinetic and capacity studies. *Colloid Surf A* 287:1–9
28. Vijayaraghavana K, Balasubramanian R (2010) Single and binary biosorption of cerium and europium onto crab shell particles. *Chem Eng J* 163:337–343
29. El-Naggar IM, Ibrahima GM, El-Kady EA, Hegazy EA (2009) Sorption mechanism of Cs^+ , Co^{2+} and Eu^{3+} ions onto EGIB sorbent. *Desalination* 237:147–154
30. Ali IM (2009) Sorption studies of ^{134}Cs , ^{60}Co and $^{152+154}\text{Eu}$ on phosphoric acid activated silico-antimonate crystals in high acidic media. *Chem Eng J* 155:580–585
31. Metwally E, Elkholy SS, Salem HAM, Elsabee MZ (2009) Sorption behavior of ^{60}Co and $^{152+154}\text{Eu}$ radionuclides onto chitosan derivatives. *Carbohydr Polym* 76:622–631
32. Chunhua X, Zhanwang Z (2010) Evaluation of D113 cation exchange resin for the removal of Eu(III) from aqueous solution. *J Rare Earth* 28(6):862–867
33. Kadous A, Didi MA, Villemin D (2011) Removal of uranium(VI) from acetate medium using Lewatit TP 260 resin. *J Radioanal Nucl Chem* 288:553–561
34. Abderrahim O, Didi MA, Villemin D (2009) A new sorbent for uranium extraction: polyethyleniminephenylphosphonamidic acid. *J Radioanal Nucl Chem* 279(1):237–244
35. Metilda P, Sanghamitra K, Mary Gladis J, Naidu GRK, Prasada Rao T (2005) Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium(VI). *Talanta* 65:192–200
36. Ferrah N, Abderrahim O, Didi MA, Villemin D (2011) Removal of copper ions from aqueous solutions by a new sorbent: polyethyleneiminemethylene phosphonic acid. *Desalination* 269:17–24
37. Alguacil FJ (2003) A kinetic study of cadmium(II) adsorption on Lewatit TP260 resin. *J Chem Res S* 3:144–146
38. Guan W, Pan J, Ou H, Wang X, Zou X, Hu W, Li C, Wu X (2011) Removal of strontium(II) ions by potassium tetratitanate whisker and sodium trititanate whisker from aqueous solution: equilibrium, kinetics and thermodynamics. *Chem Eng J* 167(1):215–222
39. Arichi J, Goetz-Grandmont G, Brunette JP (2006) Solvent extraction of europium(III) from nitrate medium with 4-acyl-isoxazol-5-ones and 4-acyl-5-hydroxy-pyrazoles. Effect of salts and diluents. *Hydrometallurgy* 82:100–109