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Solid–liquid extraction of heavy rare-earths from phosphoric acid solutions using Tulsion CH-96 and T-PAR resins

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ABSTRACT

Wet phosphoric acid produced industrially from natural rock phosphates generally contains uranium in appreciable amounts and rare-earths in trace concentrations. In this paper, the solid-phase extraction of mixture of seven heavy rare-earths (HREs) such as terbium (Tb), dysprosium (Dy), holmium (Ho), yttrium (Y), erbium (Er), ytterbium (Yb), and lutetium (Lu) from phosphoric acid solutions using Tulsion CH-96, a macroporous bifunctional phosphinic acid resin and T-PAR resin, a phosphoric acid resin has been investigated. The parameters studied include time, H_3PO_4 concentration, ratio of volume of aqueous phase to mass of resin, metal concentration, and temperature. Effect of H_3PO_4 concentration from 0.5 to 5 M in the aqueous phase containing 25 mg/L of each metal using Tulsion CH-96 indicated that the percent extraction of metals decreases with increase in acid concentration at any given mass of resin. Mechanism of metal transfer follows ion exchange type. The separation factors were evaluated based on the distribution coefficients in order to estimate the potential of the results for the separation of individual/pair of rare-earths from others.

1. Introduction

The lanthanide elements, as a group, have magnetic, chemical and spectroscopic properties that have led to their application in a wide range of end uses. High-value market sectors include phosphors, optical glass, lasers, advanced ceramics and capacitors. With the increasing demand for rare-earth elements in the international market the separation and purification of these elements has gained considerable importance.

The principal commercial sources of rare-earth elements are monazite, xenotime, and bastnasite. In addition to these, rock phosphate which is used for the production of fertilizer-grade phosphoric acid also contains minor quantities of rare-earth elements considered as secondary source for rare-earth elements. Phosphate rocks generally contain about 50–300 mg/kg uranium and other rare-earths at less than 100 mg/kg of ore, depending on the source of rock phosphate used [1]. Singh et al. [2] reported the extraction and recovery of uranium with synergistic mixture of di-nonyl phenyl phosphoric acid and tri-n-butyl phosphate from fertilizer-grade phosphoric acid. Kabay et al. investigated the recovery of uranium employing various chelating ion exchange resins from phosphoric acid solutions [3]. Using solvent extraction and ion exchange methods, Koopman et al. reported the removal of heavy metals and lanthanides from phosphoric acid process liquors [4].

Separation of individual lanthanides from each other is very difficult due to their chemical similarity. Solvent extraction and ion exchange are the common methods used for the recovery and removal of metal ions from aqueous solutions. Literature review reveals that much of work has been done on solvent extraction of rare-earths employing organophosphorus reagents such as di(2-ethylhexyl)phosphoric acid (D2EHPA), bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC 88A), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302), bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301), alkylated phosphine oxides (Cyanex 921, Cyanex 923, Cyanex 925) and their mixtures [5–13] from chloride and nitrate media.

Even though solvent extraction method has several advantages, it is difficult to operate for dilute metal ion solutions over a wide range of acidities. On the other hand, ion exchange is an ideal method for removing trace levels of metal ions from aqueous solutions. Li et al. [14,15] reported the extraction of heavy rare-earths using extraction resins containing Cyanex 272 and extraction resin containing 1-hexyl-4-ethyloctyl isopropylphosphonic acid (HEOPPA) from hydrochloric acid solutions. They reported that adsorption of rare-earths on the resin as a function of pH follows the order as Lu(III) > Yb(III) > Tm(III) > Er(III) > Y(III) > Ho(III). An extraction resin containing PC 88A was used by Park et al. to separate Gd and Tb [16,17] employing extraction chromatography

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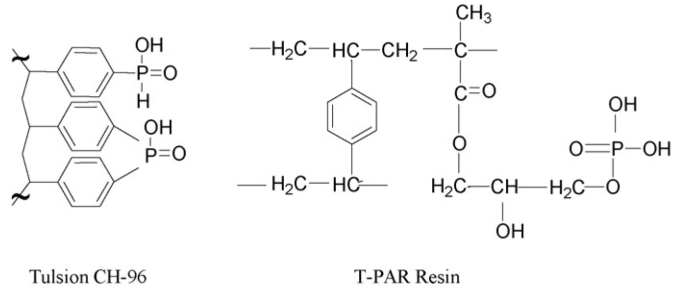

Tulsion CH-96 T-PAR Resin

Fig. 1. Structures of Tulsion CH-96 and T-PAR resins.

method. El-Sofany [18] investigated the removal of lanthanum(III) and gadolinium(III) from nitrate medium using Amberlite XAD-4 resin impregnated with Aliquat-336.

Conventional strong cation and anion resins cannot be used over a wide range of acidities. Alexandratos et al. synthesized bifunctional phosphinic acid resin by Friedel-Crafts phosphination reaction on polystyrene-divinylbenzene using $AlCl_3$ as catalyst [19–21]. It is well documented that these resins utilize both an access mechanism to bring the metal ions into polymer matrix and a recognition mechanism to selectively react with the metal ions, hence called dual-mechanism bifunctional polymers [22–24]. This bifunctional phosphinic acid resin was proved as a potential candidate for the recovery of uranium and actinides from different acid media [25–27]. In our previous work we reported the extraction behavior, mechanism of metal transfer and separation factors of terbium from other rare-earths using this bifunctional phosphinic acid resin, Tulsion CH-96 from phosphoric acid medium [28]. Recently phosphoric acid resin, RGP, with a large acid capacity was prepared by the addition of phosphoric acid to epoxy groups of macroreticular poly(glycidyl methacrylate-co-divinylbenzene). RGP exhibits high affinity towards Pb(II), Ti(IV), U(VI), and Zr(IV) [29–31]. There are no reports on the extraction of HREs from phosphoric acid solutions using Tulsion CH-96 and T-PAR type ion exchange resins. The structures of these resins were shown in Fig. 1.

The objective of the present study is to determine the extraction efficiency of mixture of HREs using Tulsion CH-96 and T-PAR resins in order to determine distribution coefficient (D), separation factor (β) and ultimately possibility of one/or group of metals separation from others in the acid range 3–4 M similar to actual wet phosphoric acid (WPA) concentration obtained from rock phosphate mineral.

2. Materials and methods

2.1. Reagents

Tulsion CH-96 resin, a phosphinic acid resin with polystyrene-divinylbenzene matrix, T-PAR resin, a phosphoric acid resin with cross linked polyacrylic matrix, were obtained as gift samples from M/s. Thermax India Ltd., Pune, India. The ion exchange capacities of Tulsion CH-96 and T-PAR resins were estimated by titrating with NaOH and calculated to be 2.39 and 2.36 meq/g, respectively. The ion exchange reaction can be given as

$$> P(=O)OH + Na^+ \leftrightarrow (> P(=O)O)Na + H^+$$

All rare-earth oxides (>99.99%) were purchased from Treibacher Industrie AG, Austria. The stock solutions of rare-earth ions were prepared by digesting the corresponding rare-earth oxide in concentrated hydrochloric acid. Solution samples of various H_3PO_4 concentrations were prepared by mixing fixed volumes of the stock solutions with varying volumes of concentrated H_3PO_4 and double distilled water. Analytical Reagent grade phosphoric acid, H_3PO_4 (88%, specific gravity 1.75) was used. Working solutions were prepared after suitable dilution. All other reagents used were of analytical grade.

2.2. Apparatus

An inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XDL, Thermo Jarrel Ash) was used to determine the rare-earth ions in the aqueous solutions. A Jeio-Tech temperature controlled shaking water bath was used for equilibrium experiments.

2.3. Method

For solid–liquid extraction studies, appropriate amount of resin was added to aqueous solution in reagent bottles and agitated for different time intervals (1–12 h) in a thermostatic shaking water bath. Agitation was stopped after fixed times, separated the aqueous phase and determined the residual metal concentration using ICP-OES. The amount of metal ion transferred into the resin phase was calculated by difference of metal concentration before and after equilibrium.

The distribution ratio (D) between the resin phase and the aqueous phase is defined as the concentration of metal on the resin phase per gram of the resin divided by the concentration of metal in the aqueous solution per milliliter of the solution and calculated using the equation

$$D = \frac{([\mathrm{M}]_\mathrm{t} - [\mathrm{M}]_\mathrm{o}) \times V/m}{[\mathrm{M}]_\mathrm{o}}$$

where $[M]_t$ denotes the total metal concentration, $[M]_o$ is the residual metal concentration in the solution, V is the volume of the aqueous phase (mL), and m is the mass of resin (g). The separation factor (β) refers to the possibility of separation of two metals from each other, which depends on D values under particular experimental conditions.

3. Results and discussion

3.1. Effect of equilibration time

The effect of time in the range from 1 to 12 h on the extraction of HREs was studied using aqueous solutions containing 25 mg/L of each rare-earth ion and 4 M phosphoric acid at a ratio of volume of aqueous phase to mass of resin (Tulsion CH-96/T-PAR), of 33.3:1 at 303 K (Fig. 1). It was observed that 4 h (Fig. 2(a)) time is sufficient to reach equilibrium for Tulsion CH-96 and 6 h (Fig. 2(b)) for T-PAR resin. However, to ensure that complete equilibrium achieved, all the subsequent experiments were carried out for 10 h equilibration time.

3.2. Effect of acid dependency at an aqueous to resin ratio of 100:1

Effect of H_3PO_4 concentration from 0.5 to 5 M in the aqueous phase containing 25 mg/L of each metal was studied keeping ratio of volume of aqueous phase to mass of resin (Tulsion CH-96/T-PAR) at 100:1 (Fig. 3). It was found that the percent extraction of metal decreases with increase in acid concentration, confirming the metal transfer to the resin phase follows ion exchange type mechanism [28]. Further, the results suggest large differences in percentage extraction of some metals over the others at certain acidities, thereby showing separation possibilities.

At 0.5 M H_3PO_4 concentration using Tulsion CH-96 resin, about 80% extraction of Lu and Yb was observed (Fig. 3(a)), where as the extraction of other metals (Tb, Dy, Ho, Y, and Er) was 30–40% only. The observed difference in percent extraction is due to their

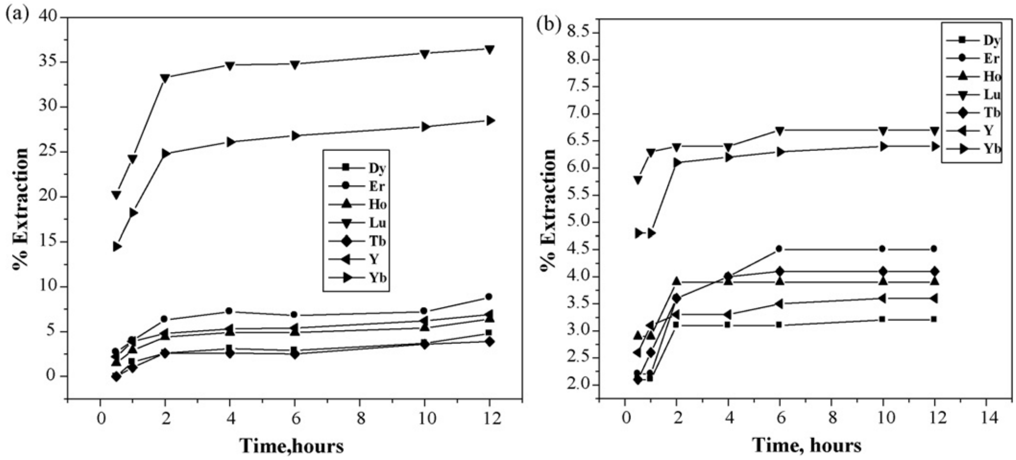

Fig. 2. Effect of equilibration time on uptake of [RE^{3+}] (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: mass of resin = 0.3 g, volume of aqueous phase = 10 mL, [H_3PO_4] = 3 M, [RE^{3+}] = 25 mg/L, temperature = 303 K.

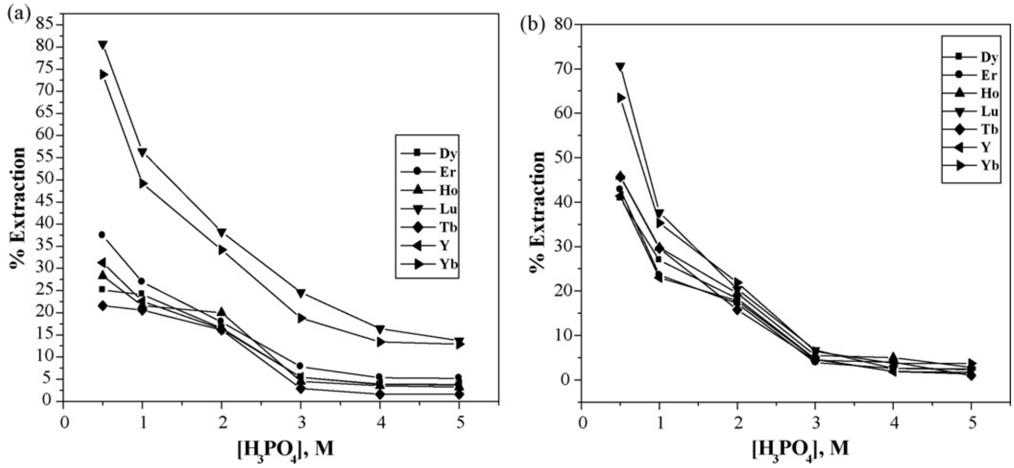

Fig. 3. Effect of acid concentration on percent extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: ratio of volume of aqueous phase to mass of resin = 100:1, [H_3PO_4] = 0.5–5 M, [RE^{3+}] = 25 mg/L, temperature = 303 K, time = 10 h.

ionic radii. Ion exchange resins, generally, have greater selectivity for ions with increasing valence or charge. Among the ions with the same charge, higher affinities were seen for ions with higher atomic number. The percent extraction decreases with increasing ionic radii. The results are in good agreement with the reported literature [8,14,15,28]. The separation factors (Table 1) of Lu for Tb and Dy are 16.7 and 10.9, respectively at 0.5 M acid concentration. Low β values were found in 3–4 M acid region. It was observed that a separation factor of 28.1 for Lu and Yb pair with Tb at 0.5 M acid (Table 2). However, it is difficult to separate Lu and Yb pair from Tb and Dy pair at 4 M acid. Hence, at a ratio of volume of aqueous phase to mass of resin of 100:1, there is a possible separation of Lu/Yb from Tb or Dy at 0.5 M acid. However, we follow-up our next experiments to get high β values at 3–4 M acid region (which is equivalent to WPA concentrations) by increasing ratios of volume of aqueous phase to mass of resin to 20:1 and 5:1.

Table 1
Separation factors of rare-earths with Tulsion CH-96 at an aqueous to resin ratio of 100:1.

[H_3PO_4], M	Metal	Tb	Dy	Ho	Y	Er
0.5	Lu	16.7	10.9	10.7	8.5	6.7
1	Lu	5.4	4.8	4.7	4.6	4.4
3	Lu	7.6	8.3	5.4	5.3	4.9
4	Lu	9.6	8.6	5.6	5.4	4.7
0.5	Yb	11.4	7.4	7.3	5.8	4.6
1	Yb	3.7	3.4	3.3	3.2	3.1
3	Yb	5.7	6.3	4.1	4.1	3.8
4	Yb	8.2	7.4	4.8	4.4	4.0

On the other hand, using T-PAR resin, the β values are low compared to Tulsion CH-96 even at 0.5 M acid. The magnitude of percent extraction is almost same as that of Tulsion CH-96. The percent extraction of rare-earths follows the ionic radii in case of T-PAR resin (Fig. 3(b)) also. But the extraction results are not that selective compared to Tulsion CH-96.

3.3. *Effect of acid dependency at an aqueous to resin ratio of 20:1 and 10:1*

Effect of H_3PO_4 concentration (0.5–5 M) on the extraction of HREs was studied at the volume of aqueous phase to mass of

Table 2
Separation factors of rare-earths with Tulsion CH-96 at an aqueous to resin ratio of 100:1.

[H_3PO_4], M	Metal pair	Tb	Dy	Tb + Dy
0.5	Lu + Yb	28.1	18.3	11.1
1	Lu + Yb	9.1	8.2	4.3
3	Lu + Yb	14.5	13.4	6.9
4	Lu + Yb	17.9	16.0	8.5

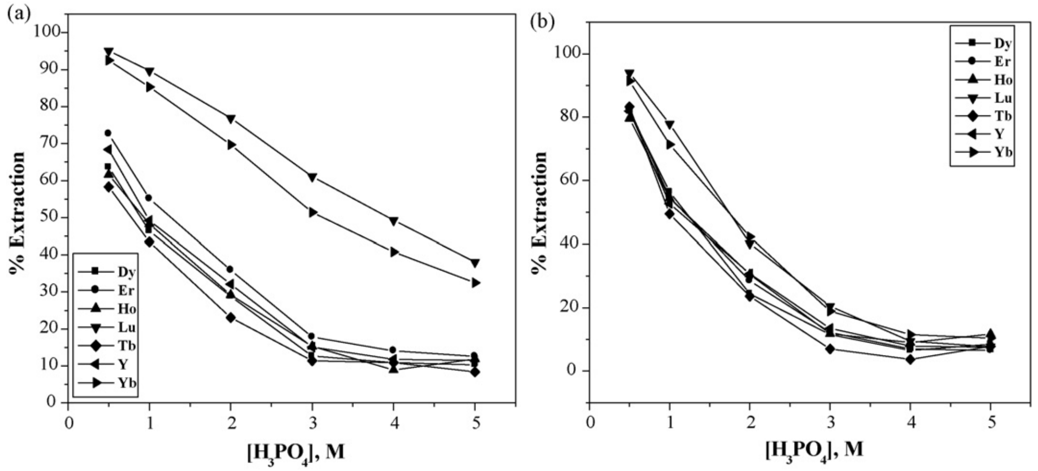

Fig. 4. Effect of acid concentration on percent extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: ratio of volume of aqueous phase to mass of resin = 20:1, [H_3PO_4] = 0.5–5 M, [RE^{3+}] = 25 mg/L, temperature = 303 K, time = 10 h.

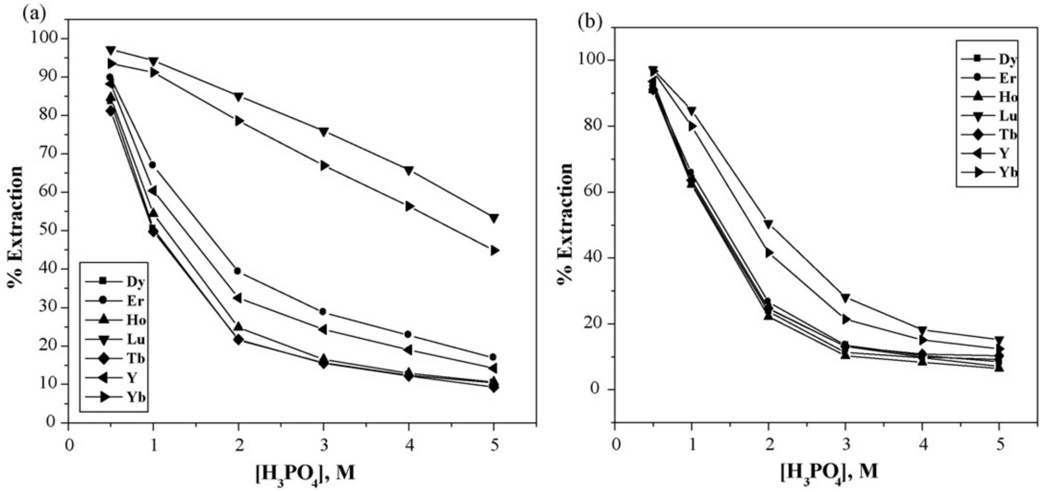

Fig. 5. Effect of acid concentration on percent extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: ratio of volume of aqueous phase to mass of resin = 10:1, [H_3PO_4] = 0.5–5 M, [RE^{3+}] = 25 mg/L, temperature = 303 K, time = 10 h.

resin ratio of 20:1. Using Tulsion CH-96, in low acid region of 0.5–1 M, the percent extraction of Lu and Yb are about 95% and decreased to 50% at 3–4 M acid region (Fig. 4(a)). The percent extraction of HREs increases when the ratio of volume of aqueous phase to mass of resin altered from 100:1 to 20:1 as expected. The percent extraction of HREs with T-PAR resin (Fig. 4(b)) also increases.

When the ratio of volume of aqueous phase to mass of resin set at 10:1, at 0.5 M acid Lu and Yb are about 95% extracted where as the other five elements are about 85% extracted with Tulsion CH-

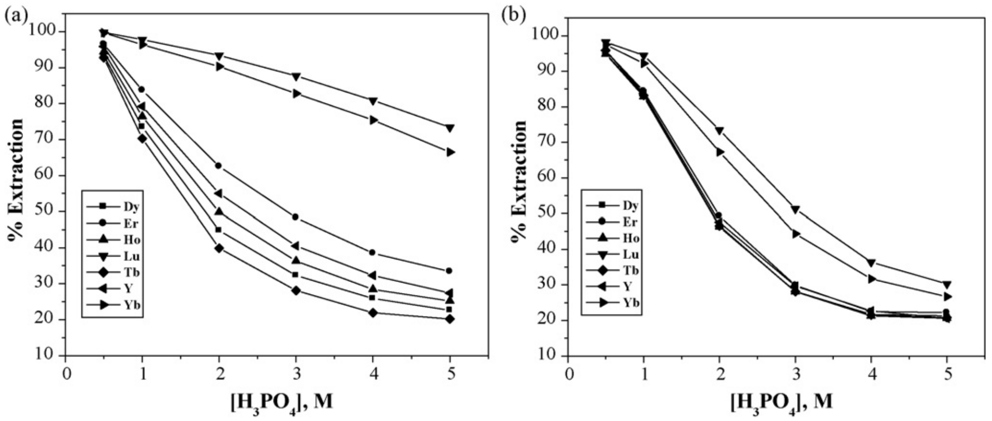

Fig. 6. Effect of acid concentration on percent extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: ratio of volume of aqueous phase to mass of resin = 5:1, [H_3PO_4] = 0.5–5 M, [RE^{3+}] = 25 mg/L, temperature = 303 K, time = 10 h.

Table 3
Separation factors of rare-earths with Tulsion CH-96 at an aqueous to resin ratio of 5:1.

[H_3PO_4], M	Metal	Tb	Dy	Ho	Y	Er
0.5	Lu	5.1	4.6	3.9	2.7	2.4
1	Lu	18.9	16.2	13.8	11.5	8.7
2	Lu	21.3	17.2	14.3	11.5	8.5
3	Lu	18.7	14.8	12.7	10.5	7.7
4	Lu	15.2	12.5	11.2	8.8	6.8
0.5	Yb	2.4	2.2	1.8	1.3	1.1
1	Yb	11.9	10.2	8.7	7.2	5.5
2	Yb	14.1	11.3	9.5	7.6	5.6
3	Yb	12.7	10	8.6	7.1	5.2
4	Yb	11	9.1	8.1	6.4	4.9

Table 4
Separation factors of rare-earths with Tulsion CH-96 at an aqueous to resin ratio of 5:1.

[H_3PO_4], M	Metal pair	Tb	Dy	Tb + Dy
0.5	Lu + Yb	7.5	6.8	3.6
1	Lu + Yb	30.9	26.4	14.2
2	Lu + Yb	35.4	28.5	15.8
3	Lu + Yb	31.4	24.8	13.8
4	Lu + Yb	26.2	21.6	11.8

96 (Fig. 5(a)) indicating no separation possibility at this condition. But, in 3–4 M acid region the percent extraction of five elements (Tb, Dy, Ho, Y, and Er) drastically decreased to about 15–28%, where as the percent extraction of Lu and Yb are 76–56% indicating possible separation of Lu and Yb from other metals. In case of T-PAR resin (Fig. 5(b)), separation possibility is not observed at any studied acid concentration.

3.4. Effect of acid dependency at an aqueous to resin ratio of 5:1

The percent extraction of HREs as a function of concentration of H_3PO_4 from 0.5 to 5 M was studied using Tulsion CH-96 at the volume of aqueous phase to mass of resin ratio of 5:1. It was observed that at 0.5 M acid, all the metals were extracted to about 99% using Tulsion CH-96 (Fig. 6(a)) suggesting very low separation possibility, while at 2–4 M acid, separation factors (Table 3) are high, indicating the applicability of results to actual WPA of fertilizer grade. A separation factor of 21.3 was found for Lu with Tb at 2 M acid concentration. The results clearly demonstrate that the decrease in separation factors follow their increase in ionic radii except for Y. It was falling in between Ho and Er, which is in good agreement with the results reported by Li et al. [14,15].

At high phosphoric acid concentration, 4 M, interestingly, the separation factor tendency is reversed with mass of resin as observed above (Table 1). It was observed that a separation factor of 15.2 for Lu with Tb using a ratio of 5:1 whereas it is 9.6 at a ratio of 100:1 with Tulsion CH-96 and similar behavior for Lu with other metals also. The situation is same for Yb as well. The separation factors for Lu-Yb pair with Tb–Dy were also given in Table 4.

Using T-PAR resin no appreciable separation factors were found. It is extracting HREs, but it cannot be used for separation of HREs under studied experimental conditions. The total ion exchange capacity of Tulsion CH-96 and T-PAR resin for HREs was calculated to be 1.32 and 1.35 meq/g, respectively.

From the Figs. 3 to 6, we can arrive at the possibility of binary separation of Lu with Tb/Dy and Yb with Tb/Dy and it is possible to separate Tb/Dy from solution containing Lu or Yb or both or it is possible to separate a solution containing Lu, Yb, Tb and Dy into two concentrates of Lu, Yb and Tb, Dy. The separation factor values are small to separate Lu, Yb from other five metals (Tb, Dy, Ho, Y, and Er) by using 2 g of Tulsion CH-96 at 0.5 M acid concentration or using 0.1 g of Tulsion CH-96 at 4 M acid concentration. Based on the separation factors, we can conclude that, in order to get high separation factor at high acid concentration, the resin amount needs to be increased.

3.5. Effect of metal concentration

The effect of metal concentration in the range 5–25 mg/L on the extraction of HREs was studied using Tulsion CH-96 and T-PAR resins from aqueous solutions containing 3 M H_3PO_4 and aqueous to resin ratio maintained at 14.3:1 (Fig. 7). There was a marginal effect on percent extraction of HREs with both resins. Using Tulsion CH-96, the percent extraction decreases from 78 to 71% for Lu, 71–61% for Yb and around 31–18% for other metals. Increase of metal concentration (5–25 mg/L) results in decrease of separation factors of Lu with Tb from 23 to 15.9, Lu with Dy from 18.9 to 12.3 where as this decrement is little with others (∼1). Similarly, the separation factors of Yb with Tb and Yb with Dy decreases from 15.3 to 10.6 and 12.5–8.3, respectively. Using T-PAR resin, the variation of percent extraction is 20 ± 4% for Lu and Yb, and 10 ± 2% for other metals. The variation of metal concentration has no effect on separation factors of Lu/Yb with other metals (2.5 ± 0.1).

3.6. Effect of temperature

By keeping the aqueous and resin phase conditions constant (10 mL of aqueous solution containing 25 mg/L HREs with 3 M

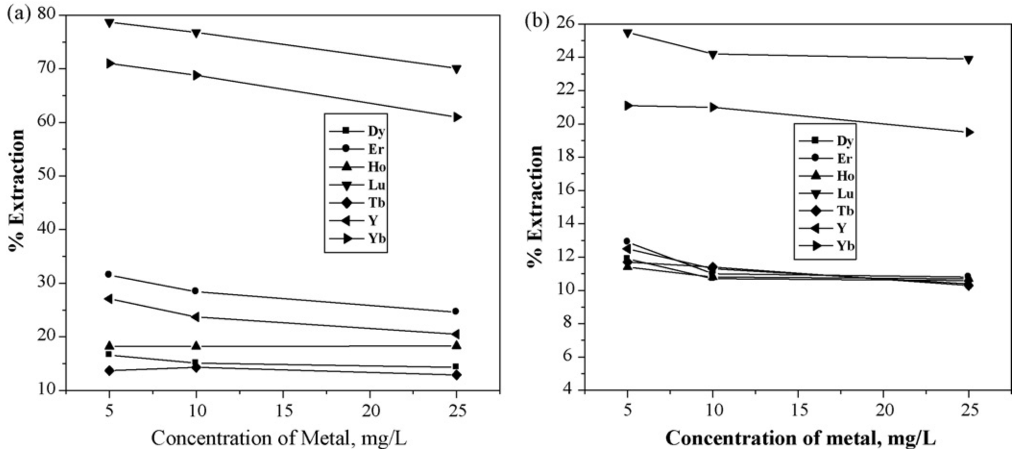

Fig. 7. Effect of metal concentration on extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: mass of resin = 0.7 g, volume of aqueous phase = 10 mL, [H_3PO_4] = 3 M, [RE^{3+}] = 5–25 mg/L, temperature = 303 K, time = 10 h.

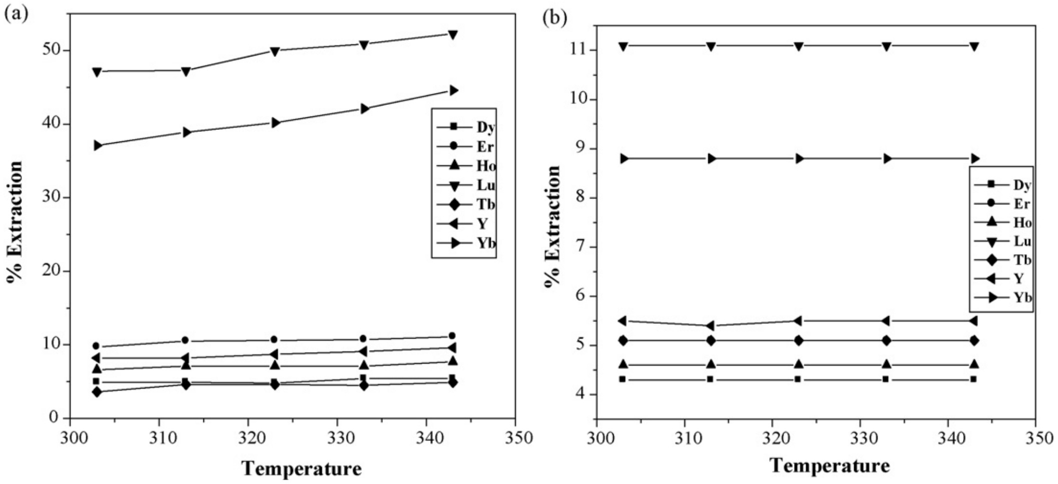

Fig. 8. Effect of temperature on extraction of HREs (a) using Tulsion CH-96 and (b) using T-PAR resins. Experimental conditions: mass of resin = 0.3 g, volume of aqueous phase = 10 mL, $[H_3PO_4]$ = 3 M, $[RE^{3+}]$ = 25 mg/L, time = 10 h, temperature = 303–353 K.

H_3PO_4 and 0.3 g of Tulsion CH-96 and 0.3 g of T-PAR resin, 10 h), the effect of temperature from 303 to 343 K on the extraction of HREs was investigated (Fig. 8). Marginal increase in percentage extraction of Lu (47–52%) and Yb (37–44%) with Tulsion CH-96 and no effect for others was observed. The variation of temperature from 303 to 343 K has marginal effect on the separation factors of Lu with Tb (22 ± 2.0), Dy (18 ± 1.5), Ho (12 ± 1.0), Y (10 ± 0.5) and Er (8 ± 0.5). The separation factors of Lu/Yb with other five metals decreases with increase in ionic radii except for Y as it was falling in between Ho and Er. The separation factors of Lu/Yb with other five metals from 303 to 343 K follows in the order Tb > Dy > Ho > Y > Er. Using T-PAR resin, the variation of temperature has no effect on percentage extraction of HREs and thereby separation factors.

4. Conclusions

We investigated for the first time the sorption behavior of HREs from phosphoric acid solutions with regard to their separation using two kinds of resins, Tulsion CH-96, a macroporous bifunctional phosphinic acid resin and T-PAR, a phosphoric acid resin. An equilibration time of 4 and 6 h is adequate for Tulsion CH-96 and T-PAR resins. The transfer of metal to the resin phase follows ion exchange type mechanism. Under studied experimental conditions, the variation of temperature and metal concentration has no effect on separation factors of HREs with T-PAR resin and marginal effect with Tulsion CH-96. The present results can be applied to the binary separation of Lu with Tb/Dy and Yb with Tb/Dy and to separate Tb/Dy from phosphoric acid solution containing Lu or Yb or both using Tulsion CH-96. T-PAR resin needs modification to get better separation factors of HREs.

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