



Extraction Studies of Middle Rare Earths from Chloride Medium Using Tulsion CH 90 Resin

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Abstract

In the present study, we report the solid-liquid extraction behaviour of middle rare earths from chloride medium using Tulsion CH-90 resin. Rare earths (REs) were widely used as raw materials for high-purity individual rare earth elements, strong magnets and rechargeable batteries. For the process development of Samarium (Sm (III)) separation from other REs, the fundamental parameters were studied to establish optimized conditions. These parameters include effect of equilibration time, effect of equilibrium pH, effect of mass of resin and regeneration and recycling capacity of the resin. The loading and elution of resin was not changed up to six cycles, indicating greater stabilities of the resin. Studies on effect of associated metals gave the information of binary/ group separation of Sm (III) from other rare earths.

Keywords: Samarium; Chloride medium; Tulsion CH-90; Separation factors

Introduction

Rare-earth elements (REEs) are a group of 17 elements, consisting of the lanthanides (14elements) and two more elements scandium and yttrium. REEs are used in a wide range of modern technologies such as fluorescent lamps, magnets, superconductors, lasers, ceramics, semiconductors and catalysts [1]. Many of these applications are important for the development of environmentally friendly technologies for lighting, energy storage, and the manufacturing of chemicals. The REEs are presently considered to be among the most critical elements by the European Union (EU) and the United States (USA), since they are mined in only a few countries and their prices have varied in recent years. Hence the demand for REEs is increasing [2].

Even though many types of new extractants like calixarenes and ionic liquids have been developed in recent years, such as, calix [4] arenes suspending extractive groups, diglycolamic acids and ionic liquids, most of the them are difficult to apply to industrial RE separations because of small separation factors for adjacent heavy REs [3-5]. From literature search it is well known fact that much of work has been done on solvent extraction of rare-earths using organophosphorus reagents such as di(2-ethylhexyl) phosphoric acid -D2EHPA, bis(2,4,4- tri methyl pentyl) phosphinic acid-Cyanex 272, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester -PC 88A [6-9].

Previously from our group, we reported extraction behaviour and separation possibilities of rare earths from phosphoric acid using organophosphorus reagents [10, 11]. Reddy et al., studied synergistic solvent extraction of rare earths with bis(2,4,4- trimethylpentyl) dithiophosphinic acid -Cyanex 301 [12].

Although solvent extraction method has several advantages, it is difficult to operate for dilute metal ion solutions over a wide range of acidities. Alternatively, ion-exchange is an ideal method for removing trace levels of metal ions from aqueous solutions. The extraction behaviour of uranium and other actinides were studied from different acid media using bifunctional phosphinic acid resins [13-16]. Some of the synthesized resins were evaluated for their cation affinity, bifunctionality and dual mechanism of the resin [17-19]. Rao et al. Synthesised styrene-divinyl benzene based resins and applied for inorganic trace metals extraction [20].

For the first time, in the present study we are reporting commercially available Tulsion CH-90 resin for chloride medium. The importance of the present work is to examine the fundamental studies, separation possibilities of Sm (III) from other rare

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earths and comparison of obtained results with previous studies. The distribution of Sm (III) depends on various experimental conditions like, equilibrium pH, concentrations of metal ions, and weight of the resin.

Material and Methods

Reagents

All rare-earth oxides (>99.99%) except Ce (Cerium chloride) were purchased from Treibacher Industry AG, Austria. The stock solutions of rare-earth ions were prepared by digesting the corresponding rare earth oxide in minimum concentrated hydrochloric acid and evaporated to near dryness and then made up to the mark with double distilled water. NaCl ($\mu = 0.1\text{molL}^{-1}$) was used to maintain constant ionic strength. All the other chemicals used were of analytical grade. Tulsion CH-90, with amino diacetic acid functionality was obtained as gift samples from M/s. Thermax India Ltd., Pune, India.

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.

Method

For solid-liquid extraction studies, appropriate amount of resin was added to aqueous solution in reagent bottles and shaken 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 loaded 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 millilitre of the solution and calculated using the equation.

$$D = \frac{([M]_t) - [M]_o \times \frac{V}{m}}{[M]_o}$$

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.

Results and Discussion

Effect of equilibration time

The effect of time on the distribution of 50 mg/L of Samarium (2.13 pH) was studied from chloride solutions using 0.1 g of Tulsion CH-90 resin at 303K. The effect of time in the range 5-780 minutes was investigated and observed that equilibrium was attained at 540 minutes (Figure 1).

Effect of equilibrium pH

Effect of equilibrium pH (1.66 - 3.53) on the percent extraction of Samarium (50 mg/L) was studied using 0.1 g of Tulsion CH-90. The percent extraction increases from 23.7% to 99.7%. (Figure 2). Further the plot of log D verses equilibrium pH yields a straight line with a slope value of 1.65 (Figure 3). The

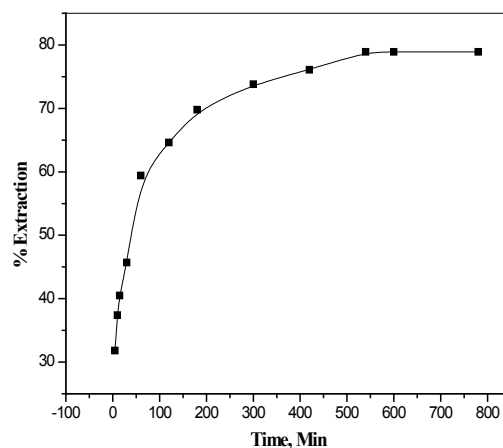


Figure 1: Effect of equilibration time on distribution of Samarium.

Experimental conditions: Tulsion CH-90= 0.1 g, Equilibrium pH = 2.13, [Sm(III)] = 50 mg/L, temperature = 303°K

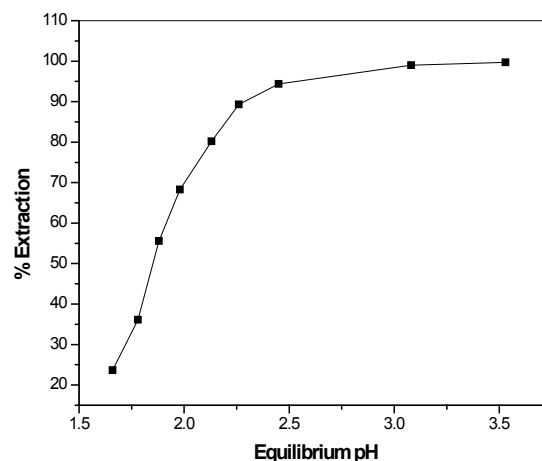


Figure 2: Effect of equilibrium pH on distribution of Samarium.

Experimental conditions: Tulsion CH-90= 0.1 g, Equilibrium pH = 1.66-3.53, [Sm(III)] = 50 mg/L, temperature = 303°K

ion exchange mechanism was confirmed, with release of 2 moles of H^+ for every mole of metal extracted.

Effect of weight of resin

Effect of weight of resin on the percent extraction of 50 mg/L of samarium at equilibrium pH 1.67 and 1.88 of constant aqueous phase conditions was shown in figure 4. It was observed that, by increasing weight of Tulsion CH 90 resin from 0.05 g to 3 g, the percent extraction of metal increases from 17.8% to 100%.

Effect of metal concentration

Effect of metal concentration on the extraction of samarium was studied by varying metal concentration in the range 10-700 mg/L at pH 2.45 with 0.1g of Tulsion CH-90 resin. It was observed that the percent extraction decreases with increase in metal concentration. The amount of metal transferred into resin phase increased from 1.3 to 22.4 mg per gram of resin and remained constant thereafter. This is significantly high compared to loading

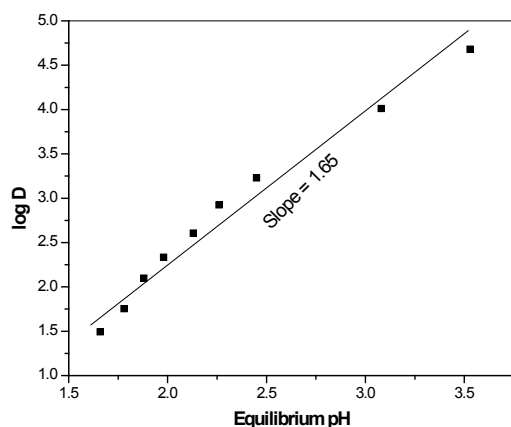


Figure 3: Plot of log D vs. equilibrium pH.

Experimental conditions: [Sm(III)] = 50 mg L⁻¹, Tulsion CH-90 = 0.1 g, temperature = 303 K, equilibrium pH = 3.53-1.66

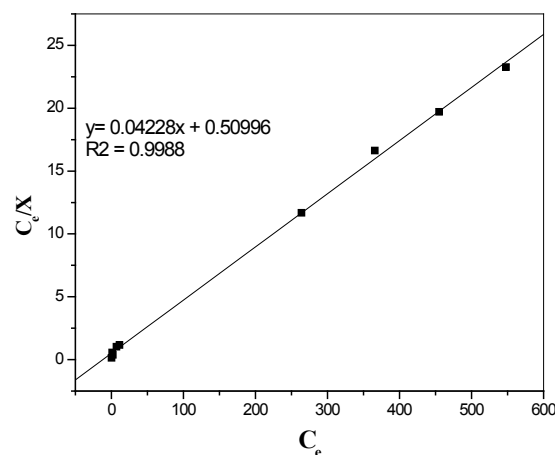


Figure 5: Langmuir adsorption isotherm

Experimental conditions: Tulsion CH-90 = 0.1 g, Equilibrium pH = 2.45, [Sm(III)] = 10-700 mg/L, temperature = 303 K

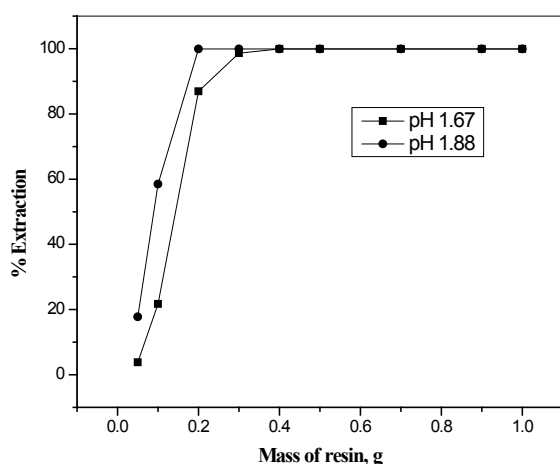


Figure 4: Effect of mass of resin on extraction of Samarium using Tulsion CH-90.

Experimental conditions: [Sm(III)] = 50 mg L⁻¹, [Tulsion CH-90] = 0.05-3 g, Equilibrium pH 1.67 and 1.88, Temperature = 303 K

capacity of Tulsion CH 90 for Gadolinium-10mg/g of resin [21].

Langmuir adsorption isotherm

The loading of samarium into the resin increases with increase in the metal concentration in the aqueous phase. The linearized Langmuir adsorption isotherm for the extraction of samarium by Tulsion CH-90 resin was shown in Figure 5. The Langmuir model assumes that, the metal ion uptake occurs on a homogeneous surface by monolayer adsorption and there is no interaction between sorbed species. The linearized Langmuir equation relating the amount of metal extracted by resin and equilibrium concentration of metal is given by the equation.

$$\frac{C_e}{X} = \frac{1}{bX_m} + C_e/X_m$$

Where C_e is the concentration of samarium at equilibrium (mg/L), X is the amount of samarium extracted by resin (mg/g), b is Langmuir constant (L/mg), X_m is the maximum adsorption capacity (mg/g). The experimental capacity (X_m) is obtained from slope of the straight line shown in Figure 5 and is calculated as 23.6 mg/g.

Loading capacity of the resin

Loading capacity of Tulsion CH-90 resin is determined by contacting 2 g of resin for 2 hours, repeatedly with the 100 mL of aqueous solution containing 100 mg/L of samarium at 1.9 pH. After equilibrium, the aqueous phase was analysed for samarium. The amount of samarium transferred into resin phase in each contact was calculated by difference of samarium in the aqueous phase after each contact and the cumulative increase in the concentration of samarium in the resin phase after each stage of contact was determined. The results indicate that transfer of metal from aqueous phase to resin phase occurs after each contact. Complete loading of the resin is possible after sixth stage. The loading capacities of Tulsion CH-90 resin for samarium is 23.6 mg/g of the resin confirming the results of Langmuir adsorption isotherm data.

Elution studies

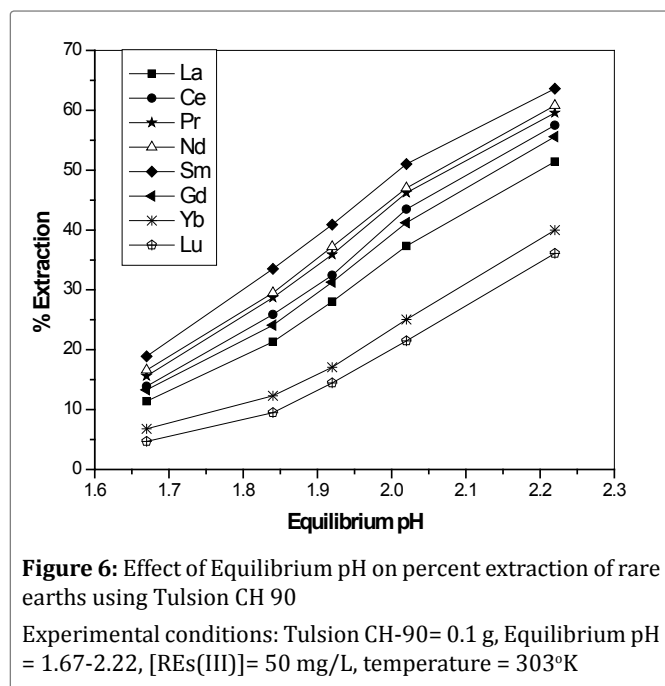
Elution studies are very important in any commercial extraction process to back extract the metal from the loaded resin phase. With this objective, samarium elution from the loaded Tulsion CH 90 resin containing 16.5 mg per gram of the resin has been studied using various eluants such as HCl, HNO₃, H₂SO₄ in the concentration range of 0.1-1M and the results showed that among mineral acids, HNO₃ with 0.5 N concentration was the best eluant with a recovery percent of 100% for Tulsion CH 90 resin.

Regeneration and recycling

Studies on the recycling capacity of Tulsion CH-90 (2.14 pH) for the extraction of samarium were carried out. First the resin (0.1g) was loaded with aqueous phase containing 50 mg/L of samarium. The shaking time for the single stage of extraction (73%) of samarium was 5 h using Tulsion CH-90 resin. Quantitative elution of samarium from loaded Tulsion CH-90 was obtained by 0.5 N of HNO₃. The regenerated resin was used for extraction using fresh aqueous phase with same conditions. The results indicate that there was no change in extraction and elution efficiency of resin up to five cycles of extraction indicating greater stabilities of the resin.

Comparison of the extraction behaviour of Sm(III) with other rare earths using Tulsion CH-90 resin

The commonly associated rare earths (REs) with samarium were studied. The extraction behaviour of La, Ce, Pr, Nd, Gd, Yb



Equilibrium pH	Metal pair	
	Sm-La	Sm-Lu
2.22	1.6	3
2.02	1.7	3.8
1.92	1.8	4.3
1.84	1.8	5
1.67	1.9	5.7

Table 1: Separation factors of Sm(III) from other associated metals using Tulsion CH-90 resin (0.1g)

and Lu (50 mg/L each) has been studied from chloride solutions (1.67-2.22 pH) using 0.1g of Tulsion CH-90 (Figure 6). It was observed that the percent extraction of all the REs using this resin increases with increasing equilibrium pH following cation exchange mechanism. Using 0.1g of Tulsion CH-90 resin, the percent extraction of rare earths (REs) at 1.67 pH increased from 11.4% (La) to 18.9 % (Sm), where as in case of heavy rare earths (HREs) - Lutetium (Lu-4.7%) and Ytterbium (Yb-6.8%) the percent of extraction decreases. But here the possibility of separation of REs from HREs is not possible because of low extraction.

At 1.84 pH, Sm(III) showed a percent extraction of 33% and Lu(III) is extracting only 9%, so the binary separation of Sm/Lu can be tried at this pH. High percent extraction for Samarium (64%) was observed at pH 2.22 and it can be separated from Lutetium (36%) and Ytterbium (40%) which are extracting below 40%.

There is equal chance of separation possibility for Sm(III) from HRES and other REs at low pH (1.67), whereas with increasing pH, at 2.22 pH there is only binary separation of Sm (III) from HRES possible but not from other REs. The separation factors of samarium from other REs were calculated and given in Table 1. From the associated metals extraction data it was observed that samarium is highly extracted among studied REs and Sm was considered for determining the separation possibilities from other REs. From the separation factor data it can be concluded that the equilibrium pH from 1.67 to 2.02 is suitable for the separation of Sm from other REs. Based on the above results, further studies on separation of individual metal ions or separation of binary metals from other will be taken up employing column method.

Conclusion

For the first time, we are reporting the extraction behavior of Sm(III) from chloride medium using commercially available Tulsion CH-90 resin. Metal extraction follows cation exchange mechanism. Under the studied experimental conditions the loading of Tulsion CH-90 for Sm(III) was 22.4 mg/g. Among the various eluting agents studied, 0.5 N concentration of HNO_3 was the best eluant for the loaded Tulsion CH-90. Extraction of metals which are generally associated with Sm(III) showed that there is a possibility for separation of Lu and Yb from other rare earths using Tulsion CH-90 at 1.67 pH and 2.22 pH. The separation of Sm(III) was possible from other rare earths such as La, Ce, Pr, Nd, Lu and Yb using Tulsion CH-90 resin.

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