Separation of La(III) Using Functionalized Material on Fixed Bed Column

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Lanthanum belongs to the category rare earth elements (REEs) and it is found in the Earth's crust. Lanthanum is used in many manufacturing processes such as: electronic products, petroleum refining, in the glass industry, in ferroalloys and for rechargeable batteries. All these industries have a different impact on the environment. This study presents the possibility of removing of lanthanum (III) from aqueous solutions using a column filled with an adsorbent material. The adsorbent material is magnesium silicate impregnated with tetrabutylammonium dihydrogen phosphate dissolved in ethyl alcohol. It was characterised by FTIR analysis. The residual concentration of lanthanum, the removal degree for the volume of solution passed through the column and the contact time were determined in order to establish the maximum adsorption capacity. The residual La(III) concentration was determined using inductively coupled plasma mass spectrometry. The number of sorption-desorption cycles of the material was determined. The desorption of the material was made after every sorption process, with a 10% hydrochloric acid solution. Considering that the material was impregnated with a relatively small amount of tetrabutylammonium dihydrogen phosphate, the number of sorption-desorption cycles was rated as four.

Keywords: lanthanum, magnesium silicate, fix bed column, functionalized material

Lanthanum is one of the most used rare earth metals REE's in the past years. Because of its metallurgical, optical and electronic proprieties La(III) is used in many fields like electronics, medicine, ceramics and agricultures [1,2].

They have an essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries and catalysis. Because of the increasing use of hybrid and electric cars, compact lamps and wind turbines the demand of REEs including La(III) raises [3]. China is one of the countries that have the greatest exploitation of La(III) and uses significant amounts in all domains. Lanthanum is used as microelement in fertilizers and in animal husbandry. Lanthanum concentrations were found in cereal, vegetables, meat and eggs. Lanthanum is also found in many sources of fresh water, surface water and groundwater. It is estimated that a Chinese intakes 3% of daily accepted intake of REE's. Lanthanum is used in medicine in renal failure as carbonate because of the reduction phosphate absorption. This can lead in time to harmful effect on the environment and people [4,5].

Many separation and preconcentration methods like liquid-liquid extraction, ion-exchange, coprecipitation, solid phase extraction have been studied [5-7].

In the last years for the selective recovering and separation of some metals and non-metals ions was impetuous required the obtaining of advanced materials with applies in this process. In order to improve the adsorption properties of were developed new methods of chemically modification of the inorganic and organic solid supports, through functionalization with different extractants dissolved in various solvents [8-16].

This research work presents study presents the possibility of removing of lanthanum (III) from aqueous solutions using a column filled with an adsorbent material, magnesium silicate impregnated with tetrabutyl ammonium dihydrogen phosphate.

Experimental part

Materials and methods

The adsorbent material used was obtained as follows: 10 g magnesium silicate was impregnated with 2% of tetrabutylammonium dihydrogen phosphate, using as solvent 50 mL ethyl alcohol and kept in contact for 24 h. After that, the samples were dried at 323K for another 24 h.

The glass column (inner diameter of 2.5 cm and height of 6 cm) was filled for ever sorption-desorption with known amounts of material: 10.0011 g, 8.1363 g, 7.9074 g, 5 g, respectively. For every sorption-desorption cycle, with the help of a peristaltic pump (Heidolph Pumpdrive 5206) 3000, 2000, 1000 and 500 mL La(III) solution respectively, were passed through the column. The lanthanum solution had a concentration of 10 mg/L. The column was loaded with La(III) solution in the up-flow mode, with a volumetric flow rate of 7 mL/min. Sequences of 10 mL samples were collected for which the residual concentration of La(III) was determined using inductively coupled plasma mass spectrometry (ICP-MS Bruker aurora M90).

After every sorption, the desorption of the material was made with 250 mL hydrochloric acid solution, with a concentration of 10 mg/L.

Results and discussion

Characterisation of the impregnated material

The adsorbent material was characterized by FTIR analysis. The FTIR spectra (KBr pellets) of the adsorbent material were recorded on a Shimadzu Prestige- 21 FTIR spectrophotometer in the 4000–400 cm^{-1} range.

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Figure 1 shows the FTIR spectrum of the impregnated solid support after using it in the removal process by adsorption on column of La(III). Stretching vibrations bands appear at 1649 cm^{-1} and 1093 cm^{-1} characteristic for the bonds $C_{aliphatic}$-O-$C_{aliphatic}$ and at 1093 cm^{-1} characteristic for the P-O bonds from the extractant. Characteristic bands of the solid support are also visible on the FTIR spectrum at 806 cm^{-1} and 470 cm^{-1} corresponding to stretching vibrations of the Si-O bonds. The weak band at 1240 cm^{-1} can be attributed to Si-O vibrations and the band 750 cm^{-1} are bending vibrations of the Si-O-Si bonds. Stretching vibrations of the OH group can be seen at ~1600 cm^{-1} [17, 18].

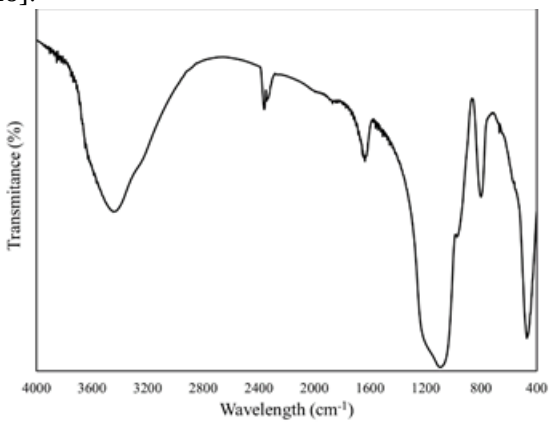

Fig. 1. FTIR spectrum of the functionalized adsorbent material after adsorption of La(III)

Adsorption on column

Adsorption studies were carried out in order to establish the adsorption capacity of the functionalized material. The adsorption capacity of the functionalized material for lanthanum separation was calculated using the equation (1):

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where:

C_0 is the initial lanthanum concentration (mg/L) ,

C_e is the equilibrium concentration (mg/L),

V is the volume (L),

m is the amount of adsorbent material (g).

Figure 2 show the adsorption capacity of the functionalized material for La(III) separation for the volume of solution passed through the column for all tree sorption-desorption cycles.

From all the tree sorption-desorption cycles, the first cycle presents the highest adsorption capacity 3 mg/g until reaching the breakthrough volume at ~ 2000 mL. For the second and third cycle the obtained capacities were lower 0.5 mg/L and 0.15 mg/L, respectively. The breakthrough volumes of cycle two and tree are 950 mL and 400 mL, respectively. In this study, with each sorption-desorption cycle, the desorbed amount of lanthanum decreases, but not with maximum efficiency; this explains the limited number of sorption-desorption cycles. The TBAH2P to support ratio remains constant (0.2 g TBAH2P to 10 g support). For all sorption-desorption cycles, the breakthrough curves are presented in figure 3.

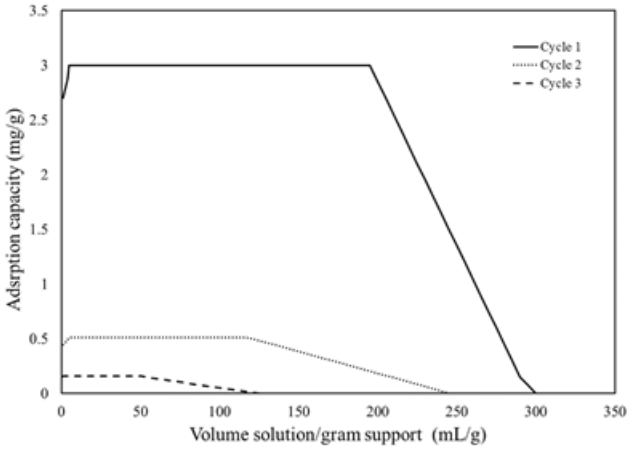

Fig.2 Adsorption capacity of the studied material for La(III) separation

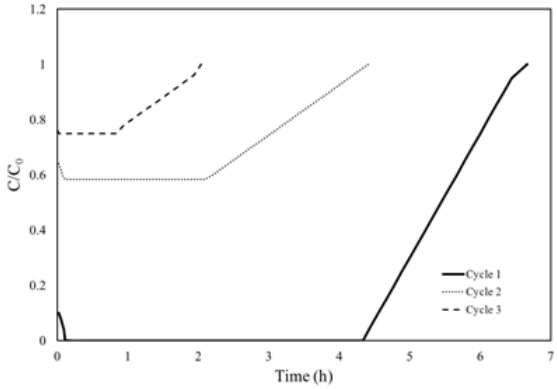

Fig. 3. Breakthrough curves of the first sorption-desorption cycle

In order to determine the efficiently of the column the logit method was used to designed the fix bed column. The equation (2) defines the logit method.

$$\ln\left[\frac{C/C_0}{1-C/C_0}\right] = -\frac{KNX}{V} + KC_0t \quad (2)$$

where:

C is the solute concentration at any time mg/L,

C_0 is the initial concentration mg/L,

V is the approach velocity (~85.56 cm/h),

X is the bed depth,

K is the adsorption rate constant L/mg' . h,

N is the adsorption capacity coefficient mg/L.

The logit equation is rearranged as in equation (3).

$$\ln\left[\frac{C}{C_0 - C}\right] = -\frac{KNX}{V} + KC_0t \quad (3)$$

By plotting ln[C/(C_0-C)] against t, N and V can be calculated from the slope KC_0 and the intercept KNX/V. The logit method in linearized form for all sorption-desorption cycles is given in figure 4. The adsorption rate coefficient K and the adsorption capacity coefficient N are given in table 1.

Figure 5 shows the efficiency of the four cycles of sorption-desorption. The highest efficiency has the first cycle ~96%. It is visible a sharp decline is between the first and the second cycle. The efficiency decreases

Table 1

ADSORBTION PARAMETERS OF La(III) ON FIXED BED COLUMN

Sorption-desorption cycle	Adsorption rate coefficient K, L/mg·h	Adsorption capacity coefficient N, mg/L
1	0.25	774
2	0.28	183.20
3	0.37	30.09

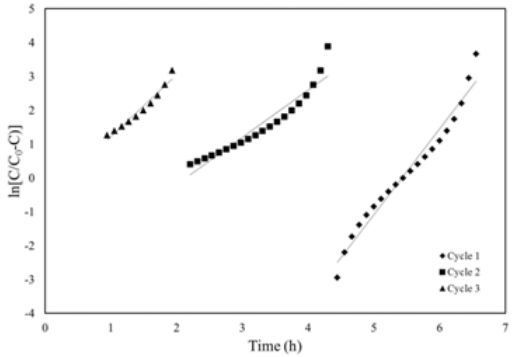

Fig. 4. Linearized form of logit model for the first sorption-desorption cycle

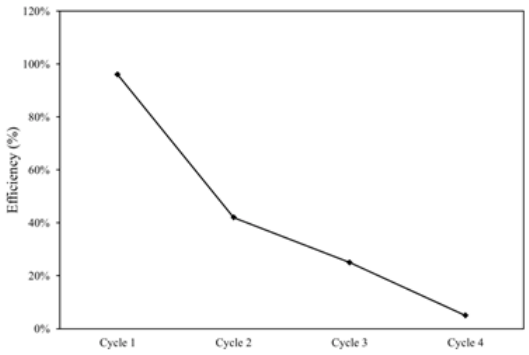

Fig. 5. The efficiency of the sorption-desorption cycles

smother from the second cycle (~42%) to the fourth cycle to less than 10%. The material has a very low efficiency at the fourth cycle. We established that the functionalized material can be used for four sorption-desorption cycles.

Conclusions

In this paper the adsorption process of La(III) on a column filled with adsorbent material was studied. The adsorbent material used was magnesium silicate impregnated with tetrabutylammonium dihydrogen phosphate. It was characterised by FTIR analysis shows a successful impregnation. The first sorption-desorption cycle revealed the highest removal degree of 100% for about 2000 mL 10% La(III) aqueous solution. The removal degree decreased with every cycle performed down to less 20 % in the fourth sorption-desorption cycle, therefore the number of regeneration cycles was established as been four.

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