Article

Evaluation of La (III) and Ce(III) Adsorption from Aqueous Solution Using Carbon Nanotubes Adsorbent

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Abstract: Since the 1960s Rare earths (REs) applications gradually have expanded to everyday life. REs have a great strategic importance in industrial and technological development, so it is expected an increase of their demand. Among the REs the European Commission considered Cerium and Lanthanum as critical raw materials. This research article studies the adsorption of Ce and La onto two carbon nanomaterials, multiwalled carbon nanotubes (MWCNT) and carboxylic functionalized multiwalled carbon nanotubes (MWCNT_ox). The latter has slightly more affinity for REs than MWCNT. The recovery percentage for Ce were 89 and 98% and in the case of for La were 99 and 92% using 0.8 g of MWCNT and 0.2 g of MWCNT_ox respectively. The adsorption process fits a pseudo second order kinetic model and the Langmuir isotherm best represented the metal uptake.

Keywords: adsorption; Lanthanum; Cerium; carbon nanotubes; rare earth

1. Introduction

Since 1960s, REs applications gradually have increases to everyday life until become to be elements which are critical in industrial development and modern technology, in this context these materials are designed also as technology-critical elements [1]. Although rare earths are more abundant than precious metals, the extraction of these are arduous, mainly due to two main reason, they are dispersed in ores deposit and they have similar chemical properties between them, making difficult their individual separation.

REs are widely used in different sectors such as clean energy, nuclear energy, chemical engineering, consumer electronics, advanced transportation, communication, metallurgy or medicine [2,3]. Their great applications are due to the configuration of their electrons in atomic structure and their extraordinary luminescent, catalytic, magnetic, optical, nuclear, electrical, metallurgical and chemical properties [4]. Moreover, the REs importance is also increasing due to their use in green carbon technologies, such as rechargeable car batteries, electronic devices, permanent magnets, wind turbines, and so on. [5].
The global demand of REs is increased and it is expected to experiment a notable growth over time [3]. The REs worldwide reserves are 120 million tons [6]. China is one of the highest supplier of these elements, with more than 70% of the global supply [7]. REs are considered by the European Commission as the most critical raw materials group with the highest supply risk [7]. However, in spite of their great applications and the larger amounts of REs-waste their recycling is still poorly development, in the EU only the 6% of the heavy REs and the 7% of the light REs are recovered [5][4][8][9].

Among REs, Nd (magnets include computer hard disk drive, mobile phones, electric hybrid vehicles, etc. [9][10][11]), Eu and Y (phosphors and luminescence in fluorescence lamps, LEDs, plasma screens, etc. [12][13]), and Ce and La (metal alloys, batteries, glass and catalysts, and rechargeable lithium-nickel batteries[14][15]) are considered the most critical one until 2025 [5].

Currently, the recycling of electric car batteries is a great social and technological challenge. Due to the environmental problem associate to their dangerous compounds, such among others, heavy metals. And the presence of valuable metals, particularly REs, cerium, lanthanum, neodymium and praseodymium which are forming part of the anode in the Ni-MH cell [6][16]. Nowadays, these kind of batteries are one of the most used [17].

Pyrometallurgical and hydrometallurgical process could be used in the battery recycling with the aim of REs recover. In the hydrometallurgical methods the batteries components are leaching in alkaline or acid medium, after machining [17], other stage included in hydrometallurgy methods is the selective separation and concentration from liquid effluent of the valuable metals, REs [6]. Some methods carried out to achieve it are among others, liquid-liquid extraction [18][19], adsorption[20], bioadsorption [21], ion exchange [14], precipitation [16][22][23].

Adsorption is an important methodology to recover these strategic elements from liquid effluents due to simplicity, flexibility, low cost and high efficiency [24][25][26][27]. Thus due to their high economic and technological value of REs joint to their supply risk it is essential the development or improvement technologies to recover them [28]. This article studies the viability to recover two strategic REs present in batteries, La and Ce.

In the last decades the study and the development of new adsorbent has been constant. Crane et al. studied the behavior of La adsorption onto nanoscale zero valent iron in an acid drainage medium [29], Iftekhar et al. [30] reviewed the factors that affect the La adsorption with different adsorbents, biosorbent, inorganic nano/composites, magnetic, silica, graphene oxides, activated carbon, etc. Celso et al. [10] also presented a deep review about the adsorption capacity of different kind carbon nanomaterials.

In this sense this research article is focused on the adsorption of two of the most critical REs, Ce (III) and La(III) onto multiwalled carbon nanotubes (MWCNT) and carboxylic functionalized multiwalled carbon nanotubes (MWCNT-ox) in order to recover these valuable elements from liquid effluent.

2. Materials and Methods

2.1.- Reagents:

Commercial multiwalled carbon nanotubes (MWCNT) and multiwalled carbon nanotubes functionalized with carboxylic groups (MWCNT_ox) from Sigma-Aldrich were used as adsorbent without any further manipulation, Table 1 presents their main characteristic. All chemical,
lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O) and cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O) from Sigma Aldrich, were used in AR grade.

<table>
<thead>
<tr>
<th>Table 1.- MWCNT and MWCNT$_{ox}$ characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity (%)</td>
</tr>
<tr>
<td>MWCNT</td>
</tr>
<tr>
<td>MWCNT$_{ox}$</td>
</tr>
</tbody>
</table>

CVD: Chemical vapour deposition

2.2. Z potential measurement and batch adsorption experiments:

Z potential was measured using a Zetasizer Malvern Nano ZS at 25°. Aqueous suspensions were prepared in pH solutions between 1 and 13 using solutions of HCl and NaOH. The concentration of activated carbon was adjusted to a value of 0.1 g L$^{-1}$. The suspensions were dispersed with a Bandelin Electronic Sonopuls HD 3100 sonicator, using an amplitude of 60% for 150 s.

The adsorption of REs by nanomaterials were studied via batch adsorption experiment performed in a 0.5 L glass reactor provided of mechanical shaking. Standard aqueous solutions of 1 g L$^{-1}$ concentration of La and Ce respectively were prepared. The working REs solutions were prepared by diluting these. Different initial pH of the solutions was obtained with an acid solution of 0.1M HNO$_3$. The working REs solutions were put in to contact with the nanomaterials according to the different experimental conditions.

The residual concentration of Ce and La in aqueous solutions were determined by ICP (Agilent Technologies 5100 ICP-OES). The adsorption percentage was defined as:

$$R_{Ce/La} = \left[\frac{C_0 - C_t}{C_t}\right] \times 100 \quad (1)$$

Where $C_0$ and $C_t$ are the initial and time rare earth concentrations in the aqueous solution respectively (mg RE L$^{-1}$).

REs load capacity onto the nanomaterials was calculated by mass balance, according to:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (2)$$

Where $q_t$ is the amount La and Ce adsorbed (mg RE g$^{-1}$ adsorbent), $V$ is the volume of the solution (0.2 L) and $m$ is the sorbent dosage (g).

3. Results

It is assumed that the adsorption of both, La and Ce by the MWCNT responded to an adsorption process such as:

$$\text{MWCNT} + \text{M}^{n+} \rightarrow \text{MWCNT}[\text{M}^{n+}]_s.$$  \hspace{1cm} (3)

Where MWCNT stands for the solid adsorbent an M for the meals.

Moreover, in the case of the functionalized carbon nanotubes the next reaction must be also considered.

$$3\text{(MWCNT-COOH)}_a + \text{M}^{n+} \rightarrow (\text{MWCNT-COOH})[\text{M}^{n+}]_a.$$  \hspace{1cm} (4)

Thus an ion exchange mechanism is also responsible for metal adsorption.
3.1.- Stirring speed

Figure 1 shows La and Ce adsorption percentage against time at different stirring speed, the other experimental parameters were kept constant. REs adsorption onto MWCNT-Ox are not affected by the stirring speed, so the maximum REs percentages of removal become virtually independent of the stirring speed in the range between 500-1000 min\(^{-1}\), which indicates that the thickness of the aqueous diffusion layer and the aqueous resistance to mass transfer are minimum. Diffusion contribution of the aqueous species to the mass transfer process is assumed constant [31],[32].

![Graph showing adsorption percentage vs time for different stirring speeds](image)

**Figure 1.-** Stirring speed effect on the adsorption of La and Ce onto the MWCNT and MWCNT-ox. (a) MWCNT: Experimental conditions: [Nanomaterials]= 0.8 g, liquid 0.2 L of [RE] = 0.01 g L\(^{-1}\), pH= 6, T= 298 K, \(\theta\)= variable rpm. (b) MWCNT_ox: Experimental conditions: [Nanomaterials]= 0.2 g, liquid 0.2 L of [RE] = 0.01 g L\(^{-1}\), pH= 6, T= 298 K, \(\theta\)= variable rpm.

However, the behavior of MWCNT on REs adsorption was different, an increase in the stirring speed showed a decreases in the adsorption percentage at first elapsed time. This could be due to the
agglomeration of carbon particles due to the Wan Der Waals Force and the consequent reduction in the active surface area of the adsorbent [33].

Figure 2 represents Ct/Cm vs time. Ct/Cm values are independent of the stirring speed when MWCNT_ox are used as adsorbent. However, in the case of the MWCNT, it is observed a slightly dependence at different stirring speed.

(a)

(b)

Figure 2.- Ct/Co versus time to the adsorption of La and Ce onto the MWCNT and MWCNT-ox. (a) MWCNT: Experimental conditions: [Nanomaterials]= 0.8 g, liquid 0.2 L of [RE] = 0.01 g L⁻¹ pH= 6, T= 298 K, θ= variable rpm. (b) MWCNT_ox: Experimental conditions: [Nanomaterials]= 0.2 g, liquid 0.2 L of [RE] = 0.01 g L⁻¹ pH= 6, T= 298 K, θ= variable rpm.

It should be noted here that the use of the functionalized carbon nanotubes greater improve the metal uptake, since these values are presented in Table 2 for the two adsorbents used in this investigation.

<table>
<thead>
<tr>
<th></th>
<th>Ce (mg g⁻¹)</th>
<th>La (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>MWNT_ox</td>
<td>8.8</td>
<td>9.1</td>
</tr>
</tbody>
</table>

The equilibriums were reached for both carbon nanomaterials and both REs at 60 min, all tests were carried out at 180 min ensuring to reach the equilibrium time.
3.2. pH influence

In adsorption, one of the most important parameters is the pH of the solution, as it could affect the surface charge of the adsorbent and modify the adsorbate form. Therefore, it is essential to study its influence [34].

Figure 3 shows the Z potential of MWCNT and MWCNT_ox at different pH values. The isoelectric points (IEP) are 1.22 and 0.26 for MWCNT and MWCNT_ox, respectively. At pH values lower than the pH(IEP), the charge of the adsorbent surface is positive; however, when the pH increases, the surface has a negative charge. This change in the surface charge has a great influence on the adsorption properties of the adsorbent.

Figure 3. Z potential Vs pH

pH adsorption tests revealed that La and Ce uptake onto the nanomaterials are strongly pH-dependent, see Table 3.

Table 3.- La and Ce adsorption percentage at different pH values. Experimental conditions: a) MWCNT: Experimental conditions: [Nanomaterials]= 0.6 g, liquid 0.2 L of [RE] = 0.01 g L⁻¹, pH variable, T= 298 K, θ= 500 rpm. b) MWCNT_ox: Experimental conditions: [Nanomaterials]= 0.2 g, liquid 0.2 L of [RE] = 0.01 g L⁻¹, pH= variable, T= 298 K, θ= 1000 rpm.

<table>
<thead>
<tr>
<th>pH</th>
<th>MWCNT</th>
<th>MWCNT_ox</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>La</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>12.8</td>
</tr>
<tr>
<td>4</td>
<td>74.3</td>
<td>78.5</td>
</tr>
<tr>
<td>6</td>
<td>92.6</td>
<td>99.7</td>
</tr>
</tbody>
</table>

In strong acidic conditions (pH=1) the adsorption percentage for La and Ce onto MWCNT and MWCNT-ox was negligible. This is due to the repulsive effect of the positive surface charge on the nanomaterials, see Figure 3.

However, an increase in the pH, increases the adsorption percentage of La and Ce in both nanomaterials. This behavior could be due to that nanomaterials surface charge turns negative at pH values higher than the pH(IEP) 1.22 and 0.26 for MWCNT and MWCNT_ox, respectively, reaching a maximum adsorption percentage at pH 6, R_Ce=92.6% and R_La=99.7% for MWCNT and R_Ce=89.3% and R_La=92.4% for MWCNT-Ox at 180 min, see Table 2. At pH higher than 6, La and Ce precipitate such
as the hydroxides, La(OH)$_3$ and Ce(OH)$_3$, see Figure 4. For further experiments, were performed at pH 6.

![Graphs showing chemical speciation](image)

**Figure 4.-** Influence of the pH in chemical speciation

3.3.- Effect of the REs concentration

The adsorption behavior of solution with different concentrations of La and Ce at pH=6 using MWCNT and MWCNT-Ox have been studied. Results shows in Figure 5.

The removal percentage depends on the initial metal concentration. An increase in the RE concentration decreases the adsorption percentage in both nanomaterials and both REs. This behavior is more noticeable when the concentration of the REs is high, around 0.04 and 0.08 g L$^{-1}$. This decrease could be due to that both adsorbents have a fixed number of active sites, this higher metal concentrations could saturated these active sites [35]. The $q_m$ values are maximum to REs concentration of 0.04 g L$^{-1}$ for both REs, being $q_{Ce}$= 9.8 mg g$^{-1}$, $q_{La}$=6.5 mg g$^{-1}$ to MWCNT and $q_{Ce}$=49.3 mg g$^{-1}$, $q_{La}$=54.2 mg g$^{-1}$, to MWCNT$_{ox}$.

![Graphs showing adsorption behavior](image)

**Figure 5.-** Influence of the nanomaterial dosage. (a) MWCNT: Experimental conditions: [Nanomaterials]= 0.6 g, liquid 0.2 L of [RE] = variable g L$^{-1}$ pH= 6, $T= 298$ K, $θ= 500$ rpm, at equilibrium time. (b) MWCNT$_{ox}$: Experimental conditions: [Nanomaterials]= 0.1 g, liquid 0.2 L of [RE] = variable g L$^{-1}$ pH= 6, $T= 298$ K, $θ= 1000$ rpm, at equilibrium time.
3.4.- Dependence on nanomaterials dosage

A series of experiments were done to investigate the influence of nanomaterials dosage in the adsorption of La and Ce. Figure 6 shows the REs adsorption percentage vs time. An increases in the MWCNT and MWCNT_ox dosages increased the RE adsorption. These results indicate that no agglomeration of carbon nanomaterials were observed, so these amounts are not enough to observe an adsorbent aggregation effect [35].

The adsorption percentage for both rare earths is higher than 95% using 3.0 or 4.0 g L\(^{-1}\) of MWCNT. However, it could be obtained similar values of adsorption percentage with a lower dosage of MWCNT-Ox nanomaterials, 1.0 g L\(^{-1}\). This behavior indicates that MWCNT_ox have more effective towards La and Ce adsorption to these experimental conditions, this could be due that the carboxylic group also contributes in rare earths adsorption.

![Figure 6](image.png)

Figure 6.- Effect of nanomaterial dosage on the adsorption of La and Ce. (a) MWCNT: Experimental conditions: [Nanomaterials]= variable g, liquid 0.2 L of [RE] = 0.01 g L\(^{-1}\) pH= 6, T= 298 K, θ= 500 rpm. (b) MWCNT_ox: Experimental conditions: [Nanomaterials]= variable g, liquid 0.2 L of [RE] = 0.01 g L\(^{-1}\) pH= 6, T= 298 K, θ= 1000 rpm.

3.5.- Kinetic study
Experimental data were fit to various kinetic models to evaluate the adsorption rate.

- **pseudo-first order** [36]
  \[ \ln(q_e - q_t) = \ln q_e - k_1 t \] (5)

- **pseudo-second order** [37]
  \[ \frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \left( \frac{1}{q_e} \right) t \] (6)

- **Elovich model** [38]
  \[ q_t = \frac{q_e}{\beta \ln \alpha \beta + 1} \ln t \] (7)

Where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the sorption capacities at equilibrium and at time \( t \) (min) respectively, \( k_1 \) is Lagergren first-order adsorption rate constant (min\(^{-1}\)), \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is pseudo-second order constant. \( \alpha \) is the initial adsorption rate (mg min\(^{-1}\)) at contact time \( t=0 \) min and \( \beta \) is the extent of surface coverage and activated energy (g mg\(^{-1}\)). Table 4 and 5 summarized the calculated results.

### Table 4.- Kinetic parameters for La(III) and Ce(III) adsorption onto MWCNT

<table>
<thead>
<tr>
<th>REs</th>
<th>Equation</th>
<th>Constant</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>Pseudo-first</td>
<td>0.0485 min(^{-1})</td>
<td>0.9853</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second</td>
<td>0.0445 g mg(^{-1}) min(^{-1})</td>
<td>0.9945</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha=41.0593 ) mg g(^{-1}) min(^{-1}), ( \beta=2.185 ) g mg(^{-1})</td>
<td>0.9532</td>
</tr>
<tr>
<td>La</td>
<td>Pseudo-first</td>
<td>0.0560 min(^{-1})</td>
<td>0.9445</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second</td>
<td>0.0360 g mg(^{-1}) min(^{-1})</td>
<td>0.9925</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha=41.059 ) mg g(^{-1}) min(^{-1}), ( \beta=2.184 ) g mg(^{-1})</td>
<td>0.9790</td>
</tr>
</tbody>
</table>

### Table 5.- Kinetic parameters for La(III) and Ce(III) adsorption onto MWCNT_ox

<table>
<thead>
<tr>
<th>REs</th>
<th>Equation</th>
<th>Constant</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>Pseudo-first</td>
<td>0.1311 min(^{-1})</td>
<td>0.9332</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second</td>
<td>0.0596 g mg(^{-1}) min(^{-1})</td>
<td>0.9998</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha=0.4237 ) mg g(^{-1}) min(^{-1}), ( \beta=0.363 ) g mg(^{-1})</td>
<td>0.9190</td>
</tr>
<tr>
<td>La</td>
<td>Pseudo-first</td>
<td>0.1352 min(^{-1})</td>
<td>0.9448</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second</td>
<td>0.0398 g mg(^{-1}) min(^{-1})</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>Elovich</td>
<td>( \alpha=0.4425 ) mg g(^{-1}) min(^{-1}), ( \beta=0.343 ) g mg(^{-1})</td>
<td>0.9403</td>
</tr>
</tbody>
</table>

The data, in all the cases, fit better to the pseudo-second order kinetic model. The result obtained suggested that the adsorption could be also contributed with a pseudo-chemical adsorption process [39]. The rate law governing the adsorption of the rare earths onto the carbon nanomaterials was also evaluated. Three possible mechanism were studied [40].

- **Film diffusion controlled process.**
  \[ \ln \left( 1 - \frac{q_t}{q_e} \right) = -Kt \] (8)

- **Particle diffusion controlled process.**
  \[ \ln \left( 1 - \frac{(q_t)^2}{q_e} \right) = -Kt \] (9)

- **Moving boundary process**
  \[ 3 - 3 \left( 1 - \frac{q_t}{q_e} \right)^2 - 2 \frac{q_t}{q_e} = Kt \] (10)

Where \( K \) (min\(^{-1}\)) is the rate constant model, \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the sorption capacities at equilibrium time respectively and \( t \) (min).
Table 6.- Adsorption mechanisms kinetic parameter for La(III) and Ce(III) adsorption onto MWCNT

<table>
<thead>
<tr>
<th>REs</th>
<th>Equation</th>
<th>Constant</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>Film diffusion</td>
<td>0.0504</td>
<td>0.9788</td>
</tr>
<tr>
<td></td>
<td>Particle diffusion</td>
<td>0.0429</td>
<td>0.9905</td>
</tr>
<tr>
<td></td>
<td>Moving boundary process</td>
<td>0.0131</td>
<td>0.9667</td>
</tr>
<tr>
<td>La</td>
<td>Film diffusion</td>
<td>0.0375</td>
<td>0.9834</td>
</tr>
<tr>
<td></td>
<td>Particle diffusion</td>
<td>0.0221</td>
<td>0.9934</td>
</tr>
<tr>
<td></td>
<td>Moving boundary process</td>
<td>0.0079</td>
<td>0.9866</td>
</tr>
</tbody>
</table>

Table 7.- Adsorption mechanisms kinetic parameter for La(III) and Ce(III) adsorption onto MWCNT_ox

<table>
<thead>
<tr>
<th>REs</th>
<th>Equation</th>
<th>Constant</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>Film diffusion</td>
<td>0.1191</td>
<td>0.8153</td>
</tr>
<tr>
<td></td>
<td>Particle diffusion</td>
<td>0.0874</td>
<td>0.90601</td>
</tr>
<tr>
<td></td>
<td>Moving boundary process</td>
<td>0.9601</td>
<td>0.8435</td>
</tr>
<tr>
<td>La</td>
<td>Film diffusion</td>
<td>0.1575</td>
<td>0.9047</td>
</tr>
<tr>
<td></td>
<td>Particle diffusion</td>
<td>0.1038</td>
<td>0.9870</td>
</tr>
<tr>
<td></td>
<td>Moving boundary process</td>
<td>0.0131</td>
<td>0.9667</td>
</tr>
</tbody>
</table>

According to the value of R², the model used to explain the REs adsorption onto these carbon nanomaterials is particle diffusion.

3.6.- Adsorption isotherm models

To obtain information about the adsorbent capacity and the amount of adsorbent required to effectively adsorption of the REs, it is necessary to obtain the corresponding adsorption isotherm [35]. The isotherm models used in this study were Freundlich and Lagmuir ones. The data were obtained varying the quantity of adsorbent. The linearized form of isotherm equations used [41][42] are shown in equations (11) and (12).

Langmuir model

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \\
R_L = \frac{1}{1 + bC_o} 
\]  (11) (12)

Freundlich model

\[
lnq_e = ln K_F + \frac{1}{n} ln C_e 
\]  (13)

Where qe (mg g⁻¹) is the sorption capacities at equilibrium time, Ce (mg L⁻¹) is RE concentration in the aqueous phase at equilibrium, qm (mg g⁻¹) is the maximum sorption capacity and b (L mg⁻¹) is the Lagmuir sorption constant. RL is a dimensional constant separation [43], it provides an idea if the adsorption is considered favourable (RL<1) and unfavourable (RL>1), C0 (mg L⁻¹) is initial REs concentration. KF is the Freundlich constant (L g⁻¹) and 1/n is a heterogeneity factor constant, their value must be lesser than 1 for a favourable adsorption.

Table 8. Calculated isotherms parameters. MWCNT_ox Ce and La
Table 9. Calculated isotherms parameters. MWCNT Ce and La

<table>
<thead>
<tr>
<th></th>
<th>Lagmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>qm (mg g⁻¹)</td>
<td>B (L mg⁻¹)</td>
</tr>
<tr>
<td>La</td>
<td>50.51</td>
<td>0.88</td>
</tr>
<tr>
<td>Ce</td>
<td>53.76</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 8 and 9 show the isotherm parameters for both nanomaterials and both REs. The fit values, R², show that the adsorptions were carried out by the Langmuir model, the isotherm assumed a monolayer sorption, where each adsorption position retains one atom. The adsorption being energetically and sterically independent of the adsorbed quantity, these are sites identical. According to the value of the adimensional Langmuir constant RL <1, the adsorption process is considered favourable.

3.7. Desorption

Desorption studies were also carried out. Based on the result of the pH influence, see Table 3, an increase in the pH promoted the adsorption percentage. Desorption studies were carried out in an acid medium. Accordingly, MWCNT and MWCNT_ox charged with La and Ce, were put in contact with 0.25 L of 0.1 M HNO₃, HCl and H₂SO₄ solutions, during 30 min, at ambient temperature. The solid/liquid relation was 0.4 g L⁻¹, Table 10 shows the La and Ce concentration in nanomaterials.

Table 10.- La and Ce concentration in nanomaterials

<table>
<thead>
<tr>
<th></th>
<th>MWCNT</th>
<th>MWNT_ox</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>La</td>
</tr>
<tr>
<td>qe (mg g⁻¹)</td>
<td>2.5</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Preliminary results show that the desorption percentage for MWCNT and MWXNT_ox using HCl and HNO₃ are lower than 10% independently of the rare earth. An increase in the desorption percentage was observed with H₂SO₄ solution, the desorption percentage obtained for MWCNT and MWCNT_ox was 75 and 79% for Ce and La and 84 and 87% for Ce and La respectively.

4. Conclusions

One of the main conclusion is the viability on the adsorption of La and Ce by multi-walled carbon nanotubes and carboxylic multiwalled functionalized.

The best conditions in the case of MWCNT are:
- Cerium: Stirring speed 500 rpm, pH 6, Ce concentration 0.01 g L⁻¹ and MWCNT dosage 0.8 g (4.0 g L⁻¹), Ce adsorption percentage was 98%.
- Lanthanum: Stirring speed 500 rpm, pH 6, Ce concentration 0.01 g L⁻¹ and MWCNT dosage 0.6 g (3.0 g L⁻¹), La adsorption percentage was 99%.

The best conditions using MWNT_ox are:
- Cerium: adsorption percentage is independent of the stirring speed between 500 and 1000 rpm, pH 6, Ce concentration 0.01 g L⁻¹ and MWNT_ox dosage 0.2 g (1.0 g L⁻¹). The adsorption percentage of Ce was 89%.
- Lanthanum: adsorption percentage are independent of the stirring speed between 500 and 1000 rpm, pH 6, Ce concentration 0.01 g L⁻¹ and MWNT_ox dosage 0.2 g (1.0 g L⁻¹), adsorption percentage of La was 92%.

The result shows that MWNT_ox is more effective than MWCNT in the adsorption of La and Ce from aqueous solutions. In the systems studied the adsorption process fits to a pseudo-second order
kinetic model, and Langmuir isotherm. The rate law which govern the adsorption is the particle diffusion model.

The higher desorption percentage of La and Ce for both nanomaterials were obtained using 0.1 M H$_2$SO$_4$ solution rather than HCl and HNO$_3$.

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