Original Article

Purification, characterization and application of cherty rocks as sorbent for separation and preconcentration of rare earths

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ABSTRACT

Cherty rocks, most abundant byproduct of mining industry, were used as adsorbent for the extraction of rare earth elements. Purified chert was characterized by various analytical methods (XRD, FX-ED, MEB, FTIR, laser granulometry). XRD patterns showed diffraction peaks of quartz, tridymite, cristobalite and clinoptilolite-Ca phases. SEM micrographs showed granular morphology of studied chert and particle size distribution was lower than 100 μm and unimodal. Adsorption behaviors of La(III) and Ce(III) ions on chert were investigated with various chemical methods and ICP-AES. Various experimental parameters were optimized such as contact time, initial rare earth concentration, temperature, agitation rate, and calcination of chert. Stable adsorption of Ce(III) and La(III) on chert were observed at stirring speed 400 and 200 rpm respectively. However the process of calcination does not affect the adsorption capacity of the two rare earths. The adsorption kinetics, the effect of various parameters influencing the adsorption capacity and adsorption isotherms were determined. Results showed instantaneous adsorption, fast kinetics and maximum percentages of adsorption ranged between 80 and ~100%. Highest correlation coefficients were obtained for the pseudo-second order kinetic that are described satisfactorily by the Langmuir model. Thermodynamic parameters obtained indicate an endothermic and spontaneous adsorption process for lanthanum and exothermic and nonspontaneous adsorption process for cerium. Adsorption of rare earths on chert showed similar adsorption capacities to commercial diatomaceous earth and low matrix effect was observed when chert is used as an adsorbent of REE from a phosphogypsum leachate.

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1. Introduction

Rare earth elements (REEs) known as lanthanides, are grouped depending on their atomic number in ‘light’ REEs (La, Ce, Pr, Nd), and ‘middle & heavy’ REEs (Sm, Eu, Gd, Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) [1]. During the last decades, REEs have been widely used in many kinds of industrial products, such as magnetic alloys, photoluminescence materials, optical glasses, electronics and computer apparatus… They are also widely used as catalysts for petroleum refining or as reagents for diagnosis of magnetic resonance imaging (MRI) in medicine and in some fertilizers in agriculture [2–10].
The most widely used techniques for separation and preconcentration of trace REEs include coprecipitation, liquid-liquid extraction, ion exchange, membrane filtration, coagulation and flocculation, electrochemical treatment etc. [11–20]. These processes present some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost etc. [21,22]. Recently, solid-liquid extraction technique has become more and more popular in trace elements preconcentration compared with the other methods cited above. Sorbents such as activated carbon, nanostructured materials, biological substances, ion imprinted polymers, hybrid sorbents, chelating resin and modified silica are all used and tested for pre-concentration of REEs from various samples [16,21–29]. The use of solid-liquid extraction provides high enrichment factor and recovery, a rapid separation with low consumption of organic solvents. The major advantage of sorption method is the use of inexpensive sorbents [21–23,29–32] provide from abundant or recycled by-product such as the highly silicified sedimentary rocks which is called chert [33–35]. It is a hard, dense or compact sedimentary rock composed mainly of one, or combination, of different forms of silica [33–37].

The first part of this study is based on the physical and chemical characterization of chert sample coming from Gafsa-Metlaoui (south-western Tunisia) throughout the purification steps. In the second part of this study, the potential of chert for La(III) and Ce(III) adsorption and desorption from aqueous solution and phosphogypsum leachate was studied. The study is further unique as there is no existing report for the removal of any lanthanide elements by cherty materials.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Nitric acid (HNO₃, 65%), hydrofluoric acid (HF, 40%), perchloric acid (HClO₄, 70%), and hydrochloric acid (HCl, 37%) were from Scharlau Chemicals.

Diatomaceous earth was obtained from Sigma-Aldrich. Working standard solutions of REEs (Ce(III) and La(III)) were prepared on a daily basis from Ce(Cl₃)·7H₂O and La(Cl₃)·7H₂O obtained from Sigma-Aldrich by dissolving appropriate amounts in ultrapure water.

2.2. Purification and characterization of chert

Silica from cherty rocks of Gafsa-Metlaoui basin characterizes the Ypresian phosphatic series of Chouabine formation. In general, the cherty levels are located at the base of the main phosphatic series between CVI and CVII phosphatic layers and they are composed principally of opal CT (cristobalite/tridymite) [38]. Qualitative and quantitative analyzes were performed by X-ray fluorescence spectrometer (XRF) and atomic emission spectrometry inductively coupled plasma (ICP-AES). The structure was determined from analysis by X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FT-IR). The morphology was determined by scanning electron microscopy (SEM) and the particle size was measured by laser granulometry.

At first the sample was ground into a fine powder and then dried in an oven for 24 h at the temperature 60 °C. Then successive purifications were applied to the material to remove carbonates, iron oxides, clays...

To remove carbonates (present in the forms of calcite and dolomite) and iron oxide, an acid attack (HCl, 12%) at room temperature was performed on the chert finely crushed. Several washings with ultrapure water, followed by centrifugation were carried out to remove the excess of acid and iron chloride. The material was finally dried in an oven at 60 °C.

A volume of ultrapure water was added to the decarbonated chert in order to eliminate by centrifugation the clay suspension. This process was repeated several times.

The structural study was performed by a diffractometer PANalytical, X’Pert PRO’ equipped with a copper anticathode (Cu Ka λ = 1.540598 Å). Analysis of diffractograms was performed using a system based on data sheets ASTM (American Society for Testing and Materials) matching the interplanar spacing (d) 2θ angles recorded software. Conditions of the analyses were maintained constant for all samples in the interval 3–100° in 2θ, for a step of 0.015°/s.

The IR analyzes were carried out using a Fourier transform infrared spectroscopy (FTIR) type ‘FTIR VERTEX 70 ATR Bruker Diamant’. We proceeded with a resolution of 4 cm⁻¹ and 40 scans. FTIR was recorded in the range 400–4000 cm⁻¹.

Major elements and silica content of the raw chert, treated chert and diatomaceous earth were determined using ‘Magix PW2403’ X-ray fluorescence. Analyzes of rare earths elements were performed using atomic emission spectrometry inductively coupled plasma (ICP-AES) type ‘HORIBA Jobin Yvon’.

Spectrometric analysis by ICP-AES requires a pretreatment of the samples of chert before analysis. Sample preparation is based on their dissolution, for that an acid attack was carried out: in a Teflon bottle, the sample was mixed with 8 mL of hydrofluoric acid (HF, 40%), 2 mL of perchloric acid (HClO₄, 70%) and 2 mL of nitric acid (HNO₃, 65%). The dissolution was carried out for 48 h at room temperature and then on a hot plate set at 150 °C for 24 h until complete evaporation of the mixture. Hydrofluoric acid attacks the silicates to form silicon tetrafluoride (SiF₄) which evaporate during heating. The solid residue obtained was taken up with a mixture of 0.6 mL of nitric acid and UP water. The solutions obtained were subsequently analyzed by ICP-AES in order to analyze the rare earths present in the samples.

In this study, observations of surface morphology were performed using equipment of environmental scanning electron microscope (ESEM) ‘FEI Quanta 200’ category. This device can provide rapid information on the morphology and chemical composition of a solid object.

Granulometric analyses of chert and diatomaceous earth samples were determined by Granulometer Lazer Masteriser ‘2000 Marlven’ using wet method. The samples have been analyzed in water suspension and a suitable ultrasonic sound time has been applied (120 s). In order to compare the granulometric parameters from different samples, mass medium diameter (MMD; the average particle diameter by mass) has been calculated. The D₅₀ corresponds to diameter size in
microns that splits the distribution with half above and half below and the D90 describes the diameter where ninety percent of the distribution has a smaller particle size and 10% has a larger particle size.

2.3. Adsortion of rare earth elements on purified chert

2.3.1. Adsorption kinetics
To study the adsorption kinetics of REEs on purified chert, a volume of 200 mL of lanthanum or cerium salt solution with C_0 concentration was placed in contact with 0.40 g of purified chert. To determine the instantaneous concentration C_i of ions, a volume of 2 mL was taken at chosen times, then filtered using a syringe filter and by ICP-AES. These manipulations were performed at room temperature with stirring. PH of all solutions in contact with adsorbent was found to be in the range of 4-5 and initial concentration of lanthanum and cerium were ranged between 0.37-149.66 mg L\(^{-1}\) and 0.37-150.42 mg L\(^{-1}\), respectively.

Adsortive uptake (Q_t) of studied REEs by chert, for any time t, was determined by the difference between the initial and final ion concentrations. It is expressed by the following equation:

\[ Q_t = \frac{(C_0 - C_i)V}{m} \text{ (mg g}\^{-1}\text{)} \]

where C_0 and C_i are concentrations of La(III) or Ce(III) (mg L\(^{-1}\)) in the solution at t = 0 and any t, V is the volume of the solution (L) and m is the weight (g) of purified chert.

To quantify the changes in the adsorption of La(III) and Ce(III) with time, an appropriate kinetic model would be necessary. For that reason, different kinetic models were tested (intraparticle diffusion model and model based on the composition of the media) [39–44]:

- **Intraparticle diffusion model** (Weber and Morris) is expressed as:
  \[ Q_t = K_t t^{1/2} + C \]
  where K_t is the rate constant of the intraparticle diffusion (mg g\(^{-1}\) min\(^{-1/2}\)) and C is the parameter of the equation of Weber and Morris (mg g\(^{-1}\)).

- **Models based on the composition of the media**: A solution containing the studied ions is contacted with a known mass of adsorbent. The adsorption of the solute results of the simultaneous variations of concentration in solution and solid surface. The reaction rate V_t, regardless of the reactor in which it takes place is written as follows:
  \[ V = \frac{dQ_t}{dt} = KQ_t^n \]
  where K is the constant of velocity and \( n \) is the global order of the reaction.

- **zero order model** (\( n = 0 \)) equation is expressed in a nonlinear form as:
  \[ V = \frac{dQ_t}{dt} = K_0 \]

  This equation integration and rearrangement yield linear form:
  \[ Q_t = K_0 t \]

  where \( K_0 \) is the rate constant of the zero order model, expressed in mg g\(^{-1}\) min\(^{-1}\).

- **First-order model** (\( n = 1 \)) may be expressed in the form:
  \[ V = \frac{dQ_t}{dt} = K_1 Q_t \]

  Integration of this differential equation yield linear form:
  \[ \ln(Q_t) = K'_1 t \]

  where \( K'_1 \) is the rate constant of the first order kinetic, expressed in min\(^{-1}\).

- **Second-order model** (\( n = 2 \))
  \[ V = \frac{dQ_t}{dt} = K'_2 Q_t^2 \]

  where \( K'_2 \) is the rate constant of the second order kinetic, expressed in g mg\(^{-1}\) min\(^{-1}\). A linear form of the second-order model can be expressed as:
  \[ \frac{1}{Q_t} = K'_2 t \]

- **Pseudo-first order model** equation (Lagergren) is expressed in nonlinear form as:
  \[ V = \frac{dQ_t}{dt} = K_1 (Q_1 - Q_t) \]

  where Q_s and Q_t are the amounts of metal ions adsorbed on the adsorbent (mg g\(^{-1}\)) at equilibrium and at time t, respectively and K_1 is the rate constant of the first-order adsorption in min\(^{-1}\). Equation integration gives the linear form:
  \[ \ln(Q_1 - Q_t) = \ln(Q_t) - K_1 t \]

- **Pseudo-second order model** can be expressed in a non-linear form as:
  \[ V = \frac{dQ_t}{dt} = K_2 (Q_2 - Q_t^2) \]

  After adding the initial conditions of t = 0 to t = t and Q_1 = 0 to Q_t = Q_t, the equation becomes the following linear form:
  \[ \frac{t}{Q_t} = \left( \frac{1}{K_2 Q_2^2} \right) + \left( \frac{1}{Q_2} \right) \]

  where K_2 (g mg\(^{-1}\) min\(^{-1}\)) are the rate constant of pseudo-second order adsorption process.

2.3.2. Adsorption isotherms
An adsorption isotherm describe the equilibrium relationships between sorbent and sorbate in solution at equilibrium and constant temperature. In this study, mechanisms of adsorption of La(III) and Ce(III) on purified chert surfaces were examined. The adsorption equilibrium data were analyzed with Langmuir, Freundlich and Temkin sorption isotherm models [45–47]. Freundlich isotherm is describing the non-ideal and reversible adsorption. This empirical model can be applied to the monolayer adsorption even to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The Freundlich equation was represented in a linear equation as:

\[ \log(Q_s) = \log(K_f) + \frac{1}{n} \log(C_0) \]
where $K_f (\text{mg g}^{-1} \text{L g}^{-1})^{1/n}$ and $1/n$ are the Freundlich constants corresponding respectively to adsorption capacity and adsorption intensity.

The Langmuir isotherm takes into account the assumption that the adsorption occurs at specific homogeneous sites within the adsorbent. This isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites and each molecule possess constant enthalpies and sorption activation energy, with no transmigration of the adsorbate in the plane of the surface. The well-known Langmuir equation is represented as:

$$\frac{C_r}{Q_r} = \left( \frac{1}{bQ_m} \right) + \left( \frac{C_r}{Q_m} \right)$$

where $Q_r$ is the adsorbed amount of La(III) or Ce(III) at equilibrium on the adsorbent (mg g$^{-1}$), $C_r$ is the equilibrium concentration of La(III) or Ce(III) in solution (mg L$^{-1}$), $Q_m$ is the monolayer capacity of chert (mg g$^{-1}$), and $b$ is the adsorption constant of Langmuir (L mg$^{-1}$) related to the free energy of adsorption.

The Temkin isotherm contains a factor that explicitly taking into account the adsorbent–adsorbate interactions while ignoring the extremely low and large value of concentrations. However, this model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, in one hand, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy, in the other hand. The Temkin model is given by the following equation:

$$Q_r = B \ln(A_T) + B \ln(C_r)$$

where $B = (RT)/b_T$ is a constant related to heat of sorption (J mol$^{-1}$), $b_T$ is Temkin isotherm constant, $R$ is universal gas constant (8.314 J/mol*K) and $A_T$ is Temkin isotherm equilibrium binding constant (L g$^{-1}$).

### 2.4. Desorption

Desorption experiments were performed using 0.10 g of metal loaded chert with known amount of lanthanum or cerium, immersed under stirring in 50 mL of hydrochloric acid solution (HCl, 4 mol L$^{-1}$) for 5 h.

To determine the instantaneous concentration $C_r$ of desorbed ions, a volume of 2 mL was collected at defined times. It will be then filtered and dosed by ICP-AES. Desorption capacity
and percentage of desorption are calculated from the following equations [47-49]:

\[ Q_{\text{des}} = C_\text{t} \frac{V}{m} \quad (\text{mg g}^{-1}) \]

\[ \% \text{Desorption} = \left( \frac{\text{Quantity of desorbed ions}}{\text{Quantity of absorbed ions}} \right) \]

3. Results and discussion

3.1. Characterization of chert samples

Fig. 1 presents the XRD patterns of the raw and purified chert. The main diffraction peaks, in both cases, are of the crystalline phases: quartz, tridymite and cristobalite.

The raw chert contains opal-CT as major mineral silica. Opal CT precipitates at low temperature, its dissolution and recrystallization results in the minerals cristobalite and tridymite, which are more stable forms of silica. The opal CT in turn changes to microcrystalline quartz which is the final and most stable form of silica [35,38]. Further peaks are also observed, with the raw material, they correspond to the hydroxyapatite and carbonate (the latter is observed under calcite and dolomite forms).

However, with the purified chert we notice the disappearance of the crystalline phases of hydroxyapatite, calcite and dolomite on the one hand and the appearance of clinoptilolite-Ca phase on the other hand. Clinoptilolite appears to be present in the sample from the beginning and its identification
has been possible due to the elimination of certain mineral phases during the purification performed on the raw chert.

FT-IR has been used to follow the specific chemical changes that occur in cherty material during purification steps. Fig. 2 shows FT-IR spectra of cherty and diatomaceous earth samples. Infrared spectra show characteristic bands due to silicate structure which are seen between 1400 and 400 cm\(^{-1}\). Absorption bands at 447 and 791 cm\(^{-1}\) are assigned to the Si–O bonds in the tetrahedral sheet and the wide bands centered at 1090 cm\(^{-1}\) should be due to Si–O–Si in-plane vibration (asymmetric stretching) [38,50]. The IR spectra of all studied samples have at least one absorption band characteristics of cristobalite phase that appears at 619, 795, 1090, and 1202 cm\(^{-1}\) [38]. FT-IR results showed the disappearance of absorption bands characteristics of O–H at 1420 cm\(^{-1}\) and C–O bonds at 1420 cm\(^{-1}\), 874 cm\(^{-1}\) and 710 cm\(^{-1}\). Absorption bands of hydroscopic water and calcite phase are identified only in raw chert.

Scanning electron microscopy micrographs of purified chert and diatomaceous earth are presented in Fig. 3 and showing a great difference between these two materials. Results show a granular morphology of studied chert. Grains of different shape and size are observed. At high magnification (Fig. 3b) granular surface can be clearly seen and when analyzed by EDAX gives the Si-rich profiles (Fig. 4) with the presence of oxygen, Mg, Al, K and Fe. SEM photograph of diatomaceous earth illustrate a complex morphology that contains numerous pores, cavities and channels [51] which confirms its biogenic origin. Bedded fossiliferous chert contains remains of siliceous organism as diatoms, radiolarians, and sponge spicules which it forms when siliceous ooze recrystallize. Our cherty sample and according to SEM results show a chemogenic origin. It may be the result of dissolution and re precipitation of a bedded chert by hydrothermal waters where most of the silica dissolved is immediately reprecipitated leaving no trace of the fossil [52].

Laser granulometry analyses present the relative quantities of particles having particular size. Information on the particle size distribution is important for understanding physical and chemical properties of the material and influence the reactivity of solids in chemical reactions. Granulometric distribution of cherty sample is illustrated in Fig. 5 and the particle size distribution is represented in terms of the particles volume. Obtained results showed a granulometry lower than 100 \(\mu\)m and unimodal particle distribution between 1 and 100 \(\mu\)m.

Purified chert (Table 1) showed 50% of particles having diameter equal to or less than 8.61 \(\mu\)m and 90% having diameter less than 19.70 \(\mu\)m. Their greatest dispersion was founded around 9 \(\mu\)m. But, 50% of diatomaceous earth particles have a diameter less than or equal to 15.51 \(\mu\)m, 90% have a diameter less than 38.02 \(\mu\)m and the largest dispersion extended around 12 \(\mu\)m (Fig. 5).

### 3.2. Chemical analyses of cherty materials

The chemical analyses of raw chert, purified chert and diatomaceous earth, samples are shown in Table 2. Silica is the main constituent of chert and about 97% were reached after purification steps. This purification allowed a complete elimination of carbonate and reduced until 22.50% of the other oxides. REEs content determined in purified chert and diatomaceous earth are presented in Table 3. Results showed very low quantities of REEs in chert compared with

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**Table 1 – Laser granulometry analyses.**

<table>
<thead>
<tr>
<th></th>
<th>(D_{10}) ((\mu)m)</th>
<th>(D_{50}) ((\mu)m)</th>
<th>(D_{90}) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chert</td>
<td>3.77</td>
<td>8.61</td>
<td>19.70</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>5.03</td>
<td>15.51</td>
<td>38.02</td>
</tr>
</tbody>
</table>

\(D_{90}\) corresponds to the particle size for which x% of the population is below this value.

**Table 2 – Chemical analyses by XRF of diatomaceous earth and cherty samples.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Diatomaceous earth (%)</th>
<th>Raw chert (%)</th>
<th>Purified chert (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>90.60</td>
<td>60.70</td>
<td>97.29</td>
</tr>
<tr>
<td>CaO</td>
<td>2.62</td>
<td>10.59</td>
<td>–</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.22</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>FeO(_3)</td>
<td>1.40</td>
<td>2.15</td>
<td>–</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.42</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>4.62</td>
<td>4.47</td>
<td>2.87</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.17</td>
<td>1.88</td>
<td>–</td>
</tr>
<tr>
<td>MgO</td>
<td>0.94</td>
<td>4.02</td>
<td>0.43</td>
</tr>
<tr>
<td>BaO</td>
<td>0.12</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>–</td>
<td>0.64</td>
<td>–</td>
</tr>
</tbody>
</table>

Content is lower than limit of quantification of XRF.

**Table 3 – REE contents of chert and diatomaceous earth samples, expressed in (mg kg\(^{-1}\)).**

<table>
<thead>
<tr>
<th>Element</th>
<th>Purified chert</th>
<th>Diatomaceous earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>5.44</td>
<td>18.48</td>
</tr>
<tr>
<td>La</td>
<td>9.44</td>
<td>11.84</td>
</tr>
<tr>
<td>Y</td>
<td>7.20</td>
<td>8.96</td>
</tr>
<tr>
<td>Pr</td>
<td>2.56</td>
<td>6.55</td>
</tr>
<tr>
<td>Yb</td>
<td>1.60</td>
<td>2.56</td>
</tr>
<tr>
<td>Dy</td>
<td>1.36</td>
<td>2.40</td>
</tr>
<tr>
<td>Sm</td>
<td>0.96</td>
<td>2.08</td>
</tr>
<tr>
<td>Nd</td>
<td>–</td>
<td>6.56</td>
</tr>
<tr>
<td>Gd</td>
<td>–</td>
<td>2.96</td>
</tr>
<tr>
<td>Eu</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Content is below the limit of quantification of ICP-AES.
Table 4 – Adsorption capacity at different temperatures and calculated thermodynamic parameters.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Adsorption capacity Qe (mg g⁻¹)</th>
<th>ΔG (kJ mol⁻¹)</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>ΔS (kJ K⁻¹ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>3.244</td>
<td>–4.6412</td>
<td>0.8807</td>
<td>0.0188</td>
</tr>
<tr>
<td>303</td>
<td>3.933</td>
<td>–4.8296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>8.072</td>
<td>–5.0181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>16.208</td>
<td>–5.3950</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293</td>
<td>3.102</td>
<td>7.5910</td>
<td>–0.1297</td>
<td>–0.0263</td>
</tr>
<tr>
<td>303</td>
<td>2.201</td>
<td>7.8545</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>2.225</td>
<td>8.1180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>1.620</td>
<td>8.6451</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6 – Adsorption kinetics of Ce (III) at (a) low and (b) high initial concentrations.

Diatomaceous earth [53] and even in other phosphate by-products according to literature [54].

3.3. Effect of temperature and thermodynamics study

Adsorption is a phenomenon that may be exothermic or endothermic depending on the adsorbent material and the nature of the adsorbed molecules. In this study, temperature effect was studied at 293, 303, 313 and 333 K. It was performed with 400 mg of purified chert which were mixed with 200 mL of La(III) or Ce(III) solution prepared at 37.40 mg L⁻¹ and 37.60 mg L⁻¹ respectively. The pH of solutions was set between 4 and 5. The residual concentration of the rare earth elements was determined by ICP-AES and the adsorption capacity is presented in Table 4.

As we know the adsorption capacity decreases with temperature with exothermic reactions and increases in case of endothermic reactions. According to results illustrated in Table 4, the La(III) adsorption on chert showed an endothermic process whereas that of Ce(III) was exothermic. Adsorption depends on the nature of the reaction and its parameters. With endothermic process, the adsorption increase with the increase of surface coverage at higher temperature and the expansion and creation of reactive and active sites. However, the exothermic process is attributed to the physical adsorption which is dominated by dispersive force and driven by enthalpy thoroughly [55,56]. The equilibrium relationship between liquid phase and adsorbed phase concentrations is commonly referred to Henry’s law and adsorption equilibrium (partition or distribution coefficient K_d) can be expressed by the Henry constant (1) [23,56]:

\[
K_d = \frac{Q_e}{C_e}
\] (1)

where C_e is the equilibrium concentration in solution (mg L⁻¹) and Q_e is the adsorption capacity at equilibrium (mg g⁻¹).

Thermodynamic parameters, such as free energy change ΔG°, enthalpy change ΔH° and entropy change ΔS° can be determined using following Eqs. (2)–(4) where R is the universal
Fig. 7 – Adsorption kinetics of La (III) at (a) low and (b) high initial concentrations.

Fig. 8 – Equilibrium adsorption of Ce (III) on purified chert.

Fig. 9 – Equilibrium adsorption of La(III) on purified chert.
gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and T is the temperature expressed in Kelvin [23]:

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (2)
\]

\[
\Delta G^o = -RT \ln K_d \quad (3)
\]

\[
\Delta G^o = \Delta H^o - T \Delta S^o \quad (4)
\]

Free energy change of adsorption \(\Delta G^o\) was calculated by using Eq. (3). \(K_d\) is the thermodynamic equilibrium constant for the adsorption process. It was determined by plotting \(\ln(C_e/Q_a)\) versus \(C_e\) and extrapolating to zero \(C_e\) [57].

The other thermodynamic parameters, enthalpy change \(\Delta H^o\) and entropy change \(\Delta S^o\) were calculated from the slope and intercept of the plot of \(\ln K_d\) against 1/T. \(\Delta H^o\) was obtained from the slope of the straight line and \(\Delta S^o\) was determined from the intercept of the graph.

All these parameters are calculated for both studied REE at different temperature. Results are listed in Table 4. As it can be seen, the negative values of \(\Delta G^o\) show a spontaneous nature of adsorption of La(III) on purified chert and the positive value of \(\Delta H^o\) indicate an endothermic process.

Adsorption process of Ce(III) onto chert is presented negatively for the adsorption process and positive values of \(\Delta G^o\) which increase with increasing the temperature of the solution. Positive values of \(\Delta G^o\) indicate either the spontaneous nature of the adsorption process or the presence of an energy barrier. When the ions approach the particle surface, some of the water molecules forming hydration shell of ions are stripped off and simultaneously the degree of freedom of Ce ions declines [58].

Negative value of \(\Delta S^o\) (in case of Ce ions) indicate that there is a decrease in state of disorderliness during process, which in turn is due to the binding of both Ce ions and water molecules with adsorbent surface [59]. Whereas, positive value of \(\Delta S^o\) indicates that the release of the attached water molecules took place as La(III) adsorbed on the substrate and contribute to the increase in the degree of freedom of the entire system [60].

3.4. Effect of contact time

The effect of shaking time on the adsorption of Ce and La ions on purified chert at different initial concentration of the two ions was studied (Figs. 6 and 7). For low initial concentrations (between 3.76 and 0.37 mg L\(^{-1}\) for both La and Ce), results in Figs. 6a and 7a showed instantaneous adsorption, fast kinetics, the equilibrium is reached within the first 5 min and the maximum percentages of adsorption approach their maximum values (ranged between 80 and ~100%).

At low concentration the REE ions adsorption onto adsorbent was found to be concentration dependent. As can be observed, increasing initial REE ions concentration increases the equilibrium adsorption uptake of the adsorbent. It can be due to the fact that adsorption onto the adsorbents is a diffusion based process.

At high initial concentration from 18.70 to 149.66 mg L\(^{-1}\) for lanthanum and 18.80 to 150.42 mg L\(^{-1}\) for cerium (Figs. 6b and 7b), it was clearly that the adsorption capacity of chert was significantly improved. The percentage of adsorption calculated is found proportionate to La(III) concentration until vacant adsorbent sites were fully attached by these ions. While, the percentage of adsorption was inversely related to the concentration of Ce\(^{3+}\) and high affinity of the adsorbent was observed for the Ce\(^{3+}\) at lowest concentration. As can be observed from Figs. 6b and 7b, the adsorption capacity decreases in the order Ce\(^{3+}\) > La\(^{3+}\) this due to the lanthanide contract [61-63].

3.5. Effect of initial concentration

The effect of initial concentration of La(III) and Ce(III) ions at the adsorbed amount at equilibrium by chert was studied with varying solution concentrations (Figs. 8 and 9). Their shapes vary with the nature of exchangeable cations. The isotherm of La\(^{3+}\) ions form is of ’S’ class. It indicates that at low concentrations the surface has a low affinity for the adsorptive, which increase at higher concentrations. Ce\(^{3+}\) ions form for the ion exchanger is ’L’ class which is characterized by a high affinity of the adsorbent for the adsorptive at low concentrations since vacant adsorption sites decrease as the adsorbent becomes covered.

3.6. Adsorption isotherm models

Parameters of Langmuir, Freundlich and Temkin isotherms equations (\(Q_m, K_d, K_f, A_f, R^2\ldots\)) are given in Table 5. The values of the correlation coefficients showed good correlation between the experimental data and the Langmuir model. This suggests that the adsorption of La(III) and Ce(III) ions by chert was monolayer-type.

3.7. Adsorption kinetics

The kinetic adsorption data can be processed to understand the dynamics of the adsorption reaction in terms of the order and rate-limiting step. All the parameters determined by kinetic models are presented in Table 6. Among them, semi-empirical kinetic model, the pseudo-second-order, which is based on adsorption equilibrium capacity, had very high value of \(R^2\) and confirms the kinetic behaviors of the two studied REE.
### Table 6 - Equilibrium model parameters for adsorption of La(III) and Ce(III) ions by chert.

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>Parameters</th>
<th>Ce(^{3+}) (mg L(^{-1}))</th>
<th>La(^{3+}) (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial concentration</td>
<td>0.37</td>
<td>3.76</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td>(R^2)</td>
<td>0.0620</td>
<td>0.6345</td>
</tr>
<tr>
<td></td>
<td>(K_t)</td>
<td>1 E-0.4</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>(C)</td>
<td>0.107</td>
<td>0.912</td>
</tr>
<tr>
<td>First order</td>
<td>(R^2)</td>
<td>0.0016</td>
<td>0.6885</td>
</tr>
<tr>
<td></td>
<td>(K')</td>
<td>8</td>
<td>0.0005</td>
</tr>
<tr>
<td>Second order</td>
<td>(R^2)</td>
<td>0.0902</td>
<td>0.5743</td>
</tr>
<tr>
<td></td>
<td>(K_2)</td>
<td>0.0002</td>
<td>-0.0002</td>
</tr>
<tr>
<td>Pseudo-first order</td>
<td>(R^2)</td>
<td>0.1985</td>
<td>0.8385</td>
</tr>
<tr>
<td></td>
<td>(K_1)</td>
<td>0.0006</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>(Q_e)</td>
<td>0.0099</td>
<td>0.045</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>(R^2)</td>
<td>0.9999</td>
<td>0.9890</td>
</tr>
<tr>
<td></td>
<td>(K_2)</td>
<td>87.024</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>(Q_{2e})</td>
<td>0.1090</td>
<td>1.087</td>
</tr>
</tbody>
</table>

Fig. 10 – Effect of agitation rate on the adsorption capacity of Ce (III) on the purified ‘Chert’, \([\text{Ce(III)}]_0 = 37.631 \text{ mg L}^{-1}\).

Fig. 11 – Effect of agitation rate on the adsorption capacity of La(III) on the purified ‘Chert’, \([\text{La(III)}]_0 = 149.66 \text{ mg L}^{-1}\).

### 3.8. Effect of agitation rate

In case of solid-liquid system, the role of stirring is to homogenize the distribution of particles in the liquid phase and to maximize contact with adsorbent [64]. To study the effect of agitation rate on the adsorption kinetics of REEs on purified chert, a volume of 200 mL of lanthanum (149.66 mg L\(^{-1}\)) or cerium (37.63 mg L\(^{-1}\)) salt solution was placed in contact with 0.40 g of purified chert. Stirring speed going from 0 to 600 rpm was tested and results obtained are shown in Figs. 10 and 11. Better and stable adsorption of Ce(III) on chert were observed at stirring speed 400 rpm as long as we do not exceed stirring time of 240 min. Indeed, a phenomenon of desorption of Ce(III) is observed beyond 240 min for all tested stirring speed. With
Fig. 12 – Effect of calcinations of ‘Chert’ on the adsorption capacity of Ce(III) and La(III). $m_{ads} = 0.4 \text{ g}$, $V = 200 \text{ mL}$, $[\text{Ce (III)}]_0 = 37.631 \text{ mg L}^{-1}$, $[\text{La(III)}]_0 = 149.66 \text{ mg L}^{-1}$, reaction time: 2 h.

Fig. 13 – Adsorption kinetics of Ce (III) on the purified ‘Chert’ and diatomaceous earth.

Fig. 14 – Adsorption kinetics of La (III) on the purified ‘Chert’ and diatomaceous earth.

Fig. 15 – Desorption kinetics of La(III) and Ce(III) loaded chert using HCl media (4M).
the exception of 200 rpm, the other stirring speeds show significant fluctuation of $Q_t$ with stirring time and affect stability of the adsorbed amounts of La(III) on chert.

3.9. Effect of calcination

The samples of chert were calcined at different temperatures (200, 400, 600, 800 and 1000 °C). The adsorbed amounts of Ce(III) and La(III), on the calcined cherts, were calculated and the obtained results are given in Fig. 12.

The XRD characterization of calcinated cherts showed improvement in the purity and composition of the adsorbent. However, the process of calcination (Fig. 12) does not affect the adsorption capacity of the two rare earths. For lanthanum, this capacity remains unchanged and she begins to decrease slightly starting from the calcination temperature 800 °C. For cerium, a slight decrease of the adsorbed amount is observed staring from the calcination temperature 400 °C.

3.10. Comparative study

A comparative study of the adsorption of La(III) and Ce(III) on purified chert and diatomaceous earth was conducted with initial concentrations $37.40 \text{mgL}^{-1}$ of La(III) and $37.6 \text{mgL}^{-1}$ of Ce(III) (all other experimental conditions are maintained constant).

According to curves shown in Figs. 13 and 14, the same adsorption phenomenon is observed with the two adsorbents. In both studied cases equilibrium is reached quickly. The adsorbed amounts of cerium on the both adsorbents lead to adsorption values very close. However, diatomaceous earth had better adsorption of La(III) than the chert.

3.11. Desorption kinetics

Mineral acids are considered to be protons exchanging agents. Ion exchange is the mechanism in which adsorbing ion take place of another ion already associated with the sorbent surface leading to its desorption. For this purpose, HCl was tested and Fig. 15 shows the desorption kinetics of Ce$^{3+}$ and La$^{3+}$ from the ion-loaded chert.

The Ce$^{3+}$ formed a stronger ion-mass bond with chert which leads to its better adsorption percentages as compared to lanthanum. So due to its higher affinity with chert, it was more difficult to desorb. Consequently, lanthanum showed better desorption behavior as compared to cerium under the same conditions. Results showed that up to 60% of lanthanum and 46% for cerium were desorbed in concentrate HCl media (4 M).

3.12. Application on a sample of phosphogypsum

Phosphogypsum is an acidic by-product from the phosphate fertilizer industry, that large quantities are produced world-wide. Phosphogypsum is mainly composed of gypsum and contains interesting quantities of impurities such as phosphates, fluorides, heavy metals, and rare earth.

In order to study matrix effects on the adsorption capacity of ‘chert’, adsorption was studied using leachate of a phosphogypsum from the Gafsa-Metlaoui doped with a volume of Ce (III) at concentration 0.376 ppm. From Fig. 16, a minor matrix effect is observed. Indeed, adsorbed amount of Ce(III) from the phosphogypsum leachate by chert $(0.126 \text{mgg}^{-1})$ is close to that achieved when cerium is prepared in ultra-pure water $(0.11 \text{mgg}^{-1})$.

4. Conclusion

The chert, low cost and abundant byproduct material of phosphate mining industry, has suitable adsorption capacity with Ce and La ions. After purification steps, obtained chert is a siliceous phase SiO$_2$ composed mainly of Opal GT (cristobalite and tridymite), clinoptilolite-Ca and traces of quartz.

Various experimental parameters such as contact time, initial rare earth concentration, temperature, agitation rate, and calcination of chert were optimized.

The results demonstrate that La(III) and Ce(III) sorption to the chert reached equilibrium in 5 min. Highest correlation coefficients were obtained for the pseudo-second order kinetic that are described satisfactorily by the Langmuir model and the thermodynamic parameters obtained indicate an
endothermic adsorption process for lanthanum and exothermic adsorption process for cerium.

The study of the stirring rate showed a stable and better adsorption at 200 rpm and 400 rpm respectively for lanthanum and cerium, while the calcination of chert did not show a significant effect on the adsorption capacity.

Comparative study of adsorption of La(III) and Ce(III) on purified chert and diatomaceous earth was performed. Adsorbed amounts of cerium in both materials are very close, however the diatomaceous earth showed a better adsorption of La(III) than on chert.

Desorption test of the two rare earths from chert showed promising results. Finally, as an application, we tested the effectiveness of chert as an adsorbent of cerium from a phosphogypsum leachate. The result shows low matrix effect therefore this can suggest a possible application on phosphogypsum.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


