LANTHANUM UPTAKE BY CLAYS AND ORGANO-CLAYS: EFFECT OF THE POLYMER

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Abstract

Two natural smectite clays (STx-1b and SWy-2) were studied as solid sorbents for uptake and release of lanthanum. Since the obtained global efficiencies of lanthanum recovery were about 30-35%, the same considered natural clays were modified by intercalating a PEGylated ethylene diamine having chelating properties, in order to evaluate a possible improvement effect of the polymer. The pristine and the organo-clays were characterized by XRD analyses while the amounts of intercalated polymer and captured lanthanum were estimated respectively by COD and ICP-OES analyses. The results showed that pristine clays and modified clay had similar lanthanum uptake efficiencies while modified clays presented a better behaviour towards release processes, ensuring a recovery global efficiency of 43%.

Keywords: clays, organo-clays, rare earths, recovery, solid phase extraction

1. Introduction

Nowadays there is an increasing need of REs due to their usage in numerous high-technology applications (Iannicelli-Zubiani et al., 2013a). Increasing demand for the different products containing REs has resulted in a restriction of supply from producing Countries, particularly China. Since currently each EU citizen produces about 17 kg of...
WEEE per year and since these wastes are rich in precious and strategic metals, the study of a targeted and efficient REs recovery from WEEE can only lead to undeniable both socio-economic and environmental benefits (Iannicelli-Zubiani et al., 2012).

Different methods have been proposed for REs recovery and recently the use of Solid-Phase Extraction (SPE) is obtaining more and more attention because of its advantages of high recovery, short extraction time, high enrichment factor, low cost and low consumption of organic solvents. In particular, clays as solid-phase are characterized by some outstanding advantages, such as low cost, high mechanical intensity, good acid tolerance, convenient solid-liquid separation and excellent reusability. Furthermore, clay minerals show a natural adsorption behaviour towards REs (Coppin et al., 2002).

Since the compositions of leached electronic scraps are very complex, a model solution with one RE ion was studied: lanthanum was chosen as representing elements of REs family.

2. Objectives

In this context, the main objective of the present study was to recover REs, in particular lanthanum, by solid-liquid extraction. The solid sorbents used are of different kind: two pristine clays (STx-1b and SWy-2) and two ad hoc synthesized organo-clays.

Another objective of this work was to obtain the release of the captured lanthanum varying the operating conditions such as the pH, since the final aim is not only the uptake but also the recovery of valuable metals from WEEE. Further, the results obtained with the clays and the organo-clays were compared, both in the adsorption and in the release phases. Finally an analysis of the global process efficiencies was carried out.

3. Outline of the work

This work is divided in three main parts:

- The first part is about the synthesis of the organo-clays, compared during the study with the pristine clays for what concerns the adsorption and release capability of lanthanum.
- The second part covers the lanthanum adsorption tests by using the different solids.
- The third part covers the release experiments obtained varying the pH conditions.

4. Materials and methods

STx-1b and SWy-2 are two natural standard smectite mineral clays, respectively a Ca-montmorillonite and a Na-rich montmorillonite (supplied by the Clay Mineral Society). The polymer used as intercalating agent is a PEGylated ethylene diamine (POL in the following), whose formula is reported in Fig. 1. It was supplied by Bozzetto Group. Lanthanum (III) nitrate pentahydrate and nitric acid ACS reagent, both of them from Sigma-Aldrich, were the other reactants used in this study.

![Fig. 1. Chemical formula of POL](image)

Hybrid materials were obtained following a standard procedure developed elsewhere (Zampori et al. 2010). In brief, 2.5 g of clay (STx or SWy) were mixed, in a closed reactor under vigorous stirring, with 50 mL of aqueous polymer solution for a fixed time of 90 min.
The initial polymer concentration \( (CP_0) \) was of 35 mM. All the intercalation experiments were carried out at 30°C while the pH of the solutions was measured before and after dispersing the clays using a Mettler Toledo FE20/EL20 digital pH meter and it was constant throughout the preparation at about pH 11. After the intercalation reaction, the solid phase was separated by the liquid one using a centrifuge (HETTICH 32 RotoFix). The solid, upon drying (one day at room temperature) was ground in a mortar.

A determined amount of the different solids (clays and organo-clays) was contacted with an aqueous solution of La(NO\(_3\))\(_3\) at known concentration \( (C_0 = 19 \text{ mM}) \), vigorously stirred at room temperature and separated from liquid using a centrifuge. In a previous paper it was demonstrated that the lanthanum uptake was not quantitatively affected by contact time, thus very fast (Iannicelli-Zubiani et al., 2013a). Accordingly, in this study, the adsorption contact time was fixed at 1.30 h, long-lasting enough to be sure of the equilibration between solid and solution and fast enough to avoid lanthanum release at this step. The contact experiments were carried out using a solid/liquid ratio of 0.04 g/mL and the amount of lanthanum captured by the solid phase \( (C_S) \) was determined by ICP-OES of the liquid solution before and after the contacting experiments and calculated by difference.

Release tests were performed on the different samples in order to verify the solid capability not only to capture, but also to release metal ions (Fig. 2). The release was obtained contacting the enriched lanthanum solids with solutions of HNO\(_3\) 1M since previous studies (Iannicelli Zubiani et al., 2013b) proved that effective release was obtained at very acidic pHs. The operating conditions were: 1.30 h of contact time, solid/liquid ratio of 0.026 g/mL, room temperature and stirring at 500 rpm. Also in this case, the lanthanum content in the liquid phase after release \( (C_w) \) was achieved by ICP-OES.

The metal-ion concentrations were measured by an Optima 2000DV inductively plasma optical emission spectrometer (Perkin Elmer).

X-ray diffraction (XRD) measurements were carried out on powder samples with a Bruker D8 Advance diffractometer using graphite monochromated Cu-K\(_\alpha\) radiation; the scan step was 0.02° 2\( \theta \) and the measurement time 1 s per step.

The Chemical Oxygen Demand (COD) analyses were carried out using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidised by heating for 120 min at 150 °C.

5. Results and discussion

The XRD measurements provided that the polymer intercalation occurred since the basal reflection related to pristine clays showed for both organo-clays the typical shift towards lower 2\( \theta \) angles (from 5.7 to 5 for \( STx \) samples and from 7.4 to 5 for \( SWy \) samples), resulting from the interlayer enlargement due to the polymer intercalation (Fig. 3).
The amount of intercalated polymer ($CP_S$) was calculated by difference between the initial and the residual amount using the COD (Chemical Oxygen Demand) analysis (Zampori et al., 2010) on the liquid solutions and the results are reported in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$CP_0$ [g/g-clay]</th>
<th>$CP_S$ [g/g-clay]</th>
</tr>
</thead>
<tbody>
<tr>
<td>STx+POL</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>SWy+POL</td>
<td>0.8</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The lanthanum adsorption experiments (Table 2) showed that both pristine and organo-clays were effective in lanthanum uptake and that the uptake efficiencies obtained with organo-clays ($C_S/C_0$ [(mg/g-clay)/(mg/g-clay)] = 41/80 for STx+POL) were not higher but just comparable than the ones obtained using pristine clays ($C_S/C_0$ [(mg/g-clay)/(mg/g-clay)] = 35/67 for STx), thus the presence of the polymer was in this step, apparently, not significant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake [%]</th>
<th>Release [%]</th>
<th>Global efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>STx</td>
<td>52</td>
<td>62</td>
<td>32</td>
</tr>
<tr>
<td>STx+POL</td>
<td>51</td>
<td>83</td>
<td>43</td>
</tr>
<tr>
<td>SWy</td>
<td>47</td>
<td>74</td>
<td>35</td>
</tr>
<tr>
<td>SWy+POL</td>
<td>43</td>
<td>83</td>
<td>36</td>
</tr>
</tbody>
</table>

Lanthanum release was obtained in any case but it is evident (Table 2) how pristine clays were less effective to release the captured lanthanum ions ($C_W/C_S$ [(mg/g-clay)/(mg/g-clay)] = 22/35 for STx compared to $C_W/C_S$ [(mg/g-clay)/(mg/g-clay)] = 34/41 for STx+POL).

6. Concluding remarks

From the comparison between pristine and organo-clays the following conclusions can be drawn: the experimental procedure was appropriate to intercalate the polymer in both clays; similar uptake efficiencies were obtained with both natural and modified clays (around 50% for STx and STx+POL and around 45 for SWy and SWy+POL); the release efficiency was higher using organo-clays (83%) than using pristine clays (62-74%), thus the polymer seems to play an important role in the release step; from the global efficiencies data: the
modified clay $STx+POL$ ensured the best global process efficiency. Accordingly, the proposed clay-polymer system seems promising for the proposed application.

References


