Microscopic analysis of bentonite used for adsorption of lead ions in water

E. Manriquez Reza¹, J. J. Perez Bueno*¹ and A. Hurtado Macías²

¹Centro de Investigación y Desarrollo Tecnológico en Electroquímica, S.C.; Parque Tecnológico Queretaro-Sanfandila, Pedro Escobedo, Qro. Mexico. C.P. 76703. E-mail: jperez@cideteq.mx
²Centro de Investigación en Materiales Avanzados, S.C. Ave. Miguel de Cervantes 120. Complejo Industrial Chihuahua, Chihuahua, Chihuahua, Mexico. C.P. 31109.

Bentonite is mainly composed of montmorillonite, which is a mineral from the smectite group. Bentonite is considered a great candidate as an adsorbent material for heavy metal ions such as Pb²⁺ in aqueous solution due to its typically elevated surface area, high availability and low cost. Smectites have a typical layered structure consisting of an alumina octahedral sheet between two silica tetrahedral sheets. Isomorphic substitutions result in a negatively charged clay, which is compensated by exchangeable cations like Ca²⁺ and Na⁺. These hydrated cations in the interlayer surface can be easily exchanged for heavy metals, resulting in a high cation exchange capacity. High resolution transmission electron microscopy (HRTEM) was performed under Z-contrast annular-dark-field imaging mode with a scanning transmission electron microscope (STEM). Moreover, the adsorption capacity of bentonite for lead was evaluated. The results show a very high removal percentage of lead in aqueous solution, with values above 96%. These results were complemented with microanalysis by STEM in a diffraction mode.

Keywords: bentonite; HRTEM; water; remediation.

1. Introduction

Clay minerals are in the mineral group of phyllosilicates, a term applied to a broad group of hydrous silicates with layered structures of colloidal dimensions in a range of 1 nm - 2 μm [1]. Smectites are clays of type 2:1, which have a typical layered structure consisting of an alumina octahedral sheet between two silica tetrahedral sheets. Isomorphic substitutions in sheets result in negatively charged clays. The negative charge is balanced by cations intercalated between layers. These cations may be ions such as Ca²⁺, Mg²⁺ and Na⁺. When Ca²⁺ cations are mainly intercalated in a montmorillonite surface, the clay is known as Ca-montmorillonite [2-4]. These hydrated cations in the interlayer surface can be easily exchanged by heavy metals, resulting in a high cation exchange capacity [5].

Bentonite is mainly composed of montmorillonite of the smectite group [6]. Since bentonite is widely present in nature, low-cost, and has a high specific surface area and high exchange capacity, it is considered a great potential adsorbent for the treatment of heavy metal ions such as Pb²⁺, Fe²⁺, Zn²⁺ and Cr³⁺ [7-9] in aqueous solutions. Surface complexation contributes mainly to the adsorption of Pb²⁺ on bentonite, and it is dominated by outer-sphere surface complexation and ion exchange with cations on interlayer surfaces at low pH [10].

2. Experimental

Ca-bentonite capacity for lead ion adsorption was tested. Sample solutions of lead nitrate (100 mg/L) were prepared and equilibrated with 0.1 g of Ca-bentonite in polyethylene flasks. These were placed in an isothermal bath at 25°C with a stirring speed of 300 rpm during 24 h. After this time, the solutions were centrifuged. Resulting lead solutions were analyzed by ICP. Contaminated bentonite was washed several times and dried at 100°C.

X-ray diffraction was carried out on a Bruker AXS - D8 Advance diffractometer. Diffraction pattern was measured with CuKα radiation (λ = 1.5406 Å), 40kV/40mA, with a 20 range of 2 – 30°, a scanning speed of 2.5 s/step, and an increment of 0.03752-theta°. The high resolution STEM with Z contrast and TEM images were taken with a JEM-2200FS microscope with a U-1000 CCD camera (GATAN). Cu cells with a carbon lattice were used. The reflectance and absorbance measurements were carried out using an ocean optics USB2000 spectrometer with an integrating sphere and a flat Teflon surface as a white reference.

3. Results

The Ca-bentonite used in this work had a pale gray tone and decanted as two phases that can be observed after hydration and sedimentation. This heterogeneity of texture of Ca-bentonite results in the presence of other minerals beside montmorillonite. Fig. 1a show images of Ca-bentonite as a powder. Once wet, Ca-bentonite expands around 7% and usually precipitates into two main strata. The upper stratum corresponds to an almost pure montmorillonite, while the bottom stratum corresponds to a mixture of denser matter, such as quartz or cristobalite (Fig. 1b).
Fig. 1 Ca-bentonite pictured as a dry powder a), and precipitated forming two strata b).

Fig. 2a and Fig. 2b show reflectance and absorbance spectra, respectively. Ca-bentonite and Na-bentonite were analyzed as powders under dry and wet conditions. Since no transmittance or luminescence was considered to occur, reflectance and absorbance may be considered as reciprocal. Ca-bentonite was darker than Na-bentonite under both dry and wet conditions. The reflectance dropped around 40% for both bentonites upon wetting. Particularly, Na-bentonite was more reflective in the near infrared region than a white reference (Teflon), surpassing 100%.

Table 1 shows CIE-Lab color scale parameters for Ca-bentonite and Na-bentonite under dry and wet conditions. The bentonites were similar in their color parameters. Nevertheless, there was an increase of color purity upon wetting. This, together with a 40% drop in reflectance, demonstrates a well-known effect of wetting a light colored fabric. The square root of $L^*a^*b^*$ parameters allows us to identify a higher color change for a Na-bentonite from a dry powder to a wet dough.

Table 1 Color parameters corresponding to Ca-bentonite and Na-bentonite as powders under dry and wet conditions.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$y$</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>Purity</th>
<th>Dominant $\lambda$ (nm)</th>
<th>$\sqrt{L^{*2}+a^{*2}+b^{*2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-B dry</td>
<td>0.4734</td>
<td>0.4086</td>
<td>88.8</td>
<td>8.1</td>
<td>12.1</td>
<td>0.19</td>
<td>593.1 nm</td>
<td>14.595</td>
</tr>
<tr>
<td>Ca-B wet</td>
<td>0.4821</td>
<td>0.4083</td>
<td>68.3</td>
<td>8.9</td>
<td>13.0</td>
<td>0.24</td>
<td>592.6 nm</td>
<td>16.529</td>
</tr>
<tr>
<td>Na-B wet</td>
<td>0.493</td>
<td>0.3995</td>
<td>75.9</td>
<td>15.7</td>
<td>14.1</td>
<td>0.26</td>
<td>595.9 nm</td>
<td>21.197</td>
</tr>
<tr>
<td>Na-B dry</td>
<td>0.4749</td>
<td>0.4051</td>
<td>94.9</td>
<td>10.5</td>
<td>11.4</td>
<td>0.17</td>
<td>599.5 nm</td>
<td>16.007</td>
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</table>

The SEM and HRTEM techniques allow a morphological characterization of clays with a greater magnification, which permits a better understanding of bentonite structure. The typical crystalline conformation of clays can be observed in Fig. 3. Clay crystals consist of several stacked layers. The image reveals some crystals that were stacked by superposition on the c plane with a reduced spacing between faces, forming an aggregate with a size around 10 µm.
Fig. 3. Scanning electron micrograph showing a typical smectite clay layered structure.

Images presented in Fig. 4a-b were obtained with HRTEM in STEM mode and Z contrast (annular angle dark-field). Fig. 4a shows a bentonite particle around 2 μm in size, which corresponds to a colloidal particle size. The particle presents an anhedral shape, which is a very commonly observed clay form.

Fig. 4b shows a higher magnification of a Ca-bentonite particle, which represents layers arranged in parallel. The bright lines correspond to (001) planes. The distance between these lines corresponds to basal spacing of Ca-bentonite. This laminar structure can be observed in a representation in Fig. 4c, a structural model of Ca-montmorillonite. This structure presents Al-O and Si-O bonds in octahedral and tetrahedral sheets, respectively. The tetrahedral sheets are forming hexagonal cavities that can be observed in superior faces of the image (a-b planes). The interlayered structure shown in Fig. 4b can be better appreciated in this image. Additionally, the exchangeable cations between layers and oxygen atoms linked to the superficial siloxane framework are present in this structure. This allows a better understanding of mechanisms involved during adsorption of heavy metals on Ca-bentonites, as well as at which sites this adsorption occurs.

Fig. 4. a) HRTEM micrograph with Z-contrast of a bentonite particle. b) Image showing the interlaminar layers as parallel lines. C) Structural model of montmorillonite clay with a unit cell represented in the middle.

Fig. 5 shows a X-ray diffractogram corresponding to Ca-bentonite, which complements images in Fig. 3 and Fig. 4. The graph shows three different types of crystalline contributions present in a bentonite material. The Rietveld method was applied to confirm the mineralogical phases of bentonite, obtaining that Ca-montmorillonite represents 51% of the clay. The Ca-montmorillonite presents a characteristic peak of interlayer space, (001) planes, with a basal spacing of 13.6 Å in accordance with results obtained with the image present in Fig. 4b. Two other principal mineral phases were detected, cristobalite and quartz, at 48 and 1 %, respectively.
Fig. 5 X-ray diffractogram of Ca-bentonite indicating montmorillonite planes (001) and (100).

Fig. 6 shows a STEM analysis of Ca-bentonite after adsorption of lead. The EDS results are shown in an inserted table. The rectangle indicates the analyzed region. This image reveals 78.9% of lead in the superficial edges of the material. This confirms lead adsorption on the Ca-bentonite surface as expected, since Si-O bonds were very high in this area as represented in Fig. 4c.

The bentonite lead adsorption was tested. Fig. 7 shows that lead adsorption decreased when bentonite concentration increased. However, the relevance of this tendency was diminished, since the decrease was less than 2% in this interval of adsorbent concentration, maintaining a removal above 96%. It is important to mention that this overall removal percentage is higher than EDS analysis indicated (Fig. 6).

Fig. 6 EDS microanalysis in STEM of a bentonite with adsorbed lead.
In addition, a comparison study was performed for lead adsorption on different adsorbent materials. Such study was carried out until approaching equilibrium under the same conditions of temperature, agitation, lead concentration and adsorbent weight. Table 2 shows clear evidence of a far better lead adsorption capacity of Ca-bentonite with respect to a well-known adsorbent like activated carbon and other trendy materials, such as corn cob, which is an abundant agricultural waste. Although both bentonites have a significant adsorption, Ca-bentonite always had lead adsorption efficiencies above 96%.

### Table 2 Comparison of lead adsorption by different adsorbent media.

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>Removal %</th>
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<tbody>
<tr>
<td>Corncob</td>
<td>11.88</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>10.73</td>
</tr>
<tr>
<td>Ca-bentonite</td>
<td>96.44</td>
</tr>
<tr>
<td>Na-bentonite</td>
<td>69.19</td>
</tr>
</tbody>
</table>

### 4. Conclusions

Ca-bentonite can be potentially efficient for lead removal from aqueous media due to its peculiar structure, which has many sites with cations that are interchangeable for heavy metals. These sites are mainly located at the bentonite interlayer region. On the other hand, siloxane bonds located at its edges and external surfaces allow removal of lead ions in solution, carried out mainly by cation exchange and by complexation with oxygenated groups. The characterization of Ca-bentonite before and after lead adsorption confirms a high presence of lead in its structure due to adsorption. Also, comparing Ca-bentonite with other adsorbent materials under similar conditions evinces its high removal capacity, always above 96%.

### Acknowledgements

The authors gratefully acknowledge the financial support from the Mexican Council for Science and Technology (CONACyT, Grant CB-2009-01 133157). Also, the first author acknowledges CONACyT for her graduate fellowship. The authors are especially grateful to Darlene Garey of the US Peace Corps for her valuable suggestions for this work.

### References


