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Structural modification of a lamellar solid by thermal treatment. Effect on the Cd and Pb adsorptions from aqueous solution

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Abstract

The clay minerals, lamellar solids of aluminum silicate hydrate of layer structure, present physical and chemical properties that are attractive for applications in different industries. These materials represent a promising option to achieve retention of certain contaminants present in the aqueous solution, due to their natural ability for adsorption. Heavy metals such as lead, cadmium, mercury, cooper and zinc, etc., contained in effluents produced by various anthropogenic activities constitute an important phase of pollution. Adverse effects on the health of the population because of the deteriorating quality of watercourses require reversing the current situation. This study evaluates the adsorption of lead and cadmium in aqueous solution by a bentonite, a rock composed majorly by clay minerals of the smectite group. The adsorption capacity was analyzed in the natural condition of the bentonite and after thermal treatment up to 750ºC.

Keywords: Adsorption, thermal treatment, lead, cadmium, bentonite.

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1. Introduction

Bentonites are rocks composed mainly by smectite and minor constituents such as quartz and feldspar. These materials are exploited to meet the demand for many industries. The physicochemical properties of the essential components of these rocks are due to particle size that is smaller than 2 µm, lamellar morphology and cationic exchange capacity.

The term smectite is used to identify a group of clay minerals characterized by their structural conformation type 2:1 (T-O-T), where two layers of tetrahedral Si^{+4} ions are joined by and octahedral layer of Al^{+3} ions (A.C.D. Newman, 1987). In these minerals, isomorphic replacements at the tetrahedral Si^{+4} and octahedral Al^{+3} sites may take place with ions of similar ionic radius but different charge. The resulting electric charge unbalance is compensated by alkaline and alkaline earth ions located in the interlayer which are easily exchanged, thus resulting in a high cation exchange capacity.

These solid laminates have been tested as adsorbents of heavy metals, among other pollutants, in order to mitigate the serious environmental problem caused by such ions that is well documented in scientific literature.

Although these materials naturally have high adsorption capacity, it is possible to modify them in order to increase retention. Among the structural changes pillaring, homoionization and heat treatment may be mentionated, Danyun Li et. al., 1996 and Tryantafyllou, 1999. The latter modification has been studied, as well as the material in both powdered and pelletized form for large scale application of the adsorbent, for which mechanical strength is required to maintain the capacity to remove, Rueda et. al., 2010 and Barrera et. al., 2010.

In the present study, the structural changes of the smectite clay mineral by thermal treatment at different temperatures and their effect on Cd and Pb adsorption from aqueous solution were evaluated.

Interest in these laminar materials arises from the fact that they occur in substantial volume and are therefore widely available, have low cost, are easily removable and can be used in conjunction with other materials for the treatment of wastewater.

2. Experimental

To carry out laboratory experiments that led to this study, a sample of bentonite, identified as M4, belonging to a site located in the Plateau Barda Negra, Department Zapala, Neuquén Province, was used (Impiccini et. al., 2002).

The particle size of the material was reduced by grinding down to 74µm.

The chemical composition, determined by Inductively Coupled Plasma (ICP), and the mineralogical composition, determined by X-Ray Diffraction (XRD), were published in previous papers,(Venaruzzo et. al., 2006). Thermal Analysis (DTA-TG) was performed using a Netzsch STA409 equipment, at a heating rate of 10°C/min using α-Al_2O_3 as a reference.

Different fractions of the sample M4 were treated in the temperature range between 150°C and 750°C, identified as: M415, M430, M445, M455, M465 and M475.

Adsorption tests were conducted using a batch system, placing the sample in contact with different monosolute solutions of Cd and Pb, with 1000ppm concentration and a solid/liquid ratio of 2% during 24 hours at 25°C.

The supernatant of the system obtained by centrifugation was extracted in order to quantify the remaining Cd and Pb, making measurements by Atomic Adsorption Spectrometry (AAE).

3. Result and Discussion

Figure 1 shows the results obtained by the DTA-TG technique, typical of a dioctahedral smectite, Mackenzie, 1970. The first endothermic peak of the DTA curve at 150°C corresponds to the loss of adsorbed water and water of hydration of the interlayer cations, Cerezo et. al., 2003. A second peak (double in this clay) was observed at temperatures between 500°C and 700°C, which corresponds to loss of OH^-, and an endothermal peak near to 900 ºC attributed to collapse of the smectite structure.

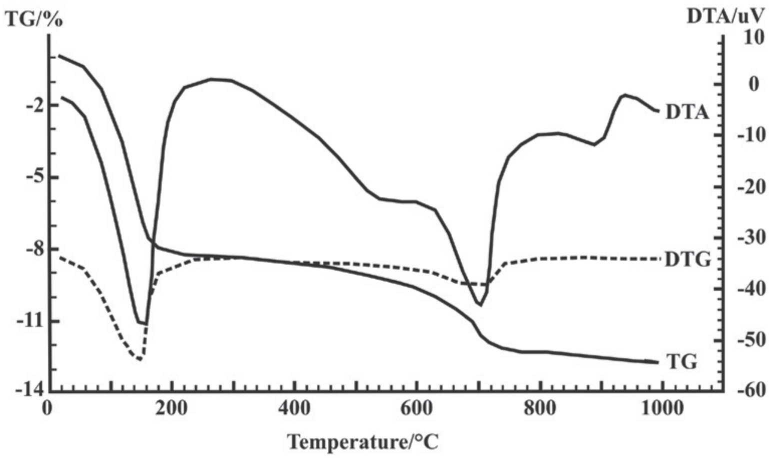

Fig. 1. Thermal analysis using ATD-TG

The results of the retention Cd and Pb cations by natural and calcined clay, obtained by the difference between the initial concentration of the cations and the concentration of the system to reach equilibrium are shown in Table 1.

Table 1. Adsorption Cd and Pb

Sample	Retention Cd (ppm)	Retention Pb(ppm)
M4	490.5	209.6
M415	496.3	194.01
M430	443.1	216.2
M445	439.1	241.0
M455	362.8	330.7
M465	120.6	186.7
M475	42.6	16.8

The amount of Cd retained by the laminar solid was approximately half of the initial concentration of the liquid (1000ppm). The obtained results show that the adsorption of Cd by the native sample, M4, was reduced slightly by thermal treatments up to 450°C and decreased strongly when the temperature applied to the solid was superior. In contrast, removal of Pb decreased when the heat treatment was greater than 550°C. This behavior could be related to the dehydroxylation temperature of the smectite, being more sensitive to changes in the retention of Cd adsorption values for both contaminants. The retention values were very low when the solid was calcined at 750°C. At this temperature, as shown in the TGA results in Figure 1, the mass loss was near the total value, close to that of the collapsed structure.

Figure 2 shows the different retention of each cation with respect to thermal treatment of the solid. The retention value of Cd was twice than Pb by the clay and the values were maintained up to near to 500ºC. After that the retention starts to decrease due to the beginning of the structural collapse.

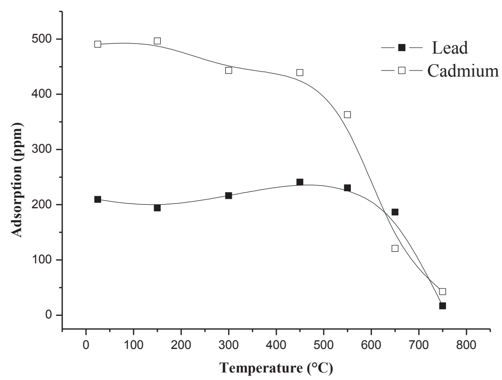

Fig. 2. Adsorption of Cd and Pb vs temperature

Table 2 exhibits pH values obtained from the different suspensions, after removing the supernatant volume required for analysis by Atomic Absorption (AAS). This pH measurement estimates the type of Cd or Pb cation species that are present in solution, Saha et. al., 2001. The pH results indicated a high probability of the presence of Cd^{+2} and Pb^{+2} species in solution, discarding precipitation.

Table 2. pH of the substrates contacted with Cd and Pb

Sample	Cd (pH)	Pb (pH)
M4	6.73	7.06
M415	6.58	6.28
M430	6.20	6.29
M445	6.26	6.24
M455	6.42	6.14
M465	6.59	6.31
M475	6.25	6.12

4. Conclusions

The adsorption capacity for Cd and Pb of a natural bentonite clay from Plateau Barda Negra, Neuquén, Argentina, was tested. This lamellar solid can retain Cd and Pb, by using the clay in natural condition and after modification by thermal treatment up to 450-500ºC. Higher temperature treatment of the solid decreases the adsorption capacity due to dehydroxylation and collapse of the clay mineral structure.

The bentonite used (with solid/liquid ratio 2%) in this work reduced by half and one-fifth the initial concentration (1000ppm) of Cd and Pb, respectively.

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