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Influence of Thermal Treatment on Bentonite Used as Adsorbent for Cd, Pb, Zn Retention from Mono-Solute and Poly-Solute Aqueous Solutions

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The retentions of Zn, Cd and Pb cations by one treated bentonite up to 750 °C were analyzed. The retentions were evaluated by using mono-and poly-solute aqueous solutions of such cations. The adsorptions were carried out in batch system at room temperature. The solid/liquid ratio was 2% $\mathrm{wt.v^{-1}}$. The solids were characterized by X-ray diffraction, thermal and chemical analyses. The Zn cation from mono- or polysolute-solutions was retained in higher amount than Cd and Pb cations in similar solution types by bentonite. The retentions were effective up to 450 °C calcined bentonite, after that, the retention capacity decreased in concordance with dehydroxylation of the structure of clay minerals.

Keywords: *adsorption, thermal treatment, clay, heavy metals*

1. Introduction

The environmental problems are the main worries of the government agencies and the scientific community, generating a change in environmental legislation, respect to remediation technologies and/or minimizing the effects of human activities on deterioration of the environment.

There are different pollution types. Water pollution, containing harmful substances, generally, come from industrial activities and their accumulation can influence on the health and the environment.

Some heavy metals such as zinc, are essential for life, however, a higher accumulation thereof in the organism, as well as those non-essential metals such as lead and cadmium can cause severe damage to the body as the often are irreversible.

There are lots of scientific papers about of the adsorptive properties of the materials, such as carbon, zeolites and clay for retaining heavy metals including Zn, Cd and Pb[1-4]. Mishraa and Patel[5] studied different adsorbents as BFS (Blast Furnace Slag), fly ash, bentonite, kaolinite and activated coals for removing lead and zinc at different pH values. The bentonite and fly ash exhibited the highest adsorption capacities for removing lead and zinc from solutions. The bentonite can be considered as a potential material for the environmental remediation technology due to physicochemical characteristics, relative abundance and easy extraction. Sometime, in order to improve the clay properties can be applied different treatments, such as acid and/or alkaline activations, purification, pillarization, etc.

The bentonite is a rock constituted by smectite clay minerals (60-90%) with quartz, feldspar, gypsum, and/or other impurities. The smectite is a 2:1 layer phyllosilicate that is one aluminium octahedral sheet between two silica tetrahedral sheets. Isomorphous substitution originate deficit of charges which are neutralized by interlayer cations.

The reaction of heavy metals in solution, chemical species, ion competition, are some variable that influence the adsorption capacity of the adsorbent[6]. Bereket et al.[7] studied the thermodynamic parameters of Pb, Cd, Zn and Cu adsorption by a bentonite. Gonzalez et al.[8] evaluated the effect of pH on the mechanism of adsorption of Pb, Cd and Zn, and they reported the influence of thermal modification on kaolin on adsorption capacities.

It was not found in literature the analysis of the adsorptions of Cd, Pb and Zn cations from mono-di-or trisolute aqueous solutions by natural and heated at high temperature of the bentonite clay. The adsorption capacity by clays decrease with temperature[4], however it is interesting analyze such behaviour when the cation is present in mono-di or trisolute conditions.

The aim of this paper was to analyze the retention of Cd, Pb, Zn from mono- or poly-solute aqueous solutions by a natural and heated bentonite up to 750 °C. The heat treatment was subject bentonite was aimed at evaluating the variation in the retention with temperature due to the possible need for a procedure of this kind to applied the adsorbent into pellets, which would be mechanically more resistant, or prevent the possible flooding of columns of treatment due to the particle size of the materials.

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2. Material and Methods

One bentonite from Neuquén province, Argentina was used in this work. The bentonite clay was named as BZ4. The bentonite is constituted by esmectite in higher content around 71.97% with a little amount of illite as clay minerals, and quartz, gypsum and feldspar as impurities[9].

The monosolute (Zn, Cd or Pb), bisolute (Cd/Zn, Cd/Pb or Pb/Zn) and trisolute (Cd/Pb/Zn) solutions were prepared with distiller water by using reactive analytical Merck® in 500, 250 and 166 ppm concentrations of each cation for different type solutions, respectively.

The thermal treatments at 150, 300, 450, 550, 650 and 750 °C were obtained at heating rate of 2 °C/min and maintained for 1 hour at temperature by using equipment Tecno Dalvo TDM6. The solids were named: BZ415, BZ430, BZ445, BZ455, BZ465 and BZ475, respectively.

The adsorptions were carried out in batch system at room temperature. The solid/liquid ratio was 2% $wt.v^{-1}$, and maintained during 24 hours. After that the solid was separated and the supernatant analyzed. The retained cations by prepared solids were calculated by difference between initial and final concentration of solutions after contacted with natural bentonite or heated bentonite. The value were obtained by X-Ray Fluorescence and carried out with a Shimadzu EDX800-HD. The supernatant solutions obtained from the test were read using calibration curves of analytical standards Merck® based on liquid specimen of polypropylene in air atmosphere.

The interlayer spacing of the samples was obtained by X-Ray Difracction (XRD) by using equipment Phillips PW 3020, Cu Kα, Ni filter, at 40 kV and 20 mA. The patterns were obtained by scanning at 1 °(2θ)/min from 3 to 20 °(2θ). Simultaneous Thermal Analysis was obtained by Differential Thermal Analysis-Thermal Gravimetric (DTA-TG) with Netzsch 409 equipment at a heating rate of 10 °C/min and a nitrogen flow rate of 35 mL/min α-Al_2O_3 was used as reference substance. The differential thermal measurements have been used in studies on the thermal behaviour of pure inorganic compounds as well as silicates, clays, oxides, ceramics, etc. The information is provided by the desolvation processes such as fusion, dehydration, oxidation, reduction, adsorption and solid state reactions[10].

3. Results and Discussion

For evaluating the adsorption capacity of the cations by bentonite treated at different temperature it was analyzed previously the thermal analysis (DTA-TGA) of the bentonite, which graphic is shown in Figure 1. Four endothermic peaks at 160 °C, 550 °C, 680 °C and 860 °C of the sample are shown in DTA diagram. The first peak is attributed to dehydratation of water in interlamellar position of the clay mineral (smectite) contained in bentonite. In this bentonite clay, the second and third peaks are due to lost of OH^- from smectite structure, attributed to presence of two smectite types, and the fourth is due to lost of structure clay[11,12]. The TGA diagram showed an important mass lost after heating up to 200 °C. There are not mass lost up to 500 °C, however 4% mass lost was observed between 500 and 700 °C. Both lost are due to dehydration and dehydroxilation, respectivey, in concordance with first, and second-third mentioned peaks (Figure 1). Then, thermal treatments at 150, 300, 450, 550, 650 and 750 °C were performed in this study.

3.1. *Retention of cations*

Figure 2 shows the retentions of Zn, Cd and Pb cations from monosolute solutions by natural bentonite (BZ4) and after treatment up to 750 °C. At room temperature the uptakes of Zn, Cd and Pb were 0.21 $mmol.g^{-1}$, 0.17 $mmol.g^{-1}$ and 0.12 $mmol.g^{-1}$, respectively. An important decrease in Cd and Zn adsorptions were observed when the bentonite adsorbent was heated at 650 °C whereas, the value of Pb adsorptions were maintained up to 550 °C and after that, small decrease was shown. A reverse behaviour in order of adsorption was reached after 550 °C (Pb > Cd > Zn). The total reduction in retention of the cations by bentonite treated at 750 °C was 95%, 50% and 33% for Zn, Cd and Pb ions, respectively, Figure 2.

Saha et al.[13] obtained similar retention values for Zn, Cd and Pb ions on Na-montmorillonite, and higher values by using OH-Al montmorillonite as adsorbents, all measured at room temperature.

Figure 3 to 5 show the retention of cations from bisolute solutions by untreated bentonite and after thermal treatments. Each initial concentration of cation was 250 $mg.L^{-1}$. The retention ions from the three bisolute solutions by bentonite at room temperature were: Zn (0.13 $mmol.g^{-1}$) > Cd (0.086 $mmol.g^{-1}$); Cd (0.09 $mmol.g^{-1}$) > Pb (0.04 $mmol.g^{-1}$) and Zn (0.135 $mmol.g^{-1}$) > Pb (0.068 $mmol.g^{-1}$).

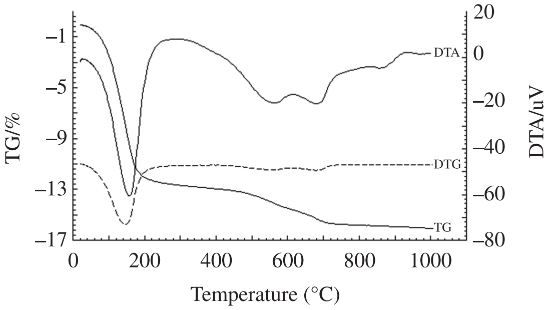


Figure 1. Thermal Analyses of BZ4 bentonite.

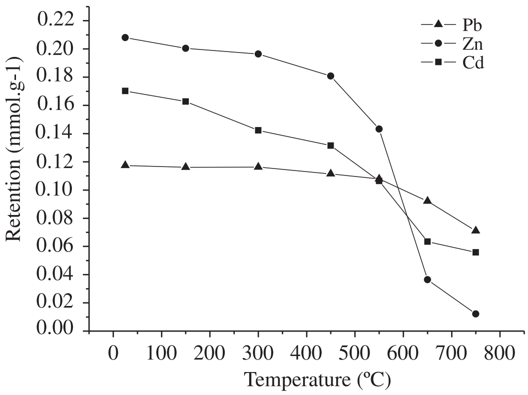


Figure 2. Retention of Zn/Cd/Pb from monosolute solutions vs. temperature treated bentonite.

The behaviour of cation retentions from bisolute solutions by heated bentonite was similar than those from monosolute solutions (Figure 2). The Pb retentions (Figures 4 and 5) were lower than Zn and Cd from both bisolute solutions (Zn/Pb; Cd/Pb).

Figure 6 shows the retention of cations from trisolute solution by natural and treated bentonite. The retentions of Zn, Cd and Pb by natural bentonite were 0.11 mmol.g^{-1}, 0.065 mmol.g^{-1} and 0.05 mmol.g^{-1}, respectively. Such values were maintained up to the bentonite was treated at 450 °C. The adsorption capacity of the solid decreased after its high thermal treatment in similar form that it was found for ions from monosolute solutions.

Table 1 shows the ionic radius and the results of adsorption cations from different type of solutions by bentonite without thermal treatment. The retained Zn, Cd, and Pb from mono-bi or trisolute solutions can be correlated in reverse way with ionic radius, and then smaller cation is retained in higher amount.

3.1.1. pH measurements

The pHs of the suspensions, constituted by bentonite (with and without thermal treatment) in contact with mono-bi-and trisolute suspensions, are shown in Table 2. According to cation or cations present in suspensions and thermal treatments, the pHs of suspensions were modified. The pH values were in the range 5.31-7.06. In general, a decrease of the pH suspension was observed with thermal treatment of the bentonite. In this pH range the zinc and cadmium species in solution are present as Zn^{2+}, Cd^{2+} ions[14]. Nevertheless, the Pb^{2+} species contributions are around 95% and 80%, in solutions at pH 5 and 7, respectively; and $PbOH^{+}$ species which complete the 100%[14].

3.1.2. XRD of bentonite before and after retained cations and thermal treatment at 650 °C

The influence of retained cations in interlayer of clay mineral was analyzed by X ray diffraction. The interlayer spacing of the clay can be defined as spacing between the top of the silica sheet up to the next top of silica sheet of the follow layer. Such value includes the thickness of 2:1 layer (9.2 Å). The spacing of smectite contained in used bentonite (BZ4), was 15.38 Å and after retention of Zn, Cd and Pb from monoionic solutions shifted to 15.22, 15.12, and 15.38 Å, respectively.

The shifting and changes in relative intensities of the peak can be attributed to presence of Zn, or Cd or Pb ions in interlayer position. When the bentonite was calcined at 650 °C (BZ465), the interlayer spacing was collapsed at 9.3 Å (Figure 7b). This value corresponds to depth of 2:1 layer of the smectite[15]. After BZ465 was contacted with Zn-, Cd-, or Pb-solutions, a little rehydration, as

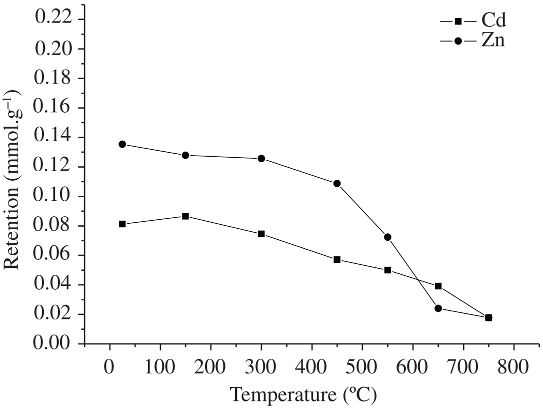


Figure 3. Retention of Cd/Zn bisolute solution by vs. temperature treated bentonite.

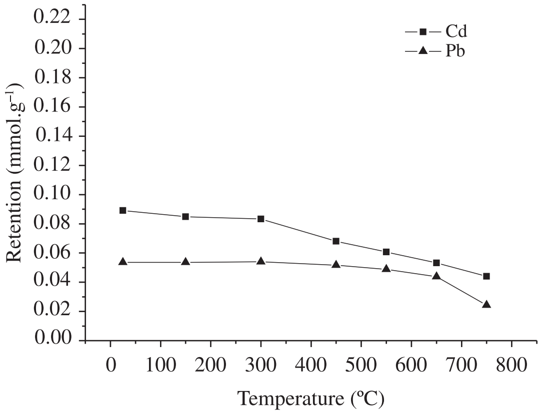


Figure 4. Retention of Cd/Pb bisolute solution vs. temperature treated bentonite.

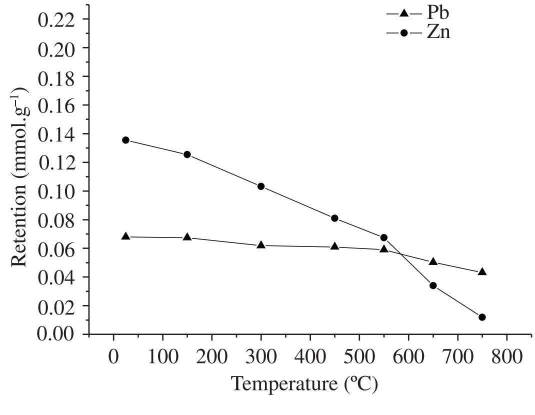


Figure 5. Retention of Pb/Zn bisolute vs. temperature treated bentonite.

Table 1. Ionic radius and retention values of Cd, Zn and Pb ions present in mono, bi and tri-solute solutions by natural bentonite.

Metals	Ionic Radius (µm)	Monosolute (mmol.g^{-1})	Cd-Pb (mmol.g^{-1})	Cd-Zn (mmol.g^{-1})	Zn-Pb (mmol.g^{-1})	Cd-Pb-Zn (mmol.g^{-1})
Zn	0.74	0.21	------	0.130	0.135	0.11
Cd	0.97	0.14	0.089	0.081	------	0.06
Pb	1.2	0.12	0.044	------	0.068	0.05

shown in Figure 7b (BZ465-Zn, BZ465-Cd, BZ465-Pb), was observed because the peak at 9.3 Å was reduced in intensity and it was observed certain recovery of original interlayer spacing. The different intensity of the broad peaks of BZ465-Zn > BZ465-Cd > BZ465-Pb in Figure 7b, may be correlate with size of ionic radius. Nevertheless, the intensities of the recuperated peaks were minor than the intensity peaks of the BZ4-Zn, BZ4-Cd, BZ4-Pb as it is shown in Figure 7a, then these decrease may be related to low retention of cation capacities by calcined bentonite.

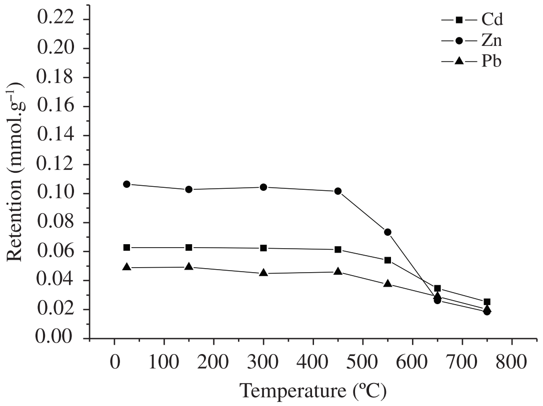


Figure 6. Retention Zn/Cd/Pb polysolute vs. temperature treated bentonite.

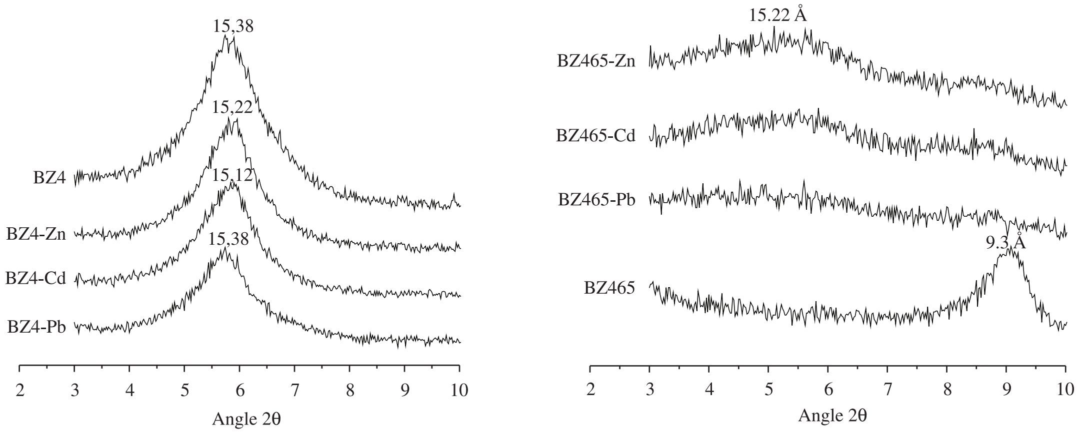
4. Conclusions

The order of cation retention from solutions by natural bentonite was: Zn > Cd > Pb in concordance with reverse ionic radius value. Such tendency was maintained although such cations were present in mono-di-or trisolute solutions.

The bentonite capacity for Zn and Cd cation retentions slightly decreased with thermal treatment up to dehydroxylation temperature of the clay mineral (smectite), after that the capacity drastically falls. However, the value of Pb retention by bentonite was maintained up to higher temperature treatment. The reduction of capacity retention was attributed to collapse interlayer spacing to the clay minerals.

The results of the paper indicate that the values in the retention of Pb were maintained up to the temperatures of 750 °C, where in a decrease of 40%, while the retention of Cd and Zn decreased by 64% and 95% respectability.

The amount of cation retention by bentonite was not exactly proportional to percentage of such cation in original solution. That is, the amount of retained Zn, Cd or Pb cations from prepared monosolute solutions (100% pure cation) were 0.21, 0.14 and 0.12 mmol.g^{-1}; whereas 0.11, 0.06 and 0.05 mmol.g^{-1} from prepared trisolute solutions (33% each one), respectively. Such behaviour, also observed by using dissolute solution, can be attributed differences in pH solutions and some competition of cations present in the same solutions.



(a)

(b)

Figure 7. X ray diffraction: a) natural Zn/Cd/Pb-bentonites; b) bentonite heated at 650 °C after retention of Zn/Cd/Pb.

Table 2. pHs of bentonite in mono-, bi- and trisolute suspensions.

Solutions Mono	BZ4 pH	BZ415 pH	BZ430 pH	BZ445 pH	BZ455 pH	BZ465 pH	BZ475 pH
Cd	6.73	6.58	6.20	6.26	6.42	6.59	6.25
Pb	7.06	6.28	6.29	6.24	6.14	6.31	6.12
Zn	6.50	6.23	6.61	5.89	5.62	5.09	5.31
Bi							
Cd/Pb	6.34	6.39	5.95	6.34	5.78	5.79	6.14
Zn/Pb	6.94	6.39	6.48	6.20	6.30	5.45	5.48
Zn/Cd	6.13	6.33	6.28	5.93	5.76	5.47	5.47
Tri							
Zn/Cd/Pb	6.10	6.13	6.26	6.09	5.99	5.61	5.56

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