



## Research paper

# Influence of pH and ionic strength on Cd, Cu and Pb removal from water by adsorption in Na-bentonite

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## ARTICLE INFO

## Article history:

Received 8 January 2015

Received in revised form 16 June 2015

Accepted 3 September 2015

Available online xxx

## Keywords:

Clay mineral

Heavy metal

Bentonite

Adsorption

Earthen liner

## ABSTRACT

This article presents a study on cadmium, copper and lead removal by means of adsorption in a natural Na-bentonite. Influence of pH and ionic strength on clay fabric and its role on cation removal are analyzed by means of Zeta potential and sedimentation tests. Batch adsorption and kinetics tests were carried out to quantify the adsorption capacity of the bentonite at monospecies and multispecies conditions, where ion competition was analyzed. Experimental results show that ionic strength strongly affects clay structure and cadmium removal, but has little influence on lead and copper removal. Adsorption kinetics was fast in all cases, which was mostly related to reaction kinetics than to diffusion kinetics. Cadmium adsorption can be explained by linear adsorption models, while copper, lead and the multispecies tests showed good agreement with both the linear and Freundlich models within the tested concentration range. The results confirm that tested Na-bentonite possesses a high capacity for the removal of Cd, Cu and Pb.

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## 1. Introduction

Heavy metals are one of the major environmental concerns due to their toxicity, persistency, and accumulation and magnification in the trophic chain. These contaminants find their way into the soil, air and water due to natural processes, such as physical erosion or chemical degradation, but mostly due to anthropogenic sources. In particular, environmental dispersion of cadmium is associated with mining, insecticides, pigments, semiconductors and anticorrosive uses, and the incorrect disposal of Ni–Cd batteries (USGS, 2010). Copper exposure is related to inhalation in copper meltings, and to water contamination due to fumigation or leachate migration from municipal solid wastes (MSW) (ATSDR, 2004), while human sources of lead are mining and smelting industries, industrial spills or soil or wastes leaching by acid rain (ATSDR, 2007).

Once these metals reach the soil and groundwater, the main concerns are their containment and remediation. The containment refers to in situ management of contaminated areas, and is potentially applicable to any pollutant. This technique incorporates physical, hydraulic, chemical or biological barriers to avoid the mobilization of contaminants (Chien et al., 2006; Houben et al., 2012). In particular, heavy metals containment has been achieved in municipal solid waste

(MSW) and hazardous waste (HW) landfills by low permeability earthen liners, while contaminant plumes migration can be controlled by means of cement based and slurry clay cutoff walls (Musso et al., 2014; Sharma and Reddy, 2004). On the other hand, in situ remediation of contaminated soils and aquifers has reached extraordinary levels of acceptance due to the low cost of operation, low environmental impact, high efficiencies and large versatility (Mena et al., 2015; Obiri-Nyarko et al., 2014). In situ treatment of heavy metal contaminated water focuses on reactive barriers due to its wide spectrum of treated contaminants and reactive media (Ott, 2000; Hashim et al., 2011; Melichová and Hromada, 2012; Majone et al., 2015). Reactive materials are quite varied but, despite the high removal efficiencies obtained with synthetic or modified materials, most researches are currently paying attention to the use of natural materials (clays, wood chips, algal biomass, etc.), and waste products (steel slag, fly ash, among others), due to their low cost, and high availability and removal capacity (Hegazi, 2013; Wantanaphong et al., 2005).

Natural bentonite can be used for either containment or treatment of metal-contaminated wastewater due to the low hydraulic conductivity of this clay (Francisca and Glatstein, 2010; Guney et al., 2014; Ozcobañ et al., 2013), and its high specific surface and cation exchange capacity, which may lead into the removal of the metallic ions from the solution (Kayabali, 1997; Rowe et al., 2004; Mazziari et al., 2013).

The purpose of this research is to determine the simultaneous effect of the ionic strength and solution pH on the clay fabric, and the influence of these parameters on the containment and remediation of Cd, Cu and Pb by a natural bentonite. Particle–fluid interactions are

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evaluated by physical tests (Zeta potential and sedimentation), while removal capacities and remediation kinetics results are determined by frequently used models. The results obtained show that the tested natural bentonite has significant potential for the in situ treatment of contaminated water and could, also, be applied in ex-situ removal systems.

## 2. Materials and methods

### 2.1. Metallic solutions

Cadmium, copper and lead solutions were prepared to obtain a metal concentration of 1000 mg/L, by dissolving cadmium nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Anedra), copper (II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , Taurus) and lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ , Anedra), respectively. All reagents were in an analytical grade and were used without further purification. Different dilutions were prepared with distilled water in order to attain concentrations of between 1 mg/L and 500 mg/L of each metal for separate tests that may be typical in wastewater from the chemical industry.

### 2.2. Bentonite

The bentonite used in this work was extracted from northern Patagonia deposits in Argentina and, according to the provider (Minarmco S.A.), consists of more than 92% sodium montmorillonite. As bentonite is expected to act as reactive material in earthen barriers, its consistency limits were tested by following D854 standard (ASTM, 2007). Its high Liquid Limit and Plasticity Index of 301 and 231, respectively, classifies this natural clay as CH (clay of high plasticity), according to the US Classification System. Additionally, grain size analyses were carried out by following D421 and D422 standards (ASTM, 2007), showing that 100% of the material is finer than 0.074 mm and 84.77% is finer than 0.002 mm. Due to the importance of surface charges on aqueous adsorption, the specific surface of the bentonite was determined by means of the methylene blue method (Santamarina et al., 2002), resulting in 731  $\text{m}^2/\text{g}$ . Cation exchange capacity (CEC) was calculated by means of Eq. 1 (Cokca and Birand, 1993), from the methylene blue adsorption test, and found to be 18.7 meq/100 g of clay.

$$\text{CEC} = \frac{100}{m_s} V_{cc} N_{mb} \quad (1)$$

where  $m_s$  is the mass of the tested solid (g),  $V_{cc}$  is the volume of the methylene blue titrant (mL) and  $N_{mb}$  is the normality of the MB substance (meq/mL).

The composition of the sample, analyzed with a LEO 1450VP scanning microscope, and coupled with EDAX energy dispersive spectrometers, is presented in Table 1.

### 2.3. Sedimentation test

The influence of pH and ionic strength on clay fabric was analyzed by means of a sedimentation test. Bentonite (2% w/v) was dispersed in

100 mL acrylic cylinders with 1 M,  $10^{-1}$  M,  $10^{-3}$  M and  $10^{-5}$  M NaCl solutions, at pH values of 3, 5, 7 and 9. The pH of the samples was monitored and corrected for 72 h, until equilibrium was reached. The dispersions were then agitated, and the dispersion height (measured as the interface between the dispersed medium and the clear solution) was recorded at regular intervals during 32 days, with a precision of 1 mm.

### 2.4. Physicochemical analysis

The electrophoretic mobility of the bentonite was analyzed in a DelsaNano HC apparatus (Beckman Coulter) by means of photon correlation spectroscopy. The Zeta potential of the clay fraction ( $\zeta$ ) was obtained from electrophoretic mobility measurements and by means of the Smoluchowski's equation (Vane and Zang, 1997). Bentonite samples were previously washed with distilled water to remove impurities and then, the solution pH was modified from 1 to 11 with 1 M HCl or NaOH. The test was carried out at three different ionic strengths (Eq. 2), modified with the addition of NaCl, to reach NaCl concentrations of 1 M,  $10^{-3}$  M,  $10^{-5}$  M. The pH of samples was measured before and after the test, and the determination was repeated if a variation higher than 0.5 units of pH was found.

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (2)$$

where  $I$  is ionic strength, and  $c_i$  and  $z_i$  are concentration and valence of  $i$  species.

Dissolved Cd, Cu and Pb were determined spectrometrically with a visible range Aquamate®, Thermo Fisher Scientific spectrophotometer. Commercial test kits were used for cadmium (Merck), copper (Hach) and lead (Merck), following the standard procedures, and diluting with distilled water in order to obtain Cd, Cu and Pb concentrations within the quantification range for each metal, when necessary.

### 2.5. Remediation kinetic test

The kinetic of the remediation process was tested in magnetically stirred beakers. Individual ions (Cd, Cu and Pb) were tested at a 50 mg/L concentration, while combined ions were tested at individual concentrations of 25 mg/L (75 mg/L in total). In all cases, bentonite content was 250 mg/L.

Cadmium, copper and lead solutions were added to bentonite dispersions, and these mixtures were then stirred for 48 h. A representative sample of the dispersion was extracted at different times to measure the metal concentration, while pH and Eh were monitored in the remaining solution. Prior to analysis, the sample was centrifuged for 10 min at 13,000 rpm to avoid interferences in the chemical analysis by the solids. Removal efficiency (RE) was computed from initial concentrations ( $C_0$ ) and instant concentrations ( $C_t$ ) as follows:

$$\text{RE} = \frac{C_0 - C_t}{C_0} \quad (3)$$

Observed pH values were lower than the precipitation pH (pHp) of each cation (cadmium pHp = 7, copper pHp = 6, lead pHp = 7). However these precipitation values are indicative for metal–water systems, no further interactions with the clay, other than adsorption, are expected (Takeno, 2005).

Obtained results were analyzed by reaction kinetic models (pseudo-first order, pseudo-second order and Elovich's equation) and diffusion kinetic models (liquid film diffusion, intraparticle diffusion and mass transfer), to confirm which mechanism controls the observed decreases of metal concentration in the solution.

**Table 1**  
Clay sample composition.

Main constituent	Mass %
Na <sub>2</sub> O	2.9%
MgO	2.4%
Al <sub>2</sub> O <sub>3</sub>	17.8%
SiO <sub>2</sub>	68.5%
K <sub>2</sub> O	1.1%
CaO	0.9%
TiO <sub>2</sub>	0.8%
FeO	5.7%

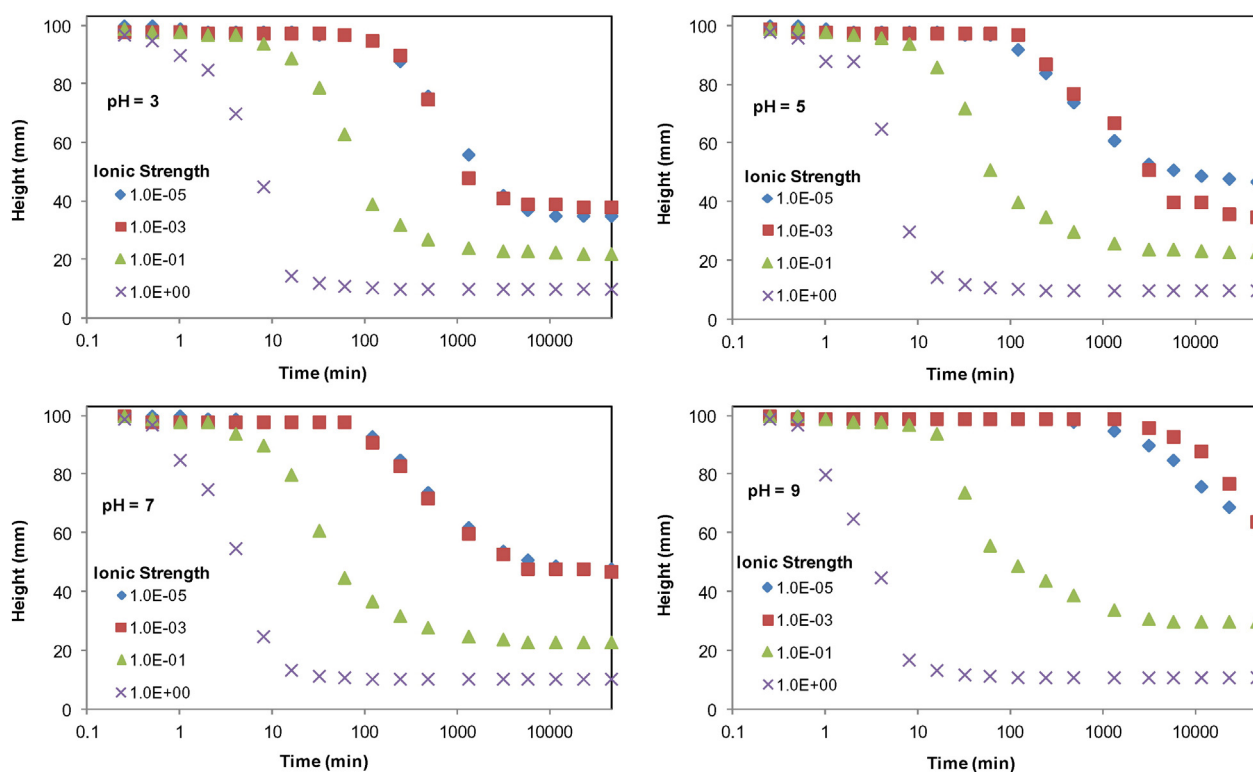


Fig. 1. Sedimentation kinetics of bentonite-NaCl dispersions at different pH and ionic strengths.

## 2.6. Adsorption test

Adsorption tests were carried out in 50 mL Falcon tubes, orbitally shaken for 24 h, at a constant temperature of 20 °C. Initial metallic concentrations ranged from 0 to 365 mg/L for individual ions, from 1 mg/L to 200 mg/L of each metal for combined tests, and the bentonite content was set in all cases equal to 250 mg/L. After 24 h, the pH and Eh of the dispersion were monitored, reaching similar conditions than those for kinetics tests. Collected samples were centrifuged at 3500 rpm for 30 min in 50 mL Falcon tubes, and the supernatant was then centrifuged for 10 min at 10,000 rpm in 1.5 mL Eppendorf tubes. The new supernatant was then analyzed to determine the final metal concentration as described in Section 2.4.

These measurements were performed without the addition of NaCl to isolate the interaction between the metals and the adsorbent. Obtained results were analyzed by conventional adsorption models, which were implemented by means of the non-linear least square fitting technique.

## 3. Testing results and analysis

### 3.1. Sedimentation behavior

Fig. 1 shows the change in sedimentation height with time, for different pH and ionic strengths. Most significant changes were found between different ionic concentrations; however, pH showed a fundamental role at low ionic strengths.

There was a difference of at least one order of magnitude in the time at which the dispersions started to descend and separate from solutions, and in the time at which dispersions reached a constant height, between dispersions with ionic strengths equal to 1,  $10^{-1}$  and  $10^{-3}$  M. However, there was no significant difference in the observed behavior for the dispersions tested at  $10^{-3}$  and  $10^{-5}$  M. Additionally, the final height of the dispersions decreased with the ionic strength for the specimens tested at 1,  $10^{-1}$  and  $10^{-3}$  M, while negligible differences were

observed in the  $10^{-3}$  and  $10^{-5}$  M solutions. In most cases, these trends increased as pH did.

Several authors have discussed sedimentation behavior for different clay systems, being kaolinites (Kaya and Durukan, 2004; Ma and Pierre, 1999; Palomino and Santamarina, 2005), and montmorillonites (Durán et al., 2000; Pierre and Ma, 1999; Tombácz and Szekeres, 2004), two of the most studied. In general, a dispersed structure is expected when the solution pH is higher than the isoelectric point of the particles edges ( $IEP_e$ ), but also when it is lower than the isoelectric point of the particle faces ( $IEP_f$ ). As tests were carried out above the theoretical  $IEP_f$  of bentonite (around 2 according to Benna et al., 1999) due to mineral dissolution, the dispersed system is only visualized at pH higher than  $IEP_e$  (around 6.5 according to Zhou et al., 2012). Between the isoelectric point of the faces and edges, different particle interactions may develop, depending on the ionic strength of the solution. Particle arrangement tends to be dispersed and deflocculated when bentonite precipitates in a very low ionic concentration and  $pH > IEP_e$ , resulting in lower final height (Fig. 1). As the ionic strength increases, the diffuse double

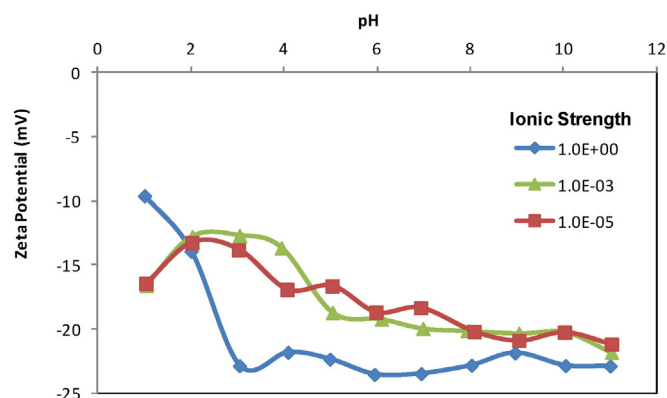


Fig. 2. Zeta potential of bentonite particles at different ionic strengths.

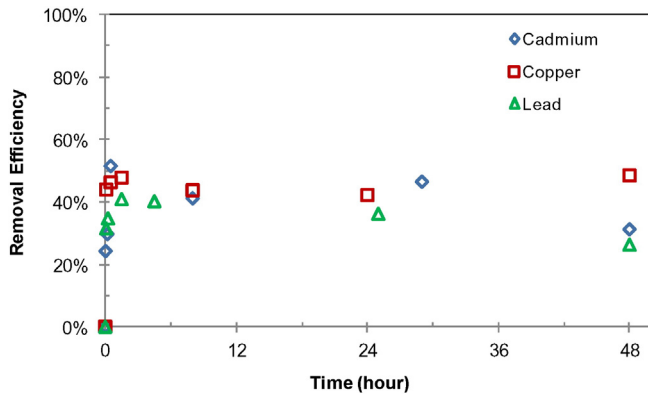


Fig. 3. Adsorption kinetics of individual metal removal with bentonite.

layer of the particles decreases, changing the microstructure from edge-to-face flocculation (EF) to face-to-face aggregation (FF) and, therefore, increasing the final height of the precipitated particles (Pierre and Ma, 1999).

### 3.2. Zeta potential

The Zeta potential indicates the net surface charge of solids, and its dependence on pH and ionic strength (Fig. 2). Bentonite particles show no isoelectric point (IEP), with a negative net surface charge within the analyzed pH interval. No differences were observed between dispersions at  $10^{-3}$  and  $10^{-5}$  M NaCl concentration, while the dispersion with 1 M NaCl concentration presented lower Zeta potentials for  $\text{pH} > 2$ . However, tests at  $\text{pH} < 3$  may not represent the real behavior of the solid, since dissolution of minerals phases can be expected (Palomino, 2003; Bibi, 2012).

The negative Zeta potential, indicative of a majority of negative surface charges through the whole pH spectrum analyzed, puts forward the application of this clay for the removal of metallic cations, as reported for similar minerals by different authors (Shaheen et al., 2013; dos Anjos et al., 2014; Musso et al., 2014).

### 3.3. Adsorption kinetics

Fig. 3 shows the removal kinetics of individual ions with bentonite. Equilibrium is reached in a very short time, and the removal efficiencies are relatively similar for all the metals, until the last analysis (48 h) when Cd and Pb adsorption seems to decay.

For the combined treatment of the metals, Cd, Cu and Pb solutions were mixed and added to the bentonite dispersion (25 mg/L of each metal). The removal efficiency of each ion is shown in Fig. 4, as well as

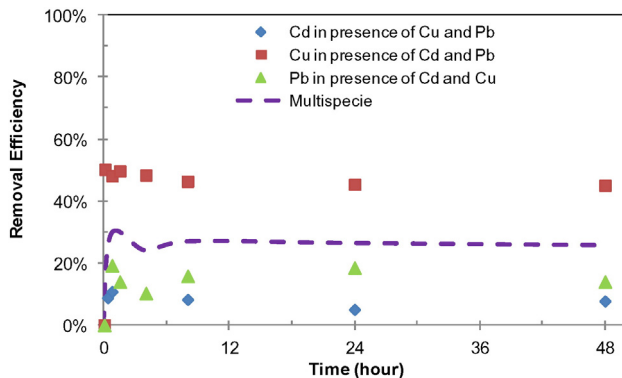


Fig. 4. Adsorption kinetics of combined metals removal with bentonite. Data points represent the remediation of each cation, while the discontinuous line indicates the global removal.

the combined removal reached. This combined efficiency is the sum of the three cations adsorbed, considering the total initial concentration (75 mg/L). As for the behavior of individual ions, the combined treatment is also rapid, indicating that adsorption is controlled by the reaction kinetic, more than the diffusion kinetic (Ho et al., 2000).

From the comparison of Figs. 3 and 4, it can be deduced that the combined treatment affects more the adsorption behavior of cadmium and lead, which could be related to the ions competition. On this matter, copper may have an advantage over lead and cadmium, due to its smaller covalent radius (138 pm, 147 pm and 148 pm, respectively), and its lower atomic mass (63.5 uma, 207.2 uma and 112.4 uma, respectively). Additionally, the increase in the ionic strength of the solution has been reported to affect cadmium and lead adsorption on montmorillonite, but to have little effect on copper removal (dos Anjos et al., 2014).

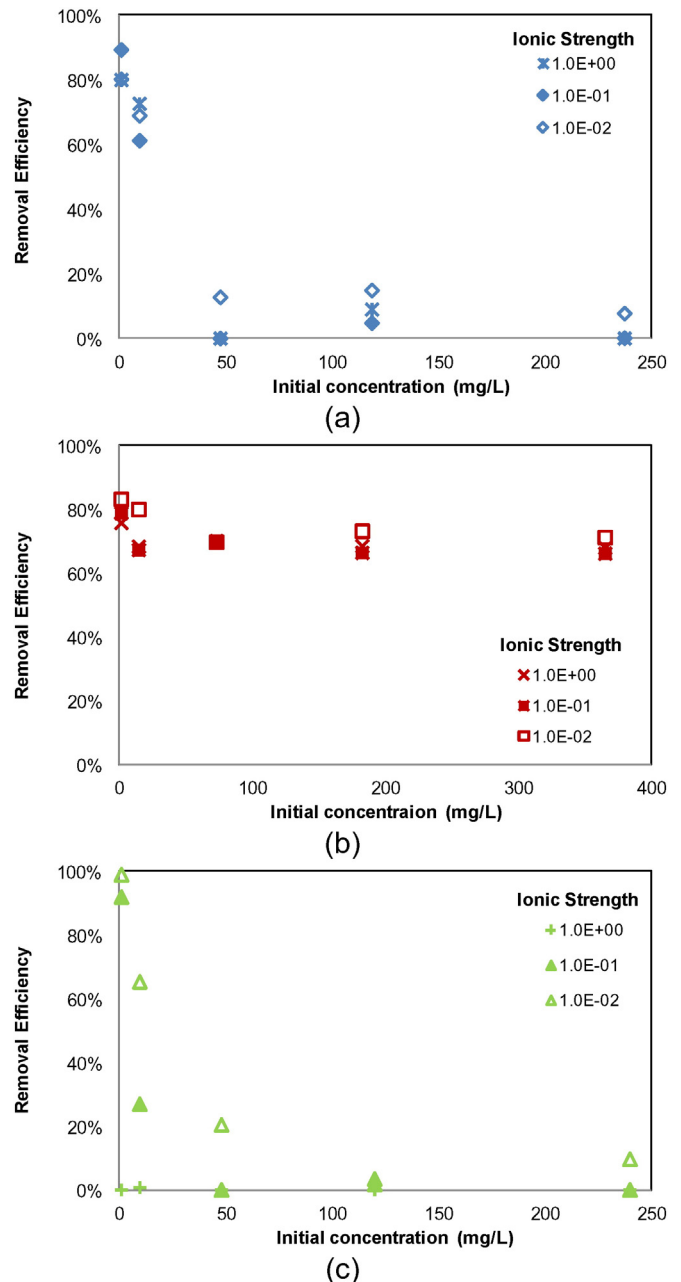


Fig. 5. Removal of (a) cadmium, (b) copper and (c) lead with bentonite in solutions with different ionic strengths.



3.4. Adsorption behavior

The ionic strength of the solution clearly affected the removal of metal-contaminated solutions tested at different initial metallic concentrations and 250 mg/L bentonite concentration (Fig. 5). The ionic strength had little effect on Cu removal (Fig. 5b), while affected Cd and, more considerably, Pb removal (Fig. 5a and c, respectively), in accordance with what was observed for kinetic tests and previously reported by dos Anjos et al. (2014). At low concentrations, the higher removal efficiencies were obtained for Pb and Cd respectively but with a significant decrease when the initial concentration rose. Conversely, at initial concentrations higher than 10 mg/L, higher removal efficiencies were obtained for Cu regardless of the ionic strength of the solution.

3.5. Adsorption isotherms

Removal of metallic ions from the solution is only related to particle–fluid interaction mechanisms. Fig. 6 presents the adsorption tests results and the better fitting with adsorption models for each case with the corresponding correlation coefficient,  $R^2$ . Cadmium adsorption is best represented by the linear adsorption model, while copper and lead adsorption are best described by Freundlich and Brunauer, Emmett and Teller (BET) models, having the linear model, however, very good correlations in both cases as well. The total removal of the three metallic ions in the multispecies test followed a linear behavior but, similarly to the individual behaviors of copper and lead, the remediation was also described properly by the Freundlich and BET adsorption models.

Despite the results of correlation coefficients ( $R^2$ ), most remediation tests show a plateau and a further increase in adsorption, which was

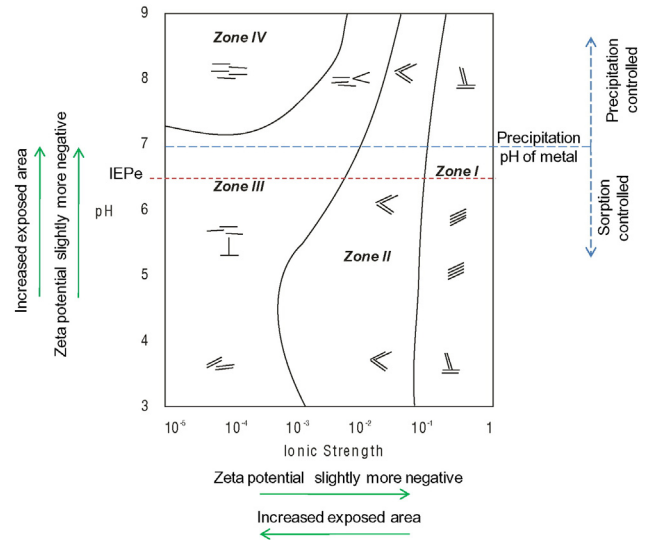


Fig. 7. Fabric map for bentonite and its relationship with metal removal.

described as a Type II isotherm, and is indicative of a physical multilayer adsorption (Hiemenz and Rajagopalan, 1997). BET model was initially developed for gas adsorption on solids (Foo and Hameed, 2010), but it has been increasingly applied for aqueous systems to model multilayer coverage (Morley and Gadd, 1995; Šćiban et al., 2007; Febrianto et al., 2009; Staudt et al., 2013; Agarwal et al., 2014).

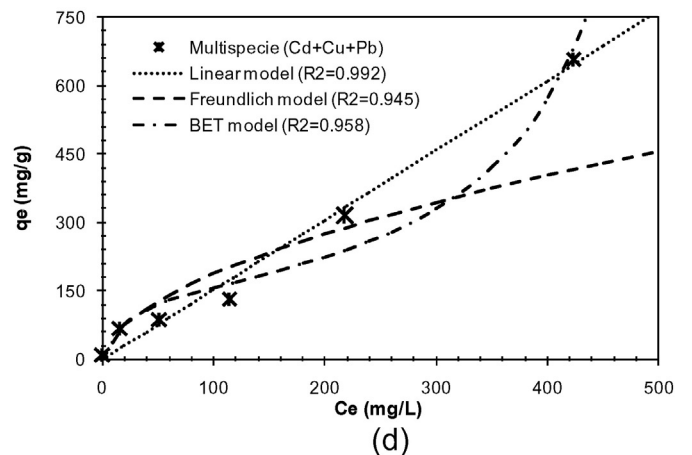
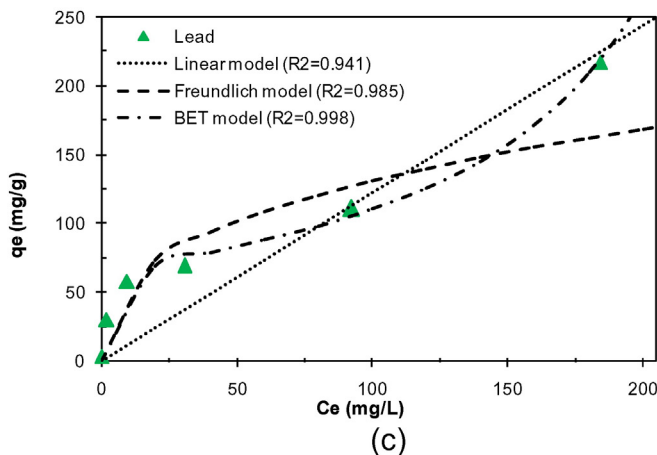
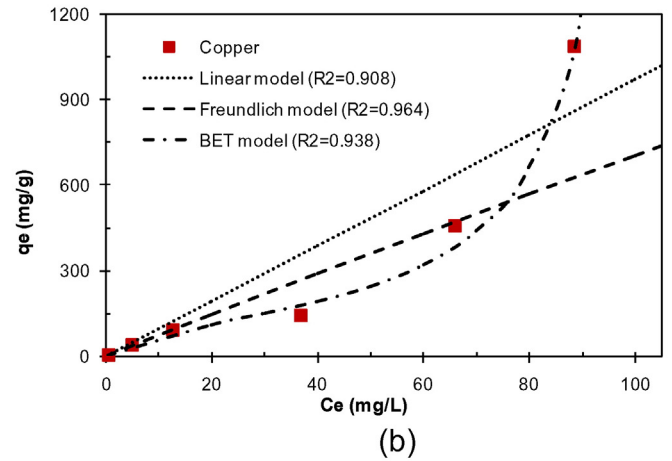
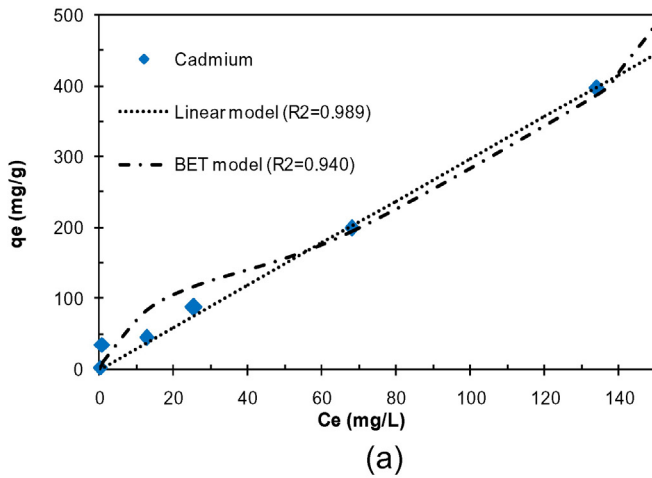


Fig. 6. Better fitting adsorption models with  $R^2 > 0.9$  for metals with bentonite. a) cadmium, b) copper, c) lead, d) cadmium–copper–lead solution.

## 4. Discussion

### 4.1. Relevance of electrochemical interactions

Fluid chemistry and pH have a strong effect on the fabric of fine grained soils. However, this impact has been addressed mostly from the mechanic and hydraulic points of view in most geoenvironmental studies (Al-Taie and Pusch, 2014). The arrangement of soil particles at micro-scale controls macroscopic emergent behaviors, such as plasticity index, shell index, compressibility, hydraulic conductivity and shear strength (Cuevas et al., 2012). Santamarina et al. (2001) and Palomino and Santamarina (2005) developed fabric formation maps showing the expected particle arrangement at different ion concentrations and pH for bentonite and kaolinite, respectively. These particle arrangements affect the final heights registered on the bentonite sedimentation tests (Fig. 1) and also the interaction between the clay minerals and surrounding metallic ions, resulting in different removal mechanisms (Fig. 7). The interaction–removal map proposed in Fig. 7 was elaborated from the obtained results, using a Krigging type interpolation. The isoelectric point of the particles edges  $IEP_{edge} = 6.5$  according to Zhou et al. (2012) and a  $pHp = 7$  (mean for tested metal precipitation) are included as reference values.

By dividing the range of final heights (10 to 64 mm) into four quartiles, four zones can be obtained within the range of analyzed ionic strengths ( $10^{-5}$ –1 M) and pH (3–9). Zone I is characterized by a high ionic strength, pH-independent and low sedimentation heights, which is consistent with face-to-face aggregated or edge-to-face flocculated systems. Zone II is defined by an intermediate ionic concentration and partially affected by pH, and presents edge-to-edge interactions, which are between the dispersed and the aggregated states. A second transitional state (Zone III) presents moderate to low ionic concentrations, which imply extended diffuse double layers (DDL). In this Zone, at pH values higher than the  $IEP_e$ , structures are rather dispersed, while a decrease in pH promotes the formation of flocculated edge-to-face structures. Finally, Zone IV is characterized by a low ionic concentration and a  $pH > IEP_e$ , which gives a completely dispersed structure, due to the increase in the repulsion energy of the DDL.

These interactions play a fundamental role in the environmental impact of clay barriers due to the capacity exhibited by bentonite to adsorb metallic compounds from contaminated groundwater and wastewater. From this point of view, a disperse system will present clay faces completely available to adsorption, while an increase in the ionic strength and a decrease in pH will tend to reduce the DDL of clay particles, promoting their attraction. However, if the pH is above the value that promotes metal precipitation ( $pHp$ ), the removal mechanisms will be related to precipitation rather than adsorption, as expected in Zone IV. In Zone III, there are also deflocculated–dispersed particle arrangements and, as the  $pH < pHp$ , the main removal mechanism is related to adsorption. This presents a second consideration for permeable reactive barriers: a disperse system will present a lower hydraulic conductivity than an aggregated or flocculated system (Montoro and Francisca, 2010), showing again a better potential for contaminants containment. When concentration increases and bentonite particles aggregate and flocculate, they reduce their exposed adsorption area, diminishing their capacity for ions removal (Musso et al., 2014) as expected for Zone I in comparison with Zone III at the same pH.

The adsorbed amounts of heavy metals indicate the capability of the tested bentonite to contribute to the retardation of Cu, Cd and Pb transport through compacted clay liners and slurry walls of significant relevance for contaminant isolation, retention and containment in many practical geoenvironmental applications.

## 5. Conclusions

This work presents the effects of pH and ionic strength on the physical structure of Na-bentonite, and its influence on the removal of

cadmium, copper and lead from solution. The results show that bentonite presents a negative surface charge in the whole pH spectrum analyzed. The ionic strength plays a fundamental role in the clay structure, inferred from sedimentation tests, while pH only has an effect at low salt concentrations. Clay fabric changes from aggregated F–F to flocculated E–E or E–F structures, to dispersed systems when ionic strength is low and pH is above  $IEP_e$  (6.5, according to Zhou et al., 2012). Adsorption kinetics is fast (equilibrium is reached between 15 min and 2 h), and controlled by reaction kinetics rather than diffusion kinetics. Adsorption behavior can be explained by the Linear model, in the case of cadmium, while copper, lead and multispecies removal can be either modeled by the Linear or the Freundlich models with great accuracy ( $R^2 > 0.9$ ) within the tested concentration range. However, a plateau in the adsorption and a further increase in removal with increasing sorbate concentration indicate a multilayer coverage, which was interpreted by the model with excellent correlations. The simultaneous presence of other metals slightly affects copper removal, while having a higher effect on lead and a strong influence on cadmium removal. These trends are similar regardless of the ionic strength of the metallic solution. Finally, we can confirm that analyzed bentonite can effectively remove heavy metals from solution by adsorption mechanisms. This represents an improvement in containment barriers modeling, since the slow advective transport given by the low hydraulic conductivity of the clay can be further reduced by chemical adsorption of cations on the barrier.

## Acknowledgments

This research was partially financed by CONICET (grant number 11220100100390CO), FONCyT (grant number 3101) and SECyT-UNC (grant number 05/M265). D.A.G. thanks CONICET for the doctorate and postdoctorate fellowship. Authors thank the support received from FCEfyN-UNC and ISEA-UNC.

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