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Cu(II) and Zn(II) adsorption capacity of three different clay liner materials

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ABSTRACT

Sorption of Cu(II) and Zn(II) on three natural clays meeting the international requirements for use as liners was evaluated by means of batch tests. The purpose of this research was to determine the retention capacities of the clays for metal cations commonly present in urban solid waste leachates. The pH and ionic strength conditions were set at values frequently found in real leachates. The changes observed in the XRD patterns and FTIR spectra upon adsorption can be considered an evidence of clay–metal electrostatic interaction. The Langmuir model was found to best describe the sorption processes, offering maximum sorption capacities from 8.16 to 56.89 mg/g for Cu(II) and from 49.59 to 103.83 mg/g for Zn(II). All samples remove more Zn(II) than Cu(II), which may be related to the different geometry of the hydrated Cu(II) cation. The total amount of metal sorption was strongly influenced by the total specific surface area, the presence of carbonates and the smectite content of the clays. In addition to their known quality as physical barriers, the adsorbed amounts obtained indicate the suitability of the tested clays to contribute to the retardation of Cu(II) and Zn(II) transport through clay liners.

1. Introduction

Heavy metals are frequently found in surface and subsurface water sources as well as in landfill leachates (Christensen, 1989). Migration of these contaminants can be prevented by either remediation/removal strategies or isolation. Removal of metals from water can be performed by means of adsorption on filter materials (Reddy et al., 2014) while clay linings are commonly used as barriers in landfills to prevent leachate migration and groundwater contamination (Cuevas et al., 2012; Cossu, 2013). The ability of the bottom liner to adsorb heavy metals becomes a significant design issue. The sorption properties of natural clays are thus of fundamental importance in evaluating their potential use as landfill barrier material (Thornton et al., 2001; Sezer et al., 2003; Kaoser et al., 2005; Du and Hayashi, 2006; Bezzar et al., 2010; Koutsopoulou et al., 2010; Ghorbel-Abid and Trabelsi-Ayadi, 2011; Sánchez-Giménez et al., 2012).

Smectite-rich clays are the most widely used clay liners due to their low hydraulic conductivity values, high ion exchange capacity (CEC), large specific surface area, selectivity and regenerability (Churchman et al., 2006). These properties have also generated interest in these clays as natural adsorbents for the removal of heavy metals from aqueous solutions (Ayari et al., 2005; Sdiri et al., 2011; Chaari et al., 2008; Ghorbel-Abid et al., 2009).

Cu(II) and Zn(II) cations are among the most common and abundant heavy metal pollutants in landfill leachate and these are potentially toxic to plants and animals (El-Fadel et al., 1997). The concentration of these cations in a leachate may vary between facilities, based on waste properties, waste age, moisture availability, temperature, and other factors (Jensen and Christensen, 1999). Typical concentrations of these metals in a leachate produced in a municipal solid waste landfill in Argentina are 6.6 mg/L for Cu(II) and 13.5 mg/L for Zn(II) (Francisca and Glatstein, 2010). Groundwater, frequently used for drinking, may be affected by leachate migration in old waste storage areas from landfills due to mass transport through the bottom liners (Christensen et al., 2001). The World Health Organization (WHO) maximum acceptable

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concentrations of Zn(II) and Cu(II) in drinking water are 5.0 mg/L and 1 mg/L, respectively (WHO, 2003, 2004). Beyond these limits, these metals are toxic and are on the US EPA list of 126 priority pollutants (Code of Federal Regulation, 2014).

Sorption of metal ions by clay minerals depends on the charge characteristics of the adsorbent (surface charge magnitude and type of charge) as well as the metal properties of ionic charge and radius and their hard-soft acid–base characteristics. Other factors such as metal concentration, pH, ionic strength, type and concentration of competing ions, the liquid–solid ratio and temperature also affect sorption processes (Ding et al., 2009). Adsorption of metallic ions on a clay surface is responsible for the retardation effect observed during mass transport in porous media (Fetter, 2002; Francisca et al., 2012).

In the Neuquén basin, Argentina, clay-rich formations are abundant, and bentonites occur overlying and underlying other smectite-rich claystones that are also of high interest due to their similar properties with the bentonites (Musso et al., 2010). These bentonites, as well as the smectite-rich claystones, meet the common hydraulic requirements for use as part of compacted clay liners (Musso et al., 2012, 2013). However, the adsorption of heavy metals by these natural Argentinean clays has not been extensively explored. The study of sorption capacity of these clay materials is important to provide additional protection when used in landfill liners and given their high abundance and the low cost of extraction and supply in the study area. Thus, considering that clays are usually modified to improve their sorption ability (Mockovciaková et al., 2010), the use of natural clays as geochemical barriers without any pre-treatment constitutes a more sustainable and economically viable alternative.

The main purpose of this study is to evaluate the adsorptive capacity of three different natural clays that already meet hydraulic requirements for use as clay liners, to retain heavy metals from aqueous solutions. The presence of Cu(II) and Zn(II) ions on the clay surfaces was demonstrated through X-ray diffraction and Fourier Transform Infrared (FTIR) spectroscopy.

2. Materials and methods

2.1. Materials and chemicals

The clayey materials were selected from three formations of the Neuquén basin in Argentine North Patagonia. The following samples were studied: a sodium bentonite from Allen formation named CATAE, a calcareous mudstone from Roca formation named NTOL, and a red claystone from Anacleto formation designed as KCE. The CATAE and KCE samples are of Upper Cretaceous age, while the NTOL sample is of Tertiary age. The main physical and geotechnical properties of these specimens are presented in Table 1, while their chemical composition can be found in Musso et al. (2010, 2013). These materials meet the technical requirements outlined in the European, Japanese and American legislations for use as clay liners (Chai and Miura, 2002), having hydraulic conductivities lower than 1×10^{-9} m/s (Musso et al., 2010, 2013) (Table 1).

Sorption and characterization studies were performed on the <2 μm fraction. All chemicals [$Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$] used were of analytical grade. NaOH and HCl solutions were used for pH adjustment and 0.08 M NaCl solution was prepared for ionic strength control.

2.2. Methodology

2.2.1. Mineralogical characterization

Mineralogy of tested materials was characterized by X-ray diffraction (XRD) analysis using random powders and oriented slides. The XRD measurements were carried out with a Rigaku D-Max IIC automated diffractometer using Cu-Kα radiation, 20 mA and 40 kV, at a scanning speed of 2° 2θ min^{-1} from 2° to 65° for the random powders and from 2° to 40° for the oriented slides.

Sample-water slurries (2 g/100 mL) were prepared with the natural clayey materials. These suspensions were dispersed by mechanical stirring followed by sonication, and then the <2 μm fraction was separated by centrifugation. On random powders, the procedure proposed by Schultz (1964) was used to semi-quantify the presence of non-clay minerals in this fraction. Oriented glass slides were made in the following conditions: air-dried, treated with ethylene glycol and heated to 550 °C. The clay minerals identified were semiquantified by calculating the ratio of the basal peak areas, after applying empirical correction factors on the peak areas (Jones, 1989).

2.2.2. Physicochemical characterization

Physicochemical characterization consisted in measurements of specific surface area, cation exchange capacity and electrophoretic mobility.

The external specific surface area (SS_{BET}) of the clays was determined by BET analysis (multipoint N_2 adsorption after degassing under N_2 flow for 6 h at 250 °C) using an Asap 2000 (Micromeritics). The total specific surface area was also determined by conducting Ethylene Glycol Monoethyl Ether (EGME) absorption tests (SS_{EGME}).

The cation exchange capacity (CEC) of the clays was measured by the copper triethylenetetramine $[Cu(trien)]^{2+}$ method.

The electrophoretic mobility measurements were conducted using a Beckman Coulter, Delsa Nano C-Particle Analyzer. These measurements were performed to obtain the zeta potential of the clay fraction (ζ) by means of the Smoluchowski's equation (Vane and Zang, 1997). The dispersions were prepared by mixing 0.031 g of sample with 25 mL of solution. After agitation for 30 min in a shaker, an aliquot was taken from the suspensions and slowly poured into the electrophoresis cell. The voltage applied during the measurements was 60 V. These determinations were conducted under different pH conditions. The pH effect was evaluated, adjusting the pH of the dispersions in the range from 2.5 to 10.5

Table 1
Geotechnical and hydraulic properties of tested clays (data compiled from Musso et al., 2010, 2013).

Geotechnical characterization	Clay samples			Standard
	CATAE	NTOL	KCE	
Water content (%)	11.3	5.5	8.12	ASTM D2216 (ASTM, 2007)
Liquid limit (%)	340	117	47	ASTM D4318 (ASTM, 2007)
Plasticity index	291	52	11	ASTM D4318 (ASTM, 2007)
Swell index (mL)	36	7	9	ASTM D5890 (ASTM, 2007)
Specific gravity[a]	2.70	2.64	2.67	–
Activity	3.14	0.28	0.13	–
Soil classification	CH	MH	CL	ASTM D2487
Particles < 62.5 μm (%)	98.3	99.0	99.0	ASTM D422 (ASTM, 2007)
Particles < 1.95 μm (%)	85.9	17.7	60.1	ASTM D422 (ASTM, 2007)
k^b (m/s)	2.02×10^{-12}	1.80×10^{-11}	3.09×10^{-12}	ASTM D2434 (ASTM, 2007)
k^c mixtures (m/s)	5.34×10^{-12}	1.46×10^{-10}	1.34×10^{-10}	ASTM D5856 (ASTM, 2007)

[a] Pyknometer method on clay oven dried at 105 °C.
[b] Hydraulic conductivity of pure samples.
[c] Hydraulic conductivity of clay–sand mixtures (15% w/w).

before each measurement. In this case, NaCl (0.08 M) was used to adjust the ionic strength of the aqueous solutions. The pH that was measured after the zeta potential measurement was recorded as the final pH.

2.2.3. XRD analysis of clay–metal complexes

XRD analyses were conducted to characterize the structural changes induced by the presence of different initial concentrations of heavy metal cations (50 mg/L, 180 mg/L, 500 mg/L and 1800 mg/L) in contact with the studied clays. The solid phase of clay–metal complexes was washed with 10 mL of NaCl (0.08 M) solution and then sedimented on a glass slide for the XRD analysis. The sample thickness was 3 mg/cm^2. They were air dried and stored under controlled humidity conditions (RH = 25–30%) in a desiccator.

XRD analyses were also recorded on homoionized samples, prepared by using 20 mL of 1.5 M of Cu(II) and Zn(II) solutions and 0.05 g of sample.

2.2.4. FTIR spectroscopy of clay–metal complexes

FTIR spectra of clays and clay–metal complexes were recorded to examine functional groups of the clays after the adsorption of either Cu(II) or Zn(II). Infrared spectra were recorded over the region 600–4000 cm^{-1}. The samples were examined in KBr pellets (3 mg/300 mg KBr).

In order to observe differences between the clays and the specimens after the adsorption of metals, spectrum of complexes with 1800 mg/L were obtained. All samples were analyzed on a Lumex FTIR-08 spectrophotometer.

2.2.5. Batch experiments

The interaction between clays and heavy metals was studied by means of batch experiments. The tests were conducted by mixing 0.031 g of clay sample with 25 mL metal–nitrate solutions containing various concentrations of the studied metals (10–220 mg/L for Cu(II) and 1–210 mg/L for Zn(II)). The lower concentrations of these solutions are similar to the average Cu(II) and Zn(II) concentrations determined in urban waste leachates (Francisca and Glatstein, 2010). The solutions were prepared using NaCl (0.08 M) as electrolyte, and the pH of the metal solution was adjusted to 5.5 using an Altronix EZDO-PC pH meter. The mixtures were shaken in a rotative shaker for 24 h at 25 °C. Then, the specimens were centrifuged at 3600 rpm for 20 min and the supernatant was filtered through 0.45 μm syringe acetate filters (Scharlab) and stored in polypropylene tubes. The amount of metal adsorbed in the clays was calculated by the difference between the initial and the final metal concentrations determined by Atomic Absorption Spectrometry (METROLAB 250AA spectrophotometer). All tests were performed in duplicate in order to verify the reproducibility of results.

Experimental results were analyzed using Langmuir and Freundlich isotherms, equations (1) and (2), respectively:

$$\frac{C_e}{q_e} = \frac{1}{C_s K_L} + \frac{C_e}{C_s} \tag{1}$$

$$\log q_e = \log K_F + n_f \log c_e \tag{2}$$

where c_e is the equilibrium concentration of metal ion in liquid phase (mg/L), q_e is the equilibrium concentration of metal ion in solid phase (mg/g), C_s is the maximum adsorption capacity (mg/g), K_L is the adsorption coefficient of the Langmuir model (L/mg), K_F is the adsorption capacity constant of the Freundlich model ($\mathrm{mg}^{1-1/n}\mathrm{L}^{1/n}\mathrm{g}^{-1}$), and n_f is the adsorption intensity constant of the Freundlich equation.

Langmuir and Freundlich isotherms are commonly used to study sorption phenomena of heavy metals on clay particles (Sánchez-Jiménez et al., 2012). With the Langmuir isotherm, it is possible to calculate the maximum adsorption capacity of each metal on the solid phase and to quantify the clay–metal affinity (Aboul et al., 2001). The Langmuir model describes monolayer coverage and assumes a homogeneous adsorption surface with binding sites having equal energies (Arfaoui et al., 2008). The Freundlich equation is an isotherm model representing the adsorbent surface as heterogeneous (Chen and Wang, 2007). Both isotherm models (equations (1) and (2)) were fitted to experimental data by means of a least square fitting technique using non-linear regression and the Origin® package software (v.8.0).

3. Results and discussion

3.1. Mineralogical characterization

The mineralogical composition of the sorbent that interacted with Cu(II) and Zn(II) ions is shown in Table 2. The CATAE sample is composed only of clay minerals (smectite), while the NTOL and KCE samples also contain non-clay minerals in the <2 μm fraction. NTOL mineralogy is dominated by an R0 illite/smectite mixed layer (75% Sm) followed by calcite and illite (Table 2). The KCE sample predominantly consists of an R0 illite/smectite mixed layer (50% Sm) and illite (Table 2).

3.2. Physicochemical characterization

The results of the physicochemical characterization are shown in Table 3. The sample CATAE has the lowest external surface area but the highest total specific surface area. The differences in these values are related to a combination of the testing method characteristics and the sample mineralogy. Samples with a higher percent of swelling clay minerals will exhibit higher total specific surface values because the measurements are made in wet conditions allowing swelling (CATAE > NTOL > KCE).

In the BET technique, the dry state of the sample suppresses the interlayer space of the clays. Therefore, the surface that is measured corresponds to the micropores located at the "quasi-crystalline overlap region" (Kaufhold et al., 2010). In bentonites, the areas of crystal-overlap accessible to N$_2$ adsorption are almost negligible (Aylmore and Quirk, 1967). In this study, samples with some illite or interstratified illite/smectite mineral content exhibit higher S_{BET} values than the bentonite CATAE, matching the values observed for similar materials reported by other authors (Srasra et al., 1994; Omotoso and Mikula, 2004).

CEC values are also related to the expansible clay mineral content of the analyzed samples (CATAE > NTOL > KCE) (Table 3).

Table 2
Mineralogy of the clays.

Lower than 2 μm mineralogy	CATAE	NTOL	KCE
Clay minerals (%)	100	86	96
Smectite (%)	100	–	–
I/S[a] type R0 (%)	–	~80	~50
Sm[b] in I/S (%)	–	75	50
Illite (%)	–	~20	~50
Kaolinite (%)	–	–	<1
Quartz (%)	–	5	2
Feldspars (%)	–	<1	1
Calcite (%)	–	8.5	1

[a] Illite/smectite mixed layer.
[b] Smectite.

Fig. 1 illustrates the effect of pH on the zeta potential of clay samples dispersed in distilled water. Obtained results showed that clay surfaces had a negative electrical charge in water over a pH range of 2–10. The zeta potential of CATAE was found to be more negative than the other clays, because it is entirely constitute by smectite, and changed by only 5 mV (−17 to −22 mV) over the same pH range. This data is in agreement with previous results which indicate that zeta potential is relatively insensitive to pH changes in bentonites (Delgado et al., 1986; Vane and Zang, 1997). NTOL and KCE clays also show a slight variation of zeta potential with pH indicating that the mineralogical differences among these samples didn't affect this trend.

3.3. *XRD analysis of clay–metal complexes*

XRD patterns of the clays, clay–metal complexes (50–1800 mg/L) and the clays homoionized with Cu(II) and Zn(II) solutions, are shown in Figs. 2 and 3. Changes in XRD patterns were only observed in the smectite and I/S (001) reflections of the analyzed clays.

In the case of the clays without metal, the XRD pattern of CATAE is characterized by symmetric and narrow peaks and presents a 001 basal reflection situated at $2\theta = 7.21°$ (d001 = 1.25 nm), indicating 1 water hydration state (Fig. 2a). The (001) reflection of NTOL and KCE, having an I/S in their composition, tends to be more asymmetric and broader, as the smectite content decreases in the I/S from the NTOL to the KCE sample (Fig. 2b, c). In these samples, the 001 value, without the metal, also indicates 1 water hydration state (d001 = 1.24–1.27 nm).

For all the intermediate concentrations of clay–Cu(II) complexes (50–1800 mg/L), the basal spacing slightly decreased compared with the natural samples, which would indicate that the samples are interstratified with interlayer spaces containing Cu(II) and Na^+ ions. The basal spacing for the specimens treated with Cu(II) tended to rise from the lowest concentration to a maximum near the 500 mg/L concentration and then slightly decreased for Cu(II) concentration of 1800 mg/L (Fig. 2). For the homoionic conditions with Na^+ and Cu(II), the layer water arrangement is homogeneous and equivalent to one water layer, as indicated by a d(001) = 1.26 nm. These results are in good agreement with the data reported by Oueslati et al. (2009, 2011) for montmorillonites saturated with Cu(II).

Obtained results show that the hydration of Cu(II) is very similar to that of Na^+, despite its higher charge density. This is due to the structure of the Cu(II) aqua-ion $[Cu(H_2O)_6]^{2+}$, which has a tetragonal distortion due to the Jahn–Teller effect in which the octahedral structure has been contracted along the *x*- and *y*-axes (Nicholls, 1974). This distortion causes an unbalanced structure that has to be compensated by the electrons located in the basal surface of the clay. In this way, the interaction of Cu(II) ions would be directly with the Si–O surface groups which act as ligands (Abollino et al., 2003).

The presence of copper-carbonate (JCPDS N° 70-2053) in NTOL and KCE samples can be observed only in a concentration of 1800 mg/L and is probably based on the small discrete reflections at 0.299 and 0.265 nm (Fig. 4).

Table 3
Physicochemical properties of the samples.

Property	CATAE	NTOL	KCE
SS_{BET}[a] (m^2/g)	42	99	94
SS_{EGME}[b] (m^2/g)	754.4	642.8	497.9
CEC	105.9	97.61	79.5

[a] External specific surface.
[b] Total specific surface.

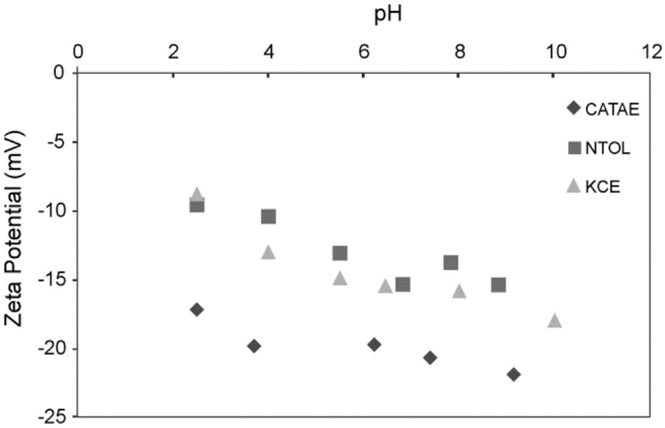

Fig. 1. pH-dependent variation of zeta potential of the clays suspended in a NaCl (0.5%) solution.

For clay–Zn(II) complexes (50–1800 mg/L), a gradual increase of the basal space from 1.25 nm to 1.30 nm can be observed as the Zn(II) concentration increases from 50 to 500 mg/L in CATAE and NTOL (Fig. 3a, b). The same trend is observed in the KCE sample although the d(001) values are lower: from 1.15 nm to 1.18 nm (Fig. 3c). At a Zn(II) concentration of 1800 mg/L, the basal spacing slightly decreases for all the analyzed samples. In all the intermediate concentrations, the basal spacing resulted more similar to Na^+ than to Zn(II), indicating a predominance of this ion in the interlayer space. Only for the homoionic condition with Zn(II) can it be seen that the basal spacing is near 1.5 nm, indicating a two-water-layer arrangement in the interlayer space.

3.4. *FTIR spectroscopy of clay–metal complexes*

One important characteristic of an adsorbent is the surface functional groups present, which are largely characterized by the FTIR spectroscopy method. FTIR spectroscopy of the clays and clay–metal complexes (1800 mg/L) is shown in Fig. 5.

The infrared spectra are in the frequency range 4000–500 cm^{-1}. The distinct increase of infrared absorbance at 3620–910 cm^{-1} confirms the dominant presence of dioctahedral smectites with [Al, Al–OH] stretching and bending bands (Sondi et al., 1996).

The absorption bands at 3400 cm^{-1} and 1630 cm^{-1} may be attributed to the –OH stretching and bending frequencies, respectively, which corresponds to the water molecule adsorbed on the clay surface. Inner hydroxyl groups, lying between the tetrahedral and octahedral layers, give the absorption near 3620 cm^{-1}. The adsorption band at 1050 cm^{-1} can be assigned to [Si–O–Si] while the band at 790 cm^{-1} confirms quartz admixture in the samples. The presence of carbonate is characterized by the band at 1410–1450 cm^{-1} (Sdiri et al., 2011). This band appears only in the spectra of the clays NTOL and KCE (Fig. 5b and c), confirming the presence of calcite in these samples.

The spectral differences between the clays and the clays on which Cu(II) and Zn(II) sorption was conducted refer to three wave number ranges (Fig. 5a–c):

- 3800–3000 cm^{-1} – the range of frequencies corresponding to the bands originating from OH group stretching vibrations;
- 1410–1450 cm^{-1} – the range of frequencies corresponding to the carbonate bands;
- 1200–600 cm^{-1} – the range of frequencies corresponding to the bands assigned to asymmetric Si–O–Si vibrations.

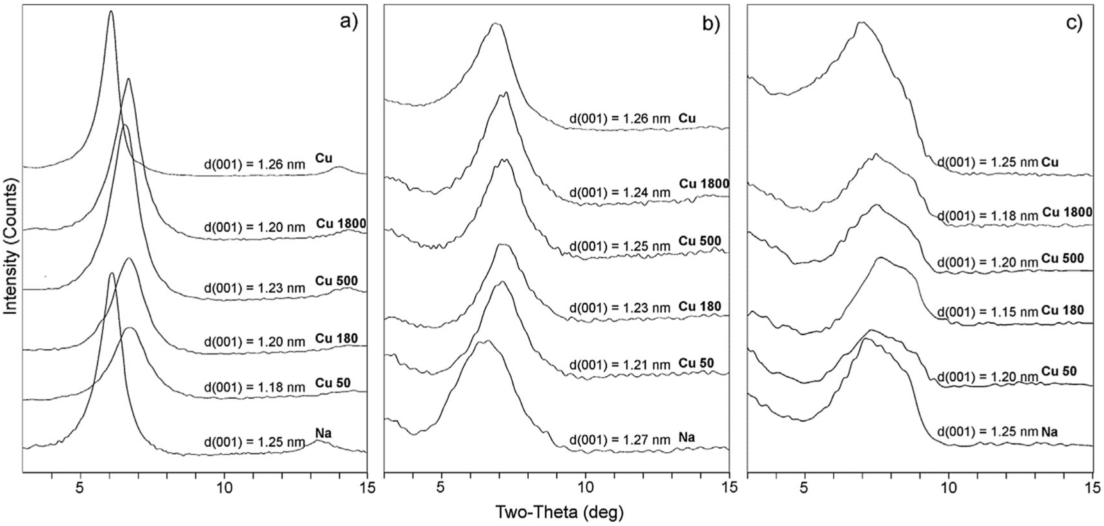

Fig. 2. XRD patterns of clay–Cu(II) sorption complexes (50–1800 mg/L) and homoionized samples with Na^+ and Cu(II). a) CATAE sample; b) NTOL sample; c) KCE sample.

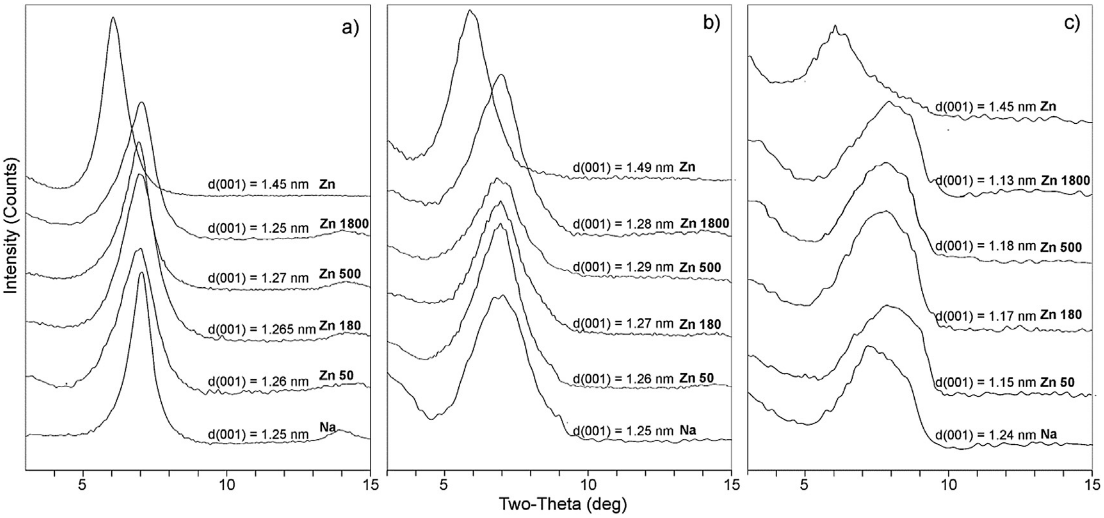

Fig. 3. XRD patterns of clay–Zn(II) sorption complexes (50–1800 mg/L) and homoionized samples with Na^+ and Zn(II). a) CATAE sample; b) NTOL sample; c) KCE sample.

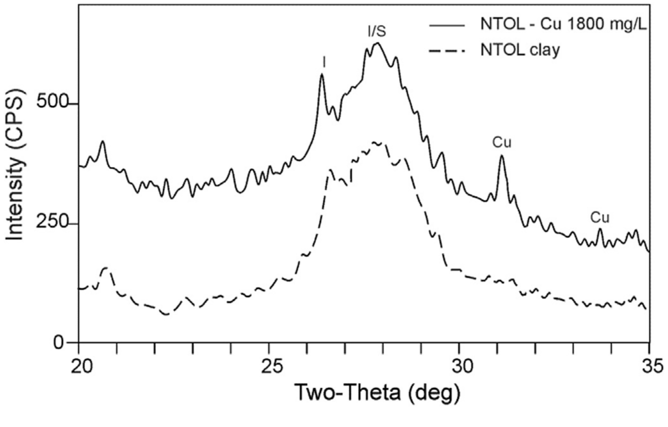

Fig. 4. XRD patterns of NTOL clay without metal and NTOL–Cu(II) sorption complex (1800 mg/L) containing copper carbonate. I: illite, I/S: illite/smectite mixed layer, Cu: copper carbonate.

In the first range, these changes are produced by different tendencies of the studied metal ions to form aqua-complexes and to hydrate in an aqueous environment. CATAE was the sample that experienced the most important change in this range after contact with the analyzed metals. This effect can be attributed to the higher amount of smectite of this clay in comparison with KCE and NTOL clays.

The carbonate bands (1410–1450 cm^{-1}) are only present in the spectra of NTOL–Cu(II) and KCE–Cu(II). Changes in the absorption frequency of this band seem to show the presence of precipitated copper-carbonate. This absorption band is not present in the Zn(II) adsorption complexes.

In the third range of bands, the 1050 cm^{-1} band is probably linked to Si–O stretching vibrations, and the 912 cm^{-1} to bending Al–OH (octahedral coordination of Al) vibrations. Only in CATAE–Zn(II) and NTOL–Zn(II) complexes can a shift of the Si–O band to the lower frequencies be seen. The presence of Zn(II) cations either in hexagonal holes and/or in the previously vacant octahedral sites may induce changes in the Si–O vibration modes (Eren and Afsin, 2008).

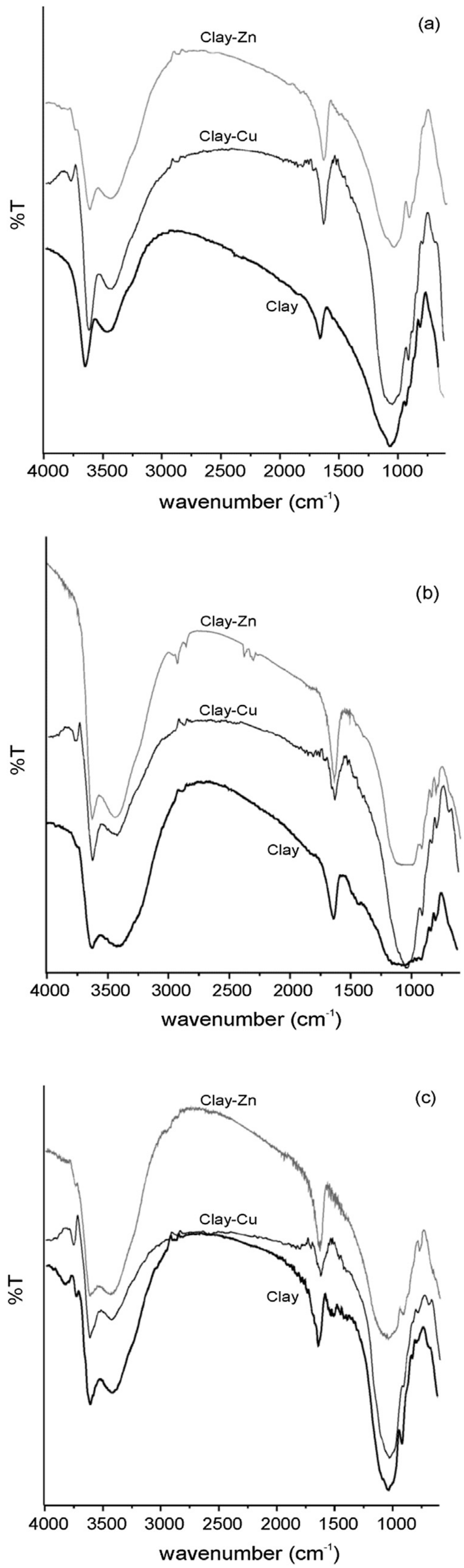

Fig. 5. FTIR spectra of the clays and the clay–metal sorption complexes (1800 mg/L). (a) CATAE, (b) NTOL and (c) KCE.

Although it is difficult to elucidate the state of adsorbed Cu(II) and Zn(II) from these data, the changes observed in the spectra upon adsorption can be considered as an evidence of clay–metal electrostatic interaction.

3.5. Adsorption isotherms

To further understand adsorption of Cu(II) and Zn(II) onto clay, adsorption isotherms of single metal solutions at pH 5.5 were evaluated. Fig. 6 presents experimental results and fitted Langmuir isotherms for Cu(II) and Zn(II) sorbed on CATAE, KCE and NTOL samples. Results are expressed as mg/g of mineral, against the metal solution equilibrium concentration expressed as mg/L. Adsorption isotherms were L-2 type (Giles et al., 1960), characterized by a steep initial slope that levels off as the equilibrium concentration of metal increases. As expressed by the percentage of adsorbed Cu(II) and Zn(II), the samples show a higher preference for both metal ions at lower concentrations. These features indicate that adsorption affinity decreased as the metal concentration increased. This may be explained by the fact that the higher surface coverage resulting from the increase of metal concentration raises the activation energy for the reaction, thereby making it more difficult for the surface to bind metal ions (Du et al., 1997).

All the samples showed higher sorption for Zn(II) than for Cu(II). Abollino et al. (2003) also detected a higher sorption of Zn(II) than Cu(II) in a Na-montmorillonite and they concluded that this is probably because the different geometry of Cu(II) aqua-ion principally hinders the complexation reactions with the surface groups of the smectite. Jung et al. (2001) also showed that the adsorption of Cu(II) was through inner-sphere surface complexes at pH 5.9 in smectite-rich clay materials. In the case of Zn(II), however, adsorption on montmorillonites was previously attributed to pH-independent cation exchange with formation of outer-sphere complexes on permanent exchange sites and to pH-dependent surface complexation on amphoteric surface hydroxyl groups (Baeyens and Bradbury, 1997; de Pablo et al., 2011).

As it is shown in Fig. 6, at high metal concentration, the sorption of Zn(II) and Cu(II) was higher than 20 mg/g and 15 mg/g, respectively, which are over the CEC of the analyzed materials. In the case of Cu(II), NTOL was the only sample which adsorbed Cu(II) amounts lower than the CEC of this clay in all tested concentrations. The fact that most of the samples adsorbed metal amounts over their CEC could be attributed to the following two types of reactions with clay surface that occur at the experimental pH (Wu et al., 2011):

a) exchange with hydronium ions:

$$2{\equiv}\mathrm{S{-}OH} + \mathrm{Cu}^{2+} \rightarrow ({\equiv}\mathrm{S{-}O})_2 - \mathrm{Cu} + 2\mathrm{H}^{+}$$

b) exchange with Na^{+} ions:

$$2{\equiv}\mathrm{S{-}ONa} + \mathrm{Cu}^{2+} \rightarrow ({\equiv}\mathrm{S{-}O})_2 - \mathrm{Cu} + 2\mathrm{Na}^{+}$$

However, more specific determinations, which include pH and ionic strength variation, need to be made in order to determine the sorption mechanisms on these clays.

The Freundlich and Langmuir model parameters that best fit the experimental data are listed in Table 4. Cu(II) and Zn(II) sorption have higher correlation values with the Langmuir than with the Freundlich model. The maximum adsorption capacity (C_s) for Cu(II) and Zn(II) on the analyzed clays, and therefore their removal efficiency, follows the order CATAE > KCE > NTOL.

The clays showed different sorption capacities and bonding affinities as a function of the tested metal and the physicochemical characteristics of the sorbent, reflecting the textural and

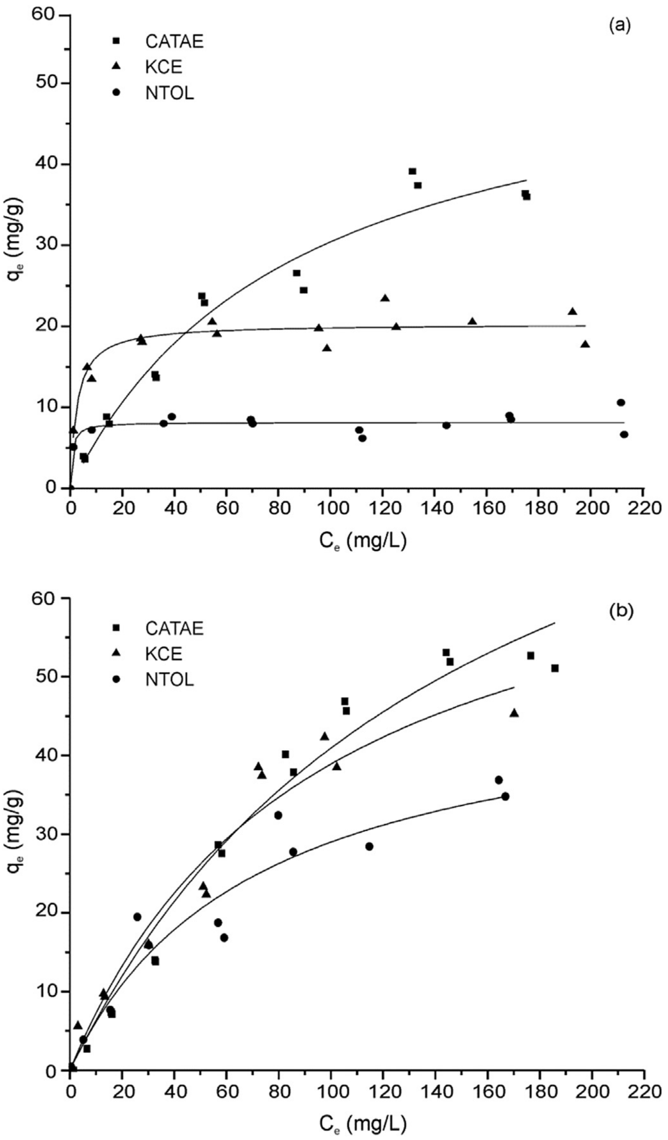

Fig. 6. Langmuir sorption isotherms of Cu(II) (a) and Zn(II) (b) on CATAE, NTOL and KCE at pH 5.5.

mineralogical differences among the clayey materials. The highest metal amounts were sorbed on the CATAE clay as a consequence of its highest amount of swelling clay minerals. The higher capacity of this clay for Cu(II) and Zn(II) retention can also be attributed to its high total specific surface area (Table 3).

The results from sorption experiments showed that the content of non-clay minerals is a very important factor for heavy metal sorption. Carbonate minerals seem to modulate the retention capacity of the clayey materials, because they can promote competitive interactions for heavy metal ions when they are dissolved, but, on the other hand, they can also induce metals precipitation as carbonates (Sánchez-Jiménez et al., 2012). For the concentration range of the obtained adsorption isotherms (10–220 mg/L), calcium carbonate is dissolved, and so NTOL, which is the sample with the highest calcite content, adsorbed the lowest amount of metallic ions. The precipitation of copper carbonate was observed through XRD and FTIR studies only at a Cu(II) concentration of 1800 mg/L, which is out of the range of adsorption isotherm concentrations.

Adsorption of Cu(II) and Zn(II) on the KCE and NTOL samples took place mainly on the smectitic clay component of the I/S mixed layer. Previous results have shown that the percentage of illite becomes an important factor in metal adsorption at pH higher than 7 where complexation reactions on the edge sites predominate (Alvarez-Puebla et al., 2005; Missana et al., 2008; Wu et al., 2011).

The percentage of smectite in the I/S mixed layer of NTOL and KCE seems to be less important than the calcite content, which would control the lower adsorption of NTOL despite its higher smectite content in the I/S. Moreover, other authors have modeled the adsorption behavior of I/S mixed layers with variable proportions of smectite (50% and 75%) and have concluded that there is a small variation in the amount of metal sorbed in these two kind of I/S (Missana et al., 2008).

3.6. Application of the clays as geochemical barriers in landfills

The Langmuir maximum adsorption capacities (C_s) of Cu(II) and Zn(II), expressed in mg/g, were compared with monolayer adsorption capacities of other natural bentonites and smectite-rich claystones reported in the literature (Table 5). This showed that the maximum adsorption capacity achieved for the bentonite CATAE is among the highest capacities reported for these metals. The maximum adsorption capacities of KCE and NTOL samples for Zn(II) are similar to the reported values for natural and raw bentonites. The adsorption of Cu(II) by KCE is comparable with the reported values for calcareous clays, whereas the maximum Cu(II) adsorption capacity of NTOL is lower than other calcareous materials.

The calculated adsorption percentages on 0.031 g of clay, from a solution with 10 mg/L of Cu(II) or Zn(II), which is a typical concentration for these metals in real leachate, were: CATAE: 50% for Cu(II) and 33% for Zn(II), KCE: 88% for Cu(II) and 68% for Zn(II), NTOL: 88% for Cu(II) and 48% for Zn(II). These results confirm that the adsorption capacity of the tested clays can successfully contribute to the retardation of Cu(II) and Zn(II) transport through clay liners. This is significant for contaminant isolation/containment in many practical geoenvironmental applications (i.e. as part of landfill liners and geosynthetic clay liners, sediment caps, slurry walls, wastewater impoundments, etc.).

4. Conclusions

The adsorption of Cu(II) and Zn(II) ions from aqueous solutions by different natural clays from North Patagonia, Argentina, was investigated. The main conclusions of this investigation can be summarized as follow:

- X-ray diffraction and FTIR spectroscopy results evidenced the presence of the metals on the clay surface.
- The Langmuir is preferred to the Freundlich isotherm to describe the adsorption of Cu(II) and Zn(II) on the analyzed clays within the ion concentration range tested in this work.

Table 4
Isotherms coefficients according to Freundlich and Langmuir.

Elements	Clay sample	Freundlich			Langmuir		
		K_F (L/g)	n_f	R^2	K_L (L/mg)	C_s (mg/g)	R^2
Cu(II)	CATAE	1.19	0.70	0.98	0.01	56.89	0.96
	NTOL	5.26	0.09	0.54	1.42	8.16	0.81
	KCE	8.40	0.18	0.79	0.39	20.3	0.88
Zn(II)	CATAE	1.09	0.64	0.88	0.01	103.83	0.98
	NTOL	0.70	0.82	0.93	0.01	49.59	0.94
	KCE	2.51	0.58	0.95	0.01	75.61	0.95

Table 5
Comparison of Langmuir maximum adsorption capacities (C_s) of natural clays for Cu(II) and Zn(II) removal from aqueous solutions.

Adsorbent	Cu(II) C_s (mg/g)	Zn(II) C_s (mg/g)	Reference
Natural bentonite (30 °C, pH 6.76)	–	68.49	Sen and Gomez (2011)
Raw bentonite (25 °C, pH 6.5)	–	73.5	Zhang et al. (2011)
Wy Na-montmorillonite (Swy-2) (pH 5.5)	132.9	–	Zhu et al. (2011)
Calcareous clays (pH 6)	27.39–17.88	22.72–15.60	Sdiri et al. (2011)
Raw bentonite	32.17	–	Eren and Afsin (2008)
Na-bentonite (22 °C, pH 5 for Cu, 6 for Zn)	30	23.1	Alvarez-Ayuso and García-Sanchez (2003)
Natural bentonite (20 °C, pH 4.5)	–	52.91	Mellah and Chegrouche (1997)
CATAE (Allen Fm.) (25 °C, pH 5.5)	56.89	103.83	This work
NTOL (Roca Fm.) (25 °C, pH 5.5)	8.16	49.59	This work
KCE (Anacleto Fm.) (25 °C, pH 5.5)	20.3	75.61	This work

- The total amount of metal sorption is strongly influenced by the total specific surface area, the presence of carbonate minerals and the content of smectite.
- The efficiency of the Cu(II) and Zn(II) removal from aqueous solutions was clearly demonstrated by means of batch tests and follow the order: CATAE > KCE > NTOL. From aqueous single ion solutions, the analyzed samples remove more Zn(II) than Cu(II) which would be related to the different geometry of the hydrated Cu(II) cation.
- All analyzed clays have a good adsorption capacity of Cu(II) and Zn(II) compared to previous results reported for natural clays. The adsorption of Cu(II) and Zn(II) over the CECs of the samples could be attributed to ion exchange with Na^+ ions located in the basal surfaces of the clay and with H^+ ions located at the edge of clay particles. The calculated maximum adsorption capacity is produced when all the sites of the clay are occupied, as will be the case in contact with landfill leachates where saturation is expected.
- The clays' sorption capacity for Cu(II) and Zn(II) was high enough to consider its use in a clay barrier to isolate urban waste leachate. This ability can also be explored in treatment technologies since these materials are low cost, abundant and locally available.

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