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Mudstones as Landfill Liner Material for Heavy Metal Removal: Equilibrium and Dynamic Sorption Study

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Abstract Clay materials used as low-permeability barriers at landfill sites can also chemically attenuate inorganic contaminants (heavy metals) in leachate. In this study, Cu(II) removal capacity from aqueous media of a raw calcareous mudstone, used as a liner material, was evaluated through both batch and column tests. Batch experiments were conducted varying contact time, pH, and Cu(II) concentration. In order to simulate waste leachates composition, the effect of the presence of some organic compounds on Cu(II) uptake was also evaluated. Column tests of compacted calcareous mudstone-sand mixtures were performed to evaluate sorption in dynamic systems. The studied calcareous mudstone exhibited higher removal capacity in a wider pH range than a commercial Na-bentonite, which is a widely used heavy metal sorbent and clay liner. It was evidenced that calcite, an important component of the calcareous mudstone and found as very small and highly porous calcareous nannofossils, contributed to its sorption properties playing a significant role in the Cu(II) removal. The presence of an anionic surfactant or phenol slightly affected the removal of Cu(II). In the clay fraction (< 2 μm), Cu(II) sorption was favored by the presence of humic acids, which add new adsorption sites

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for this metal. The extremely high retardation factor obtained for the raw calcareous mudstone is in good agreement with the high adsorption capacity experimentally proved in batch tests and demonstrated a great ability of this material to retain heavy metal mass during the transport in solution within porous media.

1 Introduction

One of the main concerns in urban landfills is the possible migration of leachate with the consequent soil and groundwater contamination. Leachates represent complex mixtures of substances including dissolved organic matter, inorganic matter (ammonia–nitrogen, nitrate-nitrogen, total phosphorus), inorganic macro-components, heavy metals, and a wide range of xeno-biotic organic compounds (Kjeldsen et al., 2002; Ye et al., 2019). Many of these substances are hazardous and toxic to human health and the environment (Vaverková et al., 2019). Heavy metals such as Cu(II), Zn(II), Cd(II), and Ni(II) are considered harmful for human health when exceed the tolerance levels and are frequently founded in large amounts in different kinds of waste and landfill leachates (Cuevas et al., 2008; Kylefors, 2003; Lo et al., 2009; Long et al., 2011; Suna Erses et al., 2005). Therefore, migration of these compounds must be avoided and leachate should not migrate outside landfill cells to reduce their impact on the ecosystems.

Leachate migration is commonly controlled by a multiple barrier system that includes geomembranes and compacted clay liners with a low hydraulic conductivity and a high adsorption capacity (Bouazza & Van Impe, 1998; Rowe, 2005). Bentonites have been used for many years as a component of clay liners due to their suitable physical and chemical properties to isolate flow and adsorb heavy metals (Atkovska et al., 2016; Ayari et al., 2005; Koch, 2002; Li et al., 2015; Mishra et al., 2011; Musso et al., 2016; Nath, 2020; Scalia et al., 2018). In this application, they are generally utilized in combination with natural soils or sand and synthetic materials (e.g., compacted clay liners (CCL) or geosynthetic clay liners (GCL)) (Daniel, 1993).

Heavy metal sorption from aqueous solutions through clay minerals is highly influenced by pH and ionic strength (Chen et al., 2011; Francisca & Glatstein, 2020; Mnasri-Ghnimia & Frini-Srasraa, 2019). In a landfill leachate, these parameters change with time. During the initial phase of a landfill, leachate pH is acid and later, in a methanogenic stage, the pH increases giving a range of pH between 4.5 and 9.0 depending on the landfill stabilization (Christensen et al., 2001). Despite studies about clay minerals behavior as adsorbents are usually referred to the adsorption of single compounds (organic or inorganic), wastewaters or leachates from waste deposits, usually contain both inorganic and organic compounds which compete for the adsorption sites (Ayala et al., 2008; Kylefors, 2003). The type and concentration of organic compounds present in a landfill leachate depend not only on the kind of waste but also on the landfill age (Paxéus, 2000; Rigobello et al., 2015). Humic substances, surfactants, and phenolic compounds are some of the organic compounds that can be found in landfill leachates (Christensen et al., 2001; Reitzel & Ledin, 2002; Sakai et al., 2000). In general, organic compounds affect the sites adsorption reactivity of clay minerals (Wu et al., 2015; Zhang et al., 2015). Moreover, humic substances play an important role retaining heavy metals due to its hydrophilic nature and ionizable oxygen groups (Covelo et al., 2007).

Most of the studies looking at heavy metal sorption by clay minerals have been conducted in batch setups and fewer studies deal with adsorption in dynamic systems. In the design of containment barriers, an understanding of the attenuation characteristics of clay liner components would improve barrier performance (Thornton et al., 2001). Column experiments can be used as an alternative to investigate the sorption and transport of metals and are considered to reflect field conditions of landfill clay liners allowing the evaluation of removal processes for large-scale applications (Contreras et al., 2017; Refaey et al., 2017).

Mudstones represent the major constituents of sedimentary basins worldwide. They are low-permeability sedimentary rocks with a high sorption capacity; consequently, they are important natural barriers that restrict leakage from waste disposal sites (Lin & Cheng, 2006). Numerous outcrops of Cretaceous-Tertiary calcareous mudstones are found in North

Patagonia Argentina. These mudstones are mainly composed of smectitic clay minerals and have suitable hydraulic properties to be used as clay liners when are compacted with sand (Musso et al., 2013). In addition to their known quality as physical barriers, some studies in equilibrium conditions performed on the clay fraction (< 2 μm) have demonstrated that these mudstones have a high heavy metal adsorption capacity from monometal solutions (Musso et al., 2014, 2017). Although this efficiency related to metal removal from aqueous solutions was previously described, there is no information on the sorption capacity of the raw material (clay minerals + non-clay minerals), which is the natural extraction condition in the quarry and the way this material is used in practical applications (e.g., landfill liners or surface impoundments). On the other hand, to the best of our knowledge, there are no adsorption studies performed on these mudstones from solutions containing organic and inorganic components as is the case of real leachates.

This paper focuses particularly on Cu(II) metal as model contaminant since it is one of greatest concern for regulators in terms of groundwater contamination through landfill leachates (Kaoser et al., 2005). Thus, the aim of the present study was to investigate the capacity of raw calcareous mudstones in the removal of Cu(II) from water through equilibrium and dynamic adsorption tests and to assess the effect of pH and organic compounds on the Cu(II) uptake.

2 Materials and Methods

2.1 Materials and Chemicals

A calcareous mudstone, named NTOL, was used to evaluate its potential as a sorbent material for Cu(II) uptake. This material belongs to Jagüel Formation of the Neuquén basin, North Patagonia Argentina. The mudstone meets the technical requirements outlined in the European, Japanese, and American legislations for use as clay liners (Chai & Miura, 2002), having hydraulic conductivities lower than 1×10^{-9} ms^{-1} permeated with water and with real leachate in mixtures with sand (Musso et al., 2017). For comparison purposes, a commercially available bentonite, named CATAE, was used as a reference material performing as well, all the tests on this clay. The mudstone and

the bentonite have the consistency of hard rock and were crushed and then milled resulting in powdered samples with a size of about 80 μm. Physicochemical and mineralogical properties of the samples were previously published (Table S1, in the supporting information).

A high resolution LEO 1530 (Zeiss) scanning electron microscope (SEM) was used to observe the morphology of the mineralogical constituents of the calcareous mudstone.

In order to complete the characterization of the sorbents, thermal analysis, both, thermogravimetric (TGA) and differential thermal analyses (DTA) were carried out by a Simultaneous Thermal Analyzer (Netzsch STA 409/c). The non-isothermal analysis was conducted in the temperature range of 20–1100 °C at 10 °C/min heating rate and in circulating air atmosphere.

For the column experiments, the clays were mixed with a commercial fluvial sand classified as poorly graded ("SP" according to the Unified Soil Classification System), to simulate typical isolation materials used in liners.

Analytical grade $Cu(NO_3)_2.3H_2O$ salt used as Cu(II) source was purchased from Sigma-Aldrich Co. and metal quantification was performed by atomic absorption spectroscopy (AAS) (Analyst 200, Perkin-Elmer). NaOH and HCl solutions were used for pH adjustment, and 0.08 M of NaCl solution was prepared for ionic strength control. Leonardite humic acid (LHA) was purchased from International Humic Substances Society. Commercial LAS (sodium salt of dodecylbenzene sulfonate, 80%) and phenol (98%) from Sigma Chemical Company Ltd. were used as received.

2.2 Methods

2.2.1 Batch Sorption Tests

Adsorption kinetics was initially done to evaluate the time needed to achieve equilibrium of Cu(II) adsorption by the raw calcareous mudstone and bentonite. A total of 0.635 g of sorbent was added to 500 mL of 3 mg L^{-1} initial Cu(II) solution at $pH = 5.5$. The flask was then placed on a shaker (200 rpm) under constant agitation at 25° ± 1 °C. At regular intervals, 10 mL of solution was withdrawn, filtered through a 0.45 μm syringe acetate filters

(Scharlab) and the concentration of the remaining Cu(II) in solution (C) was measured. The amount of Cu(II) adsorbed at a time t was calculated by the difference between the initial and the final Cu(II) concentration (Eq. 1) as follows:

$$q_e = \frac{(C_i - C_e) * V}{W} \tag{1}$$

where q_e is the equilibrium concentration of Cu(II) in solid phase (mg g^{-1}); C_i and C_e are the initial and equilibrium concentrations (mg L^{-1}) of Cu(II) in solution, respectively; and V and W represent the volume of the solution (L) and mass of the sorbent (g), respectively.

Monometal adsorption isotherms were obtained by mixing 0.031 g of raw clay sample with 25 mL of metal solutions containing various concentrations of Cu(II) (3–220 mg L^{-1}). The lower concentrations of these solutions are similar to the average Cu(II) concentrations determined in an Argentinean urban waste leachate (Francisca & 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 pH and ionic strength were selected to simulate a leachate in the acetogenic stage. The mixtures were shaken in a rotative shaker for 6 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 clay was calculated by mass balance from the initial concentration Ci, and the final (equilibrium) concentration Ce, in the supernatant following Eq. 1. All batch tests described in this section were performed in duplicate in order to verify the reproducibility of results. Experimental results were analyzed using Langmuir and Freundlich isotherm models, Eqs. (2) and (3), respectively:

$$q_e = \frac{C_s . K_L . C_e}{1 + K_L C_e} \tag{2}$$

$$q_e = K_F . C_e^{1/n} \tag{3}$$

where C_s is the maximum adsorption capacity (mg g^{-1}), K_L is the adsorption coefficient of the

Langmuir model (L mg^{-1}), and K_F and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively.

In the study of pH effect on Cu(II) removal, the same procedure to obtain adsorption isotherms was carried out. For these experiments, Cu(II) concentration was 2.5 mg/L in order to assure the exclusive presence of aqueous Cu(II) species in all the analyzed pH range. pH range studied was 3–9 to simulate the typical pH-range found in the leachate during the aging of landfills. In this case, ionic strength condition was maintained constant at 0.08 M. In order to evaluate the dissolution of calcite, a portion of the supernatant obtained from the pH effect experiment after the adsorption of Cu(II) was separated for calcium analysis by AAS.

Different concentrations of HA (1–10–50 mg/L), phenol (1–25–50 mg/L), and anionic surfactant (LAS) (1–25–50 mg/L) were tested with the aim of describing their effect on the sorption of Cu(II) on clay materials. HA effect was also evaluated on clay fraction (< 2 μm). The supernatant of clay-HA (50 mg/L)-Cu(II) complexes after they have reached equilibrium was analyzed by UV-spectroscopy to quantify the percentage of HA retained by the clay.

2.2.2 Column Sorption Test

Continuous flow columns tests were used to evaluate Cu(II) uptake in dynamic systems on calcareous mudstone-sand mixtures and bentonite–sand mixtures. The composition of the columns was 25% of NTOL and 12% of CATAE using sand as a granular material. These percentages were selected considering hydraulic requirements stipulated by international regulations to be used as isolating barriers (Musso et al., 2017). The samples were prepared by mixing sand, powder mudstone/bentonite, and tap water and cured in plastic bags for 24 h. The water content of the mixtures was 2% wet of the optimum water content (i.e., 12.5%) obtained in previous Proctor Compaction Tests (ASTM D698-07e1 2007). Subsequently, the samples were compacted in rigid wall columns and the procedure for hydraulic conductivity measurements by the falling head method was followed (ASTM D5856-95 2007). The column test set up is shown schematically in Fig. S1, in the supporting information. The samples were permeated initially with deionized water and subsequently, with

the Cu(II) solution containing 10 mg L^{-1} of Cu(II). pH and ionic strength of the solution were adjusted to 5.5 and 0.08 M respectively.

The metal concentration, C, of the effluent collected from the bottom of the column was measured over time plotting the results as solute breakthrough curves (relative concentration (C/C_0) versus pore volumes (PV)). The value of number of pore volume effluent (PVE) necessary to reach a ratio of $C/C_0 = 0.5$ is used to calculate retardation and adsorption coefficients (Sharma & Reddy, 2004). All measurements were conducted in triplicate.

Numerical Modeling of Mass Transport The expected behavior of the metal transport through the soil columns is controlled by the well-known advection and hydrodynamic dispersion with sorption equation (Sharma & Reddy, 2004):

$$D_L^* \frac{\partial^2 C}{\partial x^2} - v_e \frac{\partial C}{\partial x} \pm \frac{r}{n_e} = \frac{\partial C}{\partial t} \qquad (4)$$

where C (kg/m^3) is the contaminant concentration, D_L^* (m^2/s) is the longitudinal hydrodynamic dispersion coefficient, n_e is porosity, v_e (m/s) is the seepage velocity, $r = -(B_d/\theta).(\partial C^*/\partial t)$ (kg/m^3/s) is the rate of mass consumption due to reaction inside the porous media, B_d (kg/m^3) is bulk density of porous media, θ is the volumetric water content ($=$porosity for saturated media), and C* is the adsorbed mass on soil particles per unit weight of solids. The amount of either Cu(II) or any other metal adsorbed is related to the initial concentration by means of Eqs. (2) and (3).

Sorption columns can be simulated as 1D problem and therefore the analytical solution provided by Ogata and Banks (1961) can be used to predict the evolution of metal concentration over the space and time:

$$C_{(x,t)} = \frac{C_0}{2} \mathrm{erfc} \left[\frac{R.x - v.t}{2\sqrt{D_L^*.t.R}} \right] \qquad (5)$$

where R is the retardation factor estimated in this work from the calibrated Langmuir isotherms according to Eq. 6 (Sharma & Reddy, 2004):

$$R = 1 + \frac{B_d}{\theta} \left[\frac{K_L.C_s}{(1 + K_L.C_e)^2} \right] \qquad (6)$$

3 Results and discussion

3.1 Characterization of the Sorbents

The mineralogy of the mudstone is dominated by a R0 illite/smectite mixed layer (80% Sm), with a slightly crenulated to flaky morphology and biogenic calcite (calcareous nannofossils) (10%) (Fig. 1) (Table S1 in the supporting information). Calcareous nannofossils are mainly constituted by coccoliths which consists of minuscule CaCO$_3$ structures produced by unicellular phytoplankton (Müller 2019). The size of the coccoliths is between 2 and 3 μm and they are highly porous (Fig. 1A and C).

Thermal analyses of the samples are presented in Fig. S2, in the supporting information. The curves show that the bentonite had a higher percentage of mass loss than the calcareous mudstone in the studied temperature range (18% vs 13%, respectively). In both cases, the main losses are due to 8–10% removal of adsorbed and interlayer water (0–300 °C), 2–4% removal of OH groups (dehydroxylation) (560–690 °C), and 3–4% corresponding to a S-shaped endo-exotherm at 850–950 °C which indicates the formation of new phases (Fajnor and Kesenák, 1996). Differences in dehydroxilation temperatures between the analyzed materials are related to the existence of OH groups in various local environments in the case of the interstratified 2:1 clay mineral in NTOL. Also, in calcareous mudstone NTOL, an additional endothermic peak is observed at 811 °C related to decomposition of calcite into CaO and release of CO$_2$ (Shahraki et al., 2011) confirming also the presence of this mineral phase in the mudstone.
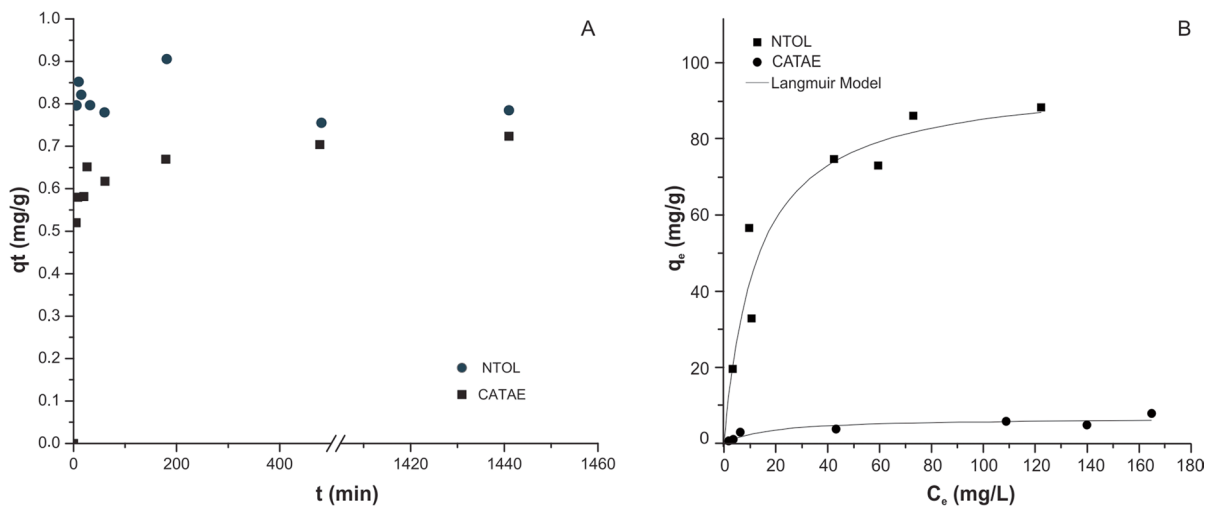
3.2 Effect of Contact Time on Cu(II) Sorption

Figure 2A shows the amount of Cu(II) removed with respect to contact time. For the bentonite CATAE, it is observed that the rate of removal from solution was initially fast in the first 50 min and then diminished gradually until an equilibrium time beyond which there was no significant increase in the removal rate (at ∼ 1400 min). On the other hand, in NTOL mudstone, the reaction was almost instantaneously achieving equilibrium removal before 5 min of contact and reveling an ultrafast removal rate compared with the bentonite. This is in agreement with other sorption studies performed on
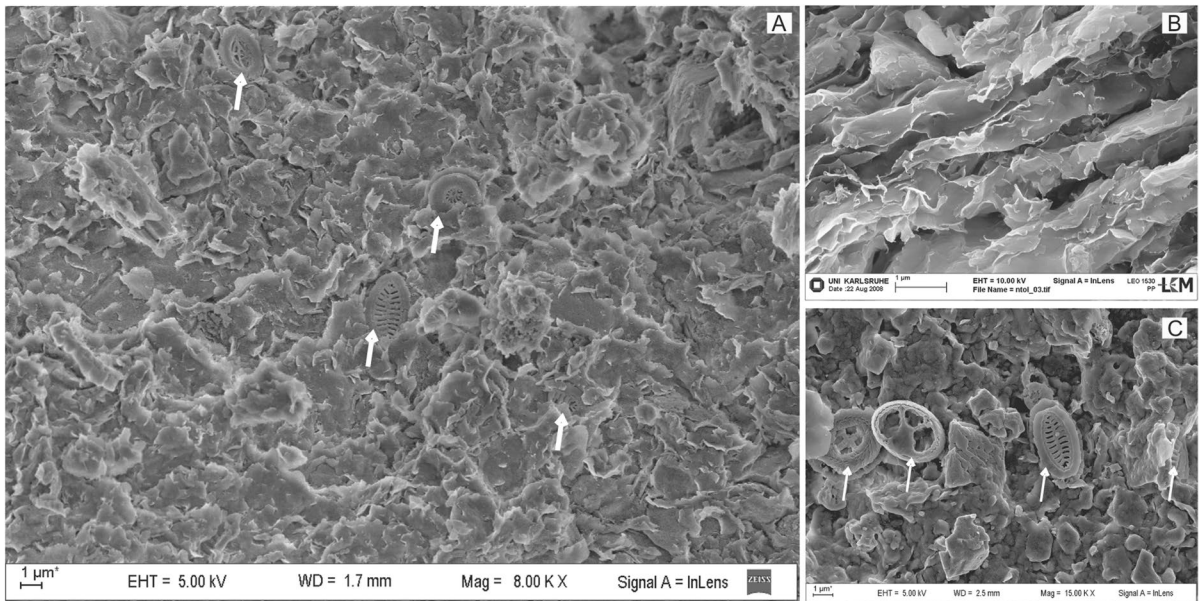
Fig. 1 **A** SEM image of NTOL calcareous mudstone showing oriented bioclasts (calcareous nanofossils) scattered in a laminated clay groundmass (white arrows). **B** Illite/smectite-mixed layer particles showing crenulated morphology and laminar microfabric. **C** Detail of the high porosity of coccoliths included in clay (white arrows)

Fig. 2 **A** Effect of contact time on Cu(II) sorption. Initial metal concentration 3 mg/L, clay dosage 0.635 g/500 mL, pH 5.5, $T = 25$ °C. **B** Sorption isotherms of Cu(II) of the calcareous mudstone NTOL and the bentonite CATAE

calcareous materials which also reported very fast kinetics (Perez-Sirvent et al. 2019). This information indicates that all adsorption data obtained after these times can be considered obtained under equilibrium conditions.

3.3 Effect of Metal Concentration on Cu(II) Sorption

Sorption isotherms of Cu(II) of the calcareous mudstone and the bentonite are shown in Fig. 2B. In both materials, sorption isotherms follow L-shaped type

similar to that described by Sposito (1984) indicating a high affinity between sorbent and solute. However, at low initial concentrations, NTOL isotherms have a much higher slope than CATAE isotherms revealing a higher affinity for NTOL which decreases as Cu(II) concentration increases.

The Langmuir and Freundlich isotherms were used to model the experimental data (Table 1). The obtained Freundlich parameters showed that the adsorption intensities (n_f) were higher than 1 (1/n closer to 0) showing that the adsorption process is more likely to be heterogeneous (Fierro et al., 2008). The Freundlich constants (K_F) show the interaction between metal ions and adsorbents, and the higher this value, the better adsorption will proceed (Kakaei et al., 2020). In this regard, NTOL sample had higher K_F than the bentonite CATAE.

The C_s value of NTOL calcareous mudstone for adsorbing Cu(II) was 15 times higher than the bentonite CATAE (Table 1) and also significantly higher than other calcareous materials (Table 2). On the other hand, the C_s of the bentonite CATAE for Cu(II) was close to those values reported in literature for other Na-bentonites (< 10 mg/g) (Abollino et al., 2003; Andini et al., 2006; García-Sánchez et al., 1999; Ling et al., 2007).

Even though the calcareous mudstone has a higher adsorption capacity, cation exchange capacity value for NTOL sample is almost the half than the bentonite CATAE (Table S1 in the supporting information). This indicates that the intrinsic ion exchange capacity of this sample is not high enough to remove large amounts of Cu(II) via ion-exchange mechanism. Therefore, these results would reflect the influence of the mineralogical differences between the calcareous mudstone and the bentonite in sorption processes.

In NTOL calcareous mudstone, three mineral components could be involved in Cu(II) removal processes from the solution: (1) the smectitic clay component of the I/S-mixed layer; (2) illite, and (3) calcite. Mechanisms of Cu(II) sorption on the smectitic clay component of the I/S-mixed layer would be cationic exchange reactions with Ca^{2+} and H^+ ions located in the basal surfaces and at the edges of clay particles, respectively (Abollino et al., 2003; Kaya & Ören, 2005; Musso et al., 2019; Vhahangwele & Mugera, 2015; Zhang et al., 2011). In the case of illite, previous results have shown that the percentage of this clay mineral becomes an important factor in metal adsorption at pH higher than 6 where complexation reactions on the edge sites predominate (Alvarez-Puebla et al., 2005; Gu & Evans, 2007; Missana et al., 2008; Wu et al., 2011).

Heavy metals can be sorbed on the surface of calcite which has been described as a significant metal-scavenging process in water and soil environments as well as in waste systems (García-Sánchez & Alvarez-Ayuso, 2002). In NTOL mudstone, calcite is in the form of very small and highly porous bioclasts (calcareous nannofossils) (Fig. 1) which would contribute with a higher BET specific surface (Table S1 in the supporting information) and therefore with sorption processes. Most common sorption processes onto calcite surface include outer-sphere or inner-sphere

Table 1 Isotherms coefficients according to Freundlich and Langmuir

|	Freundlich			Langmuir		
	K_F (L/g)	n_f	R^2	K_L (L/mg)	C_s (mg/g)	R^2
NTOL total sample	11.65	2.26	0.84	0.05	103.24	0.93
CATAE total sample	0.80	2.42	0.88	0.05	6.75	0.85

Table 2 Comparison of Langmuir maximum adsorption capacities (Cs) of other natural calcareous materials for Cu(II) removal from aqueous solutions

Adsorbent	Reference	Cu(II) C_s (mg/g)
Calcareous soil (38% $CaCO_3$) (pH 5)	Baghernejad et al., 2015	45.5
Calcareous soil (27% $CaCO_3$) (pH 5)	Baghernejad et al., 2015	50.0
Calcareous clay (26.7% $CaCO_3$) (25 °C, pH 6)	Sdiri et al., 2014	27.39–17.88
Calcareous soil (12% $CaCO_3$) (20 °C)	Rodríguez-Rubio et al., 2003	6.93
Calcareous soil (25 °C)	Echeverría et al., 1998	19.46
Calcareous mudstone NTOL (25 °C, pH 5.5)	This work	**103.24**

adsorption of ions at the calcite-water interface, ion-exchange reactions in the calcite surface monolayer, and the incorporation of trace elements into calcite (Heberling et al., 2014). Coprecipitation processes have been also described when the concentrations of trace elements are rather high (Gaskova et al., 2009; Perez-Sirvent et al., 2019).

As calcite is an important component of the NTOL calcareous mudstone, the differences between Cu(II) sorption capacities may be due to its affinity to the surface of calcite.

The precipitation of Cu(II) on the surface of sorbents is probable considering the dissolution of calcite under the conditions of this study. According to Al-Degs et al. (2006), the precipitation of heavy metals (M) as carbonate (MCO_3) or hydroxycarbonate ($M_2(OH)_2CO_3$) can occur in the presence of calcite. It can be calculated that the formation of metal hydroxycarbonates ($M_2(OH)_2CO_3$) is not possible for Cu(II) under the experimental conditions of this study, as follows. Hydrolysis of Cu(II) ions by water can be presented as:

$$Cu^{2+}(aq)H_2O(L) \rightleftharpoons Cu(OH)^+(aq) + H^+(aq) \quad K_{a1} = 1.096 \times 10^{-8} \tag{7}$$
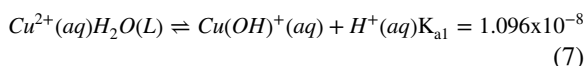
The equilibrium constant expression can be written as:

$$K_{a1} = \frac{[H^+][Cu(OH)^+]}{[Cu^{2+}]} \tag{8}$$

By calculating the value of $[H^+]$ at equilibrium from the studied pH (5.5), and substituting the K_{a1} and H^+ values into Eq. 8, the ratio $[Cu^{2+}]/[Cu(OH)^-]$ is reduced to the following equation:

$$\frac{[Cu^{2+}]}{[Cu(OH)^+]} = 288 \tag{9}$$

This indicates that the concentration of free divalent Cu^{2+} is much higher than $Cu(OH)^+$ at pH 5.5, therefore, the following reaction is more likely to occur:

$$Cu^{2+}(aq) + CO_3^{2-} \rightleftharpoons CuCO_3 \tag{10}$$
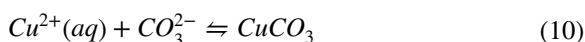
According to Harris (2010), the K_{sp} value for this reaction is 2.3×10^{-10}, thus, the minimum concentration of Cu(II) necessary to produce precipitation is 0.2 mg/L. Cu(II) equilibrium concentrations obtained

in this study exceed the maximum solubility value. Therefore, the presence of precipitated forms of $CuCO_3$ is highly probable in all the studied concentration range and tests conditions.

Based on the above analysis, the sorption mechanism of metals by the calcite in the calcareous mudstone can be represented by the following surface reactions (Al-Degs et al., 2006):
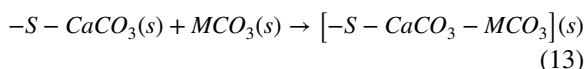
Dissolution of calcite that is present in the sorbent:

$$-S - CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) + S \tag{11}$$
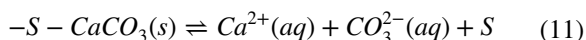
Interaction between the free metal (M^{2+}) in solution and (CO_3^{2-}) in solution can be described as:

$$M^{2+}(aq) + CO_3^{2-} \rightleftharpoons MCO_3 \tag{12}$$
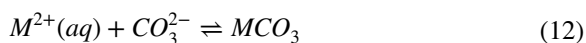
Deposition of MCO_3 on the sorbent surface:

$$-S - CaCO_3(s) + MCO_3(s) \rightarrow \left[-S - CaCO_3 - MCO_3\right](s) \tag{13}$$

where M^{2+}, $-S-CaCO_3$, and $-S-CaCO_3-MCO_3$ stand for the free metal cation in solution, the surface active sites for adsorption, and the metal-carbonate complex on the sorbent surface, respectively.

3.4 pH Effect on Cu(II) Sorption

The effect of solution pH on Cu(II) removal for NTOL and CATAE is presented in Fig. 3. In order to elucidate the contribution of $Cu(OH)_2$ chemical (or bulk) precipitation to the Cu(II) sorption, the change in removal percentage without the sorbent was examined under the same pH range. At pH lower than 6, the removal of Cu(II) from the solution by precipitation is lower than 10%, while at pH higher than 6, this percentage increases until a maximum value of 60% is reached at pH higher than 7.5. For the bentonite CATAE, a strong dependence of Cu(II) sorption with pH values was observed having low removal efficiency at low pH values which sharply increased at pH 6–7, and a constant maximum removal (90%) at pH > 7 (Fig. 3A). Compared with the curve without sorbent, the shape is very similar to that and a beneficial effect of bentonite in removal can be considered at pH > 6.5. The difference between the total removal and the removal by precipitation at pH > 6.5 is 30%, and this percentage could be attributed to the adsorption mechanism on the deprotonated aluminol and silanol groups of the clay, located at variable surface
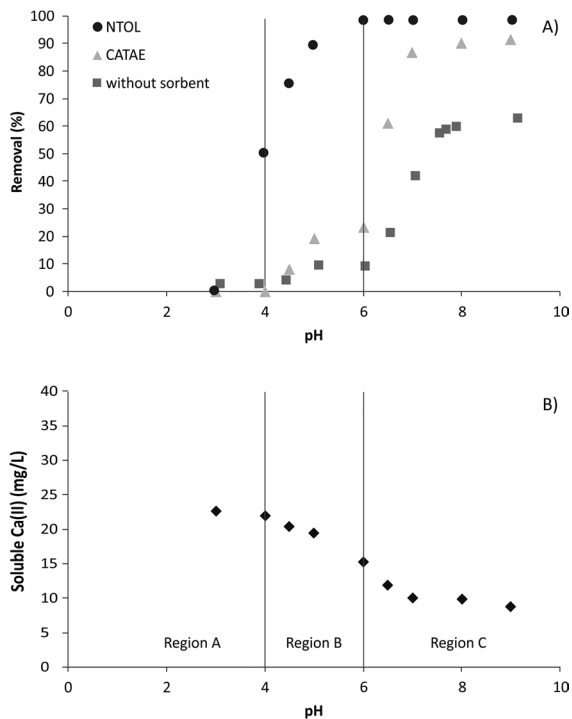
Fig. 3 Variation in removal percentages of Cu(II) as a function of pH (dose of adsorbent 1.24 g/L, ionic strength: 0.08 M, initial concentration of Cu(II): 2.5 mg/L) (**A**) and comparison between the removed Cu(II) by NTOL and calcium concentration of NTOL supernatants (**B**)

charged sites and on siloxanic groups located in permanent negative surface sites.

pH effect on Cu(II) sorption on NTOL was also evident but a very different pattern was observed. The curve can be divided into three regions (Fig. 3A). A region A (pH < 4) where no removal is possible, a region B (pH range ≤ 4 to < 6) where the removal efficiency is highly improved by the presence of the calcareous mudstone in a percentage between 50 and 80% more than the bentonite and the solution without the sorbent. Finally, a region C (pH > 6) where the calcareous mudstone removes a 10% more than the bentonite CATAE, reaching a 100% of removal.

In region B, the presence of Ca(II) in solution, in NTOL supernatants, indicated that dissolution of calcite is possible between pH 4 and 6 (Fig. 3B). Ca(II) liberation in this zone could be presumably caused by Cu(II) sorption which involves surface replacement of Ca(II) by Cu(II) towards the formation of a Cu-bearing co-precipitate. Thus, in this region, the higher removal could be related to the precipitation

of compounds that can be formed due to the dissolution of calcite. Apart from precipitation on the surface of the calcite, a small metal quantity could be also retained via ion-exchange mechanism with the released Ca(II) from calcite (Elzinga et al., 2006; Heberling et al., 2011).

At pH > 6, the removal is very high but the concentration of Ca(II) in solution decreased. In this case, a 60% of removal is by chemical precipitation and the remaining could be attributed to adsorption mechanisms on the smectitic component of the I/S, favored by a higher external specific surface compared with CATAE bentonite (Table S1 in the supporting information), where a higher contribution of deprotonated aluminol and silanol groups of the clay, located at variable surface charged sites on the edges of clay particles, is possible.

3.5 Organic Compounds Effect on Cu(II) Sorption

In order to evaluate the influence of some organic compounds in the adsorption capacity of heavy metals by the calcareous mudstone, experiments including additions of HA, phenol, and surfactant to monometallic solutions of Cu(II) were performed. Figure 4A shows Cu(II) removal in the presence of HA for raw and clay fraction of NTOL calcareous mudstone. In the case of the total sample, Cu(II) removal decreased by 11% at 1 mg/L HA content and this value remained constant at higher HA contents. For clay fraction, Cu(II) removal increases as the HA content increased. When the HA concentration increased 10 times, an increment of 6% of the removal percentage was observed. When this concentration is 50 times the initial value, the removal increment arises to 26%. On the other hand, the capacity of the total sample and clay fraction of bentonite CATAE to remove Cu(II) ions in the presence of HA was the same. In this case, the percentage of removal increased with the increment of HA content (Fig. 4B).

The HA percentage retained by the calcareous mudstone and bentonite after equilibrium was 88% and 90%, respectively, showing a high interaction between HA and the clays (data not shown). The HA can form either inner sphere or outer sphere coordination complexes onto clay minerals through surface carboxylic and hydroxyl functional groups, hydrogen bond, and hydrophobic forces (Chen et al., 2017; Filius et al., 2000; Weng et al.,
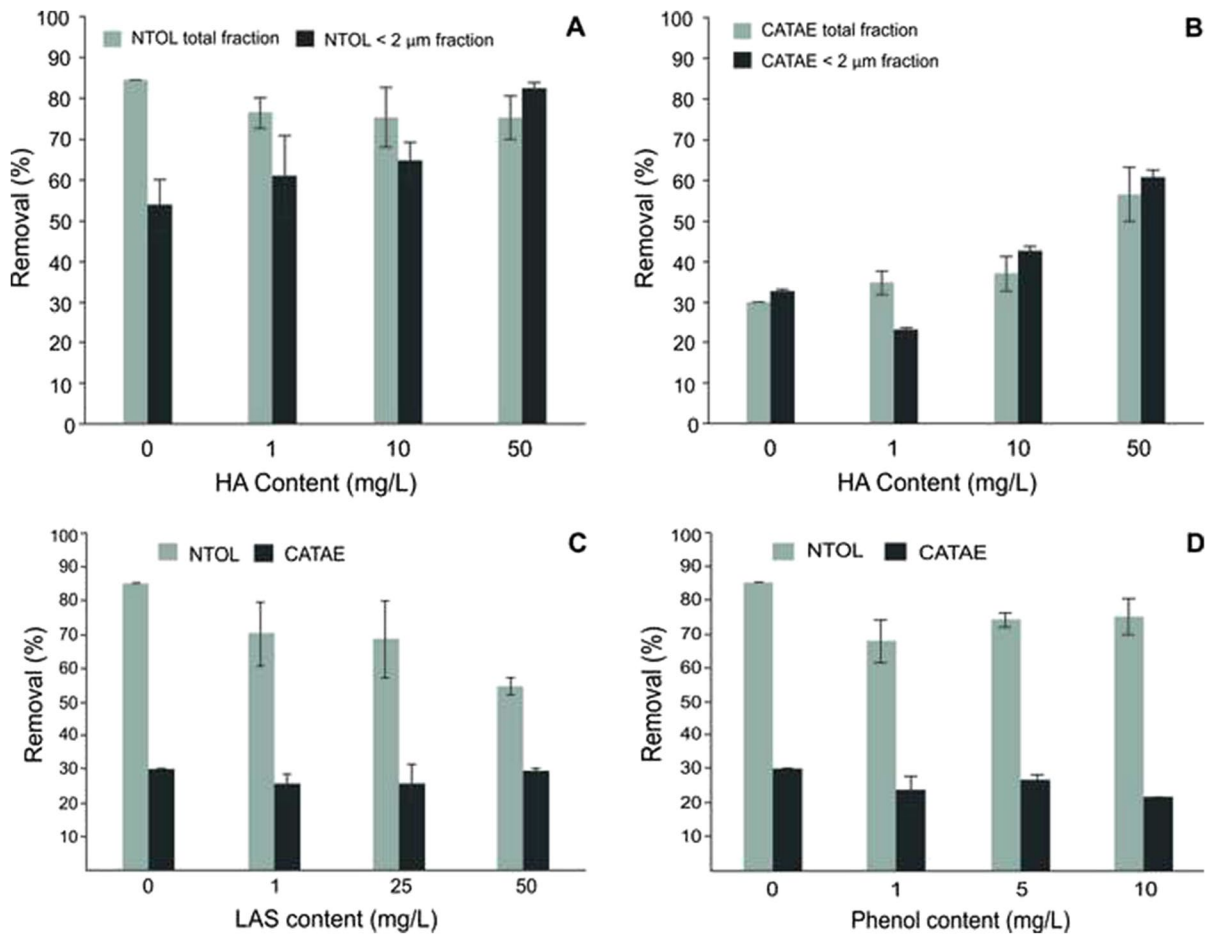
Fig. 4 Cu(II) removal effect in the presence of organic compounds. Cu(II) removal percentage in the presence of HA on calcareous mudstone NTOL (**A**) and bentonite CATAE (**B**); Cu(II) removal percentage in the presence of anionic surfactant (LAS) (**C**); Cu(II) removal percentage in presence of phenol (**D**). pH 5.5, $T = 25$ °C, ionic strength 0.08 M, initial concentration of Cu(II) 3 mg/L

2006). At the same time, humic acids have been well known to exert strong effect on the sorption of heavy metal ions because of its high complexation ability (Chen et al., 2012; Tang et al., 2014; Yang et al., 2011). In this way, Cu(II) sorption could occur on the surface of the clay minerals or on the surface of the adsorbed HA. According to Jada et al. (2006), Cu(II) ion decreases HA surface charge promoting the formation of HA-Me complexes.

Cu(II) removal in NTOL clay fraction is favored in the same way than in CATAE clay fraction due to the probed affinity of HA with clay minerals. This is also valid for total sample of the bentonite which is also mainly constituted by smectite.

Anionic surfactant (LAS) effect on Cu(II) uptake was different for each material (Fig. 4C). In calcareous mudstone NTOL, the Cu(II) removal decreased in a 35% at high LAS concentration (50 mg/L). Other studies have demonstrated that anionic surfactants can be effectively sorbed by carbonates and Ca^{2+} montmorillonites (Ma et al., 2013; Yang et al., 2007). In calcareous mudstone NTOL, calcite and a Ca^{2+} smectitic I/S-mixed layer are present. Thus, the LAS could interact with these minerals decreasing the active sites available for sorption and co-precipitation of Cu(II).

In bentonite CATAE, the Cu(II) uptake for different LAS concentrations remained very similar than

the obtained without the presence of the surfactant. Adsorption of surfactant in hydrophilic minerals may result from a direct interaction between the solid surface and the adsorbate species due to electrostatic, chemical, or other forces (Ananthapadmanabhan & Somasundaran, 1985; Ou et al., 1996). Potential Z studies performed on bentonite CATAE indicated that this material has a very high density of negative charges at the studied pH (Musso et al., 2014). Therefore, it is expected that electrostatic repulsion occurs between the surface negative charge of the solid and the LAS. For this reason, this component would not interact with bentonite active sorption sites and the Cu(II) sorption would not be affected.

The Cu(II) uptake in calcareous mudstone and bentonite as a function of the concentration of phenol is shown in Fig. 4D. Within the experimental condition tested, the effect of the presence of phenol on both materials is quite similar, causing a slight decrease of Cu(II) removal (5–10%). Experiments of phenol binding to calcite and montmorillonites from aqueous solutions have demonstrated that this compound interacts with these minerals (Awad et al., 2019; Djebbar et al., 2012; Marcano et al., 2019). A decrease in the adsorption of Cu(II) ions with the increase of phenol concentration was observed by other studies, which have evaluated the competitive adsorption of phenol and Cu(II) onto a heat treated bentonite (Banat et al., 2001). However, in the experimental conditions of this study, phenol did not evidence a significant effect on Cu(II) removal.

3.6 Column Test Results

Commonly, the determination of transport adsorption parameters is achieved by using breakthrough curves (BTCs), which show the relationship between the effluent concentration and time (Shackelford, 1994). The number of pore volume effluent (PVE) and testing time obtained from column test is shown in Table 3.

It can be observed the time consuming nature of this kind of tests and the low number of PVE obtained for both materials, especially for the bentonite CATAE which has the lowest hydraulic conductivity. The measured eluted concentration of Cu(II) from the PVE of NTOL filled columns was negligible (<0.1 mg/L). Physicochemical reactions between metals and NTOL particles produced a high retardation on the advancing front of contaminant inside the soil column. The magnitude of the calibrated sorption resulted very significant and therefore was not possible to determine the retardation factor in direct way. Then, retardation factor was computed from the calibrated Langmuir isotherm (Eq. 6) and then incorporated in the analytical solution of the advection–dispersion equation (Eq. 5). The calculated R values, considering the percentage of these clays in the columns were 3576 for NTOL and 113 for CATAE, demonstrating a greater ability of the calcareous mudstone to retain heavy metal mass during the transport in solution within the soil. Common retardation factors for other heavy metals observed in sand-bentonite mixtures are in the same order than the obtained here for CATAE (Chalermyanont et al., 2008).

Figure 5 presents the expected Cu(II) transport in the tested fixed-bed columns filled with NTOL according to Ogata and Banks (1961) (Eq. 5). Reactions between the metals in solution and NTOL particles are responsible for the negligible eluted concentration of Cu(II) indicating that the calcareous mudstone in the column did not reach its adsorption capacity. The oncoming front of heavy metals being transported through the column had

Table 3 Hydraulic conductivity values (k), testing time (time in which the test is finished according to the criteria published in ASTM D5856-95 2007 norm) and pore volume effluent (PVE) of compacted sand-mudstones mixtures and sand-bentonite mixtures obtained from the column test

Column composition	Permeant fluid	$k\ (m/s)^{*}$	Std Dv	Testing Time (days)*	PVE*
NTOL 25%	Deionized water	1.37×10^{-10}	3.91×10^{-11}	70	1
	Monometal Cu(II)	4.67×10^{-10}	9.70×10^{-11}	365	18
CATAE 12%	Deionized water	4.00×10^{-11}	5.82×10^{-12}	250	1
	Monometal Cu(II)	2.50×10^{-11}	7.99×10^{-12}	507	1

* mean values

Fig. 5 Model calculated Cu(II) breakthrough curve for compacted calcareous mudstone-sand mixtures filled column. The experimental conditions were as follows: column length 50 mm; column diameter 43 mm; hydraulic gradient 16–25; metal concentration 10 mg/L
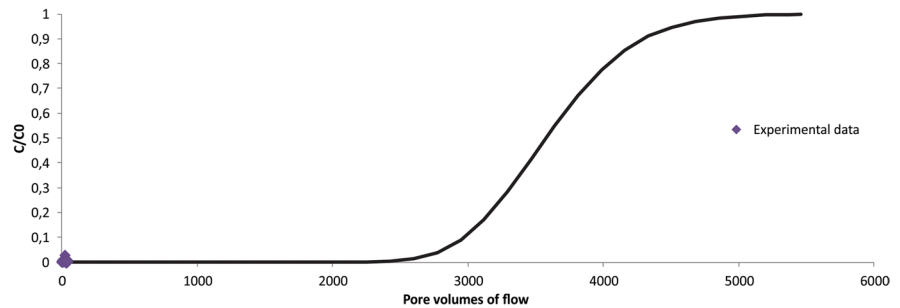
very low displacement in the experimental time (365–490 days) given the retardation due to the sorption mechanisms demonstrated by means of batch tests. The expected percolation of the Cu(II) front is close to pore volume of effluent $PVE = 3500$, which is equivalent to 11 years.

Data shown in Fig. 5 indicate that a clay barrier constructed with NTOL calcareous mudstone would have a very good performance to restrict the displacement of Cu(II) metal ion.

4 Conclusions

The results of this study indicate that the calcareous mudstone can be successfully used for Cu(II) ions removal from aqueous solutions. The kinetic studies indicated that the equilibrium for Cu(II) sorption was almost instantaneously reveling an ultrafast adsorption rate. This material, as it is extracted from the quarry, exhibited higher removal capacity in a wider pH range (4–9) than a commercial Na-bentonite which is a widely used heavy metal sorbent. The difference in the mineralogical composition of these materials would be the responsible for the higher Cu(II) removal capacity of the calcareous mudstone. In NTOL calcareous mudstone, calcite is present as an important constituent in the form of very small and highly porous calcareous nannofossils which contributed with the Cu(II) removal probably mainly through precipitation.

Cu(II) sorption was favored by the presence of humic acids in the clay fraction (< 2 μm) of both materials revealing the high affinity of this compound with the surface of clay minerals and the subsequent formation of HA-Me complexes. The presence of an anionic surfactant or phenol slightly affected the removal of Cu(II) indicating a low interaction of these compounds with the reactive minerals of the sorbents (calcite and smectite).

Column test results complemented the batch type experiments with a closer approximation to field conditions. In this study was observed that the period to breakthrough can be too long for materials with low hydraulic conductivities and high sorption capacity. Estimated retardation factor and numerical simulations of the expected Cu(II) transport in the tested fixed-bed columns filled with NTOL indicated that the migration of Cu(II) in the columns was significantly retarded by the calcareous mudstone. The extremely high retardation factor obtained for NTOL as raw material is in good agreement with the high adsorption capacity experimentally proved in batch tests. Calculated Cu(II) breakthrough curve indicated that Cu(II) ions would begin to percolate after 11 years of testing. The introduction of a calcareous mudstone in compacted clay barriers design is highly recommended to ensure long term retention of heavy metals.

References

Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., & Mensasti, E. (2003). Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research, 37*, 1619–1627. https://doi.org/10.1016/S0043-1354(02)00524-9

Al-Degs, Y., El-Barghouthi, M. I., Issa, A. A., Khraisheh, M. A., & Walker, G. M. (2006). Sorption of Zn(II), Pb(II) and Co(II) using natural sorbents: Equilibrium and kinetic studies. *Water Research, 40*, 2645–2658. https://doi.org/10.1016/j.watres.2006.05.018

Alvarez-Puebla, E., Dos Santos Jr, D. S., Blanco, C., Echeverria, J. C., & Garrido, J. J. (2005). Particle and surface characterization of a natural illite and study of its copper retention. *Journal of Colloid and Interface Science, 285*, 41–49. https://doi.org/10.1016/j.jcis.2004.11.044

Ananthapadmanabhan, K. P., & Somasundaran, P. (1985). Surface precipitation of inorganics and surfactants and its role in adsorption and flotation. *Colloids and Surfaces, 13*, 151–167. https://doi.org/10.1016/0166-6622(85)80014-7

Andini, S., Cioffi, R., Montagnaro, F., Pisciotta, F., & Santoro, L. (2006). Simultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite. *Applied Clay Science, 31*, 126–133. https://doi.org/10.1016/j.clay.2005.09.004

ASTM Standard D698–07e1 (2007). Standard test methods for laboratory compaction characteristics of soil using standard effort (12 400 ft-lbf/ft3 (600 kNm/m3), ASTM International. http://www.astm.org/cgi-bin/resolver.cgi?D698.

ASTM Standard D5856–95 (2007). Standard test method for measurement of hydraulic conductivity of porous material using a rigid-wall, Compaction-Mold Permeameter, ASTM International, http://www.astm.org/cgi-bin/resolver.cgi?D5856-15.

Atkovska, K., Bliznakovska, B., Ruseska, G., Bogoevski, S., Boskovski, B., & Grozdanov, A. (2016). Adsorption of Fe(II) and Zn(II) ions from landfill leachate by natural bentonite. *J Chem Technol Metall, 51*(2), 215–222.

Ayala, J., Vega, J. L., Alvarez, R., & Loredo, J. (2008). Retention of heavy metal ion bentonites from Grau Region (Northern Peru). *Environmental Geology, 53*, 1323–1330. https://doi.org/10.1007/s00254-007-0740-8

Ayari, F., Srasra, E., & Trabelsi-Ayadi, M. (2005). Characterization of bentonitic clays and their use as adsorbent. *Desalination, 185*, 391–439. https://doi.org/10.1016/j.desal.2005.04.046

Awad, A. M., Shaikh, S. M. R., Jalab, R., Gulied, M. H., Nasser, M. S., Benamor, A., & Adham, S. (2019). Adsorption of organic pollutants by natural and modified clays: A comprehensive review. *Separation and Purification Technology, 228*, 115719. https://doi.org/10.1016/j.seppur.2019.115719

Baghernejad, M., Javaheri, F., & Moosavi, A. A. (2015). Adsorption isotherms of copper and zinc in clay minerals of calcareous soils and their effects on X-ray diffraction. *Arch Agron Soil Sci, 61*(8), 1061–1077. https://doi.org/10.1080/03650340.2014.982549

Banat, F., Al-Asheh, S., & Abu-Aitah, L. (2001). Competitive adsorption of phenol, copper ions and nickel ions on to heat treated bentonite. *Adsorp Sci Technol, 20*(2), 107–117. https://doi.org/10.1260/026361702320360531

Bouazza, A., & Van Impe, W. F. (1998). Liner design for waste disposal sites. *Environmental Geology, 35*(1), 41–54. https://doi.org/10.1007/s002540050291

Chai, J. C., & Miura, N. (2002). Comparing the performance of landfill liner systems. *Journal of Material Cycles and Waste Management, 4*, 135–142. https://doi.org/10.1007/s10163-002-0065-3

Chalermyanont, T., Arrykul, S., & Charoenthaisong, N. (2008). Transport of heavy metals and chemical compatibility of hydraulic conductivity of a compacted sand-bentonite mixture. *Songklanakarin Journal of Science and Technology, 30*(2), 269–276.

Chen, Y. G., Ye, W. M., Yang, X. M., Deng, F. Y., & He, Y. (2011). Effect of contact time, pH, and ionic strength on Cd(II) adsorption from aqueous solution onto bentonite from Gaomiaozi. *China. Environ Earth Sci, 64*(2), 329–336. https://doi.org/10.1007/s12665-010-0850-6

Chen, Q., Yin, D., Zhu, S., & Hu, X. (2012). Adsorption of cadmium(II) on humic acid coated titanium dioxide. *Journal of Colloid and Interface Science, 367*(1), 241–248. https://doi.org/10.1016/j.jcis.2011.10.005

Chen, H., Koopal, L. K., Xiong, J., Avena, M., & Tan, W. (2017). Mechanisms of soil humic acid adsorption onto montmorillonite and kaolinite. *Journal of Colloid and Interface Science, 504*, 457–467. https://doi.org/10.1016/j.jcis.2017.05.078

Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., Albrechtsen, H.-J., & Heron, G. (2001). Biogeochemistry of landfill leachate plumes. *App Geochem, 16*(7–8), 659–718. https://doi.org/10.1016/S0883-2927(00)00082-2

Contreras, S., Henríquez-Vargas, L., & Álvarez, P. I. (2017). Arsenic transport and adsorption modeling in columns using a copper nanoparticles composite. *J Water Process Eng, 19*, 212–219. https://doi.org/10.1016/j.jwpe.2017.08.001

Covelo, E. F., Vega, F. A., & Andrade, M. L. (2007). Competitive sorption and desorption of heavy metals by individual soil components. *Journal of Hazardous Materials, 140*(1–2), 308–315. https://doi.org/10.1016/j.jhazmat.2006.09.018

Cuevas, J., Leguey, S., Garralon, A., Rastrero, M., Procopio, J., Sevilla, M., Jimenez, N., Abad, R., & Garrido, A. (2008). Behavior of kaolinite and illite-based clays as landfill barriers. *Applied Clay Science, 42*, 497–509. https://doi.org/10.1016/j.clay.2008.06.017

Daniel, D. E. (1993). *Geotechnical practice for waste disposal*. Chapman and Hall.

Djebbar, M., Djafri, F., Bouchekara, M., & Djafri, A. (2012). Adsorption of phenol on natural clay. *Applied Water Science, 2*, 77–86. https://doi.org/10.1007/s13201-012-0031-8

Echeverría, J. C., Morera, M. T., Mazkiarin, C., & Garrido, J. J. (1998). Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environmental Pollution, 101*, 275–284. https://doi.org/10.1016/S0269-7491(98)00038-4

Elzinga, E. J., Rouff, A. A., & Reeder, R. J. (2006). The long-term fate of Cu^{2+}, Zn^{2+}, and Pb^{2+} adsorption complexes

at the calcite surface: An X-ray absorption spectroscopy study. *Geochimica Et Cosmochimica Acta, 70*, 2715–2725. https://doi.org/10.1016/j.gca.2006.02.026

Fierro, V., Torne-Fernandez, V., Montane, D., & Celzard, A. (2008). Adsorption of phenol onto activated carbons having different textural and surface properties. *Microporous and Mesoporous Materials, 111*, 276–284. https://doi.org/10.1016/j.micromeso.2007.08.002

Filius, J. D., Lumsdon, D. G., Meeussen, J. C., Hiemstra, T., & Van Riemsdijk, W. H. (2000). Adsorption of fulvic acid on goethite. *Geochimica Et Cosmochimica Acta, 64*, 51–60. https://doi.org/10.1016/S0016-7037(99)00176-3

Francisca, F. M., & Glatstein, D. A. (2010). Long term hydraulic conductivity of compacted soils permeated with landfill leachate. *Applied Clay Science, 49*, 187–193. https://doi.org/10.1016/j.clay.2010.05.003

Francisca, F. M., & Glatstein, D. A. (2020). Environmental application of basic oxygen furnace slag for the removal of heavy metals from leachates. *Journal of Hazardous Materials, 384*, 121294. https://doi.org/10.1016/j.jhazmat.2019.121294

García-Sánchez, A., Alastuey, A., & Querol, X. (1999). Heavy metal adsorption by different minerals: Application to the remediation of polluted soils. *Science of the Total Environment, 242*, 179–188. https://doi.org/10.1016/S0048-9697(99)00383-6

García-Sánchez, A., & Alvarez-Ayuso, E. (2002). Sorption of Zn, Cd and Cr on calcite. Application to purification of industrial wastewaters. *Minerals Engineering, 15*, 539–547. https://doi.org/10.1016/S0892-6875(02)00072-9

Gaskova, O. L., Bukaty, M. B., Shironosova, G. P., & Kabannik, V. G. (2009). Thermodynamic model for sorption of bivalent heavy metals on calcite in natural-technogenic environments. *Russian Geology and Geophysics, 50*, 87–95. https://doi.org/10.1016/j.rgg.2008.06.018

Gu, X., & Evans, L. J. (2007). Modelling the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) onto Fithian illite. *Journal of Colloid and Interface Science, 307*(2), 317–325. https://doi.org/10.1016/j.jcis.2006.11.022

Harris, D. C. (2010). *Quantitative chemical analysis* (8th ed.). W.H. Freeman and Company.

Heberling, F., Trainor, T. P., Lutzenkirchen, J., Eng, P., Denecke, M. A., & Bosbach, D. (2011). Structure and reactivity of the calcite–water interface. *Journal of Colloid and Interface Science, 354*, 843–857. https://doi.org/10.1016/j.jcis.2010.10.047

Heberling, F., Bosbach, D., Eckhardt, J. D., Fischer, U., Glowacky, J., Haist, M., Kramar, U., Loos, S., Müller, H. S., Neumann, T., Pust, C., Schäfer, T., Stelling, J., Ukrainczyk, M., Vinograd, V., Vučak, M., & Winkler, B. (2014). Reactivity of the calcite–water-interface, from molecular scale processes to geochemical engineering. *Applied Geochemistry, 45*, 158–190. https://doi.org/10.1016/j.apgeochem.2014.03.006

Jada, A., Ait Akbour, R., & Douch, J. (2006). Surface charge and adsorption from water onto quartz sand of humic acid. *Chemosphere, 64*, 1287–1295. https://doi.org/10.1016/j.chemosphere.2005.12.063

Kakaei, S., Khameneh, E. S., Rezazadeh, F., & Hosseini, M. H. (2020). Heavy metal removing by modified bentonite and study of catalytic activity. *Journal of Molecular Structure,*

1199, 126989. https://doi.org/10.1016/j.molstruc.2019.126989

Kaoser, S., Barrington, S., Elektorowicz, M., & Wang, L. (2005). Effect of Pb and Cd on Cu adsorption by sand–bentonite liners. *Canadian Journal of Civil Engineering, 32*, 241–249.

Kaya, A., & Ören, A. H. (2005). Adsorption of zinc from aqueous solutions to bentonite. *Journal of Hazardous Materials, 125*, 183–189. https://doi.org/10.1016/j.jhazmat.2005.05.027

Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., & Christensen, T. H. (2002). Present and long-term composition of MSW landfill leachate: A review. *Crit Rev Env Sci Tec, 32*(4), 297–336. https://doi.org/10.1080/10643380290813462

Koch, D. (2002). Bentonites as a basic material for technical base liners and site encapsulation cut-off walls. *Applied Clay Science, 21*, 1–11. https://doi.org/10.1016/s0169-1317(01)00087-4

Kylefors, K. (2003). Evaluation of leachate composition by multivariate data analysis (MVDA). *Journal of Environmental Management, 68*, 367–376. https://doi.org/10.1016/S0301-4797(03)00103-8

Li, B., Li, L. Y., & Grace, J. R. (2015). Adsorption and hydraulic conductivity of landfill-leachate perfluorinated compounds in bentonite barrier mixtures. *Journal of Environmental Management, 156*, 236–243. https://doi.org/10.1016/j.jenvman.2015.04.003

Lin, T. T., & Cheng, C. H. (2006). Microanalytical characterizations of eroded and slaked mudstone proposed as landfill liner material. *Practice Periodical of Hazardous, Toxic, Waste Management, 10*, 128–133.

Ling, W., Shen, Q., Gao, Y., Gu, X., & Yang, Z. (2007). Use of bentonite to control the release of copper from contaminated soils. *Australian Journal of Soil Research, 45*, 618–623. https://doi.org/10.1071/SR07079

Lo, H. M., Lin, K. C., Liu, M. H., Pai, T. Z., Lin, C. Y., Liu, W. F., Fang, G. C., Lu, C., Chiang, C. F., Wang, S. C., Chen, P. H., Chen, J. K., Chiu, H. Y., & Wu, K. C. (2009). Solubility of heavy metals added to MSW. *Journal of Hazardous Materials, 161*, 294–299. https://doi.org/10.1016/j.jhazmat.2008.03.119

Long, Y. Y., Shen, D. S., Wang, H. T., Lu, W. J., & Zhao, Y. (2011). Heavy metal source analysis in municipal solid waste (MSW): Case study on Cu and Zn. *Journal of Hazardous Materials, 186*, 1082–1087. https://doi.org/10.1016/j.jhazmat.2010.11.106

Ma, K., Cui, L., Dong, Y., Wang, T., Da, C., Hirasaki, G. J., & Biswal, S. L. (2013). Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials. *Journal of Colloid and Interface Science, 408*, 164–172. https://doi.org/10.1016/j.jcis.2013.07.006

Marcano, M. C., Kim, S., Taylor, S. D., & Becker, U. (2019). Exploring wettability by imaging the adsorption of crude oil, re-dissolved asphaltene, and phenol solutions onto calcite. Implications to sorption mechanisms and molecular structure of surface-active compounds in crude oil. *Chemical Geology, 525*, 462–478. https://doi.org/10.1016/j.chemgeo.2019.07.030

Mishra, A. K., Ohtsubo, M., Li, L., & Higashi, T. (2011). Controlling factors of the swelling of various bentonites

and their correlations with the hydraulic conductivity of soil-bentonite mixtures. *Applied Clay Science, 52*(1–2), 78–84. https://doi.org/10.1016/j.clay.2011.01.033

Missana, T., García-Gutierrez, M., & Alonso, U. (2008). Sorption of strontium onto illite/smectite mixed clays. *Physics and Chemistry of the Earth, 33*, 156–162. https://doi.org/10.1016/j.pce.2008.10.020

Mnasri-Ghnimia, S., & Frini-Srasraa, N. (2019). Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays. *Applied Clay Science, 179*, 105151. https://doi.org/10.1016/j.clay.2019.105151

Müller, M. N. (2019). On the genesis and function of coccolithophore calcification. *Frontiers in Marine Science, 6*, 49. https://doi.org/10.3389/fmars.2019.00049

Musso, T. B., Francisca, F. M., Parolo, M. E., & Roehl, K. E. (2013). Potential use of calcareous mudstones in low hydraulic conductivity earthen barriers for environmental applications. *Environmental Technology, 34*(17), 2465–2476. https://doi.org/10.1080/09593330.2013.772660

Musso, T. B., Parolo, M. E., Pettinari, G., & Francisca, F. M. (2014). Cu(II) and Zn(II) adsorption capacity of three different clay liner materials. *Journal of Environmental Management, 146*, 50–58. https://doi.org/10.1016/j.jenvman.2014.07.026

Musso, T. B., Francisca, F. M., Pettinari, G., & Roehl, K. E. (2016). Suitability of a cretaceous natural Na-bentonite as construction material for landflls liners. *Environmental Engineering and Management Journal, 15*, 2519–2528. https://doi.org/10.1007/s10706-010-9348-y

Musso, T.B., Pettinari, G., Parolo, M.E., Mesquín, L. (2017). Arcillas esmectíticas de la región Norpatagónica Argentina como barreras hidráulicas de rellenos sanitarios y agentes de retención de metales pesados. Rev Int Contam Ambie 33(1):141–152. https://doi.org/10.20937/rica.2017.33.01.13

Musso, T.B., Parolo, M.E., Pettinari, G. (2019). pH, ionic strength, and ion competition effect on Cu(II) and Ni(II) sorption by a Na-bentonite used as liner material. Pol J Environ Stud 28(4):2299–2309. https://doi.org/10.15244/pjoes/84922.

Nath, H. (2020). Variation in geotechnical behavior of bentonite-soil blends in the salty environment of liner. *Int J Innov Sci Res Technol, 5*(8), 915–920. https://doi.org/10.38124/IJISRT20AUG537

Ogata, A., Banks, R. (1961). A solution of the differential equation of longitudinal dispersion in porous media, USGS Numbered Series 411-A.

Ou, Z., Yediler, A., He, Y., Jia, L., Kettrup, A., & Sun, T. (1996). Adsorption of linear alkylbenzene sulfonate (LAS) on soils. *Chemosphere, 32*(5), 827–839.

Paxéus, N. (2000). Organic compounds in municipal landfill leachates. *Water Science and Technology, 42*, 323–333. https://doi.org/10.2166/wst.2000.0585

Perez-Sirvent, C., Martínez-Sanchez, M. J., Veiga, J. M., Bech, J., & García-Lorenzo, M. L. (2019). In situ chemical immobilisation by limestone filler of potentially harmful metal(loid) in contaminated soils: Monitoring by Raman spectroscopy. *App Geochem, 111*, 104441. https://doi.org/10.1016/j.apgeochem.2019.104441

Refaey, Y., Jansen, B., Parsons, J. R., de Voogt, P., Bagnis, S., Markus, A., El-Shater, A.-H., El-Haddad, A. A., & Kalbitz, K. (2017). Effects of clay minerals, hydroxides, and timing of dissolved organic matter addition on the competitive sorption of copper, nickel, and zinc: A column experiment. *Journal of Environmental Management, 187*, 273–285. https://doi.org/10.1016/j.jenvman.2016.11.056

Reitzel, L. A., & Ledin, A. (2002). Determination of phenols in landfill leachate-contaminated groundwaters by solid-phase extraction. *Journal of Chromatography A, 972*, 175–182. https://doi.org/10.1016/S0021-9673(02)01098-1

Rigobello, E. S., Jambers Scandelai, A. P., Lopes Corso, B., & Granhen Tavares, C. R. (2015). Identification of organic compounds in a municipal landfill leachate by gas chromatography coupled with mass spectrometry. *Quimica Nova, 38*(6), 794–800. https://doi.org/10.5935/0100-4042.20150092

Rodríguez-Rubio, P., Morillo, E., Madrid, L., Undabeytia, T. U., & Maqueda, C. (2003). Retention of copper by a calcareous soil and its textural fractions: Influence of amendment with two agroindustrial residues. *European Journal of Soil Science, 54*, 401–409. https://doi.org/10.1046/j.1365-2389.2003.00529.x

Rowe, R. K. (2005). Long-term performance of contaminant barrier systems. *Géotechnique, 55*(9), 631–678. https://doi.org/10.1680/geot.2005.55.9.631

Sakai, S., Urano, S., & Takatsuki, H. (2000). Leaching behavior of PCBs and PCDDs/DFs from some waste materials. *Waste Management, 20*, 241–247. https://doi.org/10.1016/S0956-053X(99)00316-5

Scalia, J., Bohnhoff, G. L., Shackelford, C. D., Benson, C. H., Sample-Lord, K. M., Malusis, M. A., & Likos, W. J. (2018). Enhanced bentonites for containment of inorganic waste leachates by GCLs. *Geosynthetics International, 25*(4), 392–411. https://doi.org/10.1680/jgein.18.00024

Sdiri, A. T., Higashi, T., & Jamoussi, F. (2014). Adsorption of copper and zinc onto natural clay in single and binary systems. *International Journal of Environmental Science and Technology, 11*, 1081–1092. https://doi.org/10.1007/s13762-013-0305-1

Shackelford, C. D. (1994). Critical concepts for column testing. *J Geotech Eng, 120*(10), 1804–1828.

Shahraki, B. K., Mehrabi, B., Gholizadeh, K., & Mohammadinasab, M. (2011). Thermal behavior of calcite as an expansive agent. *J Min Metall Sect B-Metall, 47*, 89–97. https://doi.org/10.2298/JMMB1101089S

Sharma, H. D., & Reddy, K. R. (2004). *Geoenvironmental Engineering*. John Wiley.

Sposito, G. A. (1984). *The surface chemistry of soils*. Oxford University Press.

Suna Erses, A., Fazal, M. A., Onay, T. T., & Craig, W. H. (2005). Determination of solid waste sorption capacity for selected heavy metals in landfills. *Journal of Hazardous Materials, 121*, 223–232. https://doi.org/10.1016/j.jhazmat.2005.02.011

Tang, W. W., Zeng, G. M., Gong, J. L., Liang, J., Xu, P., Zhang, C., & Huang, B. B. (2014). Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: A review. *Science of the Total*

Environment, 468–469, 1014–1027. https://doi.org/10.1016/j.scitotenv.2013.09.044

Thornton, S.F., Lerner, D.N., Tellam, J.H. (2001). Attenuation of landfill leachate by clay liner materials in laboratory columns: 2. Behaviour of inorganic contaminants. Waste Manage Res 19:70–88. https://doi.org/10.1177/0734242X0101900108.

Vaverková, M. D., Zloch, J., Adamcová, D., Radziemska, M., Vyhnánek, T., Trojan, V., Winkler, J., Đorđević, B., Elbl, J., & Brtnický, M. (2019). Landfill leachate effects on germination and seedling growth of hemp cultivars (Cannabis Sativa L.). *Waste Biomass Valor, 10*, 369–376. https://doi.org/10.1007/s12649-017-0058-z

Vhahangwele, M., & Mugera, G. W. (2015). The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: Simultaneous sorption of Co2+, Cu2+, Ni2+, Pb2+, and Zn2+ ions. *Journal of Environmental Chemical Engineering, 3*, 2416–2425. https://doi.org/10.1016/j.jece.2015.08.016

Weng, L., Van Riemsdijk, W. H., Koopal, L. K., & Hiemstra, T. (2006). Adsorption of humic substances on goethite: Comparison between humic acids and fulvic acids. *Environmental Science and Technology, 40*(24), 7494–7500. https://doi.org/10.1021/es060777d

Wu, X. L., Zhao, D., & Yang, S. T. (2011). Impact of solution chemistry conditions on the sorption behavior of Cu(II) on Lin'an montmorillonite. *Desalination, 269*, 84–91. https://doi.org/10.1016/j.desal.2010.10.046

Wu, P., Wen, Y., Xiang, Y., Zhou, J., Du, J., Zhu, N., Li, P. (2015). Sorption of pyrene by clay minerals coated with dissolved organic matter (DOM) from landfill leachate. J Chem 734610. https://doi.org/10.1155/2015/734610.

Yang, K., Zhu, L., & Xing, B. (2007). Sorption of sodium dodecylbenzene sulfonate by montmorillonite. *Environmental Pollution, 145*, 571–576. https://doi.org/10.1016/j.envpol.2006.04.024

Yang, S. B., Hu, J., Chen, C. L., Shao, D. D., & Wang, X. K. (2011). Mutual effects of Pb(II) and humic acid adsorption on multiwalled carbon nanotubes/polyacrylamide composites from aqueous solutions. *Environmental Science and Technology, 45*(8), 3621–3627. https://doi.org/10.1021/es104047d

Ye, W., Liu, H., Jiang, M., Lin, J., Ye, K., Fang, S., Xu, Y., Zhao, S., Van der Bruggen, B., & He, Z. (2019). Sustainable management of landfill leachate concentrate through recovering humic substance as liquid fertilizer by loose nanofiltration. *Water Research, 157*, 555–563. https://doi.org/10.1016/j.watres.2019.02.060

Zhang, W., Zhuang, L., Yuan, Y., Tong, L., & Tsang, D. C. W. (2011). Enhancement of phenanthrene adsorption on a clayey soil and clay minerals by coexisting lead or cadmium. *Chemosphere, 83*, 302–310. https://doi.org/10.1016/j.chemosphere.2010.12.056

Zhang, W., Zheng, J., Zheng, P., Tsang, D. C. W., & Qiu, R. (2015). The roles of humic substances in the interactions of phenanthrene and heavy metals on the bentonite surface. *Journal of Soils and Sediments, 15*, 1463–1472. https://doi.org/10.1007/s11368-015-1112-8