

Original Research

pH, Ionic Strength, and Ion Competition Effect on Cu(II) and Ni(II) Sorption by a Na-bentonite Used as Liner Material

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Abstract

The potential of a Na-bentonite to be used as liner material for the adsorption of Cu(II) and Ni(II) ions from mono, bi, and polycationic solutions was investigated by batch mode. pH and ionic strength effect on Cu(II) and Ni(II) sorption were evaluated. For isotherm sorption studies, metal solutions parameters (pH and ionic strength) were selected simulating common landfill leachate conditions in the acidogenic stage. The removal of these ions by the Na-bentonite is dominantly controlled by sorption (specifically, cation exchange) under acidic conditions, but it can be strongly enhanced by metal oxide/hydroxide precipitation under alkaline conditions. Adsorption equilibrium models for the single, binary, and multicomponent systems indicate that the Langmuir-type model can fit the experimental data very well for all of them. The co-presence of metals led to a decrease in the sorption of both metals due to competition for adsorption sites. Optimum conditions are obtained when the ionic strength of solution is low (<0.05 M), pH is higher than 6, and the metal concentration is lower than 20 mg/L. Adsorption rates indicate that in addition to its quality as a physical barrier this bentonite can also act as a chemical barrier, limiting the migration of heavy metals from security landfills.

Keywords: bentonite, heavy metals, co-adsorption, liner material

Introduction

Heavy metals such as Cd, Cr, Pb, Cu, Ni, and Zn are commonly found in leachates of solid urban waste [1-3]. Their presence in soils and groundwater near municipal landfills are of main concern when the disposal sites

are not properly isolated. Many of these heavy metals are listed on top of the priority pollutants list because of their high toxicity to human health as well as the ecosystems at trace levels [4]. Ni(II) and Cu(II), as representatives of these heavy metals, are chosen for this study as they are present in landfill leachates of different localities and ages. Exposure to high levels of copper in water and diet can lead to diseases of the liver and kidney [5]. The chronic toxicity of nickel to humans

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and the environment has been well reported, and high concentrations of Ni(II) cause cancer of the lungs, nose, and bone [6].

Nowadays, intelligent landfill barriers are increasingly designed to prevent liquid and chemical escape from the repository site during and after the lifetime of the landfill. For this purpose, geological materials rich in smectitic clay minerals, such as bentonites, are preferred due to its widely probed performance to reduce hydraulic conductivity of granular materials [7-9] and to remove different types of contaminants from aqueous solutions through the sorption process [10-12]. The study of sorption of heavy metals is an important part of the overall investigation required for the assessment of potential liners. However, the application of these studies on a large scale requires knowledge of the equilibrium and kinetics of the metal adsorption process [13]. pH, ionic strength, and type and concentration of ions are among the factors that affect sorption processes on clay particles, being the first main force governing the adsorption of metal cations [14]. However, sorption behavior might be significantly altered in a competing environment having multiple metals in the system as compared to a single metal system. In most cases, soil and groundwater contamination through landfill leachate involves several heavy metals, i.e., a multiple-component system. Understanding the fate and transport of heavy metals in multi-component systems is a prerequisite to identifying dominant mechanisms governing their competitive sorption behavior in the soil environment. Usually, when competitive sorption of metals is compared with their monometal behavior, it is shown that their adsorption is lower in the competitive systems [15-17].

Sorption data are frequently simulated using empirical models of the equilibrium systems, such as the Freundlich and Langmuir models. However, modifications of both the aforementioned equations by including competitive effects, due to the presence of two or more adsorbates or the presence of sorption sites with different affinities, have also been proposed [16, 18].

In this study, a Na-bentonite from northern Patagonia in Argentina was utilized to investigate its potential as a low-cost adsorbent for the adsorption of Ni(II) and Cu(II) ions from aqueous solution through batch tests. This clay is proposed as a cheap alternative adsorbent because it is present in an abundant amount in this region and is easily accessible from the main cities of northern Patagonia. The paper focuses particularly on copper and nickel as model metals, since these are generally of most concern to regulators. Zn(II) and Cd(II) are among other common heavy metals coexisting with Cu(II) and Ni(II) in landfill leachates [19], so they were selected to understand competition effects.

The objectives of the present work are: 1) to study the influence of pH, ionic strength, and metal concentration on the adsorption of Cu(II) and Ni(II) onto a Na-bentonite; 2) to investigate the effect of other metal ions coexistence on the adsorption of these ions; and 3) to determine the isotherm model that better describes adsorption behavior under different experimental conditions (mono, bi, and polycationic adsorption).

Experimental

Materials

The clay used in this study was a natural Na-bentonite manufactured by Castiglione Pes & Cía., named CATAE. This clay belongs to the Allen Formation of the Neuquén basin, Argentina. The bentonite deposit from which CATAE is extracted is one of the biggest in South America with a calculated reserve of more than 3,000,000 tons and an extension of 69 km² [20]. This clay is often used as an additive in drilling mud and as bonding of sand for the production of greensand moulds in foundries. The bentonite has a high specific surface area (754.4 m²/g), high cationic exchange capacity (105.9 meq/100g), and a unimodal pore size distribution (1-0.1 μm), which indicates that the material is dominated by macropores [21]. This material

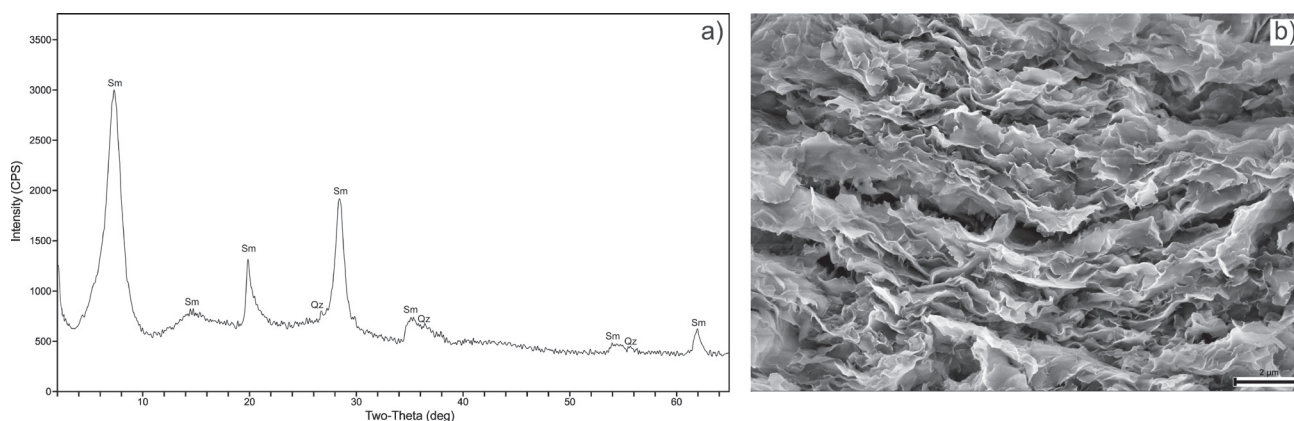


Fig. 1. X-ray diffraction pattern (XRD) of < 2 μm fraction a) and scanning electron microphotography of the Na-bentonite b) (Sm: smectite, Qz: quartz).

meets the technical requirements outlined in the European, Japanese, and American legislations for use as clay liner [22], having hydraulic conductivities lower than 1×10^{-9} m/s [23].

The bentonite is constituted by 86% of particles with a size lower than 2 microns. The mineralogy of this fraction is represented by a smectite, specifically a Na-montmorillonite classified as a Wyoming type [21], with morphology of clay flakes that have a wavy leaf appearance (Fig. 1). Clay surfaces have a negative electrical charge in water over a pH range of 2-10 [24].

The following metals were used in the sorption experiments: Cu(II), Zn(II), Ni(II), and Cd(II). Stock solutions (1000 mg/L) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade, Sigma-Aldrich) were prepared for the calibration curve and metal quantification by an atomic absorption spectrophotometer (AAS) (Analyst 200, Perkin-Elmer). NaOH and HCl solutions were used for pH adjustment, and 0.08 M NaCl solution was prepared for ionic strength control.

Batch Experiment

Two types of batch experiments were performed to evaluate Cu(II) and Ni(II) adsorption characteristics under different conditions: 1) mono, bi, and multimetal adsorption isotherms obtained simulating common landfill leachate characteristics; and 2) pH (3-9) and ionic strength (1×10^{-4} M – 1×10^{-1} M) effect in monometal systems.

Monometal adsorption isotherms were obtained by mixing 0.031 g of clay sample with 25 mL metal solutions containing various concentrations of the studied metals (10, 25, 50, 80, 120, 150, 180, and 220 mg/L for Cu(II) and 3, 5, 7, 10, 25, 50, 100, and 150 mg/L for Ni(II)). The lower concentrations of these solutions are similar to the average Cu(II) and Ni(II) concentrations determined in an Argentinean urban waste leachate [25]. 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 24 h at 25°C. Then the specimens were centrifuged at 3600 rpm for 20 min and the supernatant was filtered through 0.45 mm syringe acetate filters (Scharlab) and stored in polypropylene tubes.

Bimetal (Cu-Ni) and multimetal (Cu-Ni-Zn-Cd) adsorption isotherms were determined using the same procedure as for the monometal experiment, at a 1:1 and 1:1:1:1 molar concentration ratio, respectively. A binary and multimetal stock solution of 1000 mg/L containing Cu(II) and Ni(II) ions, and Cu(II)-Ni(II)-Zn(II)-Cd(II) ions, respectively, were prepared by dissolving appropriate amounts of their respective salts in 1 L of distilled water. From the stock solution, several working concentrations of 3-220 mg/L were prepared

by appropriate dilution. The pH of each of the solutions was adjusted to 5.5.

The amount of metal adsorbed in the clay was calculated by the difference between the initial and the final metal concentrations (Eq. 1) as follows:

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_i - C_e) * V}{W} \quad (1)$$

...where q_e is the equilibrium concentration of metal ion in solid phase (mg/g); C_i and C_e are the initial and the equilibrium concentrations (mg/L) of metals in solution, respectively; and V and W represent the volume of the solution (L) and mass of the sorbent (g), respectively.

In the study of pH and ionic strength effect on Cu(II) and Ni(II) sorption, the same procedure to obtain adsorption isotherms was carried out. 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. Ionic strength effect on Cu(II) and Ni(II) sorption was evaluated in the presence of various concentrations of NaCl electrolyte solution (0.1 M, 0.05 M, 0.01 M, 0.001 M, and 0.0001 M) at pH 5.5.

All tests were performed in duplicate in order to verify the reproducibility of results.

Adsorption Isotherms Models

Langmuir [26] and Freundlich [27] equations were first employed to describe the adsorption behavior of metals (Eqs. 2 and 3, respectively). These equations are written as:

$$\frac{C_e}{q_e} = \frac{1}{C_s K_L} + \frac{C_e}{C_s} \quad (2)$$

$$\log q_e = \log K_F + n_f \log C_e \quad (3)$$

...where 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 ($\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$), and n_f is the adsorption intensity constant of the Freundlich equation. An accurate determination of these constants (K_F and n_f) is important not only for modeling adsorption of single-component systems but also for modeling competitive adsorption, as they are included in the Sheindorf-Rebhun-Sheintuch (SRS) equation (Eq. 4).

The multicomponent adsorption isotherms are normally obtained by extending the above single component adsorption isotherms and can be classified accordingly to the single adsorption isotherm that originated the multicomponent isotherm. In this study, the Sheindorf-Rebhun-Sheintuch model was applied to the bi and multimetal experimental data (Eq. 4). The SRS equation was developed to describe competitive

sorption, where it was assumed that the single-component sorption follows the Freundlich equation [28]. The derivation of the SRS equation is based on the assumption of an exponential distribution of adsorption energies for each component. A general form of the SRS equation [28] can be written as:

$$S_i = K_i C_i \left(\sum_{j=1}^l \alpha_{i,j} C_j \right)^{n_i-1} \quad (4)$$

...where i and j denote metal components i and j , l is the total number of components, and $\alpha_{i,j}$ is a dimensionless competition coefficient for the adsorption of component i in the presence of component j . The parameters K_i and n_i are the Freundlich parameters representing a single-component system i as described in Equation 2. By definition, $\alpha_{i,j}$ equals 1 when $i = j$. If there is no competition, i.e., $\alpha_{i,j} = 0$ for all $j \neq i$, Equation 4 yields a single species Freundlich equation for component i identical to Equation 3.

Finally, from Langmuir constants obtained in single-component systems, competitive constants for binary and multi-component systems were calculated [29, 30]. Mohan and Singh [29] investigated the mutual effects of ions adsorption by measuring the adsorption capacity ratio of metal ion i in multi-component systems, q_i^{mix} , and in single-component systems, q_i^0 , such that:

$$\frac{q_i^{mix}}{q_i^0} \approx \frac{q_{im}^{mix}}{q_{im}^0} \quad (5)$$

...where q_{im}^0 and q_{im}^{mix} is the maximum amount adsorbed in a single- or multi-component system, respectively (mg/g). If $q_i^{mix}/q_i^0 > 1$, ion i enhances the adsorption of other ions. If $q_i^{mix}/q_i^0 = 1$, ion i has no effects on other ions. If $q_i^{mix}/q_i^0 < 1$, ion i competes for adsorption sites of Na-bentonite with other ions and its adsorption is suppressed by the presence of other ions.

The competitive equilibrium coefficient expresses the competition ability of ions [30]. The competitive equilibrium coefficient for component i , is the equilibrium ratio of adsorbed i to all adsorbed components (Eq. 6). The competitive equilibrium coefficient for component i among n components may be written as:

$$a_{ie} = \frac{q_{ie}/C_{0i}}{\sum_{j=1}^n q_{je}/C_{0j}} \approx \frac{q_{im}^{mix}/C_{0i}}{\sum_{j=1}^n q_{jm}^{mix}/C_{0j}} \quad (6)$$

($i = 1, 2, 3, \dots, n; \quad j = 1, 2, 3, \dots, n$)

...where q_{ie} and C_{0i} are the amount of adsorbed component i at equilibrium (mg/g) and initial concentration of component i , respectively, q_{je} and C_{0j} are the amounts of adsorbed component j at equilibrium (mg/g) and initial concentration of component j , respectively, and q_{jm}^{mix} is the maximum amount of adsorbed component j (mg/g).

Table 1. Properties of the real leachate used for batch experiments (TDS: total dissolved salts; EC: electrical conductivity; DOC: dissolved organic carbon).

Parameter	Real leachate
pH	5.20
TDS (mg/L)	15590
EC (μ S/cm)	33800
Viscosity at 20°C (cP)	1.40
Density at 20°C (g/cm ³)	1.04
Cu ²⁺ (mg/L)	6.01
Zn ²⁺ (mg/L)	9.51
Ni ²⁺ (mg/L)	2.00
Cd ²⁺ (mg/L)	0.36
Na ⁺ (mg/L)	645-29200*
Ca ²⁺ (mg/L)	42-2880*
K ⁺ (mg/L)	70-2786*
Mg ²⁺ (mg/L)	59-3860*
Phenols (mg/L)	3.45-26*
Organic N (mg/L)	24-852*
DOC (mg/L)	17.400-93.700*

* data taken from [25]

The rate of equilibrium adsorption reduction (ΔY) is the ratio of the difference between non-competitive equilibrium adsorption and competitive equilibrium adsorption to non-competitive adsorption observed at equilibrium (Eq. 7):

$$\Delta Y = \frac{q_{im}^0 - q_{im}^{mix}}{q_{im}^0} \times 100\% \quad (7)$$

Real Leachate Tests

Cu(II) and Ni(II) elimination from real leachate was assayed in batch experiments. The real leachate samples are from a landfill located in Argentina (Table 1). A typical experiment consisted in 0.031 g of Na-bentonite added to 25 mL of real leachate in polyethylene bottles, shaken for 24 h, centrifuged, and the supernatant was kept for metal analyses.

Results

pH Effect on Cu(II) and Ni(II) Sorption

The effect of solution pH on the adsorption of Cu(II) and Ni(II) on Na-bentonite is presented in Fig. 2a). In order to elucidate the contribution of precipitation to the sorption of the heavy metals, the change in removal

percentage without the sorbent was examined under the same pH range (Fig. 2b).

It was clear that sorption of Cu(II) on Na-bentonite was strongly dependent on pH values, as has been already seen by other authors [15, 31-34]. The sorption increased slowly at pH 4-6 and increased sharply at pH 6-7. At pH > 6, the removal of Cu(II) is 90% and was maintained at a constant until pH 9. This can be well understood in terms of the electrostatic interaction between the montmorillonite and the cationic species; therefore the adsorption of Cu(II) can be attributed to ion exchange between Cu(II) and H^+/Na^+ on the ion exchange sites. The increased competition between protons and metal ions for the available permanent negative sorption sites is responsible for the low removal efficiency at low pH values; additionally, a large number of active sites of variable charge may become positively charged at very low pH [32]. The Cu(II) adsorbed amount increased with increase in pH up to 7.0, this is attributed to the decrease in competition between protons and metal ions leading to a higher uptake [35]. Also, at high pH values (pH > 6.0) the oxide specie of Cu(II) in solution is precipitated (Fig. 3a), which will lead to a corresponding decrease in the removed amount of metal ions by adsorption onto a montmorillonite surface [36]. This is supported by the calculations of aqueous speciation performed with the Medusa-Hydra chemical equilibrium software for Windows (Visual

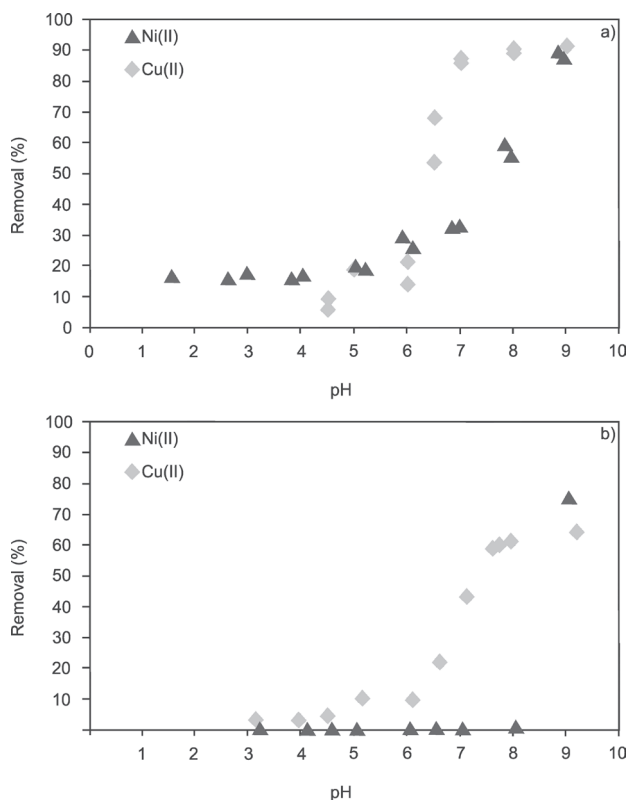


Fig. 2. Variation in removal percentages of Cu(II) and Ni(II) on Na-bentonite as a function of pH with (a) and without (b) the sorbent (ionic strength: 0.08M, initial concentration of Cu(II): 2.5 mg/L, Ni(II): 25 mg/L).

Basic) (Fig. 3). The percentage of Cu(II) removed by precipitation is shown in Fig. 2b, which can be compared with the total removal percentage (Fig. 2a). The precipitation percentage is small at pH values below 6 (<10%) and then sharply increases up to 60% at pH 7, 8, and 9. The difference between the total removal and the removal by precipitation at pH ≥ 7 is around 30%, and this percentage could be attributed to the adsorption mechanism of the main positive Cu(II) species (Cu^{2+} and $CuOH^+$) present at these pH (Fig. 3a) on the deprotonated aluminol and silanol groups of the clay, located at variable surface charged sites, and on siloxanic groups located in permanent negative surface sites.

The effect of pH on Ni(II) sorption on the Na-bentonite was less marked than in the case of Cu(II), although a very similar trend was observed. A small increase from 15% to 30% of retained Ni(II) was observed over a wide pH range from 2 to 7. Above pH 7, the removal of Ni(II) increases sharply until it reaches 90%. Other authors have also observed this pH-dependent adsorption of Ni(II) on Na-montmorillonite describing similar sorption mechanisms as in the case of Cu(II) [37, 38]. Ni(II) precipitation as $Ni(OH)_2$ plays an important role in the removal at pH 9 (Fig. 3b), being responsible for almost the total removal at this pH. For pH < 9, Ni(II) removal can be completely attributed to the adsorption process.

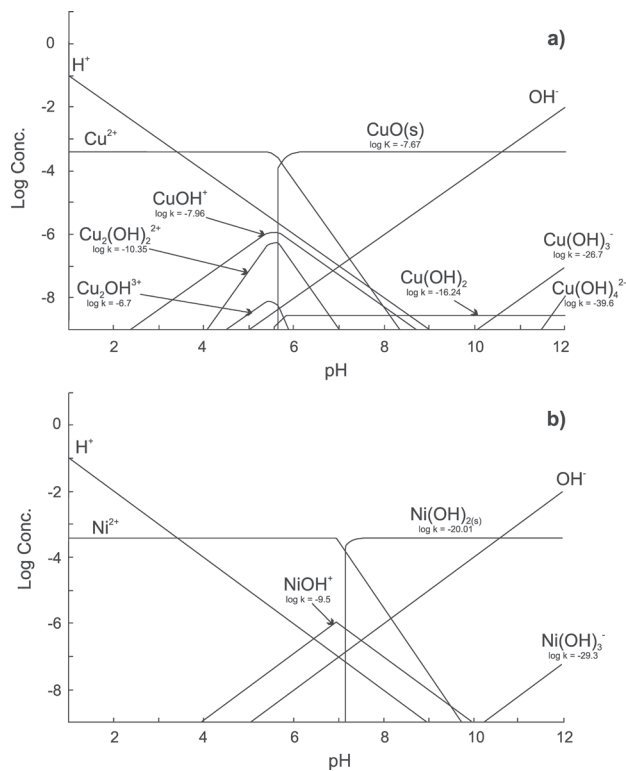


Fig. 3. Relative distribution of Cu(II) (a) and Ni(II) (b) species in aqueous solutions as a function of pH values; hydrolysis constants are indicated in the figure (initial Cu(II) and Ni(II) concentration: 0.40 mM).

Consequently, removal of Cu(II) and Ni(II) by the Na-bentonite is dominantly controlled by sorption (specifically, cation exchange) under acidic conditions, but it can be strongly enhanced by metal oxide/hydroxide precipitation under alkaline conditions.

Ionic Strength Effect on Cu(II) and Ni(II) Sorption

Fig. 4 shows the effect of electrolyte concentration on Cu(II) and Ni(II) adsorption onto the Na-bentonite.

As can be seen from Fig. 4, the sorption of Cu(II) and Ni(II) on bentonite increases with decreasing ionic strength at pH 5.5, maintaining a maximum adsorption value at NaCl concentrations lower than 0.05 M. The electrolyte concentration effect could be attributed to three reasons [32]:

- 1) Ionic strength can impact particle aggregation by influencing electrostatic interactions. Increased ionic strength can reduce electrostatic repulsion and thereby increases particle aggregation, which reduces the amount of available binding sites and thereby decreases the sorption of Cu(II) and Ni(II).
- 2) The ionic strength of solution influences the activity coefficient of Cu(II) and Ni(II) ions, which limits their transfer to the clay surfaces [39], although this effect is expected to be negligible at the metals initial concentrations used in this study.
- 3) Sorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism. Thus, the results show that electrostatic attraction plays an important role in the sorption of Cu(II) and Ni(II) on the Na-bentonite at pH 5.5, in agreement with the previous pH effects results. At high ionic strength, the increased amount of NaCl can swamp the surface of the clay and thus decrease Cu(II) and Ni(II) ions' access to the surface sites.

However, it is important to highlight some differences in ionic strength effect between the analysed metals. At high ionic strength, Ni(II) was affected stronger than Cu(II), as can be seen by a sharper

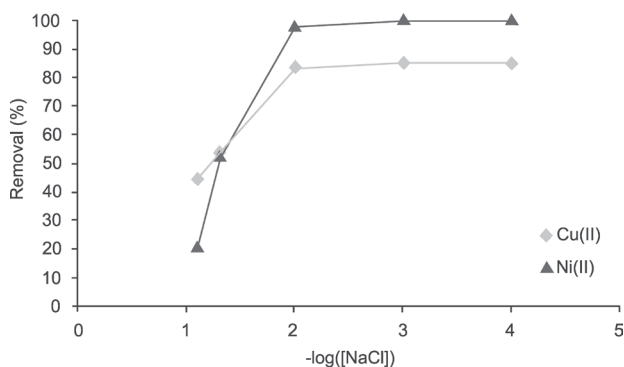


Fig. 4. Effect of ionic strength on the adsorption of Cu(II) and Ni(II) onto the Na-bentonite at ionic strength: 0.0001, 0.001, 0.01, 0.05, and 0.08 M; pH 5.5; dose of adsorbent 1.24 g/L; initial concentration of Cu(II) 10 mg/L, Ni(II) 25 mg/L.

decrease in the metal uptake from 0.01 M to 0.08 M of NaCl (Fig. 4). This would indicate that Ni(II) retention is more dependent on electrostatic interactions with solid-phase exchange sites. In contrast, Cu(II) retention is less dependent on this type of adsorption and more dependent on covalent interactions through the participation of $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})^{2+}$ species with the mineral structures, as has been already seen at this studied pH [24].

Isothermal Adsorption Characteristics of Cu(II) and Ni(II) Ions on the Na-bentonite

Adsorption isotherms of Cu(II) and Ni(II) in single, binary, and multi-component systems are shown in Figs 5a) and b), respectively. In all of them it was observed that the amount of heavy metal ions adsorbed on Na-bentonite increases with the increase in concentration of these metals in aqueous solutions. The constants of isothermal adsorption for Cu(II) and Ni(II) in single, binary, and multi-component systems are shown in Table 2. The Langmuir-type model can fit the single, binary, and multicomponent experimental data of Cu(II) and Ni(II) adsorption very well ($R^2 > 0.90$), indicating homogeneous distribution

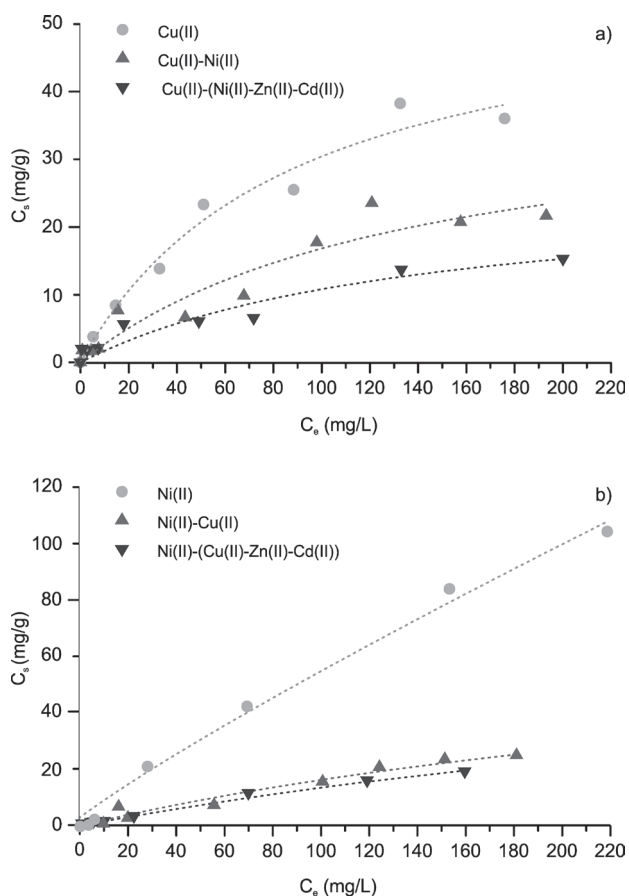


Fig. 5. Adsorption isotherms of Cu(II) and Ni(II) in single, binary, and multicomponent systems on Na-bentonite; lines represent Langmuir fitting and dots represent average sorption.

Table 2. Adsorption isotherm parameters for Cu(II) and Ni(II) in single, binary, and multi-component systems.

Model	Constants	Monometal		Bimetal		Multimetal	
		Cu(II)	Ni(II)	Cu(II)-Ni(II)	Ni(II)-Cu(II)	Cu(II) (Ni-Zn-Cd)	Ni(II) (Ni-Zn-Cd)
Langmuir	C_s (mg/g)	56.95	394.16	40.04	79.31	26.15	87.50
	K_L (L/mg)	0.011	0.003	0.007	0.002	0.007	0.001
	R^2	0.97	0.99	0.91	0.97	0.90	0.82
Freundlich	K_F	2.13	1.54	-	-	-	-
	n_F	0.56	0.87	-	-	-	-
	R^2	0.96	0.99	-	-	-	-
Sheindorf-Reb- hun-Sheintuch	a	-	-	0.72	75942	1.13	1972
	b	-	-	-	-	0.98	2266
	c	-	-	-	-	0.98	5466
	R^2	-	-	0.83	0.93	0.78	0.85

of these metals onto the surface-active sites of the montmorillonite. This is in agreement with previous works, which have also observed that the Langmuir model described the sorption data best in multi-metal systems [15, 34, 40]. Based on the values of maximum sorption capacities calculated from the fitted Langmuir equation, the sequence of metal sorption was Ni(II)>Cu(II) in non-competence and competence conditions.

An improvement in the fitting of the experimental data obtained from competitive systems with the SRS multicomponent adsorption isotherm was not observed. However, from the competition coefficient values obtained from this model, it can be observed that competition effect was stronger for Ni(II) ($\alpha \gg 1$) than Cu(II) ($\alpha > 1$), as will be analysed later.

The data in Table 2 indicate that total adsorbed amount of non-competitive adsorption is higher than total adsorbed amount of binary and multi component competitive adsorption.

This is also demonstrated by the values of $q_i^{mix}/q_i^0 < 1$ (Table 3), which indicate the mutual competitive effect of Cu(II) and Ni(II) in binary and multi component systems. Although competition reduced sorption of the two metals, the magnitude of this effect was different for each. The removal efficiency of Ni(II) decreased substantially in the presence of Cu(II) and other metals compared with the single metal system. The adsorption in a single-component system was decreased by around 80% in binary and multicomponent systems (Table 2), whereas in the case of Cu(II) its rate of adsorption equilibrium reduction was decreased by 29.6% in the Cu(II)-Ni(II) system and by 54% in the multi-component system.

The results show that Cu(II) suppresses Ni(II) adsorption more significantly and that the presence of more metals in the system does not reduce Ni(II) adsorption in a higher proportion.

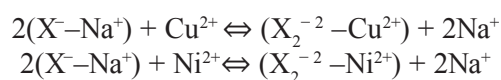
The competitive equilibrium coefficient ($a_{i,c}$) indicates that in a multimetal system Ni(II) is adsorbed in a higher proportion than Cu(II). This can be also observed comparing the maximum sorption capacities obtained from Langmuir equation (87.5 mg/g for Ni(II) and 26.15 mg/g for Cu(II)). This means that Ni(II) would have more available sites to interact with the surface of the clay, and therefore is less affected by the type of reactive site.

Discussion

Sorption Mechanisms

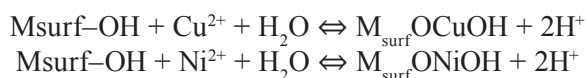
In concordance with other authors, three mechanisms are considered in the sorption experiments from the analysis of pH and ionic strength effect [41, 37, 42]: cation exchange at permanent negatively charged sites, inner-sphere complexation at variable charge surface hydroxyl groups at the crystal edges, and precipitation as metal oxides or hydroxides. At pH<6.5-7, the ionic strength-dependent adsorption indicates that the main sorption processes are:

- (i) cation exchange reactions at the permanent negative charge of faces or interlayer region of montmorillonite:



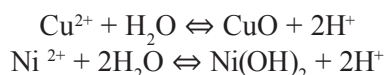
and

- (ii) formation of copper and nickel hydroxyl surface complex at the variable charge surface hydroxyl groups:



The sorption of Cu(II) and Ni(II) at higher pH is similar to metal ion uptake onto oxide surfaces [43], that is sorption increases to near 100% over a narrow pH range [44]. As demonstrated, precipitation plays an important role in the removal of Cu(II) and Ni(II) at pH>6 and pH=9, respectively, as follows:

(iii) precipitation of CuO and Ni(OH)₂:



The total metal uptake (q_T) on Na-bentonite at pH 5.5 in the competitive system was calculated by summing up the amounts of Cu(II), Ni(II), Zn(II), and Cd(II) adsorbed. The adsorption surface of q_T is shown in Fig. 6, and as it can be observed, the surface levels off at $q_T = 1.5$ meq/g, which is higher than the CEC capacity of the bentonite (CEC = 1.05 meq/g). Hence, at high metal concentration precipitation could occur at lower pH values.

Ion Competition Effect on Cu(II) and Ni(II) Sorption

In general, multi-component systems exhibit three possible types of behavior: synergism, antagonism, and non-interaction. The results showed that the presence of other metals in solution decreased the removal percentage of Cu(II) and Ni(II). This would indicate that adsorption sites of Na-bentonite for Cu(II) and

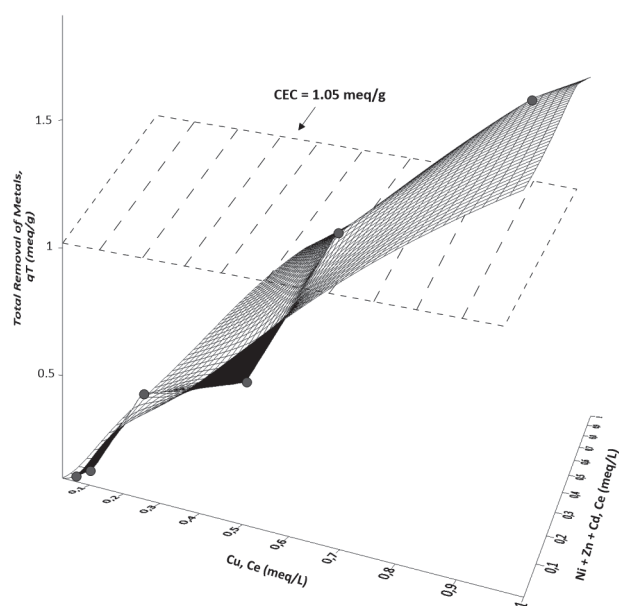


Fig. 6. Total adsorption of metal ions on bentonite in the multi-component system; the surface is predicted using the Kriging gridding method (Ce: concentration at equilibrium).

Table 3. Competitive constants calculated from Langmuir isotherm for Cu(II) and Ni(II).

Metalions	Adsorption systems	Competitive constants		
		q_i^{mix}/q_i^0	a_{ie}	DY (%)
Cu(II)	Cu(II)	1.00	1.00	0
	Cu(II)-Ni(II)	0.70	0.50	29.69
	Cu(Ni-Zn-Cd)	0.46	0.30	54.08
Ni(II)	Ni(II)	1.00	1.00	0
	Ni(II)+Cu(II)	0.20	1.98	79.88
	Ni(Cu-Zn-Cd)	0.22	3.35	77.80

Ni(II) ions are limited. Cu(II) and Ni(II) occupied the adsorption sites only once during non-competitive adsorption; but Cu(II) and Ni(II) co-occupied the same sites once during competitive adsorption, indicating an antagonistic effect (Table 3). These results are in agreement with the works of [34, 29, 45].

The cumulative amount of both metals sorbed in the Na-bentonite under competence conditions (binary and multiple systems) was similar, demonstrating that the number of sites available for sorption remained constant in these conditions.

Ni(II) adsorption was highly affected by the presence of other metals. This could be related to the fact that Cu(II) sorption through covalent interaction is stronger compared to Ni(II) dependence to electrostatic interactions which will be more affected by the presence of a higher amount of ions in the solution. The existence of specific sites for Cu(II) adsorption that are not occupied by Ni(II) or other ions when they are present explain the lesser effect of competition for Cu(II) [15]. As a result, Ni(II) might be more mobile in a mixed metal system than in a single-metal scenario and thus poses a serious ecotoxicological threat. However, in competence conditions, Ni(II) is adsorbed in a higher proportion than Cu(II) due to its lower selectivity for the adsorption sites. Also, the lower capacity for Cu(II) with respect to Ni(II) ions would depend on the different geometry of its aqution, which has a tetragonal distortion due to the Jahn-Teller effect that makes its introduction into lamellar spaces more difficult [46].

Although a reduction in Cu(II) and Ni(II) adsorption due to competition over the whole range of added metal concentrations was observed, metal isotherms show that the differences in metal sorption were evident mostly at equilibrium concentrations >20 mg/L. Thus at low metal concentrations, the effects of competition were not strong. Saha et al. [47] explained that at low added metal concentrations metals are mainly adsorbed onto specific adsorption sites, while at higher metal inputs particles lose some of their ability to bind heavy metals as adsorption sites overlap, thus becoming less specific for a particular metal.

Optimum Removal Conditions

Metal uptake capacity of a sorbent is perceived to be a function of both the surface area and the functional groups present on the surface of the material [48]. Glatstein and Francisca [49] proposed a heavy metal interaction-removal map for Na-bentonite based on pH and ionic strength of the solution and their relationship with the clay microfabric. They consider an isoelectric point of the particles edges $IEP_{edge} = 6.5$ and a precipitation pH of 7 as reference values, which make it useful to compare with our results. According to this, removal increases when the exposed area of the particles increases (dispersion mode), and this happens when the solution has a low ionic strength and the pH is higher than IEP_{edge} . This is in agreement with our results, which show that maximum removal, resulting in both sorption and precipitation, is reached when the solution has a $pH > 6$ and the ionic strength is <0.05 M.

Finally, the effect of competition is minimal when the metal equilibrium concentration is lower than 20 mg/L. Although the concentration of heavy metals in leachates from different landfills is variable, the average metal concentrations are fairly low and rarely exceed this concentration [1].

Practical Application

The comparison of Cu(II) and Ni(II) removal efficiencies by this natural liner material is shown in Fig. 7. The adsorption percentages on 0.031 g of clay, from a leachate with 6 mg/L of Cu(II) initial concentration and 2 mg/L of Ni(II) initial concentration, were 20% and 90%, respectively. This is in agreement with batch results from multimetal synthetic solution, which indicates that in competence conditions Ni(II) is removed in a higher proportion than Cu(II).

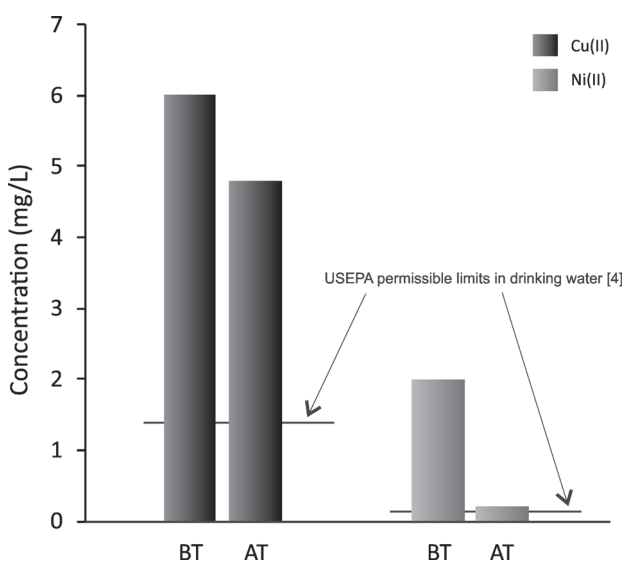


Fig. 7. Treatment of real leachate with bentonite liner (BT: before treatment; AT: after treatment).

Although the concentrations decreased during the process, the values after treatment can exceed environmental standards – especially for the Cu(II) ion. According to the current legislation, it would not be possible to discharge the leachate both into a watercourse and into a public sewage system [50] (Fig. 7). The lower adsorption rate using a real leachate can be explained because of its high ionic strength and the presence of other inorganic and organic compounds (Table 1) that possibly interacted with the analysed heavy metal, as these may affect the adsorption process and influence the application of adsorption materials in the liner system to some extent.

Conclusions

In order to evaluate the potential use of a low-cost clay liner material as efficient sorbent, a variety of experimental studies on the sorption of Cu(II) and Ni(II) heavy metal ions using a Na-bentonite from Argentina were carried out. From the results of this study we drew the following conclusions:

- 1) Ionic strength effect suggests that cation exchange is the dominant mechanism governing Cu(II) and Ni(II) sorption onto Na-bentonite at $pH < 6$. On the other hand, pH experiments without the sorbent indicated that precipitation of these metals as oxides and hydroxides contributed with the biggest percentage of removal at $pH > 6$ for Cu(II) and 9 for Ni(II).
- 2) Adsorption experiments at pH 5.5 indicated that at high metal concentration, the total adsorbed amount exceeds the CEC of the bentonite, indicating that precipitation can occur at lower pH when the metal concentration is high.
- 3) Cu(II) and Ni(II) sorption onto Na-bentonite under non-competence and competence conditions is explained better by the Langmuir sorption model. The extended Freundlich equation for competitive systems did not improve the fitting of the experimental values in relation to the Langmuir model, as R^2 values are generally lower.
- 4) The co-presence of metals led to a decrease in the sorption of both metals due to competition for adsorption sites. The effect of ion competition was higher in the case of Ni(II) than Cu(II). As a result, Ni(II) might be more mobile in a mixed metal system as would be the case of a landfill leachate. However, in multimetal systems, Ni(II) is adsorbed in a higher proportion than Cu(II), indicating that it is less affected by the type of reactive adsorption site.
- 5) Removal optimum conditions are obtained when the solution has a low ionic strength (<0.05 M), pH is higher than 6, and the metal equilibrium concentration is lower than 20 mg/L – where the competition effect is minimal.

The experimental investigation conducted here demonstrates that the Na-bentonite is able to concurrently reduce concentrations of heavy metals in

aqueous solutions. We recommend this material as an economical and efficient sorbent for heavy metals in uses related to the isolation of leachates derived from urban waste. In security landfills, in addition to its probed quality as a physical barrier, this bentonite would constitute a geochemical barrier in order to impede the dispersion of contaminants from the leakage of toxic wastes to surface and groundwater bodies.

While this bentonite is from local provenance, it is classified as a Wyoming type, with chemical, physicochemical, and technological properties comparable to this one, which is usually taken as a reference material all over the world. According to this, the results can be extrapolated to other bentonites of this type, with similar amounts of montmorillonite.

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Conflict of Interest

The authors declare no conflict of interest.

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