



Research paper

Clayey materials as geologic barrier in urban landfills: Comprehensive study of the interaction of selected quarry materials with heavy metals

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ABSTRACT

Interaction studies of clayey materials with heavy metals have been carried out at different experimental conditions to evaluate their suitability as geological barrier of landfills. For this purpose, five raw materials, usually quarried for brick making, having different mineralogical composition and geochemical and physical–chemical properties were selected. The interactions between zinc (II), lead (II), cadmium (II) and chromium (III) ions and the clayey materials were studied in solutions that simulate the characteristics (composition, majority components) and conditions of leachate from municipal solid waste landfills in the acetogenic stage (young leachate) and methanogenic stage (old leachate). Batch experiments were used to study the retention of metals on clayey materials as function of pH in non-competitive and competitive conditions. Moreover, adsorption isotherms for all the assayed metals and materials were calculated. All the clayey materials displayed lower metal sorption capacity in the young leachate conditions. The clayey materials displayed greater sorption capacity for zinc (II) and chromium (III) whereas lower sorption capacity was observed for cadmium (II). The abundance of clay minerals, carbonate content, specific surface area and the presence of smectites control the metal retention capacity of the clayey material. The obtained results showed that the selected clayey materials are suitable as components of the multibarriers in controlled urban landfills.

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1. Introduction

The geological barrier of municipal solid waste landfills is a key factor for the protection and safety issues in waste disposal (Bilitewski et al., 1997; Christensen et al., 2010; Savage, 1995). The functions of the barrier are the confining of the wastes and the buffering or attenuation of the hazardous leachate during and after the lifetime of the landfill. For this purpose, geological materials rich in clay minerals are considered among the suitable geological barriers in landfills (Koutsopoulou et al., 2010). Clay minerals, due to their small particle size and complex porous structure, have very low permeability. Their high specific surface area allows strong physical and chemical interactions with fluids and dissolved species which are subjected to electrostatic repulsion, sorption or specific cation exchange reactions. These interactions are responsible for the retention in the barrier of leachate components such as metallic cations (Churchman et al., 2006; Helios Rybicka et al., 1995). Clay minerals also have high availability and low cost (Bailey et al., 1999).

Clayey materials used as geological barrier in municipal landfills should have minimum clay content of 60% and a particle size of 2 µm (Czurda, 2006). Increased cation exchange capacity and low

permeability of the geological barrier are desirable to guarantee the longevity of the mineral barrier. The presence of smectite-type minerals in relatively small amounts (2–10%) provides a low permeability to natural soils without modifying the structural stability of the barrier (Izuka et al., 2003). Moreover, it increases the cation exchange capacity of the geological barrier allowing the retention of certain polluting agents (Gautier et al., 2010; Musso et al., 2010). Therefore, the study and characterization of the interaction between pollutants and the materials to be used as mineral barriers for landfills is an important issue that must be carried out before choosing the landfill site.

Heavy metals ions are among the most important pollutants in urban landfills. Their behavior and bioavailability are influenced by adsorption/desorption and precipitation/dissolution processes between the solid and liquid phases (Alloway, 1995). The amount of heavy metals to be adsorbed on the solid phase depends, among others, on the nature and concentration of metal, contact time, temperature or pH (Du and Hayashi, 2006; Langmuir, 1997; Msaky and Calvet, 1990). Cations are retained in the surface of the solid phase through electrostatic attractions or specific adsorption by the formation of complexes. The formation and/or rupture of the chemical bonds are the responsible for the transfer processes between the solid and liquid phases and the metal transport (Aharoni and Sparks, 1991).

The aim of this work is to evaluate the capacity of several types of clayey materials to retain heavy metals from leachate produced in municipal solid waste landfills and discuss their suitability as

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geological barrier of landfills. For this purpose, the interactions between zinc (II), lead (II), cadmium (II) and chromium (III) ions and five clayey materials of different characteristics were studied in solutions prepared to simulate the composition and conditions of young and old leachate from urban landfills.

2. Materials and methods

2.1. Materials

The clayey materials were selected from five significant quarries of ceramic raw materials in Spain. They are from the Ariño (Teruel) Q1, Pantoja (Toledo) Q2, Bailén (Jaen) Q3, Carboneros (Jaen) Q4 and Papiol (Barcelona) Q5 quarries. These materials fulfill the technical requirements of the EU Landfill directive (European Council, 1999, 2003), having hydraulic conductivity lower than $1 \times 10^{-9} \text{ m s}^{-1}$. They had a minimum clay mineral content of 50%, primarily non-expandable, to guarantee an adequate mechanical stability (Rogel-Quesada et al., 2009). Similar clayey materials have a broad distribution across the Spanish territory.

The mineralogical composition of the selected materials covers the main sheet-silicates groups, so they present different geochemical and physical–chemical properties. The Q1 clay is Cretaceous and provides high grade of kaolinitic clay (González López et al., 2005). The Q2 (García Calleja, 1991) and Q3 (González et al., 1998) clays are illitic with accessory kaolinite and smectite and have Miocene age. The Q4 clays (Vazquez and Jimenez-Millan, 2004) are Triassic and are composed only of illite. Finally the Q5 clay of Pliocene age is illitic–smectitic and is currently used as a mineral barrier under the “El Garrá” landfill (Barcelona, Spain). The Q3, Q4 and Q5 clays contain also abundant carbonates either calcite or dolomite.

All materials were sampled in situ (500 kg) and stored. 100 kg was dried in a rotary kiln at 60 °C, then ground to <5 mm size, homogenized and finally packaged in 20 kg polyethylene bags.

2.2. Synthetic leachate

The interaction studies between clayey materials and the heavy metals were carried out using two types of synthetic leachate. Leachate composition was chosen to simulate different conditions and changes of an urban landfill leachate through time. A young leachate (1–2 years) was modeled using acetic acid, to simulate characteristics of leachate in its acetogenic stage, with high organic content and a pH value near 5. The other solution was prepared to study metal adsorption in old leachate (older than 10 years). In this leachate, salinity and organic content were lower and the pH value was ~8 due to degradation of organic acids with low molecular weight to CO_2 and the reduction of sulfates to sulfides, which are characteristic processes of the methanogenic stage (Owen and Manning, 1997; Tchobanoglous et al., 1994; Williams, 2005). For interaction experiments, both synthetic leachates were doped with lead, zinc, cadmium and chromium (III).

The composition of the synthetic solutions was formulated using the computer program PHREEQC v. 2 for geochemical calculations. The Visual MINTEQ software was used to obtain the chemical speciation of each metal in the synthetic leachate. Table 1 lists the compositions of both solutions. The synthetic leachates were prepared by dissolving the corresponding salts in ultrapure water (water quality Type 1, Millipore) and adjusting the pH value to 5 for the young leachate and 8 for the old leachate. Lead and zinc were added in form of acetate salts whereas cadmium and chromium (III) were added in form of chloride salts.

2.3. Analytical methods

The mineralogy of the clayey materials was studied by powder X-ray diffraction (XRD) with a Siemens D-5000 diffractometer using Cu K α radiation, 40 mA and 40 kV, at a scanning speed of $0.48^\circ 2\theta \text{ min}^{-1}$

Table 1

Chemical composition of both types of leachate.

	Young leachate, pH = 5	Old leachate, pH = 8
	Concentration (g/L)	
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	3.92	1.427
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1.48	1.045
$\text{Mg}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$	1.14	0.3647
$\text{NH}_4\text{CH}_3\text{CO}_2$	3.51	–
KCH_3CO_2	1.35	–
KCl	–	0.4277
NaCl	–	0.1321
NaCH_3CO_2	3.47	0.2904
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	0.709	0.1160
HCH_3CO_2	3.29	–
	Concentration (mg/L)	
Cd^{2+}	10	0.10
Cr^{3+}	10	0.0050
Pb^{2+}	10	0.023
Zn^{2+}	10	0.10

from 3° to 70°. The bulk mineralogy was determined using random powders and the clay mineralogy using oriented slides using the <2 μm size fraction (Moore and Reynolds, 1989). The procedure proposed by Schultz (1964) was used to semi-quantify the minerals in the clay materials. Quantitative analysis of the sepiolite-bearing samples was obtained using the UNE standard method (UNE, 22161:1992). Semiquantitative XRD estimation of the proportion of clay minerals in the clayey fraction (mainly illite, kaolinite and smectite) was performed according to Barahona (1974).

The specific surface area (SSA) of the samples was determined by BET analysis (multipoint N_2 adsorption after degassing under N_2 flow for 18 h at 90 °C) using a micromeritics GEMINI V SSA analyzer. The cation exchange capacity (CEC) was determined at room temperature by Na^+ saturation (1 M sodium acetate at pH = 8) and displacement of Na^+ by Mg^{2+} (0.5 M $\text{MgNO}_3 \cdot 5\text{H}_2\text{O}$ at pH = 5) (Rhoades, 1982). Determination of total organic carbon (TOC) and total inorganic carbon (TIC) in the samples was carried out using a Shimadzu carbon analyzer (TOC-5000A model, equipped with the solid sample combustion unit SSM-5000A) using the optimal conditions recommended by the manufacturer. The analyzer was calibrated using anhydrous glucose (40% TC) and anhydrous sodium carbonate (12% TIC) for total carbon and inorganic carbon determinations, respectively. The percentage of TOC in sample was determined by difference between TC and TIC. The amorphous Fe_2O_3 was quantified by means of the Citrate–Ditionite–Bicarbonate (CDB) extraction method at 80 °C (Smith and Mitchell, 1989).

2.4. Interaction studies between the clayey materials and heavy metals

The interaction between clayey materials and heavy metals was studied with batch experiments in duplicates. 25.0 mL of the corresponding test solution was added to 0.250 g of the selected clayey material in 50 mL polyethylene centrifuge tubes. For each set of samples, soil-free blank solutions were also prepared. The centrifuge tubes were mechanically shaken in a thermostatically controlled orbital shaker (Selecta, model Rotavit), at 220 min^{-1} at 30 °C in the dark for 24 h. Then, the suspensions were centrifuged for 15 min at 3500 rpm (Genesys centrifuge, model Universal 16), decanted and filtered through 0.45 μm syringe acetate filters (Scharlab). The filtrates were placed in 50 mL polyethylene containers and were stored at 4 °C until the metal analysis.

In order to study the retention capacity of the clayey materials for each metal, at different pH values, solutions containing 10.0 mg L^{-1} of each heavy metal were added to the clayey materials using the previously described procedure. The pH values of the metal solutions varied between 2 and 8 to simulate the typical pH-range found in the leachate during the aging of landfills. The pH values of the filtrates were recorded. The sorption capacity under competitive conditions

was studied by adding to the five materials, young (pH = 5) and old (pH = 8) synthetic leachate, doped with the four metals at concentrations shown in Table 1. To obtain the sorption isotherms in non-competitive conditions, solutions of the young leachate doped with each individual metal at different concentrations, were added to the clayey materials according to the general procedure used for all interaction studies.

The metal concentrations in all solutions were determined by Atomic Absorption Spectrometry (AAS), using a Unicam Solaar M Serie atomic absorption spectrometer equipped with flame and graphite furnace atomizers, under the instrumental conditions recommended by the manufacturer. All standards for calibration were prepared by adequate dilution of AAS standard solutions (Fluka, USA) in the synthetic leachate solutions. The amount of metal adsorbed in the clayey material was calculated by difference between the initial concentration and the metal concentration in the filtrate analyzed by AAS.

3. Results and discussion

3.1. Characterization of clayey materials

Clayey materials were characterized before interaction with heavy metals. The mineralogical composition and other important properties of the clayey materials used are shown in Table 2.

Samples Q1, Q2 and Q4 have the highest clay mineral contents. Sample Q5 contains abundant illite, smectite and Fe-chlorite. The Q3 and Q5 materials are richer in expandable clay mineral (smectite). Other accessory minerals, such as dolomite, albite and calcite, were also present in the materials. The abundance of carbonates influences the properties of the clayey materials. For instance, the dissolution–precipitation equilibrium of carbonate minerals can cause the co-precipitation of metallic cations as carbonates or provide additional sites for sorption of metals or oxides (Lamble et al., 1997).

The SSA of the clayey materials was determined to evaluate the available surface for the interaction between the solid particles and the liquid fraction in contact with them. The highest SSA values are exhibited by Q2 and Q4 samples, which also have the highest illite content. Q1 sample with a similar content in clay minerals has a low SSA. This is attributed to the kaolinite content, which has a larger crystalline size and usually lower SSA than illite and montmorillonite (Aylmore, 1974).

The five clayey materials have similar CEC ranging between 12.3 and 15.7 cmol(+) /kg, due to the low abundance of smectite. The similar CEC values, recorded for samples Q2, containing traces of smectite, and Q5, with an estimated content of smectite of 17%, are attributed to the greater amount of clay minerals. The organic matter and carbonate contents can affect the retention of metals due to complex formation and precipitation of metals as carbonates. As can be seen in Table 2, the Q3, Q4 and Q5 materials have the highest amounts of inorganic carbon, mainly carbonates, whereas the highest values of organic carbon were observed in samples Q1 and Q3. The Q2 material has small abundance of organic carbon, inorganic carbon and accessory minerals.

3.2. Retention of metals on clayey materials as pH function

The adsorption of metals on clayey materials depends on both, the type of the metals and the liquid phase (leachate), and the characteristics of clayey materials. Moreover, the adsorption process is usually modified by the presence of different metallic species in solution due to competitive adsorption. The capacity of each clayey material to retain metals at different experimental conditions can be evaluated by estimation of the distribution coefficients (K_d) according to the equation (Sauvé et al., 2000):

$$K_d = \frac{\text{Metal retained in the clayey material}(\mu\text{g kg}^{-1})}{\text{Metal dissolved in the leachate}(\mu\text{g L}^{-1})} \quad (1)$$

The relationship between the metal retained in the clayey material and metal dissolved in the leachate is considered as a constant value.

The distribution coefficient values for all metals and clayey materials as a function of the pH measured after the interaction are shown in Fig. 1. The lower values of distribution coefficient were observed for cadmium (II) whereas the higher values were obtained for lead (II). Competition between protons and heavy metals by sorption sites of clayey surfaces was established at moderately acid pH values (Bradl, 2004), which diminished with increasing pH value due to decrease of proton concentration. So, an increase in the retention of metals was observed as pH values were increased. At higher pH values, metals could precipitate at clay surface as lead, zinc and cadmium carbonates or hydroxo-complexes (Scheidegger and Sparks, 1996) or chromium (III) hydroxide, increasing the distribution coefficient.

Table 2
Mineralogical composition and physicochemical characterization of the clayey materials.

	Clayey materials				
	Q1	Q2	Q3	Q4	Q5
Mineralogical composition					
Phyllosilicates, %	74	72	47	69	60
Kaolinite, %	62	11	6	<1	<1
Illite, %	12	60	31	69	34
Smectite, %	<1	1	10	Not detected	17
Chlorite, %	Not detected	Not detected	Not detected	Not detected	9
Quartz, %	20	14	29	17	26
Microcline, %	1	4	3	4	4
Albite, %	1	10	3	<1	2
Dolomite, %	2	<1	4	7	<1
Calcite, %	1	<1	13	<1	7
Other minerals (presence)	Siderite	Not detected	Pyrite	Hematite	Hematite
Fe ₂ O ₃ amorphous, %	0.2	0.4	0.3	1.7	1.5
Physicochemical characterization					
S_{BET} , m ² /g	20.1	42.3	29.7	38.7	19.5
CEC, cmol/kg	12.3	15.7	13.2	12.7	15.3
k, m s ⁻¹	1.93×10^{-10} (1.79)	1.69×10^{-10} (1.67)	4.07×10^{-10} (1.76)	8.21×10^{-10} (1.93)	5.22×10^{-10} (1.95)
TOC, %	1.24	0.11	1.00	0.06	0.10
TIC, %	<0.01	0.03	2.52	1.23	1.39

k: hydraulic conductivity measured in a triaxial cell (density in g cm⁻³ of dry sample).

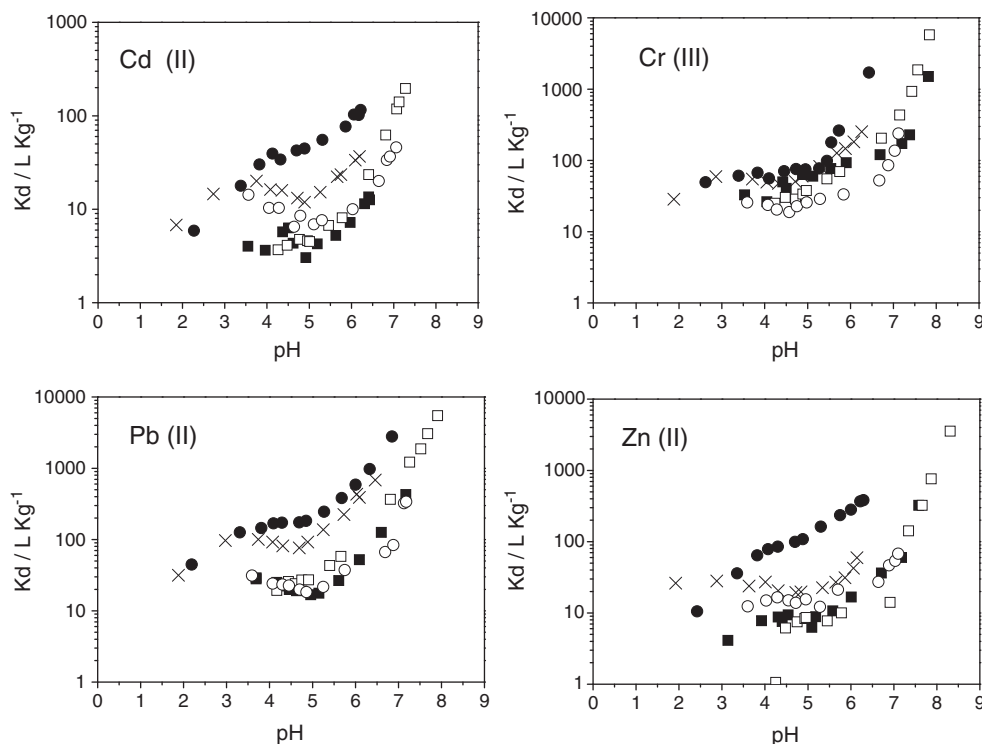


Fig. 1. Distribution coefficients (K_d) for cadmium (II), chromium (III), lead (II) and zinc (II) at the clayey materials Q1 (x), Q2 (●), Q3 (□), Q4 (■) and Q5 (○) as pH function.

The highest values of distribution coefficients and the maximum metal retention were obtained at different pH values for each clayey material. In general, samples Q1 and Q2 reached highest metal retention capacity at lower pH values than the remaining clayey materials. Both materials have high clay mineral content and carbonates are virtually absent. Moreover, the abundant kaolinite present in these materials can decrease the pH during interaction (Cama et al., 2002; Huertas et al., 1998). In Q3, Q4 and Q5 samples considerable increase of pH was observed due to the abundance of carbonates. The presence of carbonates improved the retention of the metals through precipitation of lead, cadmium and zinc carbonates or chromium (III) hydroxide. The high clay mineral content and the high SSA in Q2 affect the significant improvement in metal retention at pH values lower than 6. This material has also the highest CEC, in spite of the low smectite content. Samples Q4 and Q2 have similar characteristics in terms of clay mineral content, illitic nature and SSA, but the CEC of Q4 is lower than the CEC of Q2. This suggests the greater availability of polar surfaces in Q2 for metallic ions interactions. This fact can be responsible for the slight expandability of this illitic clay (Cuadros, 2010). In addition, the dissolution of the dolomite when sample Q4 is exposed to an acidic media would produce a competitive effect for charged sites between Mg, Ca and heavy metal ions.

3.3. Competitive sorption of metals from synthetic leachate solutions on clayey materials

In the experiments using synthetic leachate, a competition for the sorption sites of the solid phase may be established between the metals and the potassium, ammonium or sodium cations present in the leachate. Moreover, the metals can form stable and soluble complexes with chloride and organic matter. In the presence of the old leachate, the high number of negatively charged bonding sites on the surface of the clays (Helios Rybicka et al., 1995) can cause a more effective interaction between the metals and the clayey materials. In accordance with the previous study on the interaction between metal and clayey materials

as pH function, the lower sorption capacity and distribution coefficients were obtained in the experiments with young leachate solutions.

The results for the five materials are shown in Fig. 2. Sample Q2 displayed the higher sorption of metals at pH 5 possibly due to the higher SSA value and high clay minerals content. The distribution coefficients of samples Q3 and Q4, in general, were similar although Q4 has both high SSA and clay minerals content. The high capacity of metal sorption exhibited by Q3 material may be due to the presence of smectite. In general, samples Q1 and Q5 showed the lowest distribution coefficients and the lowest SSA. As it was previously shown, sample Q1 has a low SSA and the highest clay minerals content, mainly kaolinite. Sample Q5 has higher clay mineral content than Q3, but it also has low SSA. These facts indicate that trace metals were preferably adsorbed at the external surfaces of the sheet-silicates, rather than the interlayers of the smectitic components, without excluding a small contribution from cation exchange sites.

Considering the distribution coefficients values in competitive conditions (Fig. 2), lead was preferably adsorbed by samples Q1 and Q3 and zinc and lead were preferably adsorbed by Q2. Chromium was preferably retained by Q4, whereas zinc, lead and cadmium were selectively adsorbed by Q5 all showing comparable distribution coefficients. The percentages of retained metal at these experimental conditions were higher than 2%, 4%, 5% and 6% for zinc, chromium, lead and cadmium, respectively, in all the clayey materials. Heterogeneity, characteristics and different properties of the materials probably lead to different selectivity for metals.

The amount of soluble metal species in old leachate was lower than in young leachate (Table 1) because the solubility of metal species decreases as pH increases due to formation of insoluble hydroxides. Saturation of the bonding sites of clayey materials can not be reached when the metal concentration in leachate is very low. As it was previously mentioned, a more effective interaction between metals and clayey materials was observed in the presence of old leachate due to the high number of negatively charged bonding sites present in clayey surface. Indeed, the distribution coefficients in old leachate model (pH 8) were significantly higher than their counterparts at pH 5. In old leachate, Zn, Pb and Cr

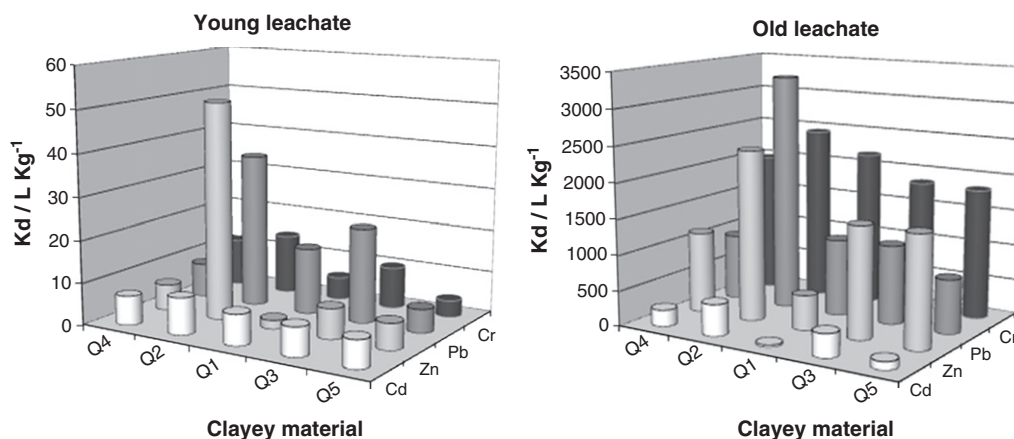


Fig. 2. Distribution coefficients (K_d) for cadmium (II), zinc (II), lead (II) and chromium (III) at the five clayey materials, in competitive conditions, using the young (left) and old (right) synthetic leachate.

were retained in percentages exceeding 83%, 88% and 95%, respectively for all the clayey materials. The lower distribution coefficients were obtained for Cd, with retention percentages ranging from 23% for Q1 to 82% for Q2. Soluble Cd is mainly present as exchangeable cation at pH values lower or close to 8 (Adriano, 2001; Undabeytia et al., 1998). Cadmium as exchangeable cation is weakly bonded on the clay surface, so a lower retention would be expected (Singh et al., 1999). Sample Q2 also displayed the highest capacity of metal retention in old leachate whereas the lower distribution coefficients were observed in Q1 and Q5. The obtained results suggest that metals were preferentially adsorbed at the external surface of clayey materials.

3.4. Sorption isotherms in non-competitive conditions

In order to perform a comprehensive study of metal adsorption in clayey materials, the adsorption isotherms in non-competitive conditions were calculated at pH 5 for all the metals and materials. Sorption isotherms allow estimation of the maximum adsorption capacity of metal onto the solid phase and quantification of the affinity between the metals and the clayey materials (Aboul-Kassim and Simoneit, 2001; Altin, et al., 1998). These parameters were determined at pH 5, because the saturation of the bonding sites of clayey materials with the metal cations could be produced at this pH value. In addition, precipitation of chromium (III) hydroxide and lead, zinc and cadmium carbonates is virtually avoided at pH 5.

The isotherm models used mainly for heavy metals follow the Langmuir and Freundlich equations. In the Langmuir isotherm model it is assumed that sorption energy is the same for all surface sites and independent of the adsorption level. However, the adsorption energy can change because real surfaces were not homogeneous. The Freundlich adsorption model contains a new parameter which considers the heterogeneity of the surface (Aboul-Kassim and Simoneit, 2001). The Langmuir equation has been generalized to include the heterogeneity of the sorbent surface too (Sohn and Kim, 2005; Tsai et al., 2005). This isotherm is the most promising extension of the Langmuir and Freundlich isotherms (Cheng et al., 2010) and it is expressed as:

$$q = \frac{Q(K_{\min} C_e)^\beta}{1 + (K_{\min} C_e)^\beta} \quad (2)$$

where q is the sorbed metal amount per unit of sorbent (clayey material), C_e is the concentration of sorbate (metal) at the equilibrium, Q is the maximum sorption capacity of the sorbent, K_{\min} is the minimum value of the bonding energy coefficient and β is indicative of the heterogeneity of the sorbent.

The experimental data were fitted to the generalized Langmuir equation using non-linear regression and the Origin® package software (v. 8.0). The sum of the residuals of root mean square error (RMSE) was used as performance function:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^m (Q_i - q_i)^2} \quad (3)$$

where Q_i is the data of batch experiments, q_i is the estimated values associated with Q_i , m is the number of data of batch experiments, and n is the degree of freedom. The goodness of fit of the fitting function, R^2 , was also calculated.

The obtained values for the parameters of the generalized Langmuir equation after fitting of experimental data are listed in Table 3. The isotherms for adsorption of zinc (II) are shown in Fig. 3. The adsorption isotherms for the four metals obtained for Q2 are plotted in Fig. 4. The clayey materials exhibited different sorption capacities and bonding affinities as a function of the tested metal and the physico-chemical characteristics of the material, reflecting the heterogeneity of the clayey materials.

All clayey materials showed lower sorption capacity for Cd. Cadmium can form complexes with acetate and chloride anions present in young

Table 3
Obtained parameters in the fitting of the experimental data of metal adsorption onto clayey materials to the generalized Langmuir isotherm.

Metal	Clayey material	Q_L , mmol kg ⁻¹	K_L , L mg ⁻¹	β	R^2
Zinc	Q1	12.83 ± 2.34	0.0192 ± 0.0070	1.12 ± 0.18	0.9972
Zinc	Q2	21.38 ± 1.30	0.0480 ± 0.010	0.62 ± 0.04	0.9994
Zinc	Q3	4.86 ± 0.70	0.0276 ± 0.0071	1.46 ± 0.32	0.9928
Zinc	Q4	5.12 ± 0.20	0.0625 ± 0.0060	1.06 ± 0.09	0.9989
Zinc	Q5	2.31 ± 0.15	0.0870 ± 0.018	0.91 ± 0.14	0.9952
Lead	Q1	2.07 ± 0.18	0.0435 ± 0.0065	1.07 ± 0.10	0.9986
Lead	Q2	9.05 ± 12.41	0.0079 ± 0.0279	0.65 ± 0.25	0.9943
Lead	Q3	2.02 ± 0.10	0.0871 ± 0.0141	0.814 ± 0.077	0.9980
Lead	Q4	1.08 ± 0.07	0.1590 ± 0.390	0.90 ± 0.16	0.9887
Lead	Q5	1.58 ± 0.23	0.0312 ± 0.0108	1.18 ± 0.26	0.9925
Cadmium	Q1	1.72 ± 0.15	0.0318 ± 0.0060	1.24 ± 0.15	0.9864
Cadmium	Q2	1.81 ± 0.05	0.0865 ± 0.0086	1.39 ± 0.13	0.9877
Cadmium	Q3	1.78 ± 0.12	0.0346 ± 0.0049	1.44 ± 0.19	0.9797
Cadmium	Q4	0.63 ± 0.03	0.0652 ± 0.0060	2.80 ± 0.68	0.9326
Cadmium	Q5	1.19 ± 0.07	0.0479 ± 0.0047	2.15 ± 0.38	0.9602
Chromium	Q1	2.61 ± 0.13	0.0225 ± 0.0007	7.0 ± 1.3	0.9896
Chromium	Q2	12.67 ± 0.79	0.0197 ± 0.0022	1.43 ± 0.14	0.9944
Chromium	Q3	11.31 ± 1.27	0.0495 ± 0.0087	1.59 ± 0.29	0.9903
Chromium	Q4	5.32 ± 0.14	0.0367 ± 0.0006	4.97 ± 0.33	0.9976
Chromium	Q5	3.89 ± 0.10	0.0383 ± 0.0010	2.55 ± 0.18	0.9977

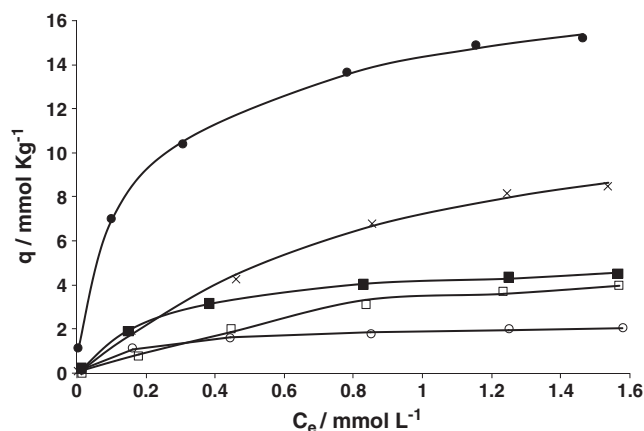


Fig. 3. Experimental data and the sorption isotherms (lines) for zinc and Q1 (x), Q2 (●), Q3 (□), Q4 (■) and Q5 (○) materials.

leachate at pH 5. These complexes can be weakly sorbed onto the surface of the clayey materials, so sorption capacity is lower compared to the free cadmium ions in the absence of acetate and chloride. All clayey materials showed higher sorption capacities for zinc and chromium. Samples Q1, Q2 and Q5 showed higher adsorption for Zn^{2+} and Q3 showed higher adsorption for Cr^{3+} . In contrast Q4 displayed similar sorption capacity for both metals. However, the highest bonding energies were observed for lead and cadmium ions in all the clayey materials except for Q5, where the highest value was showed for zinc. The lower affinity constants for chromium might be due to the higher kinetic inertia of this metal to break bonds with water molecules and the high concentration of acetate ions in the leachate. Chromium forms stable complexes with acetate. A competition between the active sorption sites of the clayey materials and the acetate ions might decrease chromium adsorption on the clayey materials and explain the observed low affinity constants notwithstanding the high retention capacities. The similar behavior exhibited by Zn^{2+} ions may be explained by formation of the monovalent ion ZnOH^+ at pH 5 (Gier and Johns, 2000).

According to the affinity constant and maximum retention capacity values of the clayey materials, a classification or “ranking” can be established for each metal (Table 4). In general, the materials with best sorption capacities were Q2 and Q1 with the highest abundances of clay minerals. In general, Q2 is the best clayey material for metallic retention in agreement with its high SSA. The results from sorption experiments showed that a high clay mineral content and a relatively high SSA are more important factors for heavy metal adsorption than the type of the clay minerals present. Moreover carbonate minerals

Table 4
Classification of clayey materials as retention capacity function for each metal.

Metal	Ranking of clayey material
Cd	$\text{Q3} \approx \text{Q1} > \text{Q2} > \text{Q5} > \text{Q4}$
Cr	$\text{Q2} \approx \text{Q3} > \text{Q4} > \text{Q5} > \text{Q1}$
Pb	$\text{Q2} > \text{Q1} > \text{Q3} \approx \text{Q5} > \text{Q4}$
Zn	$\text{Q2} > \text{Q1} > \text{Q4} \approx \text{Q3} > \text{Q5}$

seem to modulate the retention capacity of clayey materials because they can promote competitive interactions for heavy metal ions when they are dissolved, but on the other hand they can induce precipitation of metals as carbonates, hydroxo-complexes or hydroxides at high pH values. Finally the presence and abundance of organic matter was an important parameter for cadmium retention by the clayey material (Lee et al., 1996).

4. Conclusions

Interaction studies between heavy metals and clayey materials showed greater retention for Zn^{2+} and Cr^{3+} . All clayey materials showed low sorption capacity for cadmium (II). The highest retention on clayey materials was showed at conditions of old leachate (pH 8) due to formation of insoluble carbonates, when carbonate minerals are present, and hydroxides. The mineralogical composition and the physical–chemical properties are important factors affecting the behavior of the clayey materials during sorption. The clay mineral content, the SSA, the absence or presence of carbonates and the presence of small amounts of smectite are considered the most important parameters for sorption. Sample Q2 with high clay mineral content, the highest SSA and CEC values and the presence of traces of expandable smectite showed highest capacity for metal sorption.

Other factors such as the abundance of poor crystalline iron oxides and organic matter, also influence sorption processes. Metal sorption in clayey materials is a complex process affected by mineralogical composition and physical–chemical properties of materials and leachate composition. All studied clay materials meet the specifications required by the EU Landfill Directive and according with the experimental results, they all can be considered suitable as geological barriers in landfills. Additional advantages include their high availability and low cost.

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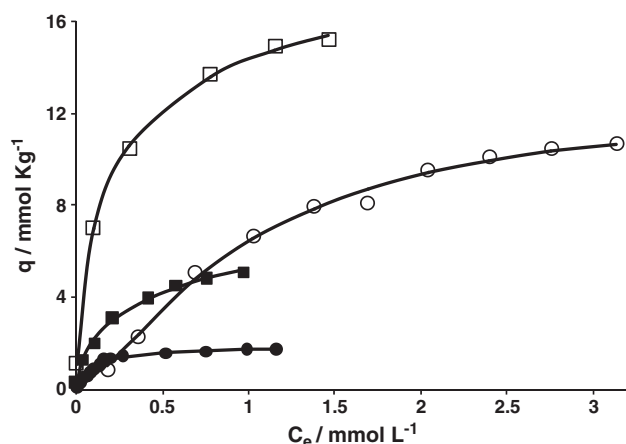


Fig. 4. Experimental data and the sorption isotherms (lines) for Q2 material and cadmium (●), lead (■), chromium (○) and zinc (□).

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