Mobility of Cr, Pb, Cd, Cu and Zn in a loamy sand soil: A comparative study

B. Fonseca *, H. Figueiredo, J. Rodrigues, A. Queiroz, T. Tavares

IBB-Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho, 4710-057 Braga, Portugal

ARTICLE INFO

ABSTRACT

Interest in soil contamination has been growing in recent years due to the ongoing degradation of soil environments. Therefore, the development of remediation techniques and the study of contaminant sorption and migration are areas of intense research.

In this study, the authors sought to evaluate the scenario of co-contamination of a loamy sand soil by multiple heavy metals. To that end, the sorption and transport of five metals—Cr, Pb, Cd, Cu and Zn—was evaluated using representative samples of a soil from the north of Portugal. The tests were conducted in batch and continuous systems using single- and multiple-metal acid solutions to evaluate the effect of metal competition. In accordance with the type of assay—batch or continuous—Langmuir or Convection Dispersion Two-Site Nonequilibrium models were adjusted to explain the sorption/transport data. FTIR analyses were performed on the final samples of the continuous systems.

Generally, the results revealed good fitting of the tested models for the metals in competitive and noncompetitive scenarios, with the exception of Zn that was originally present in soil samples at higher concentrations. As expected, the influence of competition was observed in both batch and continuous systems, but with different tendencies. The FTIR spectra also revealed a strong influence of clay minerals and organic matter on the sorption of the metals.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The release and disposal of heavy metals from anthropogenic activities have been responsible for the increasing concentrations of these contaminants in soil environments. The high loading of metals in soils may affect the growth of plants and the health of animals, thereby representing a significant threat to public health (Berti and Jacobs, 1996). Consequently, the development of effective strategies to manage heavy metal pollution is of great importance (Adhikari and Singh, 2003) but requires extensive knowledge of the sorption and transport behaviors of heavy metals and of the diverse variables affecting these processes. Several studies have been performed in order to establish the influence of different parameters on heavy metal sorption/desorption (Appel and Ma, 2002; Fonseca et al., 2009b; Fontes et al., 2000; Hanna et al., 2009; Lee et al., 2001; Liu et al., 2006; Sipos et al., 2008). Most of these studies primarily reported the results of batch tests, giving detailed information on the sorption process but little on the transport of the heavy metals. Therefore, because the simultaneous presence of competing metals is known to affect sorption processes and leaching potentials through soil profiles, this study sought to evaluate the retention of heavy metals using either batch or flow tests, simulating single- and multi-metal contamination, in order to obtain more realistic results (Serrano et al., 2005). However, it is also important to perform these types of studies for different regions and soils, as the composition of the soil matrix may result in unexpected behavior.

Some heavy metals such as cadmium (Cd), zinc (Zn) and copper (Cu) can be found in fertilizers used on agricultural lands (Tran et al., 1998; USEPA, 2009). In addition, Zn and Cu are also present in high concentrations, along with lead (Pb), in roadside soils (Miller et al., 1989). These four metals, together with chromium (Cr), are frequently identified in wastes from several industrial activities including electroplating, car manufacturing, and metallurgy (Covelo et al., 2008; Lau and Stenstrom, 2005; USEPA, 2009). Thus, these five metals can be readily found as co-contaminants in agricultural lands as well as near roads and/or automotive facilities. For this reason, a soil sample collected in a location of great agricultural activity near an automotive facility was used to study the competitive and non-competitive sorption and transport of Cr, Pb, Cd, Zn and Cu.

Batch tests were undertaken using single- and multiple-metal solutions with equimolar concentrations of the aforementioned heavy metals in order to study their sorption equilibria. The Langmuir isotherm model was adjusted to the experimental data, allowing the determination of the soil's maximum sorption capacity for each metal, with and without competition. To evaluate the retention of each metal in single- and multiple-metal flow systems, the respective solutions were pumped through soil columns. Finally, the CXTFIT code was used to fit the dimensionless two-site nonequilibrium convection–dispersion

* Corresponding author at: Biological Engineering Department, University of Minho, Campus de Gualtar, 4710-079 Braga, Portugal. Tel.: +351 253 604 400; fax: +351 253 678 986.

E-mail address: bfonseca@deb.uminho.pt (B. Fonseca).

equation to the breakthrough curves (Toride et al., 1995; van Genuchten, 1981) in order to determine the retardation factor for each metal under the tested conditions. Functional groups present in the soil that may have some role in the sorption process were identified by FTIR.

2. Material and methods

2.1. Soil characterization

Several representative soil samples of a loamy sand soil were collected at Póvoa de Varzim, Oporto, Portugal (41°25′15.58″N and 8°45′58.27″O), homogenized and characterized as described elsewhere (Fonseca et al., 2009a, 2009b). The particle distribution was determined by means of laser granulometry (Beckman-Coulter mod. LS230). The soil pH was determined according to US EPA method 9045D (USEPA, 2004). The ammonium acetate (Hendershot et al., 1993) and the Tinsley (Tinsley, 1950) methods were used to quantify the cationic exchange capacity and the organic matter content of the soil, respectively. Moreover, the concentration of each element—Cr, Cd, Pb, Zn, and Cu—was determined by flame atomic absorption (Varian SpectraAA-400), after microwave digestion (Aurora Instruments MW600) with nitric acid using US EPA method 3051A (USEPA, 2007). Iron and manganese oxides were determined by the dithionite–citrate method (Mehra and Jackson, 1958). Finally, the carbonate content and mineral composition were determined with a Scheibler calcimeter and by X-ray diffraction analysis (Philips PW3710), correspondingly. Table 1 summarizes the physical and chemical characterization performed for the studied soil.

2.2. Batch experiments

Sorption isotherm assays for Cr, Pb, Cd, Zn and Cu, with either single or mixed solutions, were performed using the batch equilibrium technique. The experiments were conducted by adding 20 mL of each metal solution or an equimolar solution of the five metals to 2 g of soil in 50 mL polypropylene centrifuge tubes. The experiments were performed using seven different solutions, prepared on a molar concentration basis, in order to prevent mass effects (Echeverria et al., 1998). The heavy metal concentration range [0.05 mM–0.48 mM] was selected considering the legislated limit for Pb, as this was the heaviest metal tested. Except for the Cr solutions, which were prepared from potassium dichromate salt, the solutions were prepared using nitrate salts of the desired heavy metals in a background of 0.01 M of $CaCl_2$. This background was used to improve centrifugation and minimize cation exchange (OECD, 2000). The solutions were acidified with concentrated HNO_3 (65%), in order to avoid the precipitation of metal cations (pH ≤ 2). It should be noted that the initial concentration of every metal

was determined by flame atomic absorption spectroscopy after the preparation of the solutions.

Preliminary studies showed that over the concentration range tested, Cr reached sorption equilibrium after 192 h, the longest equilibration time of the five metals studied (Fonseca et al., 2009a; Serrano et al., 2005; Usman, 2008; Vega et al., 2006). Therefore, all the batch equilibrium tests, including blanks, were undertaken in an orbital mixer (Certomat® S) for 192 h at room temperature (25 ± 0.5 °C) and at a shaking speed of 100 rpm. The polypropylene tubes containing the soil–solution mixtures were then centrifuged at 5000 rpm for 5 min, and an aliquot of the supernatant was collected in pre-acidified sample tubes (2% HNO_3). These samples were stored at 4 °C for future analysis by flame atomic absorption spectroscopy. The pH of the supernatant was measured and was always approximately 6 ± 0.5.

The concentration of metal adsorbed onto the soil at equilibrium— S/(mmol kg^{-1})—was calculated as:

$$S = (C_i - C)V / W \qquad (1)$$

where C is the concentration of metal in the solution at equilibrium (mM); C_i is the initial concentration of metal in the liquid phase (mM); V is the volume of metal solution (L) and W is the weight of the soil sample (kg). The results were plotted in a graph of S versus C and the Langmuir isotherm model was fitted to data:

$$S = (S_{max}bC) / (1 + bC) \qquad (2)$$

S_{max} is the maximum mass of metal that can be sorbed by a given mass of the sample (mg kg^{-1}); b is a constant related to the binding strength (L mg^{-1}) (Fonseca et al., 2009a; Langmuir, 1918; Sparks, 1995).

2.3. Continuous flow experiments

All column experiments, including duplicates, were conducted at room temperature—25 ± 1 °C—in acrylic columns 2.5 cm in diameter by 25 cm deep. The packed soil in the columns had a mean bulk density of (2.3 ± 0.3) g cm^{-3} and a bed height of (22 ± 1) cm. Single-metal solutions with 0.05 mM of each metal—Cr, Pb, Cd, Zn and Cu—and also a mixed solution with equimolar concentrations of the five metals, each with a pH lower than 2, were passed through the columns for approximately 35 h at an average flow rate of (15 ± 0.2) mL min^{-1}. To ensure saturation flow conditions and, consequently, the absence of immobile regions, the columns were operated in an upward flow mode (Papelis and Um, 1999). The samples were collected in 50 mL polypropylene tubes, and an aliquot was acidified with 2% ($^v/_v$) of concentrated HNO_3 (65%) for final analyses by flame atomic absorption spectroscopy. The pH of the effluent samples was also measured. The dimensionless two-site nonequilibrium convection–dispersion equation (TSM) was then fitted to the obtained experimental breakthrough curves (C/C_0 versus t) using the CXTFIT model (Toride et al., 1995), in order to determine the retardation factor—R—the coefficient of partitioning between the equilibrium and nonequilibrium phases—β—and the mass transfer coefficient for transfer between the two phases—ω. The hydraulic parameters, namely the dispersion coefficient—D/(cm^2 h^{-1})—and the pore water velocity—v/(cm h^{-1})—were determined independently for each column. Specifically, the equilibrium convection–dispersion equation (CDE) was fitted to the breakthrough curves of a nonreactive tracer—$CaCl_2$ (0.01 M). Consequently, a residence time of approximately 50 min was estimated for the flow experiments. The detailed procedure has been described elsewhere by Fonseca et al. (2009b).

After each displacement experiment, the soil bed was collected and homogenized, three samples of each column were digested (Fonseca et al., 2009b; USEPA, 2007), and the metal concentration in

Table 1
Chemical and physical properties of soil.

Clay (%)	2.58
Silt (%)	23.06
Sand (%)	74.36
pH (H$_2$O)	5.9
Cationic exchange capacity/(cmol$_c$ kg^{-1})	12.52
Organic matter content/(%)	3.5
[Fe$_{ox}$]/(g kg^{-1})	3.82
[Mn$_{ox}$]/(g kg^{-1})	0.10
[Cr]/(mmol kg^{-1})	0.17
[Pb]/(mmol kg^{-1})	0.58
[Zn]/(mmol kg^{-1})	4.21
[Cd]/(mmol kg^{-1})	0.01
[Cu]/(mmol kg^{-1})	0.54
[CaCO3]/(mg kg^{-1})	0.0
Clay minerals[a]	Smectite, illite, kaolinite

[a] Average of clay minerals content: smectite (18%); illite (31%); kaolinite (41%).

each sample was determined through flame atomic absorption spectroscopy. These samples were also analyzed by transmission FTIR (FTIR BOMEM MB 104) on pressed KBr pellets (100 mg of KBr and 1 mg of sample). Background correction for atmospheric air was used for each spectrum. Spectra were obtained in the range 500–4000 wavenumbers with a minimum of 10 scans and a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Soil characterization

According to the data compiled in Table 1, it can be inferred that the studied soil is slightly acidic loamy sand. It has considerable organic matter content, but low cationic exchange capacity and no carbonate (Fonseca et al., 2009a). Kaolinite was found to be the predominant mineral composing the clay fraction of the soil sample. Finally, all the heavy metals were found in concentrations below the national legislated limit for soils with pH between 5.5 and 7.

3.2. Batch experiments

Fig. 1 shows the isotherm curves obtained for each metal in competitive (multiple-metal) and noncompetitive (single-metal) systems. Generally, the isotherm curves have the shape of an L-curve isotherm, resulting from the relatively high affinity of the soil particles for the metal at low surface coverage, an affinity that decreased as the surface became saturated (Echeverria et al., 1998; Sposito, 1989). For the noncompetitive sorption of Pb and the competitive sorption of Cr, the isotherms obtained took the form of nearly vertical lines, or H-type isotherms. These are usually produced by inner-sphere surface complexation or by significant van der Waals interactions in the adsorption process (Sposito, 1989). Finally, the curves obtained for the noncompetitive sorption of Cu and Zn revealed an S-type curve. This is related to the low affinity between the soil particles and the metal at low concentrations due to the

interference of other substances, such as soluble organic matter, that can compete with soil particles for the metal cations (Sposito, 1989). Except for Cr, all the other equilibria were reached more slowly in the case of competitive sorption (Figure 1) as the ions competed for sorption sites (Markiewiez-Patkowska et al., 2005). Nevertheless, the higher sorption density of Cu may also be due to the formation of Cu–Cr precipitates, since the soil–solution at the end of the experiment had a pH of approximately 6 (Sun et al., 2006). This could also explain the higher retention of Cr when in competition with Cu and other metals (Yolcubal and Akyol, 2007).

As mentioned before, the experimental isotherm obtained for the sorption of Pb in the absence of competition was a nearly vertical line (Figure 1), revealing its total sorption and its high affinity for the soil despite the variation in the solution concentration. Given this observation and the values of the Langmuir affinity constant—b—determined for each metal in both systems (Table 2), a sorption trend can be defined as: Cr>Pb>Cd>Cu>Zn. This trend can be mainly explained by the conventional hard–soft acid–base (HSAB) principle and the nature of the ions studied. The "hard" ions are those with high electronegativity, low polarizability and small ionic size. These ions prefer hard ligands but form weak complexes with them. However, the "soft" ions have greater affinity for "soft" sites and are more strongly bounded (Ghosh and Biswas, 2003; Liu et al., 2006; Puls and Bohn, 1988; Sparks, 1995). It should be noted that, at low pH values, Cr^{6+} exists mainly as an oxyanion, which is adsorbed at positively charged sites. In fact, the equilibrium pH values of the sorption experiments, including the blank, were between 5.5 and 6.5, indicating the degree of protonation of the soil surface. Furthermore, oxyanions are "soft" bases and, according to the Pearson concept, can react strongly with Lewis acid sites created by inner-sphere surface complexation (Bailey et al., 1960; Banks et al., 2006; Fonseca et al., 2009b; Pearson, 1963; Sposito, 1989).

As the working concentration range is very narrow in these studies, the experimental maximum sorption capacities observed (Figure 1) differ largely from the estimated values (Table 2), because the trend of the isotherm curves for higher concentrations is unpredictable. However,
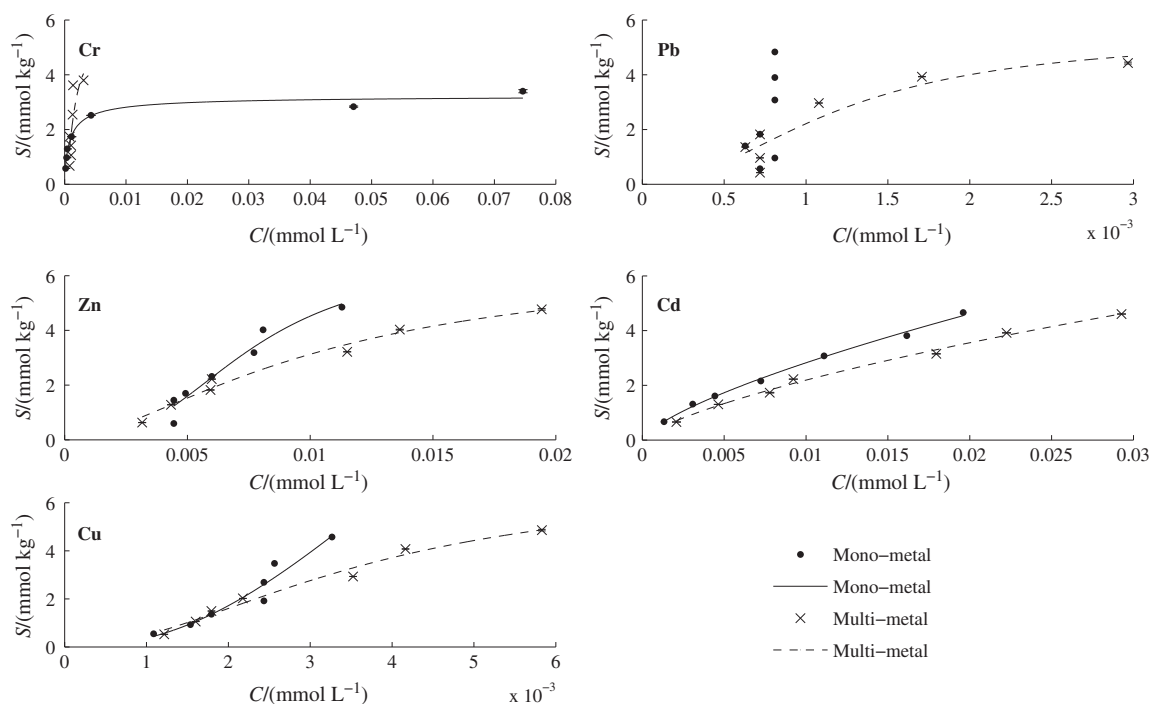

Fig. 1. Adsorption isotherms obtained for the tested metals in competitive and noncompetitive systems. Lines represent the adjusted Langmuir model. The error bars depict the confidence interval for a level of confidence of 95%.

Table 2
Values of Langmuir and Sips equations parameters determined in the mono- and multi-metal batch systems, for each tested metal. The standard deviations were under 10%.

Langmuir	Mono-metal	Multi-metal
	Cr	
S_{max}	3.10	–
b	1364	–
r^2	0.964	–
	Pb	
S_{max}	–	14.0
b	–	183
r^2	–	0.793
	Zn	
S_{max}	9879	17.0
b	0.04	21.0
r^2	0.831	0.971
	Cd	
S_{max}	10	10
b	41	30
r^2	0.988	0.991
	Cu	
S_{max}	9977	8531
b	0.1	0.1
r^2	0.735	0.956

Table 3
Quality of fit and parameter estimates based on the two-site chemical nonequilibrium convective dispersion equation, for mono- and multi-metal flow systems. The standard deviations were under 10%.

Parameters	Mono-metal	Multi-metal
	Cr	
R	107	502
β	0.11	0.00
ω	0.13	0.17
r^2	0.924	0.73
	Pb	
R	34	39
β	0.63	0.62
ω	0.01	0.02
r^2	0.999	0.995
	Zn	
R	6	–
β	0.18	–
ω	100	–
r^2	0.887	0.030
	Cd	
R	27	13
β	0.99	0.72
ω	100	0.58
r^2	0.987	0.996
	Cu	
R	49	198
β	0.99	0.09
ω	60	0.03
r^2	0.998	0.993

it is clear from the experimental data (Figure 1) that all the metals at the tested concentration range were totally sorbed in this soil, in either noncompetitive or competitive scenarios.

3.3. Flow experiments

In Fig. 2, the breakthrough curves obtained for each metal in competitive and noncompetitive flow tests are shown. The respective adjusted two-site adsorption models are also presented. Generally, the fit provided by the two-site adsorption model was good, as demonstrated by the correlation coefficient values in Table 3. However, the breakthrough curve of Zn in the competitive sorption experiment could not be fit using this model. Values of relative

concentration much higher than 1 were obtained for this assay, with more expression in the first 5 h before the breakthrough point of the other metals (Figure 1). The Zn cations can be easily exchanged when competing with other metal cations (Covelo et al., 2004). Therefore, it can be assumed that a fraction of the highly concentrated native Zn (Table 1) was washed out from the column, increasing its concentration in the effluent, especially before the saturation of the exchangeable surfaces.
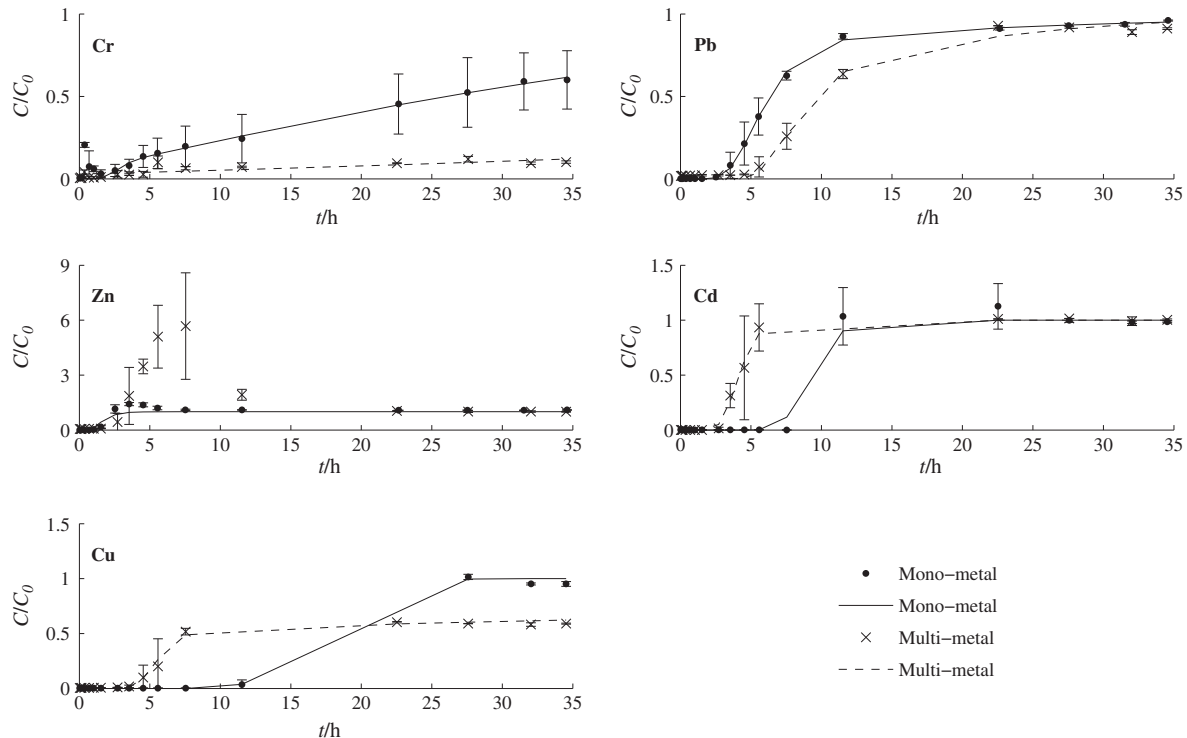

Fig. 2. Experimental breakthrough curves obtained for each metal in competitive and noncompetitive scenarios. Lines represent the adjusted two-site model. The error bars depict the confidence interval for a level of confidence of 95%.

Examining the single-metal systems, it is evident that the highest retardation factor—R—was obtained for Cr, whose affinity for the soil was already shown to be the highest among the metals studied (Table 3). Cr oxyanions were specifically sorbed to sites with high dissociation constants, making them less vulnerable to leaching. However, the batch tests revealed that the other metals were sorbed at less energetic sites, making them more susceptible to acid leaching. A trend in relative metal mobility under the conditions studied can be defined as: Zn>Cd>Pb>Cu>Cr, which is slightly different from what would be expected after the analysis of the affinity constants (b) obtained in the batch tests (Table 2), although it is known that the sorption and transportation of heavy metals in dynamic environments do not always occur under equilibrium conditions (Sposito, 1989). In fact, compared with Cd and Cu, the values of the partitioning coefficient between the equilibrium and nonequilibrium phases—β—obtained for Cr and Zn were significantly lower (Table 3). This suggests that the sorption of these metals occurs instantaneously at equilibrium sites but is time-dependent at the remaining sites, with higher sorption energy (Toride et al., 1995). However, the values found for the mass transfer coefficients ($\omega > 1$) suggest that not only Cd and Cu cations but also Zn cations are promptly sorbed at equilibrium sites. The results with respect to Pb transport and sorption are less conclusive. The mass transfer coefficient points to a nonequilibrium process ($\omega < 1$), but the value of β reveals that a larger amount of these cations are sorbed at equilibrium sites than at nonequilibrium sites (Candela et al., 2007; Seuntjens et al., 2001; van Genuchten, 1981). According to the batch experiment results, both Cr and Pb cations were retained at sites with high sorption energies; therefore, sorption at nonequilibrium sites seems to be predominant, as this reaction is kinetically controlled. When in competition, the mass transfer coefficient did not vary significantly for Cr and Pb, as these metals seemed to be sorbed more specifically. By contrast, the value of this variable decreases for the Cd and Cu cations, probably because competition stimulates the specific sorption of these ions.

The values obtained for the retardation factor—R—estimated for Cr and Cu transport in the competitive system were much higher than the values obtained for the other metals. This strengthens the aforementioned hypothesis of the precipitation of a Cu–Cr solid in the column, which is especially reasonable given that the pH of the effluent in the first 5 h was above 6 (Figure 3) due to the low acid-buffering capacity of the soil (Fonseca et al., 2009b; Sun et al., 2006). It should be noted that the hydroxides of the tested metals do not precipitate in the pH range at which experiments were conducted (Cherry, 1982). Finally, as expected, the Cd retardation factor decreased when Cd was in competition with other cations for sorption sites (Markiewiez-Patkowska et al., 2005; Serrano et al., 2005; Vega et al., 2006). Pb ions experienced a slightly higher retardation in the competitive scenario, as this metal is adsorbed specifically on sites with high dissociation constants. As can be observed, the curve correspondent to the competitive scenario in Fig. 2 grew more slowly, suggesting increasing sorption density at high-energy sites (Sposito, 1989; Strawn and Sparks, 2000).

3.3.1. FTIR spectral analysis

Fig. 4 shows the FTIR spectra obtained for an uncontaminated soil sample and from the single-metal contaminated and co-contaminated soil samples collected from the soil bed columns. The bands of clay minerals represented by the SiO–H stretches at 3706 cm^{-1} and 3622 cm^{-1} (kaolin) and the Si–O–Si stretch at 1030 cm^{-1} were slightly different from the spectra of the contaminated samples (Smidt and Meissl, 2007). The authors have reported similar results previously, when studying the noncompetitive sorption of chromium, and attributed these to the sorption of metals at the edges of the clay minerals (Alvarez et al., 2004; Fonseca et al., 2009b). However, the acidic character of the inlet solutions may have enhanced the dissolution of silicates, as these peaks decreased for the contaminated sample. However, the peaks do not overlap, revealing the persistence of these edges, even if they are less concentrated. There are two bands at approximately 2900 cm^{-1}, attributed to the C–H stretch of aliphatic structures, and a band at approximately 1634 cm^{-1} that change in all spectra (Carballo et al., 2008). However, the change is more evident in the cases of Pb and Cr. Pb forms strong complexes with soil organic matter and can compete with most other metals for sorption sites (Strawn and Sparks, 2000). Cr transport can also be significantly retarded by the presence of organic matter, as this material has been reported to reduce Cr^{6+} to Cr^{3+} under acidic conditions or to complex chromium oxyanions, as mentioned previously (Banks et al., 2006; Jardine et al., 1999). In this particular case, the bands assigned at 1634 cm^{-1} and 1384 cm^{-1} may also be related to the interactions with the free water and the organic matter fractions (Haberhauer and Gerzabek, 1999). The bands at 692 cm^{-1} and 797 cm^{-1} commonly associated with inorganic materials tended to overlap for the contaminated samples, probably due to the presence of heavy metal complexes (Du et al., 2007).

4. Conclusions

The batch and continuous tests showed that this type of soil— loamy sand—has a high affinity for all the tested metals but a different maximum sorption capacity for each one. An affinity trend was
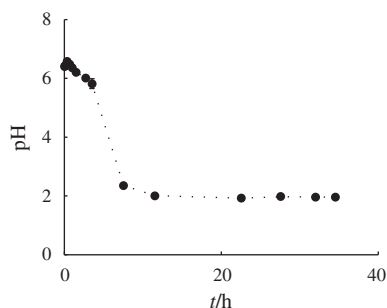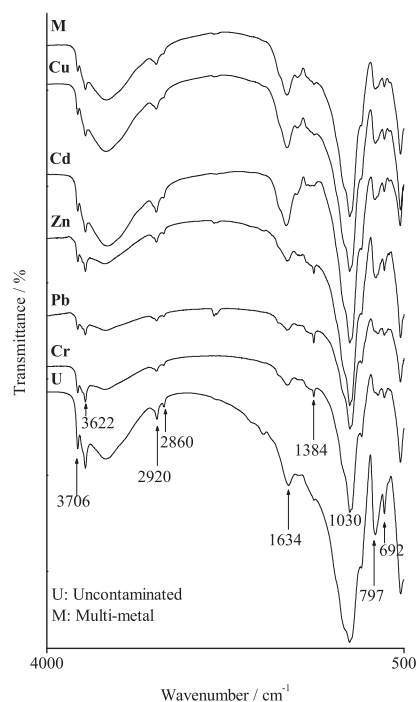

Fig. 3. Variation of the effluent pH during the course of a competitive flow test. The experiment was performed in duplicate with a standard deviation of less than 10%.

Fig. 4. FTIR spectra of uncontaminated and contaminated soil samples collected from each column after the flow tests.

defined as: Cr>Pb>Cd>Cu>Zn, according to the respective Langmuir constant—*b*. Similarly, a trend of the maximum sorption capacities of the soil—S_{max} values—was described as: Cu≈Zn>Cd>Pb>Cr. The results of the flow tests showed that in dynamic systems, reactions were not in equilibrium, and therefore, the trend of the retardation factor was different: Zn>Cd>Pb>Cu>Cr.

Generally, in competitive situations, the heavy metals were less strongly sorbed by soil, due to the competition for sorption sites. However, Cr and Cu seemed to precipitate as a Cu–Cr solid, due to the increase in the soil pH. Also, Zn is less effectively retained in flow systems, mainly due to the acid leaching of Zn ions, which were highly concentrated in this soil.

The existence of competition among heavy metals does not always reduce their retention in soil, depending on the concentration, pH and types of metals involved. Other processes besides adsorption may also occur, thereby influencing the selection of decontamination techniques.

Role of the funding source

Acknowledgments

References

Adhikari, T., Singh, M.V., 2003. Sorption characteristics of lead and cadmium in some soils of India. Geoderma 114, 81–92.

Alvarez, R., Evans, L.A., Milham, P.J., Wilson, M.A., 2004. Effects of humic material on the precipitation of calcium phosphate. Geoderma 118, 245–260.

Appel, C., Ma, L., 2002. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. J. Environ. Qual. 31, 581–589.

Bailey, N., Carrington, A., Lott, K.A.K., Symons, M.C.R., 1960. Structure and reactivity of the oxyanions of transition metals. Acidities and spectra of protonated oxyanions. J. Chem. Soc. 290–297.

Banks, M.K., Schwab, A.P., Henderson, C., 2006. Leaching and reduction of chromium in soil as affected by soil organic content and plants. Chemosphere 62, 255–264.

Berti, W.R., Jacobs, L.W., 1996. Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications. J. Environ. Qual. 25, 1025–1032.

Candela, L., varez-Benedi, J., de Melo, M.T.C., Rao, P.S.C., 2007. Laboratory studies on glyphosate transport in soils of the Maresme area near Barcelona, Spain: transport model parameter estimation. Geoderma 140, 8–16.

Carballo, T., Gil, M.V., Gomez, X., Gonzalez-Andres, F., Moran, A., 2008. Characterization of different compost extracts using Fourier-transform infrared spectroscopy (FTIR) and thermal analysis. Biodegradation 19, 815–830.

Cherry, K.F., 1982. Plating Waste Treatment. Ann Arbor Science, Michigan.

Covelo, E.F., Andrade, M.L., Vega, F.A., 2004. Heavy metal adsorption by humic umbrisols: selectivity sequences and competitive sorption kinetics. J. Colloid Interface Sci. 280, 1–8.

Covelo, E.F., Vega, F.A., Andrade, M.L., 2008. Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a fibric histosol and its organo-mineral fraction. J. Hazard. Mater. 159, 342–347.

Du, C.W., Linker, R., Shaviv, A., 2007. Characterization of soils using photoacoustic mid-infrared spectroscopy. Appl. Spectrosc. 61, 1063–1067.

Echeverria, J.C., Morera, M.T., Mazkiaran, C., Garrido, J.J., 1998. Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. Environ. Pollut. 101, 275–284.

Fonseca, B., Maio, H., Quintelas, C., Teixeira, A., Tavares, T., 2009a. Retention of Cr(VI) and Pb(II) on a loamy sand soil: kinetics, equilibria and breakthrough. Chem. Eng. J. 152, 212–219.

Fonseca, B., Teixeira, A., Figueiredo, H., Tavares, T., 2009b. Modelling of the Cr(VI) transport in typical soils of the North of Portugal. J. Hazard. Mater. 167, 756–762.

Fontes, M.P.F., de Matos, A.T., da Costa, L.M., Neves, J.C.L., 2000. Competitive adsorption of zinc, cadmium, copper, and lead in three highly-weathered Brazilian soils. Commun. Soil Sci. Plant Anal. 31, 2939–2958.

Ghosh, D.C., Biswas, R., 2003. Theoretical calculation of absolute radii of atoms and ions. Part 2. The ionic radii. Int. J. Mol. Sci. 4, 379–407.

Haberhauer, G., Gerzabek, M.H., 1999. Drift and transmission FT-IR spectroscopy of forest soils: an approach to determine decomposition processes of forest litter. Vib. Spectrosc. 19, 413–417.

Hanna, K., Lassabatere, L., Bechet, B., 2009. Zinc and lead transfer in a contaminated roadside soil: experimental study and modeling. J. Hazard. Mater. 161, 1499–1505.

Hendershot, W.H., Lalande, H., Duquette, M., 1993. Ion exchange and exchangeable cations. In: Carter, M.R., Gregorich, E.G. (Eds.), Soil Sampling and Methods of Analysis, pp. 197–206.

Jardine, P.M., Fendorf, S.E., Mayes, M.A., Larsen, I.L., Brooks, S.C., Bailey, W.B., 1999. Fate and transport of hexavalent chromium in undisturbed heterogeneous soil. Environ. Sci. Technol. 33, 2939–2944.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40, 1361–1403.

Lau, S.L., Stenstrom, M.K., 2005. Metals and PAHs adsorbed to street particles. Water Res. 39, 4083–4092.

Lee, S.Z., Chang, L.Z., Chen, C.M., Yang, H.H., Hu, P.Y., 2001. The effect of hydration on adsorption and desorption of heavy metals in soils Part A J. Environ. Sci. Health 36, 63–74.

Liu, C.L., Chang, T.W., Wang, M.K., Huang, C.H., 2006. Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective–dispersive model. Geoderma 131, 181–189.

Markiewiez-Patkowska, J., Hursthouse, A., Przybyla-Kij, H., 2005. The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brownfield deposit. Environ. Int. 31, 513–521.

Mehra, O.P., Jackson, M.L., 1958. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Clay Miner. 7, 317–327.

Miller, D.M., Sumner, M.E., Miller, W.P., 1989. A comparison of batch-generated and flow-generated anion adsorption-isotherms. Soil Sci. Soc. Am. J. 53, 373–380.

OECD, 2000. OECD Guideline 106. Guideline for the testing of chemicals: Adsorption-desorption using a batch equilibrium method.

Papelis, C., Um, W., 1999. Anion and cation transport in zeolitized tuffs from the Nevada test site: effects of ion type, pH, and ionic strength. In: Selim, H.M., Sparks, D.L. (Eds.), Heavy Metals Release in Soils. Lewis Publisher, Boca Raton, pp. 31–54.

Pearson, R.G., 1963. Hard and soft acids and bases. J. Am. Chem. Soc. 85, 3533–3539.

Puls, R.W., Bohn, H.L., 1988. Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. Soil Sci. Soc. Am. J. 52, 1289–1292.

Serrano, S., Garrido, F., Campbell, C.G., Garcia-Gonzalez, M.T., 2005. Competitive sorption of cadmium and lead in acid soils of Central Spain. Geoderma 124, 91–104.

Seuntjens, P., Tirez, K., Simunek, J., van Genuchten, M.T., Cornelis, C., Geuzens, P., 2001. Aging effects on cadmium transport in undisturbed contaminated sandy soil columns. J. Environ. Qual. 30, 1040–1050.

Sipos, P., Németh, T., Kis, V.K., Mohai, I., 2008. Sorption of copper, zinc and lead on soil mineral phases. Chemosphere 73, 461–469.

Smidt, E., Meissl, K., 2007. The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management. Waste Manage. 27, 268–276.

Sparks, D.L., 1995. Environmental Soil Chemistry. Academic Press, San Diego.

Sposito, G., 1989. The Chemistry of Soils. Oxford University Press, Inc., New York.

Strawn, D.G., Sparks, D.L., 2000. Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. Soil Sci. Soc. Am. J. 64, 144–156.

Sun, J.M., Zhu, W.T., Huang, J.C., 2006. Characterization of primary precipitate composition formed during co-removal of Cr(VI) with Cu(II) in synthetic wastewater. Environ. Sci. Pollut. Res. 13, 379–385.

Tinsley, J., 1950. The determination of organic carbon in soils by dichromate mixture. IV International Congress of Soil Science, pp. 161–164.

Toride, N., Leij, F.J., van Genuchten, M.T., 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. U.S. Salinity Laboratory. U.S. Department of Agriculture, Riverside, California.

Tran, Y.T., Bajracharya, K., Barry, D.A., 1998. Anomalous cadmium adsorption in flow interruption experiments. Geoderma 84, 169–184.

USEPA, 2004. Soil and Waste pH. Environmental Protection Agency, United States of America.

USEPA, 2007. Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils. Environmental Protection Agency, United States of America.

USEPA, 2009. In: Cameron, R.E. (Ed.), Guide to Site and Soil Description for Hazardous Waste Site Characterization. Environmental Protection Agency, United States of America.

Usman, A.R.A., 2008. The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt. Geoderma 144, 334–343.

van Genuchten, M.T., 1981. Non Equilibrium Transport Parameters from Miscible Displacement Experiments. U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

Vega, F.A., Covelo, E.F., Andrade, M.L., 2006. Competitive sorption and desorption of heavy metals in mine soils: influence of mine soil characteristics. J. Colloid Interface Sci. 298, 582–592.

Yolcubal, I., Akyol, N.H., 2007. Retention and transport of hexavalent chromium in calcareous karst soils. Turk. J. Earth Sci. 16, 363–379.