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Evaluation of metal mobility and adsorption capacity of a compacted lateritic soil by sequential extraction

Évaluation de mobilité en métod et capacité d´adsorption d´un sol lateritic par l´extraction séquentielle

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ABSTRACT
Diffusion tests were carried out on compacted soil specimens to investigate the mobility of metals, Cd and Pb, in a tropical residual soil contaminated by acidic solutions at pH 3 and 5.5. After the diffusion, sequential extraction procedure was applied to the soil specimens. This study has shown that the retention of both metals is quite relevant, despite the fact that cadmium is less adsorbed than lead, and that sequential extraction may be a very useful tool to investigate retention processes.

RÉSUMÉ
Le test de diffusion ont été exécuté sur a comprimé du speciments de sol pour examiner la mobilité de métaux dans le sol contaminé par les solutions acides, le Cd et Pb, avec la composition connue. Après la diffusion, la procédure d´extraction séquentielle a été appliquée au speciments. Cette étude a montré que la rétention des deux métaux est tout à fait pertinente, malgré le fait ce cadmium est monis a adsorbé que premier.

1 INTRODUCTION

Lateritic soils are widely used in Brazil as clay liners for waste disposal sites. Laboratory researches have indicated that these soils present significant metal retention capacity even for sandy samples, what may be reported to the expressive amount of constituent iron and aluminum oxides and hydroxides.

Usually retention evaluated in batch, diffusion and column tests, calculated by means of comparison of concentrations before and after the contact with the soil i.e. indirect evaluation, is named adsorption. It is considered reversible and related to ion exchange, which actually characterize non-specific adsorption. For a better parameter assessment and a more realistic simulation of migration through the soil, measured retention should be further investigated to define which reactions really occur: specific adsorption, non-specific adsorption, or precipitation. This is especially relevant for lateritic soils, which mineralogical composition suggests the occurrence of specific adsorption.

Sequential extraction is considered as an operational procedure employed to isolate defined species, forms or phases that are present in a material. It has been widely used in soils for agricultural purposes (plant-available species, and element deficiency or toxicity in animals and crops) and, more recently, in environmental studies, particularly in polluted solid systems. The description of types, forms and amounts of metal species, usually known as metal speciation, has been very useful to understand their mobility in contaminated soils and sediments.

This paper presents the results of a sequential extraction procedure applied to a compacted lateritic soil submitted to the diffusion of metals, cadmium and lead, in order to understand the metal speciation in these soils when used as clay liners for waste disposal sites.

2. MATERIAL AND METHODS

2.1 Material

The studied material is a lateritic residual soil of diabase from the Experimental Center of the Agronomic Institute of Campinas University, in the State of Sao Paulo, Brazil. This soil has been extensively researched for agricultural purposes for more than 40 years, resulting in a significant amount of available data. Furthermore, it is typical lateritic clay, which is a class of soils of relevant occurrence all over the country. The A horizon, enriched in organic material, was discarded, and the samples were collected at approximately a 50-cm depth.

The mineralogical composition of the bulk sample of the soil, obtained by X-ray diffraction, consists mainly of quartz, kaolinite, ilmenite, hematite and magnetite. The mineralogy of the clay fraction was additionally obtained by X-ray diffraction after separation treatments, which aimed at a better identification of the clay minerals which diffraction peaks were superimposed. Separation treatments included electromagnetic separation (non magnetic at an electric current of 0.5 A), FeO extraction, glycol addition and heating at 490ºC. Results indicated that the clay fraction is composed of kaolinite, gibbsite and vermiculite in the proportion of 73%, 22% and 5%. The magnetic fraction has 87% ilmenite, 9% hematite and 4% magnetite, suggesting that the main iron oxide in the bulk sample is ilmenite. Summarizing, the soil is mainly composed by kaolinite, iron oxides (ilmenite, hematite and magnetite), quartz, gibbsite and vermiculite.

The organic content of the soil is 26 mg/kg, according to the Walkley-Black method.

The soil is composed of 59% clay, 14% silt, 21% fine sand and 6% medium sand. The liquid limit and the plastic index are, respectively, 30% and 15%. The soil classifies as ML by USSC i.e. silt with low plasticity.

Maximum dry unit weight and optimum water content at Proctor energy are, respectively, 15.7 kN/m^3 and 10.7%, and the hydraulic conductivity is 1 X 10^{-9} m/s at this condition.

The studied soil has adequate geotechnical properties for the construction of clay liners at waste disposal sites, as indicated by the above-mentioned indices and by prior experience in the construction of embankments and dams.

The soil pH, obtained by distilled water by 4 different methods (ASTM, 2001; Yong & Phadungchewit, 1993; Boscov, 2004; Camargo et al., 1986), ranged from 5.2 to 5.5, and the point of zero charge (PZC), obtained by potentiometric titration tests, falls within the range of 4.0 – 4.5 pH units (Hemsi, 2001).

2.2 Methods

2.2.1 Diffusion test

Diffusion tests were carried out according to the procedure proposed by Barone et al. (1989). The soil samples were compacted statically inside the diffusion cells at the maximum dry unit weight and optimum water content determined at Proctor energy. After compaction, the soil was saturated by capillarity.

The cells were then filled with mono-elemental nitric acid solutions of cadmium (Cd) and lead (Pb), respectively, at the concentrations of 3 mg/L and 100 mg/L, which are based on the alert values of soil contamination according to the environmental protection agency of the State of Sao Paulo (CETESB, 2001). Cadmium and lead are toxic metals usually present in waste disposal sites; there is experimental evidence that the former is very mobile and the latter, significantly retained in the studied soil (Tsugawa, 2004). The solutions were prepared at pH 3.0 and 5.5, in order to evaluate soil performance in contact with acidic solutions and at the soil natural pH.

Diffusion was carried out for 87 days, along which samples of the reservoir solution were collected and chemically analyzed. The soil specimen was then extruded, cut into five slices, and the pore water of each slice was squeezed by the application of 25 MPa pressure and also chemically analyzed.

2.2.2 Sequential extraction

Sequential extraction has been primarily used in agronomy to evaluate the availability of soil nutrients for plant uptake. Recently, it has been used to appraise the possibility of plant intake of toxic metals, such as chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn), from contaminated soils, which has been called bioavailability.

Different sequential extraction procedures have been reported, which generally consist in applying reagents sequentially to the same soil sample. The reagents dissolve selectively constituents of the soil grains such as carbonates, oxides and hydroxides, organic material and sulfides, and silicate minerals. The number of reagents defines the steps of the extraction.

In this study, a simplified procedure proposed by the European Commission (2001) was applied, which resulted from a project supported by the Bureau of Community Reference (BCR) where current procedures were compared and evaluated (Quevauviller et al., 1993).

Four extraction steps have been used to define phases retaining metals; the stability of bonds increases and the mobility of metals decreases in the following order:

E1 = exchangeable cations, including water-soluble phases and carbonates extracted with acetic acid solution (0.11 mol/L);

E2 = easily and moderately reducible phases adsorbed and precipitated with iron and manganese oxides and hydroxides extracted with hydroxylamine chloridrate solution (0.5 mol/L);

E3 = solid organic and sulfitic phases extracted with ammonium acetate solution (1.0 mol/L);

E4 = residual fraction, occluded in primary minerals, extracted with aqua regia.

The solutions resultant from the contact of the reagents with the soil sample for pre-determined time interval, temperature and agitation procedure at each step are named extracts. The mass of a metal retained in each soil phase is calculated with the metal concentration measured in the correspondent extract. Results are expressed as mass of metal per unit mass of dry soil.

The sum of the first three steps (E1+E2+E3) has been considered as bioavailable metal. For geotechnical purposes, E1 could be considered as metals that are weakly bonded to soil particless (non-specific adsorption) and could be released by the clay liner when in contact with acidic solutions. E4 corresponds to the most stable bonds and long-term (geological scale) release of metals to the environment; metals are not adsorbed, but are actually components of the mineral lattice. E2 is related to specific adsorption and covalent reactions, indicating much stronger adsorption than E1, but not so stable as E4. The stability of adsorption at E3 phase must be further investigated.

Soil samples obtained from the diffusion test were broken up with a hammer and crushed to powder in an agate crusher. Three replicates of each sample, weighted after homogeneous mixing, were submitted to the sequential extraction procedure.

For each extraction three types of blanks were prepared: vessel blank, to evaluate the cleaning process (decontamination) of the recipients; reagent blank, to check the concentration of the studied metals in the extraction solutions used in each step before the contact with the soil; and the procedural blank for each step, which consists in running the overall procedure with a recipient without soil sample.

In order to evaluate the quality of the extraction procedure and of the chemical analysis, a complete sequential extraction was applied to a certified reference material (CRM), BCR-701 (European Commission, 2001; Quevauviller et al., 1995), which has certified concentrations of Cd, Cr, Cu, Ni, Pb and Zn. The use of CRM enabled the correction of operational mistakes and improvement of experimental conditions, such as particulate-controlled environment, proper decontamination of vessels, and statistic quality control of volume measurements, among others. It also defined the use of two chemical analytical techniques, according to the range of metal concentration.

2.2.3 Chemical analyses

Chemical analyses were carried out by spectrometry of atomic emission with inductive coupled plasma (ICP-AES) and mass spectrometry with inductive coupled plasma (ICP-MS). Analyzed samples derived from the monitoring of the diffusion cells reservoir, the soil solution from the soil slices at the end of the diffusion tests, and the extracts of the sequential extraction tests.

Concentration measurements obtained by both techniques are bases on analytical curves, which are specific for the chemical composition of the samples and the range of expected concentrations. An analytical curve consists in a regression curve obtained by the measurement of solutions with known metal concentration The closer to the samples concentration range the analytical curve is determined, the more accurate are the results.

The analyses in both techniques were carried out with analytical curves prepared in the same matrix of the samples in order to avoid matrix interference in the results.

The reservoir samples collected in the first fifteen days of diffusion were analyzed by ICP-AES due to higher concentrations of metals. From the sixteenth day on till the end of diffusion, the samples were analyzed by ICP-MS. The analytical curves for Cd and Pb were prepared in nitric acid solution, which is the matrix of the contaminant solution in the diffusion tests, in the range of 0.5 to 5 mg/L for ICP-AES analyses and 0.1 to 50 μg/L for ICP-MS analyses.

The extracts of the sequential extraction tests were analyzed by ICP-MS. Analytical curves were prepared with the extraction solutions used in each step, i.e. the same matrix. It was necessary to prepare an analytical curve for each step due to different concentration ranges, pre-determined by means of semi-quantitative analyses. For step 1, the range of cadmium concentration was 1 to 100 μg/L, and 1 to 500 μg/L for lead. For step 2, concentration ranges were 1 to 50 μg/L and 1 to 1000 μg/L, for Cd and Pb, respectively; in step 3, 1 to 50 μg/L for Cd and 1 to 500 μg/L for Pb. Because of ICP-MS sensibility, samples from steps 1 and 2 were diluted before measurement.

3. RESULTS AND DISCUSSION

3.1 Diffusion tests

Diffusion tests results are presented as metal concentration in the cell reservoir as a function of time. Figures 1 and 2 show sample data for the tests carried out with cadmium solutions,

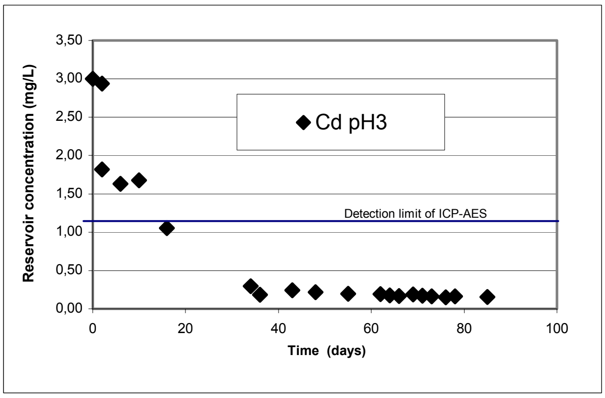

Figure 1 – Cd diffusion at pH 3.

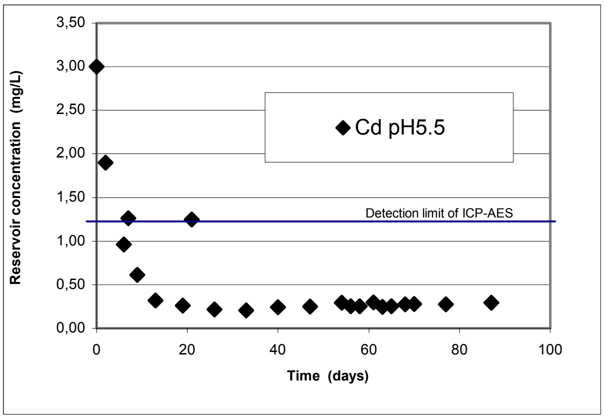

Figure 2 - Cd diffusion at pH 5.5.

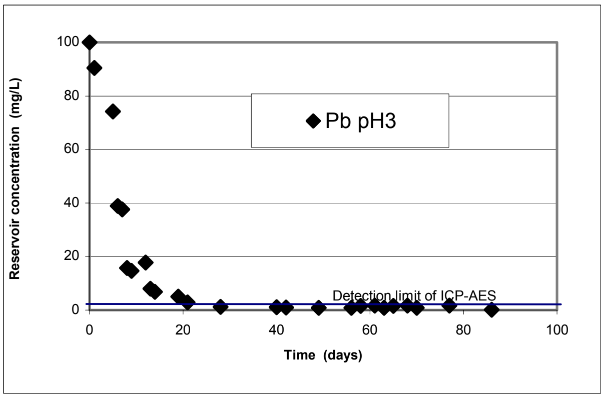

Figure 3 – Pb diffusion at pH 3.

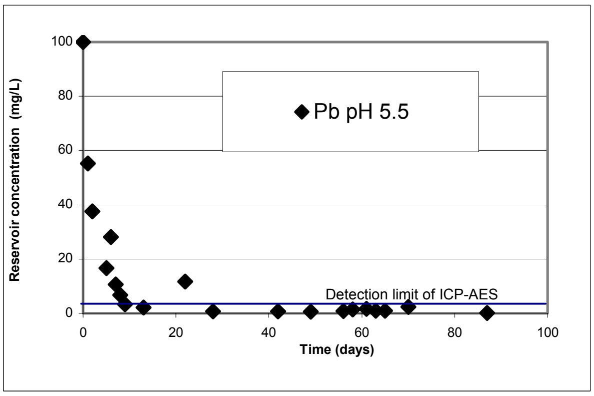

Figure 4 - Pb diffusion at pH 5.5.

respectively, at pH 3 and 5.5. Tests results for the diffusion of lead at pH 3 and 5.5 are shown in Figures 3 and 4, respectively.

Cd concentrations in the soil pore water were approximately 20 to 30 µg/L in the upper layer of the specimen, and lower than 1 µg/L in the other layers, at both pH values. Pb concentrations varied from 9 µg/L in the upper layer to less than 1 µg/L in the other layers, at both pH values. These results indicate that, for both metals, less than 1% of the metal that migrated from the reservoir solution to the soil was present in the soil pore water.

Figures 1 and 2 show that pH was not relevant for the diffusion of Cd through the compacted soil, although it can be noticed that the depletion of Cd concentration in the reservoir at pH 5.5 was slightly faster than at pH 3. However, the percentage of cadmium that was transferred from the reservoir to the soil at pH 3 was slightly higher (96%) than at pH 5.5 (90%).

Despite the fact that the initial concentration of lead in the reservoir was significantly higher, results indicate that the pH difference was not relevant for Pb diffusion either (Figures 3 and 4). However, the difference between the initial (100 mg/L) and final (0,14 mg/L) concentrations suggests that Pb was strongly adsorbed (99,9%) by the soil.

The low final concentrations of Cd and Pb in the reservoir after 87 days of diffusion and in the pore water of the respective specimens point out that these metals are strongly adsorbed by the soil. Apparently Cd was less adsorbed than Pb, although in both cases the amount of metal adsorbed was at least 90%.

Table 1 – Sequential extraction data from contaminated soil samples from diffusion test with acid solution pH 3.

Extracts	Cd pH 3		Pb pH 3	
	Cd	Pb	Cd	Pb
Step 1				
average (µg/g)	25.13	0.09	< dl	649.46
sd	1.33	0.02	-	45.84
Step 2				
average (µg/g)	17.20	16.14	0.03	1772.22
sd	0.35	0.21	0.00	21.72
Step 3				
average (µg/g)	4.85	79.72	< dl	1467.49
sd	0.38	8.34	-	121.61
Total (µg/g)	47.18	95.95	>0.03	3889.17

sd – standard deviation

Table 2 – Sequential extraction data from contaminated soil samples from diffusion test with ph solution equal to the soil (ph = 5,5).

Extracts	Cd pH 5.5		Pb pH 5.5	
	Cd	Pb	Cd	Pb
Step 1				
average (µg/g)	21.95	0.16	< dl	561.60
sd	3.14	0.01	-	34.29
Step 2				
average (µg/g)	7.53	7.94	0.02	1380.86
sd	0.35	0.54	0.01	86.63
Step 3				
average (µg/g)	2.14	32.12	< dl	1100.70
sd	0.67	11.30	-	185.24
Total (µg/g)	31.62	40.22	>0.02	2043.16

sd – standard deviation

3.2 Sequential extraction

The results of the sequential extraction tests are presented in Tables 1 and 2 for cadmium and lead, in terms of averages and respective standard deviations. It must be noticed that, despite the fact that monoelement contaminant solutions were applied to the soil in the diffusion tests, both Cd and Pb were measured in all analyzed samples.

It can be noticed that cadmium was mostly adsorbed in exchangeable phases (E1); the percentage of Cd adsorved in this phase relative to the sum of Cd mass extracted in the three steps was 53 and 69%, respectively, at pH 3 and 5.5. Secondarily, Cd was adsorved in the oxide/hydroxide phases (E2) (37 and 24 %, respectively, at pH 3 and 5.5). The retention in organic matter (E3) was 10 and 7 %, respectively, at pH 3 and 5.5.

Lead was mainly adsorbed in oxide/hydroxide phases (E2) and secondly in organic matter (E3) at both pH values. Amounts adsorved in both phases are similar. Iron oxide/hydroxide adsorved 46 and 45% of Pb at pH 3 and 5.5, respectively; organic matter adsorved 38 and 36% of Pb, respectively. Exchangeable phases retention was 17 and 19% at pH 3 and 5.5, respectively.

Pb adsorption by oxide/hydroxides was actually expected to be relevant for this soil, whereas retention in organic matter was higher than foreseen, and should be further investigated.

Soil samples contaminated with cadmium have shown some content of lead in the three steps. This is interpreted as dissolution of soil particles possibly induced by the acidic solutions.

Cadmium concentrations measured in the lead contaminated samples were lower than lead concentrations in cadmium contaminated samples. For pH 3 and 5.5, Cd concentration in the extracts E1 and E3 of the Pb contaminated samples were under the detection limit of ICP-MS.

Contents of Cd and Pb in the original soil, presented in Table 3, were obtained from 6 replicates submitted to the same procedure applied to the contaminated samples.

Table 3 – Sequential extraction data from non-contaminated soil.

Extracts	Non-contaminated soil	
	Cd	Pb
Step 1		
average (μg/g)	< dl	< dl
Sd	-	-
Step 2		
average (μg/g)	< dl	2,92
Sd	-	0,16
Step 3		
average (μg/g)	0,03	8,18
Sd	0,01	1,08

dl- detection limit

For both metals, the total mass extracted from the contaminated samples resulted higher than the mass that was introduced in the diffusion cells. Another phenomenon apparently occurred simultaneously to diffusion and adsorption, such as a partial dissolution of soil grains. This hypothesis is now being verified by means of reverse diffusion tests, where solutions of nitric acid at pH 3 and 5.5 without metals are applied to the soil. After the reverse diffusion, soil samples will be submitted to sequential extraction tests to measure masses of Cd and Pb mobilized from the soil grains by the applied solutions.

4. CONCLUSION

This study showed that cadmium is more mobile than lead in the studied soil, as expected; that both metals are significantly retained in the soil at pH 3 and pH 5.5; and that the oxide phase of the soil, mainly ilmenite, is responsible for the greater amount of retention of the studied metals. This retention could be considered stable due to the type of interaction between the surface of the oxides and the cations, i.e. specific adsorption (Sposito, 1989).

The research also highlighted the importance of organic matter phases in the adsorption of lead, which should be further investigated.

Furthermore, there was experimental evidence that other mechanisms, besides diffusion and adsorption, take place in the diffusion tests with acidic solutions, such as dissolution of solid grains, even at pH similar to soil pH. These mechanisms are being investigated by diffusion reverse tests.

Finally, this study showed that sequential extraction tests could be very useful to evaluate the mobility and retention of metals in clay liners, as they may provide additional information that is not possible to assess by diffusion tests.

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