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PERCOLATION OF LEAD(II) AND CADMIUM(II) THROUGH TWO BENTONITES USED AS LANDFILL LINER

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In order to prevent contamination of subsoil and groundwater by leachates containing heavy metals, montmorillonite linings are used on landfill bottoms. It is therefore important to understand ion uptake by this clay. In this study we have performed percolation of lead(II) and cadmium(II) through columns filled firstly with a technical bentonite and then with a reference bentonite. Elution curves provide an evaluation of metals retention. After the percolation step, columns are cut and metal ions are extracted to evaluate influence of side effects and soil depth on metal uptake. Moreover retentions of lead(II) and cadmium(II) are compared.

Keywords: Cadmium(II); clay; column; extraction; lead(II); percolation

INTRODUCTION

Solid wastes are usually stocked in landfill without prior treatment. Such an operation is dangerous for the environment because rain and runoff waters can leach soluble elements from wastes (Zavattiero and Castagnoli, 1986). These leachates contain a large amount of mineral and organic pollutants capable of contaminating groundwater. They therefore represent a potential hazard for the human organism through feeding.

Regulations require waterproofing of landfill bottoms by a double barrier in order to avoid subsoil contamination (Goubier, 1986; Gélosi and Giubilei, 1994). A draining system and a geomembrane constitute the first one. The second one corresponds to a passive barrier made up of a clay lining capable of retaining pollutants.

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Heavy metals in leachates represent a risk as they are toxic and non-degradable through time. Their migration through the passive barrier depends on the multiple mechanisms that govern soil and leachate behaviour, as cationic exchange, surface sorption or precipitation (Sposito *et al.*, 1981; Inskeep and Baham, 1983; Stadler and Schindler, 1993; Alberga *et al.*, 1994; Serpaud *et al.*, 1994). The metallic cations migration through the soil and the risk of groundwater contamination have been widely studied (Voice *et al.*, 1983; Tiller *et al.*, 1984; Di Toro *et al.*, 1986; Yong and Sheremata, 1991; Harter, 1992; Van Bladel *et al.*, 1993; Holm and Zhu, 1994). However, in most of these studies authors performed the experiments only in a static way named "batch". Moreover, only few works have been carried out with technical clays used for waterproofing landfill bottoms (Yanful *et al.*, 1988a, 1988b).

The aim of this work is to evaluate and compare lead(II) and cadmium(II) retentions by a technical clay and by a reference clay. The experiments are carried out on columns in order to be more representative of natural media, taking into account soil penetration and diffusion phenomena.

Two types of experiments can be performed on columns: contamination and leaching. Contamination consists in percolating metal solution through a non-polluted soil. The soil accumulates metallic cations progressively and it is then possible to evaluate its retention capacity (Doner *et al.*, 1982; Behra and Bourg, 1987; Plassard *et al.*, 2000). Leaching consists in percolating, through a contaminated soil, solutions capable of solubilizing metallic cations. The evaluation of retention stability is then possible (Kedziorek *et al.*, 1998). Clay linings in landfill bottoms are passive and initially not polluted. Consequently, in this study we have decided to simulate a contamination.

MATERIALS AND METHODS

Metal Solutions

Concentrations used in this study are high in order to increase the response obtained. Metal solutions are prepared by dissolving $1.8 \times 10^{-3} \text{ mol l}^{-1}$ of metal nitrate in deionized water. The nitrate counter-ion is chosen because of its non-affinity for metals (Sillén, 1977; Hirsch *et al.*, 1989). Sodium nitrate is added to the solution to maintain a constant ionic strength of 0.05 mol l^{-1} which avoids flocculation and clay mobilisation in the eluted fractions. The pH value is then adjusted with sodium hydroxide or nitric acid to 5.5, which is a current value in leachates.

Clays

Two bentonites are studied. The first one, called BSAB, is a technical commercial bentonite commonly used as landfill liner, which contains 80% of sodium montmorillonite. The second one, provided by the Clay Mineral Society, is the SWy-2 montmorillonite, used as reference. X-ray diffraction analysis of both clays are presented in Figure 1. In order to respect BSAB characteristics and to evaluate the retention phenomenon in landfill liners, these two clays have not been chemically treated.

Columns

Plexiglas columns (diameter: 4.4 cm; length: 3 cm) are filled with 2% of montmorillonite and 98% of crushed silica hydrated by a 0.05 mol l^{-1} sodium nitrate solution (Fig 2). The grain size of the silica is contained between 10 and 31.5 μm . A previous study

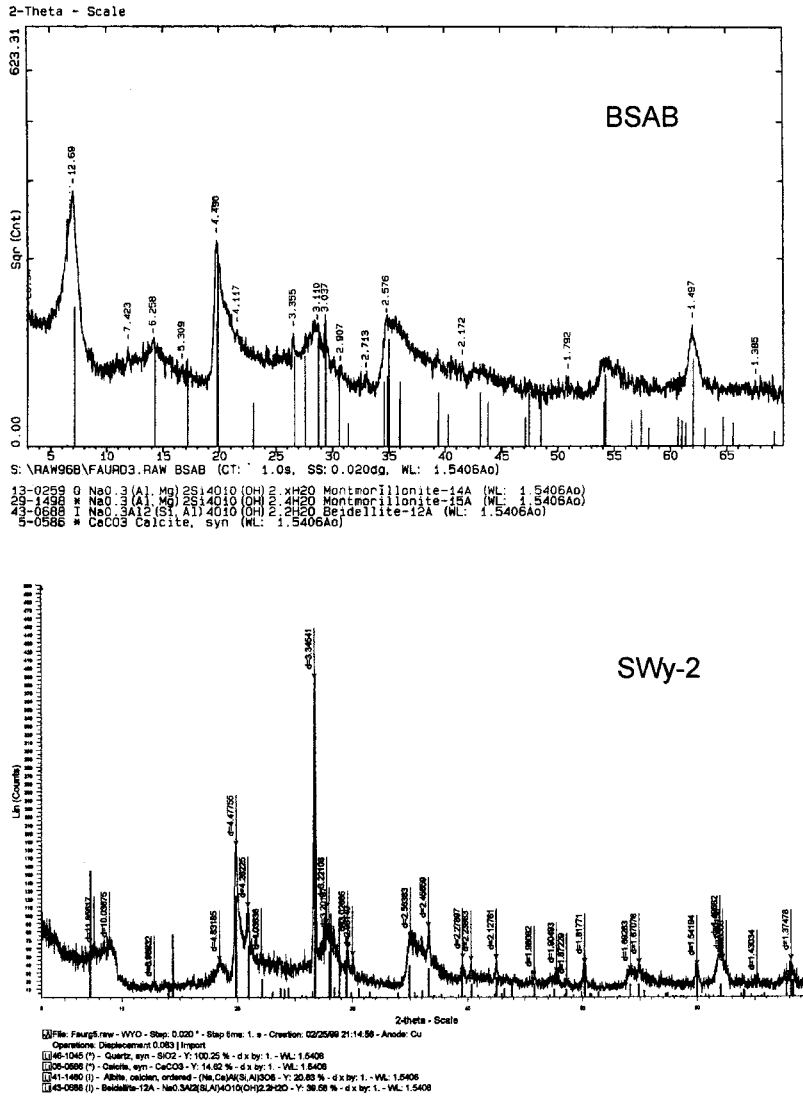


FIGURE 1 X-ray diffraction analysis of clays.

(Winiarski, 1994) showed that this silica does not have significant influence on the composition of the percolated solutions.

This synthetic mixture is packed between two Plexiglas gratings in order to obtain a density of about 1.45. A filter paper is placed between the clay and the gratings so as to immobilise clay particles in the column. Glass beads are placed between the caps and the gratings to avoid preferential flows. Columns are then hydrated by sodium nitrate 0.05 mol l^{-1} during 24 h in order to permit the complete clay swelling. With these experimental conditions, the void volume is 16 ml.

The solutions percolate from the bottom to the top of the column in order to avoid possible erosion due to the pressure reaching 90 cm of water. First, 200 ml of sodium nitrate 0.05 mol l^{-1} are percolated through the column. Tubing is drained to limit dilution

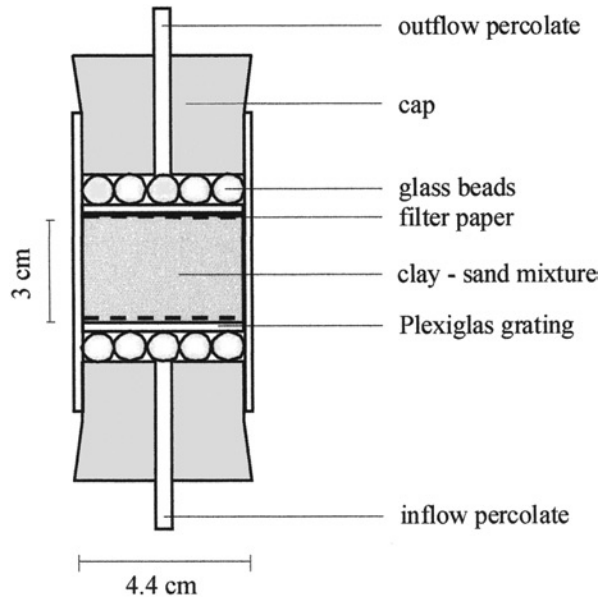


FIGURE 2 Modelling column.

effects. The solution is then introduced and the percolate is collected each 50, 100 and 200 ml. Metal concentration of the eluted solution is determined by AAS.

For extraction experiments, after percolation, soil is removed from the column and separated as described in Figure 3. This allows us to verify that side effects are negligible, and to study metallic cations retention as a function of depth. Each part of the column is dried at 60°C during 72 h and extraction by aqua regia is performed. Samples obtained are then centrifugated, diluted, filtered and analysed by AAS.

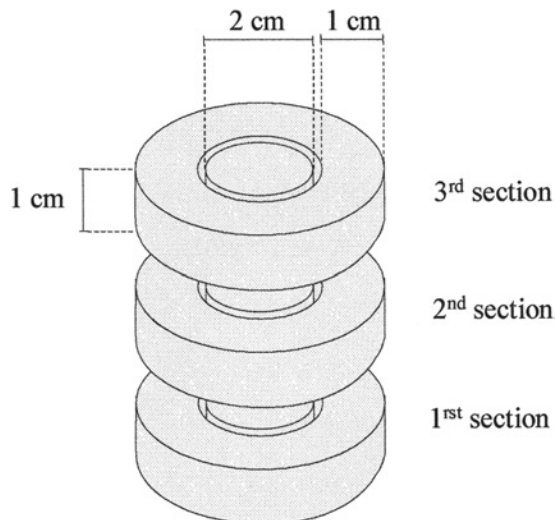


FIGURE 3 Column sections.

Percolations and extractions of lead(II) and cadmium(II) are realised separately for each clay.

RESULTS

Percolations

Total metal retention, Q_R , is calculated for each collected fraction as the difference between initial metal concentration C_i and percolated metal concentration C_n :

$$Q_R = \sum_i^n (C_i V_i - C_n V_n)$$

Lead(II) and cadmium(II) retentions by BSAB and by SWy-2 are presented in Figures 4 and 5.

Whatever clay and metal, elution curves show a horizontal asymptote from $V/V_0 = 40$. Cations are totally eluted and clay is saturated. Metallic cations retention on BSAB is 0.34 mol mg^{-1} of clay for lead(II) and 0.28 mol mg^{-1} of clay for cadmium(II). In the case of SWy-2, the results are 0.33 mol mg^{-1} for lead(II) and 0.21 mol mg^{-1} for cadmium(II).

Extractions

In order to observe a possible concentration gradient as a function of the column height, percolations have been stopped at $V/V_0 = 16$ for lead(II) and at $V/V_0 = 12$ for cadmium(II), which correspond to the half saturation of BSAB. Metallic cations retention is calculated after percolation and after extraction.

In the case of lead(II), whatever the clay, retention decreases as a function of height (Fig. 6). Moreover, we have calculated total metal retention in columns:

BSAB: percolations: $Q_R = 0.24 \text{ } \mu\text{mol mg}^{-1}$ of clay

extractions: $Q_R = 0.26 \text{ } \mu\text{mol mg}^{-1}$ of clay;

difference between internal and external part: 8%

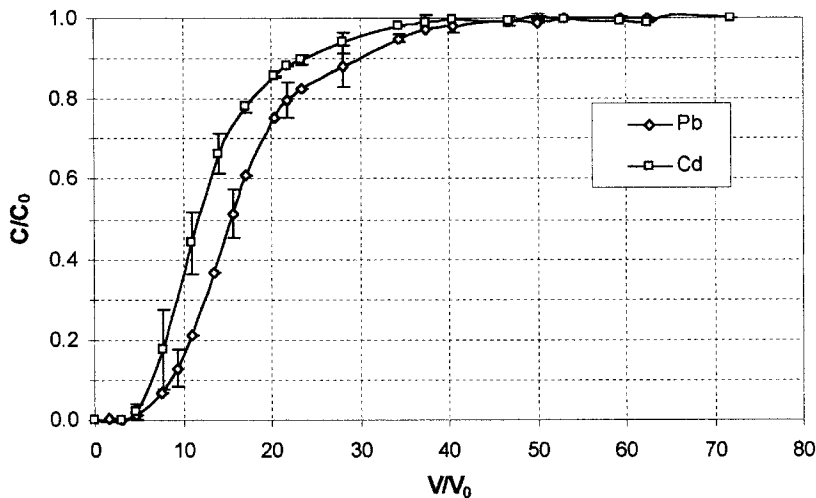


FIGURE 4 Lead(II) and Cadmium(II) percolation through BSAB.

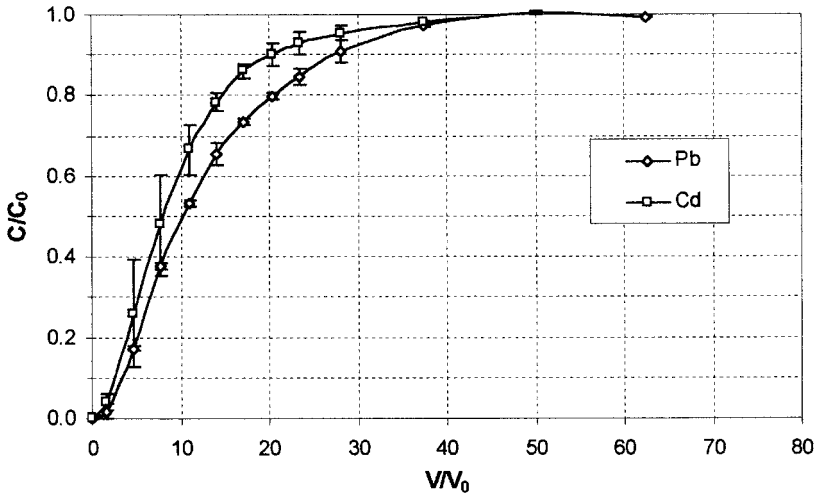


FIGURE 5 Lead(II) and Cadmium(II) percolation through SWy-2.

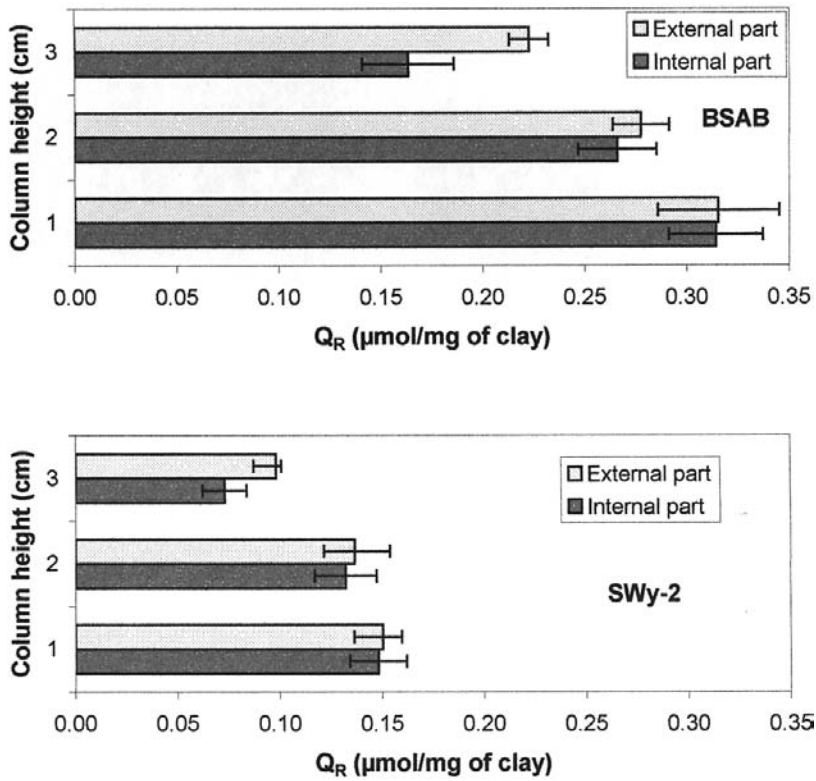


FIGURE 6 Lead(II) retention as a function of column height.

SWy-2: percolations: $Q_R = 0.13 \mu\text{mol mg}^{-1}$ of clay

extractions: $Q_R = 0.12 \mu\text{mol mg}^{-1}$ of clay

difference between internal and external part: 8%

With regard to cadmium(II), as for lead, retention varies as a function of height (Fig. 7).

Total retention of cadmium(II) in columns is:

BSAB: percolations: $Q_R = 0.18 \mu\text{mol mg}^{-1}$ of clay

extractions: $Q_R = 0.15 \mu\text{mol mg}^{-1}$ of clay

difference between internal and external part: 6%

SWy-2: percolations: $Q_R = 0.17 \mu\text{mol mg}^{-1}$ of clay

extractions: $Q_R = 0.15 \mu\text{mol mg}^{-1}$ of clay

difference between internal and external part: 0%

DISCUSSION

Percolation Assessment

In order to validate the column experiments, the retentions calculated after percolations and after extractions are compared. Statistic Fisher-Snedecor and Student tests are performed on the averages and the standard deviations: they are homogeneous with a confidence interval $\alpha = 0.005$. Consequently the metal retention evaluation from percolate is correct. However, this evaluation seems to be slightly overestimated with regard to results obtained after extractions.

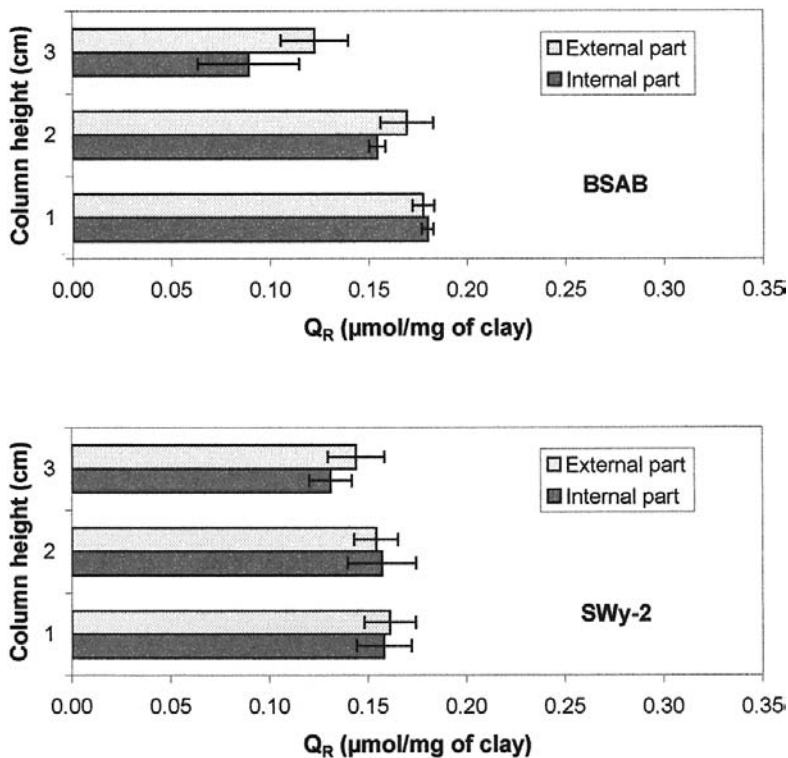


FIGURE 7 Cadmium(II) retention as a function of column height.

Moreover extractions allow the detection of possible side effects. The average between internal and external parts of the columns is always lower than 10%. We can therefore consider that side effects are negligible due to experiment repeatability. Nevertheless, side effects increase with column height. In fact, it is lower than 2% in the first centimetre of the column, it is of about 5% and always lower than 10% in the second section, but it can reach 30% in the last centimetre.

In conclusion, metal retention determined by mean of percolates is similar to that obtained after extractions. Consequently, elution curves as a function of percolate volume give a correct representation of retention in columns. Nevertheless, side effects in the highest part of the column should be taken into account.

Metal Retention

Quantities of lead(II) retained are 0.34 mol mg^{-1} of BSAB and 0.33 mol mg^{-1} of SWy-2. For cadmium(II) these quantities are 0.28 mol mg^{-1} of BSAB and 0.21 mol mg^{-1} of SWy-2. Montmorillonites affinity for lead is greater than for cadmium, which corresponds to the results found in "batch" (Barbier *et al.*, 2000). This order has been observed by Kinniburgh *et al.* (1976) on a goethite and by Plassard (1999) on a real soil. Kinniburgh *et al.* (1976) observed that this affinity depends on the pK of the first hydrolysis constant of the metal. The selectivity is then lead (pK = 6.2) > cadmium (pK = 10). Moreover, we can observe a correlation between the ionic radius and the affinity. Cationic exchange is easier, for cations of the same charge, if the hydrated radius is small, or the non-hydrated radius is large. It corresponds to the affinity observed: Pb^{2+} (0.120 nm) < Cd^{2+} (0.097 nm). This is in accordance with the results of a previous study on the sorption of lead(II) and cadmium(II) on BSAB and SWy-2 (Barbier *et al.*, 2000), where it was found that ion exchange is the most important process for metal uptake, even if surface complexation exists.

Retention as a Function of Depth

With regard to lead(II), a concentration gradient exists whatever the clay. The bottom of the column, which is first in contact with the solution, contains more metallic cations than the top: this part is saturated more rapidly. This first section of column retains about 12% more lead than the second section and 40% more than the third section. Moreover, we can notice that the two clays have different behaviour with respect to lead(II). Indeed, for the same percolated volume, the first centimetre of BSAB is saturated whereas that of SWy-2 hardly reaches the half saturation. Consequently distribution of lead(II) ions is different in spite of an identical total retention when clays are saturated. The half saturation is not obtained for the same percolated volumes. In the case of BSAB, the elution curve slope is lower than in the case of SWy-2 for the first 160 ml percolated ($V/V_0 = 10$): lead is fixed faster at the beginning of the percolation. On the contrary, from $V/V_0 = 14$ to $V/V_0 = 22$, the elution curve slope is lower in the case of SWy-2. As a consequence, even if BSAB and SWy-2 retain the same quantity of lead(II), their behaviour is slightly different.

With regard to cadmium(II), metal retention in the first centimetre is relatively similar for both clays, which indicates that BSAB and SWy-2 have a close behaviour. Nevertheless, concentration gradient as a function of depth is greater with BSAB especially for the last centimetre. In fact the first centimetre of BSAB retains 41% more cadmium(II) than the third centimetre when for SWy-2 this difference is only 14%. Cadmium(II) ions seem to be fixed on BSAB as soon as they are in contact with clay, whereas they seem to have a

more homogeneous repartition on SWy-2. However, as for lead(II), total retention of cadmium(II) ions is the same for both clays.

CONCLUSION

Two montmorillonites have been artificially contaminated by percolation of lead(II) and cadmium(II) solutions.

Extractions have been performed after percolations. Comparison between the metallic cations quantity extracted and the determination of this quantity by percolate analysis shows that this method permits a good evaluation of metal retention.

Both clays have a higher affinity for lead(II) than for cadmium(II) ions.

BSAB and SWy-2 have different behaviours with respect to lead(II) and cadmium(II). BSAB uptakes these metallic cations from the first contact, which allows preserving the deeper layer of soil from a possible pollution. As a consequence this clay seems to be a better antipollution material than SWy-2.

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