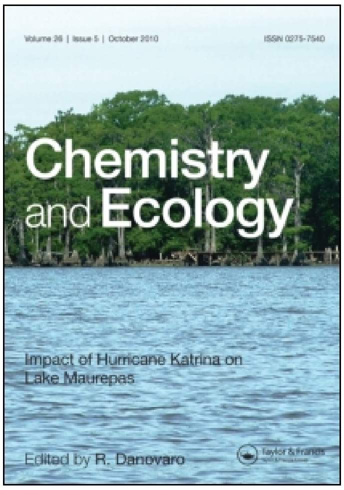

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INFLUENCE OF COMPLEXATION ON LEAD(II) AND CADMIUM(II) PERCOLATION THROUGH A CLAY LINER

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Wastes are usually stocked in waste disposals without any pre-treatment. Runoff waters lead to the formation of leachates containing mineral and organic pollutants. In order to prevent groundwater contamination, a double barrier is placed on the landfill bottom. The first one is an active barrier made up of a draining system and a geomembrane, and the second one, consisting of a clay liner allowing pollutant retention, is considered as a passive system. The aim of this work is to evaluate the complexation impact on the organic and inorganic retention. Percolations on columns filled with clay are performed, which allow a better knowledge of the transfer of metallic pollutants, complexed or not, through a model porous media, considering charge and conditional stability of complexes.

Keywords: Cadmium(II); Clay; Complexation; Lead(II); Percolation column

1 INTRODUCTION

The oldest and the most usual way of eliminating solid wastes is stocking in landfill without any prior treatment, leading to a risk of environmental contamination (Zavattiero and Castagnoli, 1985). Rain and runoff water flow leads to formation of leachates containing a large quantity of mineral and organic pollutants, whose dangerous impact toward natural media is well known. In order to protect subsoil from pollution, a double barrier is placed on the landfill bottoms. The first one consists of a draining system and a geomembrane, while the second one consists of a passive barrier made up of a clay lining capable of uptaking metal ions.

Numerous studies have shown that metallic cations are retained in clay principally by the way of cationic exchange (Sposito *et al.*, 1981; Inskeep and Baham, 1983; Alberga *et al.*, 1994; Holm and Zhu, 1994; Barbier *et al.*, 2000). Nevertheless, in leachates, metallic cations

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are in contact with various substances capable of complexing them. It is thus interesting to know if complexation modifies metal-ions retention.

In a previous work, percolations of metal ions were performed, model columns made in laboratory were tested, and metal retention was evaluated (Barbier *et al.*, in press). The aim of this paper is to study the percolation of solutions containing metal ions in presence of ligands (organic pollutants or degradation products of humic and fulvic acids) to evaluate influence of complexation on metal retention.

2 MATERIALS AND METHODS

Two types of metal solutions, based on the presence or absence of a ligand, are used. First, experiments are carried out with noncomplexed metal solutions: cations are only surrounded by hydration sphere and represent a reference state. Various ligands are then added to compare metal retention with and without ligand.

2.1 Noncomplexed Metal Solutions

Concentrations used are deliberately high in order to increase the response obtained. Moreover, metal ions and ligands can reach high concentrations in leachates (Cyr *et al.*, 1987). Metal solutions are prepared by dissolving $1.8 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ of metal nitrate in deionized water. The nitrate counter-ion is chosen because of its nonaffinity for metals (Sillén, 1977; Hirsch *et al.*, 1989). Sodium nitrate is added to maintain a constant ionic strength of $0.05\,\mathrm{mol\,l^{-1}}$, which avoids flocculation and clay mobilization in the eluted fractions. Considering the pH values frequently estimated in leachates, the pH value is adjusted to 5.5 with a diluted sodium hydroxide solution.

2.2 Complexed Metal Solutions

Selected ligands are chloride and sulfate ions, ethylenediaminetetraacetic acid (EDTA), ethylenediamine (EDA), phthalic acid (PHT), glycolic acid (GLY), and acrylamidoglycolic acid (AAG).

Chloride and sulfate ions are abundant in leachates (Bolton and Evans, 1991; Cyr *et al.*, 1987). They are added in the metal solutions by dissolving sodium chloride or sodium sulfate. A ligand–metal (*R*) ratio of 25:1 for chloride ions and 10:1 for sulfate ions allows an efficient complexation (Sillén, 1977; Martell and Smith, 1977).

Ethylenediaminetetraacetic acid, used in washing products in order to retain calcium, is a very strong chelating agent. Whatever the metal may be, a ligand–metal ratio of 2:1 is high enough to favor complexation reactions.

Ethylenediamine is a fungicidal component. It is usually found among the pesticides degradation products (Kirk-Othmer, 1981) and persists in leachates. It is also a strong chelatant, and the ligand–metal ratio of 5:1 is selected.

Phthalate ions come from degradation of plastics and soil organic matter (Brémond and Perrodon, 1989). They are found in urban rainwater (Plassard, 1999) and so in leachates. Their structure (aromatic cycle with two carboxylic functions) is representative of aromatic pollutants and produces stable complexes with metallic cations (Garg *et al.*, 1985; Gao *et al.*, 1995; Lucas Vaz *et al.*, 1996). It is added by dissolution of PHT to obtain a ligand–metal ratio of 25:1.

TABLE I Chemical Composition of BSAB.

Components	*Percentage by weight*
SiO_2	58.83
Al_2O_3	20.92
Fe_2O_3	3.26
MgO	4.39
Na_2O	3.40
CaO	1.43

Glycolic acid is a detergent component (Thoen *et al.*, 1997) and complexes a large number of metallic cations (Bottari *et al.*, 1975; Sudersanan and Sundaram, 1977; Kulig *et al.*, 1980; Kumberger *et al.*, 1992). An *R* value of 25:1 is favorable for complex formation.

Acrylamidoglycolic acid, from the same family as GLY, forms complexes with an *R* value of 25:1 and 3:1 for Cd(II) and Pb(II), respectively (Barbier, 1999).

Solutions are prepared by dissolving metal nitrate in deionized water. Sodium nitrate is added to maintain a constant ionic strength of $0.05\,\text{mol}\,l^{-1}$. Ligand is then added and the pH is adjusted to 5.5 with sodium hydroxide or nitric acid. All reagents are of analytical grade.

2.3 Clay and Percolation Column

This work is performed with a technical commercial bentonite, called BSAB, commonly used as a landfill liner. It contains 80% of sodium-montmorillonite and its chemical composition, as provided by supplier, is presented in Table I.

Plexiglas columns (diameter: 4.4 cm, length: 3 cm) are filled with 2% of BSAB and 98% of crushed silica hydrated by a $0.05\,\text{mol}\,l^{-1}$ sodium nitrate solution (Fig. 1). The grain size of the silica is contained between 10 and 31.5 µm. Winiarski (1994) showed that this silica does not have significant influence on the composition of the percolated solutions. This percentage of silica allows us to obtain a permeability close to those encountered in liners.

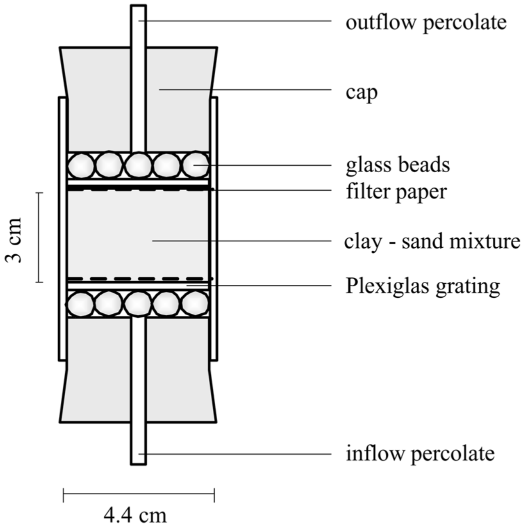

FIGURE 1 Modeling column.

This synthetic mixture, representative of a model soil, is packed between two Plexiglas gratings in order to obtain a density of about 1.45. The columns are then hydrated by sodium nitrate $0.05\,\text{mol}\,\text{l}^{-1}$ 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 to avoid possible erosion due to the pressure reaching 90 cm of water. First, 200 ml of sodium nitrate ($0.05\,\text{mol}\,\text{l}^{-1}$) is percolated through the column. Tubing is drained to limit dilution effects, and the solution is then introduced and percolate is collected at 50, 100, and 200 ml. Metal concentration of the eluted solution is determined by AAS.

3 RESULTS

Percolations of lead(II) and cadmium(II), noncomplexed and complexed, are performed separately. Total metal retention, Q_R, is the sum of metal retained on each collected fraction $(1, 2, \ldots, n)$, normalized to the clay weight. Metal retained on each collected fraction is the difference between initial metal quantity and the percolated metal quantity. The formula is as follows:

$$Q_\text{R} = \sum_i^n \left(\frac{C_i V_i - C_n V_n}{m} \right),$$

where

C_i = the initial concentration ($\mu\text{mol}\,\text{l}^{-1}$)
V_i = the initial volume of solution (l)
C_n = the concentration on the percolated solution ($\mu\text{mol}\,\text{l}^{-1}$)
V_n = the volume of the percolated fraction (l) and
m = the clay mass (mg).

Protonation and complexation constants of ligands with lead(II) and cadmium(II) are given in Table II.

Lead–sulfate, lead–GLY, lead–PHT and cadmium–EDA complexes are very weakly soluble with concentration and pH conditions of percolations. Thus, these systems have not been studied.

3.1 Lead(II)

Percolations of lead(II) nitrate solution provide the reference elution profile. Metal retention is found to be $Q_\text{R} = 0.34\,\mu\text{mol}\,\text{mg}^{-1}$ of clay. Figure 2 shows percolations of noncomplexed and complexed lead(II).

According to protonation and complexation constants of chloride ions (Sillén, 1977), for a ratio $R = 25{:}1$, the only complex in solution is the $[\text{PbCl}]^+$ species, which represents 13% of the total lead. Lead(II) retained in column is $Q_\text{R} = 0.34\,\mu\text{mol}\,\text{mg}^{-1}$ of BSAB, so this complex formation does not modify metal retention. This phenomenon can be due to

- the positive charge of the complex, which has an affinity for the clay (because of cationic exchange); and
- the low stability of the complex, which can be easily dissociated on the clay surface.

In presence of AAG, with an R value of 3:1 and at pH 5.5, the $[\text{Pb(AAG)}_2]$ complex is the dominant species and represents 50% of the total metal. Metal uptake is then $Q_\text{R} = 1.27\,\mu\text{mol}\,\text{mg}^{-1}$ of clay, which corresponds to a retention increase. It is assumed that this complex can be trapped in the column by precipitation.

TABLE II Protonation and Complexation Constants ($pM + qH + rL \rightleftarrows M_pH_qL_T$, $\beta_{p,q,r} = (M_pH_qL_T)/(M)^p(H)^q(L)^r$).

Ligand	*Protonation*	*Lead(II)*	*Cadmium(II)*
Chloride*		$\log \beta_{1,0,1} = 0.48$ $\log \beta_{1,0,2} = 0.15$ $\log \beta_{1,0,3} = 0.49$	$\log \beta_{1,0,1} = 2.12$ $\log \beta_{1,0,2} = 3.7$ $\log \beta_{1,0,3} = 4.3$
Sulfate*		–	$\log \beta_{1,0,1} = 1.0$ $\log \beta_{1,0,2} = 0.9$
GLY‡	$\log \beta_{0,1,1} = 3.63$	–	$\log \beta_{1,0,1} = 1.47$ $\log \beta_{1,0,2} = 2.0$
AAG	$\log \beta_{0,1,1} = 2.94$	$\log \beta_{1,0,1} = 2.97$ $\log \beta_{1,0,2} = 5.67$	$\log \beta_{1,0,1} = 2.36$ $\log \beta_{1,-1,1} = -2.82$
PHT†	$\log \beta_{0,1,1} = 4.97$ $\log \beta_{0,2,1} = 7.75$	–	$\log \beta_{1,0,1} = 2.82$ $\log \beta_{1,0,2} = 4.67$ $\log \beta_{1,0,3} = 6.4$ $\log \beta_{1,1,1} = 7.02$ $\log \beta_{1,-2,2} = -7.8$
EDA*	$\log \beta_{0,1,1} = 9.58$ $\log \beta_{0,2,1} = 16.25$	$\log \beta_{1,0,1} = 7.18$ $\log \beta_{1,0,2} = 8.63$	–
EDTA*	$\log \beta_{0,1,1} = 2.17$ $\log \beta_{0,2,1} = 4.92$ $\log \beta_{0,3,1} = 11.09$ $\log \beta_{0,4,1} = 21.47$	$\log \beta_{1,0,1} = 18$	$\log \beta_{1,0,1} = 16$

*Sillén, 1977.
†Lucas Vaz *et al.*, 1996.
‡Martel and Smith, 1976.

The complex mainly formed with EDA is the $[Pb(EDA)]^{2+}$ species, which represents 40% of the total metal. The quantity of lead(II) retained in column is then $Q_R = 0.12\ \mu mol\ mg^{-1}$, which implies a retention decrease of 64%.

In the case of the system lead(II)–EDTA, $[Pb(EDTA)]^{2-}$ is the major species (99%) and is not retained by clay ($Q_R = 0\ \mu mol\ mg^{-1}$). We have to notice that water in the column leads to

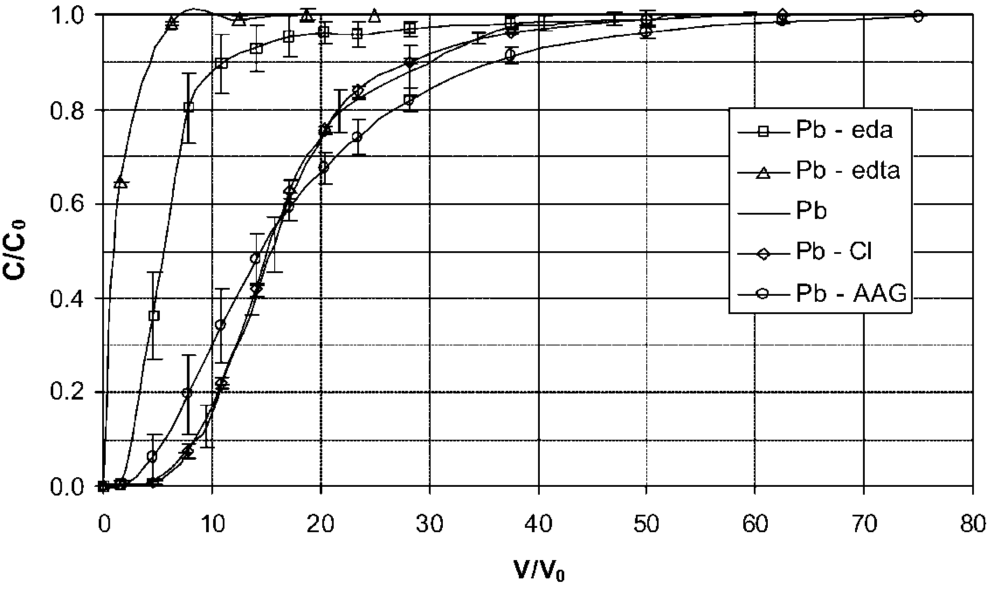

FIGURE 2 Elution profiles of noncomplexed and complexed lead(II).

the dilution of percolation solution. As a consequence, the ratio C/C_0 at $V/V_0 = 5$ is underestimated.

3.2 Cadmium(II)

Elution profile reference is given by percolation of noncomplexed cadmium(II). Metal retention is $Q_R = 0.28\,\mu\text{mol mg}^{-1}$ of BSAB.

Percolation of complexes formed with inorganic ligands are presented in Figure 3. Retention of cadmium complexed by chloride ions ($Q_R = 0.19\,\mu\text{mol mg}^{-1}$) decreases by 35% with respect to noncomplexed cadmium(II). This is in accordance with the results obtained by Plassard *et al.* (2000) for a natural alkaline soil. With our experimental conditions and with an R value of 25:1, 56% of the total metal is included in the [$CdCl_2$] neutral complex and 35% is included in the $[CdCl]^+$complex. These species are not retained by clay.

The system cadmium–sulfate ions forms the [$Cd(SO_4)$] neutral complex, which represents 14% of the total metal, with an R value of 10:1. Retention ($Q_R = 0.22\,\mu\text{mol mg}^{-1}$) is then 22% less than retention of the noncomplexed Cd^{2+} ion.

Figure 4 shows percolation of the systems cadmium(II)–GLY and cadmium(II)–AAG. In presence of GLY, with an R value of 25, the dominant $[CdGly]^+$ species represents 50% of the solution and leads to a retention decrease of 52% ($Q_R = 0.13\,\mu\text{mol mg}^{-1}$). Cd^{2+} ion seems to be the only species retained even if the complex is positively charged. Acrylamidoglycolic acid forms the [Cd(AAG)(OH)] neutral complex for a ratio $R = 25$. Metal retention is then $Q_R = 0.18\,\mu\text{mol mg}^{-1}$, which corresponds to a retention decrease of 47%.

Percolations of cadmium(II)–PHT and cadmium(II)–EDTA systems are presented in Figure 5. Both ligands form negative and stable complexes with cadmium. For PHT–cadmium(II) ratio of 25:1, the $[Cd(Pht)_3]^{4-}$ complex represents 52% of total cadmium and leads to a retention decrease of 81% ($Q_R = 0.05\,\mu\text{mol mg}^{-1}$).

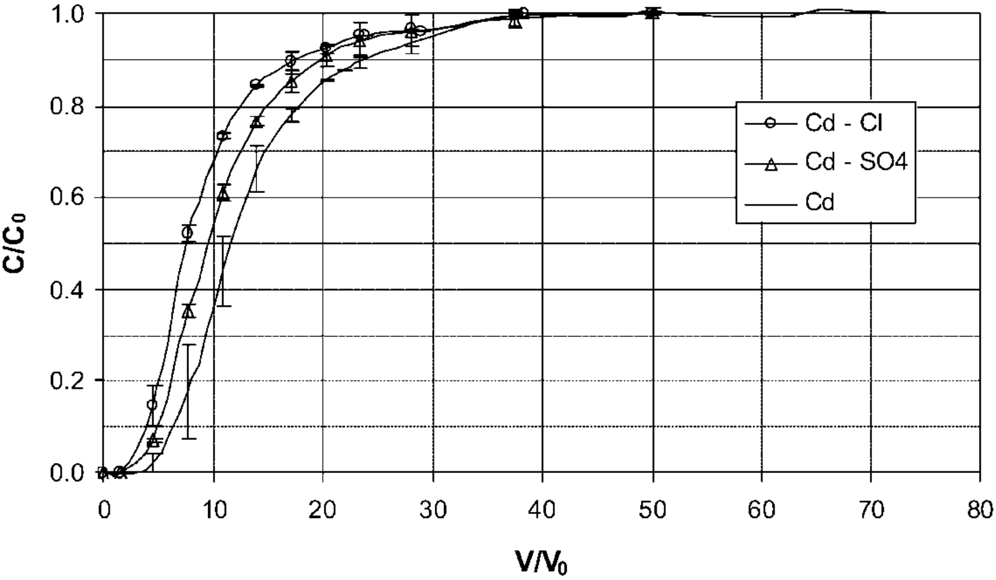

FIGURE 3 Elution profiles of cadmium(II) complexed by chloride and sulfate ions.

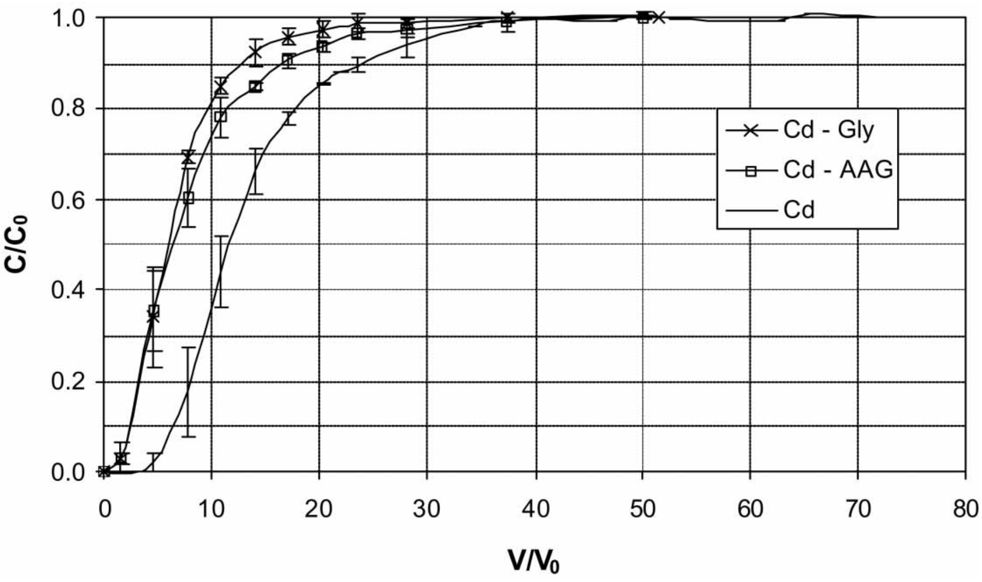

FIGURE 4 Elution profiles of cadmium(II) complexed by GLY and AAG.

In presence of EDTA and with an R value of 2, $[\mathrm{Cd(EDTA)}]^{2-}$ complex, representing 99% of the solution, is practically not retained ($Q_\mathrm{R} = 0.03\ \mu\mathrm{mol\,mg}^{-1}$) and the retention decreases 91%. As mentioned for lead, the first fraction collected is underestimated because of the dilution phenomenon. Complexes mask the metal from reactive sites of soil, according to the observations of Kedziorek *et al.* (1998) and Plassard *et al.* (2000).

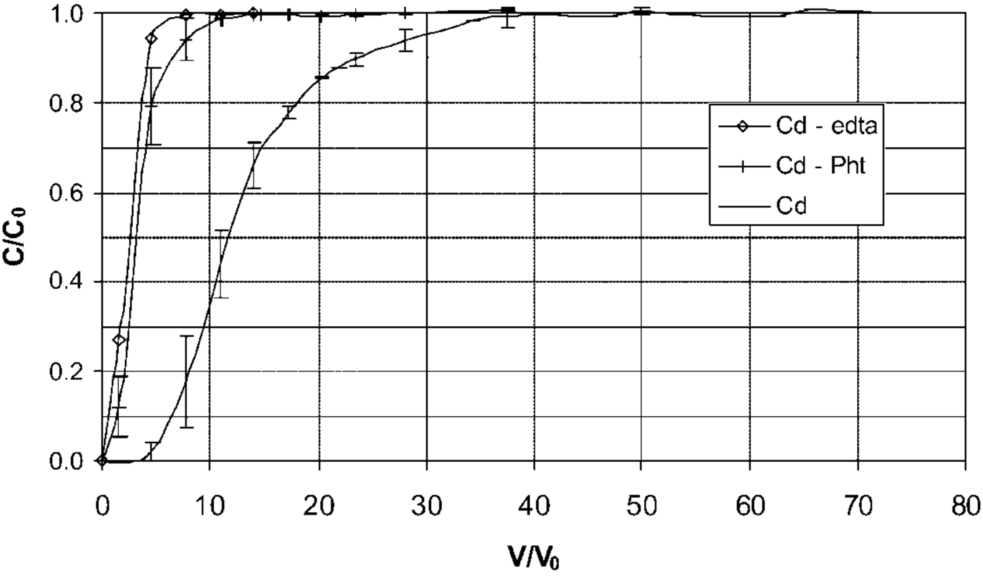

FIGURE 5 Elution profiles of cadmium(II) complexed by PTA and EDTA.

4 DISCUSSION

In most of the systems studied, it can be noticed that elution of the complexed metallic cations is faster than that of noncomplexed metals. Nevertheless, retention decrease depends on the kind of the complexes. As a consequence, it is interesting to determine the parameters having an influence on retention.

4.1 Influence of Complexes Charge

[Pb(AAG)$_2$] complex, which precipitates in the column and leads to a retention increase, is not taken into account. Table III summarizes results of the percolated complexes as a function of their charge. This table allows us to predict that complexes charge and retention decrease appear to be correlated. The retention decrease is higher when the species are negatively charged. This observation is in agreement with the fact that ionic exchange is the principle mechanism for metal uptake (Barbier *et al.*, 2000).

However, even for positive complexes we can notice that the positively charged complexes are less retained than the corresponding free cations. So there is another parameter influencing retention.

4.2 Influence of Complexes Stability

The more stable a complex, the more important is the complex quantity in solution. In order to study influence of complexes stability on metal retention, Figure 6 shows the retention decrease as a function of the percentage of the major species. As mentioned before [Pb(AAG)$_2$] complex is not taken into account.

The graph in Figure 6 shows that the higher is the major species percentage, the more important seems to be the retention decrease. As expected, it can be assumed that metal retention in column is influenced by the complexes conditional stability.

It would be interesting to know if the influence of the conditional stability is similar for positive, neutral, and negative species. Table III shows that negative species have no or small affinity for clay, so conditional stability of these complexes does not have influence on their retention and their elution is fast ($V/V_0 = 10$). Neutral species are also not so influenced by conditional stability, but are more retained than negative complexes. Positive species are

TABLE III Results of Percolated Complexes as a Function of Their Charge.

	% of major species	*Retention decrease (%)*
Negative species		
[Pb(EDTA)]$^{2-}$	99	100
[Cd(EDTA)]$^{2-}$	99	91
[Cd(Pht)$_3$]$^{4-}$	52	81
Neutral species		
[Cd(AAG)(OH)]	60	47
[Cd(Cl)$_2$]	56	35
[Cd(SO$_4$)]	14	22
Positive species		
[Cd(Gly)]$^{+}$	50	52
[Pb(Eda)]$^{2+}$	40	64
[PbCl]$^{+}$	13	0

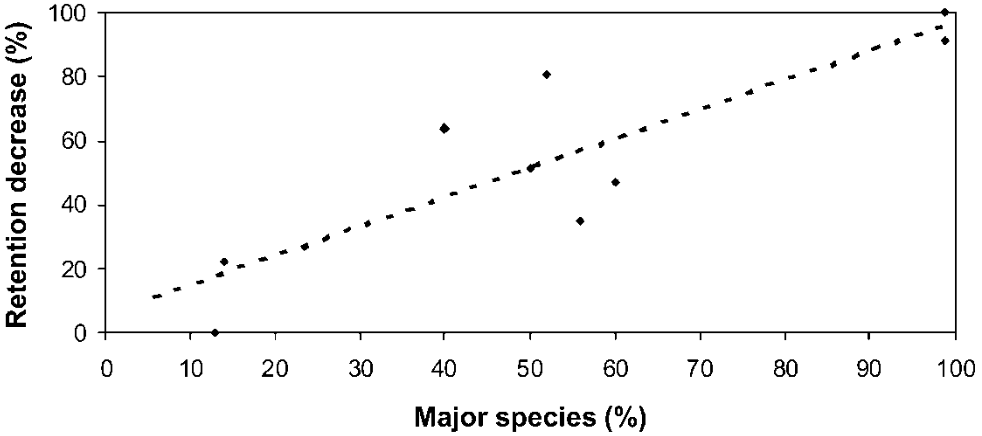

FIGURE 6 Influence of percentage of major species on retention.

greatly influenced by conditional stability. They are retained by clay, except when metallic cation forms a very stable complex (for instance, $[Pb(EDTA)]^{2-}$ or $[Cd(EDTA)]^{2-}$).

To confirm these previous results, the study should be continued by forming and testing other complexes so as to apply an appropriate statistical analysis.

5 CONCLUSION

Most of the studies concerning metal retention on montmorillonite refer to batch techniques, so hydrodynamic effects (*i.e.* depth, pollutant flow, etc.) are not taken into account. Moreover, comparison of the metal retention in terms of complex charge and conditional stability does not appear clearly in these works.

In our study, the systematic percolation of 10 complexed systems indicates that the presence of ligands usually leads to a metal-retention decrease. Complexes charge is the most influencing factor on retention, followed by complexes conditional stability. As a consequence, thermodynamic values, as conditional stability constants and solubility products, permit an evaluation of retention variations.

Transposition of these results to natural media phenomena shows that the complexed metal ions should diffuse easier than solvated cations in deep layers of soils and groundwater, which can lead to a risk of natural resources contamination.

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