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Sorption-Desorption Hysteresis of Cd and Pb on Alluvial Soils as Affected by Clay Content

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ADSORPTION hysteresis in natural sorbents has important environmental implications for pollutant transport and bioavailability. The objective was to assess and compare the competitive adsorption and desorption capacities and adsorption hysteresis of $Cd^{2+}$and Pb^{2+}on four natural soils with different clay contents (10%, 20%, 40% and 50%, hereafter referred to S_{10}, S_{20}, S_{40} and S_{50}) in terms of their physical and chemical properties. The adsorption-desorption hysteresis of $Cd^{2+}$and Pb^{2+} were characterized using linear, Freundlich and Langmuir equations. In all soils Pb^{2+} was invariably sorbed and retained to a greater extent than Cd^{2+}. Based on hysteresis index, Pb^{2+} was less mobile than Cd^{2+} in the studied soils. The adsorption and retention of Cd^{2+} and Pb^{2+}were most influenced by pH, cation exchange capacity (CEC), total amorphous material percent (TAM%), total organic carbon percent (TOC%) and clay content. In all the soils Cd^{2+} exhibited greater hysteresis than Pb^{2+}. The amounts of Cd^{2+} and Pb^{2+} desorbed from S_{10} were more than from S_{50}, indicating that S_{50} was a more effective sorbent for water and wastewater treatment and clay content was the individual soil property most markedly influencing Cd^{2+} and Pb^{2+} adsorption and retention.

Keywords: Hysteresis, Adsorption, Desorption, Heavy metals.

Regarding acute toxicity, Cd^{2+} and Pb^{2+} together with Hg^{2+} are form the big three" of heavy metals with the greatest potential hazard to humans and the environment (Volesky, 1990). Much greater effort will be needed to reduce pollution from these elements, *e.g.* through immobilization of Cd^{2+} and Pb^{2+} in soil and removal of these toxic elements from contaminated waste water. Cadmium and lead can be introduced into the soil as fertilizers, liming agents, sewage sludge urban and industrial wastes (Alloway, 1995, Kabala *et al*., 2009 and Shaheen & Tsadilas, 2010). Most studies of the behavior of Cd^{2+} and Pb^{2+} in soils have focused on the interaction of soil with solutions containing individual metal and have ignored the potential effects of mutual competition.

Since the heterogeneity of soil makes it very difficult to predict the potential mobility and distribution of even single metals, experimental data are essential. As a consequence, experiments to determine adsorption characteristics should

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always be followed by the determination of desorption. Adsorption and desorption isotherms show whether adsorption is reversible or wholly or partially irreversible (hysteretic). Most experiments have determined the distribution of metals between soil and metal ion solution following a contact period during which equilibrium is assumed to occur.

Hysteresis, or non-singularity, is a phenomenon in which the adsorption and desorption isotherms do not coincide (Strawn and Sparks, 1999). Several mechanisms have been suggested to explain hysteresis including chemical precipitation, variation of the binding mechanism with time, migration and incorporation of the solute into the soil matrix, micropore deformation and trapping (Weber & Huang, 1998, McBride, 2000 and Sander *et al.*, 2005). Pseudo-hysteresis is related to slow desorption kinetics, non-attainment of equilibrium of the adsorption before desorption was started (McBride, 2000) mass loss from vessels and adsorption to non-settling colloids (Sander *et al.*, 2005). One possible explanation for slow desorption is that chemiadsorption reactions usually require a much higher activation energy in desorption direction than adsorption, to break the energetically very favorable bonds of the sorbate with the surface (McBride, 2000 and Apple & Ma, 2002). The pseudo-hysteresis depends on conditions and can be eliminated, while the true hysteresis is reproducible in repeated adsorption-desorption cycles (Sander *et al.*, 2005). The objectives of the present work were to assess and compare the competitive adsorption and desorption capacities and the adsorption hysteresis of Cd^{2+} and Pb^{2+} in four alluvial soils with different clay content, to study the dependence of Cd^{2+} and Pb^{2+} fixation, hysteresis on soil properties.

Material and Methods

Soil sampling and analyzing

Four soils with different clay contents (10%, 20%, 40% and 50%, hereafter referred to S_{10}, S_{20}, S_{40} and S_{50}, respectively) were collected from 0-30cm depth to represent the alluvial of Egypt. The soil samples were pooled, air dried, passed through a 2 mm sieve and homogenized. Soil particle size was determined by the hydrometer method (Ashworth *et al.*, 2001). Soil pH was determined in 1:2.5 soil/water extracts with a combined pH electrode (Melero *et al.*, 2007). Cation exchange capacity was determined with sodium acetate and ammonium acetate for Na extraction (Rhoades, 1982). Total organic carbon was measured by Walkley-Black (1934) method as described by Nelson and Sommers (1982). Oxide contents were determined by the dithionite-citrate method (USSCS, 1972 and Sherdrick & McKeague, 1975) and the Fe, Al and Mn contents of the extract were determined by atomic absorption spectrophotometer (AAS), Perkin-Elmer model 1100B. The soil characteristics are summarized in Table 1.

TABLE 1. Characteristics of the studied soils.

Soil sample	pH	Clay (g kg^{-1})	OM (g kg^{-1})	CEC (Cmol$_c$ kg^{-1})	TAM (g kg^{-1})
S_{10}	7.41	105	4	15.51	32
S_{20}	7.52	204	8	30.22	38
S_{40}	7.71	408	12	42.43	42
S_{50}	7.91	509	15	52.53	55

OM: organic matter; CEC: cation exchange capacity; TAM: total amorphous material.

Adsorption and desorption experiment

Adsorption isotherms were constructed using the method of Fontes *et al.* (2000), as modified by Harter and Naidu (2001), using solutions containing both metals of Cd^{2+} and Pb^{2+} (0.01, 0.03, 0.05, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2 and 3 mmol L^{-1}) and 0.01 mol L^{-1} NaCl as background electrolyte. The concentrations were chosen in such a way as to span the range from typical values to levels of severe pollution. Triplicate suspensions of 5 g soil samples in 100 ml of solution in polyethylene tubes were shaken in a rotary shaker for 24 hr at 25°C and then centrifuged at 5000 rpm for 20 min. The pellet was saved for use in the desorption stage of the experiment; the resulting filtrate was analyzed by AAS. The amount of each metal that had been sorbed was calculated from the difference between its concentration in solution before the addition of the soil and after equilibration (shaking) with soil. Adsorption isotherms for each metal were constructed by plotting the sorbed metal content of the soil sample (mgkg^{-1}dry soil) against the metal concentration in solution at equilibrium (mgL^{-1}).The sorbed amount was calculated by mass balance equation:

$$q_e = (C_i - C_e)V/M$$

where: q_e, C_i, C_e, M and V are the sorbed amounts of the metal ions (mg kg^{-1}), initial metal concentration in solution (mg L^{-1}), equilibrium metal concentration (mg L^{-1}), mass of sorbent (g) and the volume of the solute solution (L), respectively. The adsorption isotherms were calculated for each soil using the Langmuir and Freundlich equations:

$$C_e/C_s = 1/bQ + C_e/Q$$

$$\text{Log } C_s = 1/n \text{ Log } C_e + \text{Log } K_f$$

where : C_e= equilibrium solution phase concentration (mg L^{-1}), C_s= equilibriumsolid phase concentration (mg kg^{-1}), Q=Langmuir isotherm adsorption capacity (mg kg^{-1}), b=enthalpy related adsorption constant (L mg^{-1}), n=adsorption intensity constant (k gl^{-1}) and K_f= adsorption capacity constant (L kg^{-1}).

Desorption isotherms were constructed using the pellets obtained in the adsorption stage; the pellets were dried at 45 °C and weighed. Each pellet was shaken in a polyethylene tube containing 100 ml of 0.005 mol L^{-1} DTPA solution at 25°C for 24 hr and then centrifuged at 5000 r min^{-1}; the filtrate was analyzed by AAS. The amount of each metal that had been released from the soil sample was measured. The desorption isotherms for each metal were constructed by plotting the amounts of metal retained in the soil samples (mg kg^{-1} dry soil) against the metal concentration in solution following desorption (mg L^{-1}).

Hysteresis index

The adsorption-desorption hysteresis was quantified for each sorbent-solute solution using the (n) value of Freundlich equation as defined by O'Connor *et al.* (1980) and Barriuso *et al.* (1994):

$$HI = n_{desrob}/n_{sorb} \times 100$$

where HI is the hysteresis index. The lower index values indicate increased difficulty of the sorbed metal to desorb from the sorbent (Chefetz *et al.*, 2004). The n_{sorb} and n_{desorb} are the exponent of fitted Freundlich equation in the adsorption and desorption branches, respectively. Theoretically, if there is no hysteresis n_{desrob}=$n_{sorb}$and, positive hysteresis would be characterized by n_{sorb}>n_{desorb} in the case of negative hysteresis n_{desorb}>n_{sorb}, respectively, (O' Connor *et al.*, 1980 and Barriuso *et al.*, 1994). Statistical analysis was performed using the Excel programs.

Results and Discussion

Soil characteristics

The studied soil samples were significantly different in terms of the components and properties (Table 1) which may influence metal adsorption and mobility, and therefore metal retention by the soils. The clay content was significantly different between soils and varied between 10.50% (S_{10}) and 50.90% (S_{50}). The pH of the soils ranged from 7.4 (S_{10}) to 7.9 (S_{50}), organic matter from 4.0 (S_{10}) to 15.0 g kg^{-1} (S_{50}). The S_{50} had the highest proportion of amorphous material (Table 1). The cation exchange capacity (CEC) varied from low (15.5 $Cmol_c$ kg^{-1}) in the S_{10} to high (52.5 $Cmol_c$ kg^{-1}) in the S_{50}.

Adsorption and desorption isotherms

Figure 1 shows the adsorption and desorption isotherms for Pb^{2+} and Cd^{2+}. The adsorption isotherms of Cd^{2+} for the soils was L type (typical of soils with a high affinity for the solute), with an initial slope that remained unchanged whatever the metal concentration in the equilibrium solution was. On the other hand, the adsorption isotherms of Pb^{2+} for the soils (Fig. 1) was H type, with a typically high initial slope reflecting a high affinity of the soil solid phase for the sorbate.

The competitive desorption isotherm of Cd^{2+} was mainly type L for the soils, while the competitive desorption isotherms of Pb^{2+} was H type. The competitive adsorption or DTPA-desorption isotherms of Cd^{2+} with Pb^{2+} were fitted to Langmuir and Freundlich models (R^2= 0.80 to 0.99, respectively). The fitted curves from Langmuir equation were used to estimate the maximum adsorption or retention capacity Q_m (mg kg^{-1}), and adsorption energy b (L mg^{-1}). The calculated Maximum adsorption and DTPA-desorption capacity of $Cd2^{+}$ and Pb^{2+} (Fig. 2), showed consistent increases with increasing the clay content.

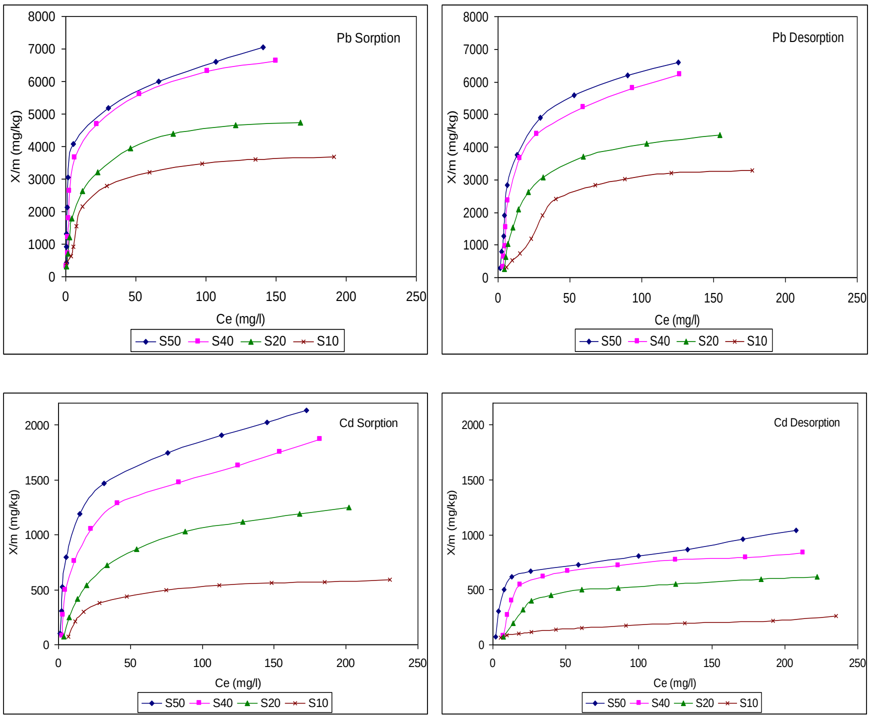

Fig.1. Competitive adsorption and desorption isotherms of Pb^{2+} and Cd^{2+} in the studied soils.

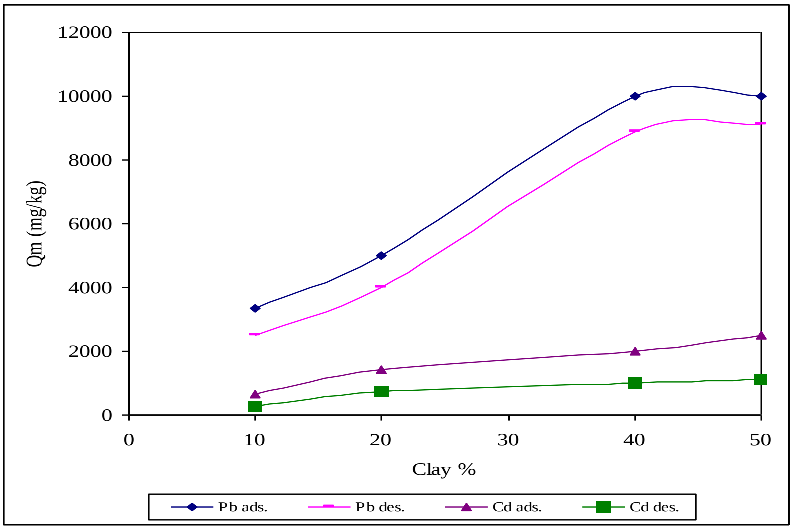

Fig.2. Effect of clay percent on Langmuir isotherm adsorption capacity of Pb^{2+} and Cd^{2+} in the studied soils.

Based on the Q_m results (Fig. 2), S_{50} soil showed the highest capacity of both adsorbed Pb and Cd either in the adsorption or desorption processes, while the lowest values were recorded for S_{10}.The maximum adsorption for S_{50} reached 10000 and 2500 mg kg^{-1} for Pb^{2+} and Cd^{2+}, respectively. The maximum adsorption or DTPA-desorption capacity were significantly higher for Pb^{2+} when compared to those of Cd^{2+} due to the high adsorption affinity of lead ion on soil samples. These differences in soil affinity for Pb^{2+} and Cd^{2+} have been observed by others for tropical soils (Lu *et al.,* 2005).

This is usually attributed to differences in metal characteristics and resultant affinity for adsorption sites (Appel and Ma, 2002). For example, the hydrated radius of Pb^{2+} is smaller than that of Cd^{2+} (Pb^{2+} 0.401 nm; Cd^{2+} 0.426 nm; Nightingale, 1959), favoring columbic interactions of Pb^{2+} with exchange sites. Furthermore, Pb^{2+} has a greater affinity for most functional groups in organic matter including carboxylic and phenolic groups, which are hard Lewis bases. This is mainly attributed to the differences in chemical properties between the two metals. Lead is a harder Lewis acid (Pb^{2+} is a borderline Lewis acid while Cd^{2+} a soft Lewis acid), has a higher electronegativity (2.33 and 1.69 for Pb^{2+} and Cd^{2+}, respectively); and has lower pK_H (negative log of hydrolysis constant; 7.71 and 10.1 for Pb^{2+} and Cd^{2+}, respectively) than Cd^{2+}. Each of these factors makes Pb^{2+} a better candidate for inner-sphere surface adsorption/complexation reactions compared to Cd^{2+} (Wulfsberg, 2000).

In addition, Moreira and Alleoni (2010) stated that the maximum adsorption capacity (MAC) values for metals were lower in the competitive than in the non-competitive system. In the non-competitive system, the most common affinity sequence was Cu > Zn > Ni > Cd, whereas the most common sequence was Cu > Cd > Zn > Ni in the competitive system. In general, the Langmuir model fitted well the adsorption data of metals on the studied soils.

Further investigation of Fig. 2 showed that the MAC values significantly decreased after the desorption with DTPA with higher magnitudes in case of Cd^{2+} ion compared to those of Pb^{2+} due to the higher accessibility of Cd^{2+} extraction by DTPA than Pb^{2+}. The statistical analysis (Table 2) showed highly significant positive correlation between Pb^{2+} or Cd^{2+} maximum adsorption capacity Q_m calculated from Langmuir model and clay, OM, CEC, total amorphous materials and pH. This could be attributed to the increase of clay content which is associated with increases in the adsorption sites expressed by high CEC, OM and total amorphous material, which is in agreement with the findings of Gurel (2006), Covelo *et al*. (2007) and (2008) and Vega *et al*. (2009). Comparing the experimental results for lead and cadmium, the general trend is that the maximum adsorption capacity Q_m increases when the pH increases. This is not only because of the hydrogen ion competition at low pH, but also because of the weakly acidic nature of the active sites on the adsorbent whose deprotonation with increasing pH, favors the metal adsorption (Pagnanellia *et al.*, 2003). The b values (enthalpy related adsorption constant (L mg^{-1}) which expresses the metal binding energy showed significant R^2 values (0.69 - 0.91) with soil properties especially with Cd^{2+} (Table 2).

TABLE 2. Correlation coefficient between Langmuir values (Q_m and b) and soil properties

Soil characteristics	Q_m (mg kg^{-1})				b (L mg^{-1})			
	$Pb_{sor.}$	$Pb_{des.}$	$Cd_{sor.}$	$Cd_{des.}$	$Pb_{sor.}$	$Pb_{des.}$	$Cd_{sor.}$	$Cd_{des.}$
pH	0.93**	0.94**	0.97**	0.92**	0.60	0.18	0.82*	0.83*
OM	0.95**	0.96**	1.00**	0.98**	0.54	0.24	0.70	0.73
TAM	0.83*	0.85*	0.95**	0.88*	0.76	0.35	0.88*	0.91**
CEC	0.95**	0.95**	1.00**	0.98**	0.55	0.28	0.69	0.72
Clay	0.97**	0.98**	0.98**	0.96**	0.48	0.12	0.74	0.73

Q_m: maximum adsorption; b: sorption energy; Pb_{sor}: sorption of Pb^{2+}; Pb_{des}: desorption of Pb^{2+}; Cd_{sor}: sorption of Cd^{2+}; Cd_{des}: desorption of Cd^{2+}; OM: organic matter; CEC: cation exchange capacity; TAM: total amorphous material; *, **Significant at $P = 0.05$ and $P = 0.01$ levels, respectively.

The fitted curves from Fruendlich equation were used to estimate the partitioning coefficient K_f (L kg^{-1}) and adsorption intensity constant n (kg l^{-1}). The calculated K_f values for both adsorption and DTPA-desorption of both Cd^{2+} and Pb^2 (Fig. 3) showed consistent increases with increasing the clay content. The K_f values were significantly higher for Pb^{2+} when compared to those of Cd^{2+} due to the high adsorption affinity of lead ion on soil samples. These differences in soil affinity for Pb and Cd^{2+} have been observed by others for tropical soils (Lu *et al.*, 2005). High K_f values were recorded for adsorption than DTPA-desorption for both Pb^{2+} and Cd^{2+} due to the additional competitive action of DTPA ligands.

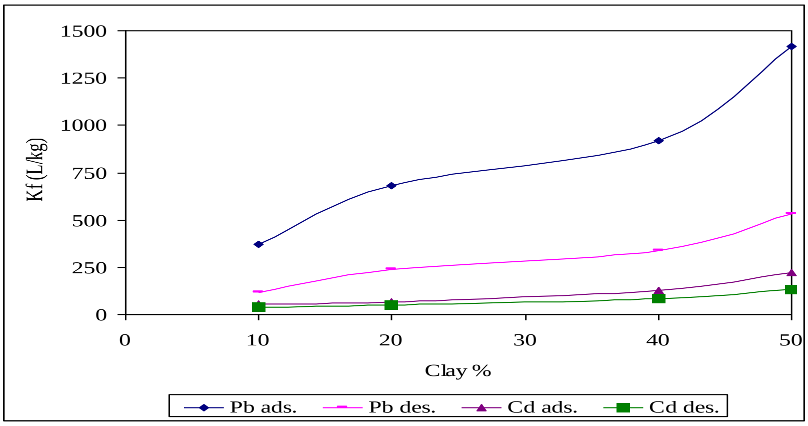

Fig. 3. Effect of clay percent on distribution (partition) coefficient (K_f) of Pb^{2+} and Cd^{2+} in the studied soils.

The statistical analysis (Table 3) showed highly significant positive correlation between Pb^{2+} or Cd^{2+} partitioning coefficient K_f (L kg^{-1}) and adsorption intensity constant n (kg l^{-1}) calculated from Freundlich model and clay, OM, CEC, total amorphous materials and pH. This could be attributed to the increase of clay content which is associated with increases in the adsorption sites expressed by high CEC, OM and total amorphous material, which is in agreement with the findings of Vega *et al*. (2009). This is confirmed by Esfandbod *et al.* (2011) who showed that Cd-partioning value (K_d) was significantly correlated with soil pH. The effect of soil properties on the adsorption intensity constant (n) was clearly noticed for both Pb^{2+} and Cd^{2+}.

TABLE 3. Correlation coefficient between Freundlich values (K_f and n) and soil properties.

Soil characteristics	K_f (L kg^{-1})				n (kg l^{-1})			
	$Pb_{sor.}$	$Pb_{des.}$	$Cd_{sor.}$	$Cd_{des.}$	$Pb_{sor.}$	$Pb_{des.}$	$Cd_{sor.}$	$Cd_{des.}$
pH	0.99**	0.99**	0.98**	0.99**	0.97**	0.89*	0.99**	0.82*
OM	0.98**	0.98**	0.92**	0.94**	0.95**	0.88*	0.96**	0.69
TAM	0.99**	0.99**	0.98**	0.99**	1.00**	0.96**	1.00**	0.84*
CEC	0.97**	0.98**	0.91**	0.94**	0.95**	0.89*	0.96**	0.67
Clay	0.96**	0.97**	0.94**	0.95**	0.93**	0.83*	0.98**	0.73

K_f: adsorption capacity constant or partition coefficient; n: adsorption intensity constant; Pb_{sor}: sorption of Pb^{2+}; Pb_{des}: desorption of Pb^{2+}; Cd_{sor}: sorption of Cd^{2+}; Cd_{des}: desorption of Cd^{2+}; OM: organic matter; CEC: cation exchange capacity; TAM: total amorphous material; *, **Significant at *P* = 0.05 and *P* = 0.01 levels, respectively.

A statistical analysis was carried out to study the correlations between the properties and components of the soils and the competitive adsorption and retention of Cd^{2+} (Table 2). The adsorption and retention of Cd^{2+} in the soils were found to be dependent not only on soil pH and CEC, but also on the contents of Fe and Mn oxides and the clay fraction.

Covelo *et al*. (2007) showed that adsorption and retention of Cd^{2+} were highly correlated with the vermiculite content of the soil. According to Bradl (2004), however, a soil would sorb a metal ion to a substantial extent only when the iron oxides were bound to the clay fraction and organic matter. Cd^{2+} is known to be preferentially fixed by soils with a moderately acid to slightly alkaline pH, especially in the presence of manganese oxides (Covelo *et al*., 2008 and Vega *et al*., 2009).

In addition to the known influence of the character rustics of each soil, one should also consider the widely accepted fact that Cd^{2+} and Pb^{2+} in soil compete with each other and also with other metal ions present, for adsorption sites (Benjamin & Leckie, 1981 and Vega *et al*., 2006 & 2009). The soils with the highest competitive adsorption and retention capacities of Cd^{2+} (*i.e.*, S_{50} and S_{40}) were also the soils with the highest pH, CEC, AM and clay content (Table 1). According to the previous studies (Benjamin and Leckie, 1980 & 1981, Serrano *et al*., 2005, Arias *et al*., 2006, Vega *et al*., 2006 and Covelo *et al*., 2008), the adsorption behaviour of a cation in soil is strongly influenced by the presence of other cations.

As can be seen, the S_{50}, of clayey texture, was the soil containing the highest proportion of clay (about 50%), which resulted in its high adsorption and retention capacities of Cd^{2+} (Fig. 2). Therefore, the soil properties, which are highly significantly positive correlated with the adsorption and retention of Cd^{2+}, enhance the ability of soils to sorb and retain this cation. Gurel (2006) found that the presence of chlorite in the clay fraction facilitated Pb^{2+} and Cd^{2+} fixation in soil.

The S_{50} was the individual soil exhibiting the highest Pb^{2+} fixation capacity. As stated above (Fig. 2), both the adsorption and retention of Pb^{2+} fitted with the Langmuir model more closely than the Freundlich model. In those soils exhibiting good fitting (*i.e.*, high R^2 values), As a rule, the soils with the highest Pb^{2+} fixation capacity were those with the highest pH, CEC and clay content, also containing very substantial amounts of AM. The soils with the lowest fixation capacity were those with the lowest clay content and pH and containing little organic carbon, which suggests the formation of insoluble organic complexes with added Pb^{2+}. It was confirmed by the correlation analysis of the characteristics of the studied soils, The Pb^{2+} fixation was significantly correlated with the pH and organic C content of each soil.

In addition, the competitive adsorption and retention of Pb^{2+} were correlated with CEC, the contents of AM and clay (Table 2). This is consistent with the results of other authors (Gurel, 2006 and Vega *et al*., 2006), who found that Pb^{2+} ion possessed a high affinity for iron oxides, and also for clay minerals. Moreover, the presence of iron and manganese oxides may have a prominent effect on Pb^{2+} adsorption by soil. Covelo *et al*. (2008) and Kabata-Pendias (1980) found that Mn oxides exhibited the highest affinity for Pb^{2+} among the most abundant oxides in soil. In addition, Pb^{2+} fixation was correlated with pH and contents of the clay fraction (Table 2). Consistent with these results, it was found that Pb^{2+} immobilization in soil to be favored by the presence of vermiculite in the soil.

The dependence of competitive Pb^{2+} adsorption and desorption on soil components and properties differed between soils (Table 2). The adsorption and retention of Pb^{2+} in the soils were highly significantly correlated with pH, CEC, and more markedly, with the clay content; therefore, clay content and organic matter are the two individual factors most strongly favoring Pb^{2+} in its competition for adsorption sites in surface soils. However, the adsorption and retention of Pb^{2+} in the presence of Cd^{2+} were influenced mainly by the soil mineral components (iron and manganese oxides).

Adsorption-desorption hysteresis

Figure 4 shows the hysteresis indices (HI) calculated from (n) value of Freundlich equation. The gap between adsorption and desorption isotherms was evaluated by the hysteresis index (HI). For both metal ions, the HI increased with decreasing of clay content on the S_{10} (Fig. 4). This could be due to the presence of limited number of high energy adsorption sites available on the sorbent, therefore the metal ions were preferentially adsorbed at those high energy adsorption sites first, and the adsorbed metals at those sites was difficult to be desorbed (Singh *et al.,* 2006). At high initial concentrations of the metals, the limited high-energy sites (resistant fraction) were first saturated by Cd^{2+} or Pb^{2+}. The rest of metal ions sorbed at the low energy adsorption sites, and hence were more easily desorbed than those at high energy adsorption sites. Thus, overall desorption was easier and the hysteresis index (HI) was higher at lower clay content.

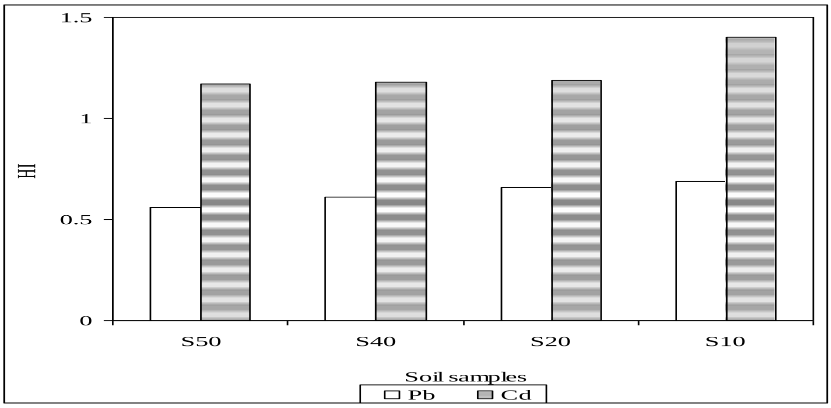

Fig.4. Hysteresis indices for Pb and Cd Adsorption-desorption in the studied soils.

Higher HI values were recorded for Cd^{2+} as compared to those of Pb^{2+} at all the investigated soils. The results showed that the Pb^{2+} adsorption was more irreversible than Cd^{2+} adsorption in all soils. The competitive adsorption of Cd^{2+} and Pb^{2+} was more irreversible in S_{50} compared with the other soils. Also, the S_{50} had a slightly alkaline pH and the highest CEC values, AM contents and clay content (Table 1). This hysteresis may be attributed to the different rates of adsorption and desorption processes as it was suggested by Strawn and Sparks (2000), assuming that 2-day period may be not sufficient to attain complete desorption equilibrium. Sorbate may undergo some transformation and being transformed may slower interact with the species in the solution.

The composition and properties of forming surface complex may be affected by the presence of DTPA in solution. For the soils low clay content, The average percentage of the sorbed metals released from S_{10} after DTPA-desorption steps, were 14% and 60% for Pb^{2+} and Cd^{2+}, while it was 10% and 36%, respectively in S_{50}. This is in agreement with the findings of Businelle *et al.* (2003).

The values of the calculated hysteresis indices (HI) were inversely proportional to the clay content of the investigated soil samples. The statistical analysis (Table 4) showed highly significant and negative correlation coefficients (R^2= -1.0 to -0.98) between HI indices and all the tested soil properties (*i.e.* pH, OM, CEC, AM and clay fraction) in case of Pb^{2+} adsorption-desorption. In case of Cd^{2+} adsorption-desorption, the HI R^2 were lower (R^2 = -0.72 to - 0.86) which is still highly significant.

In order to reliably identify the specific soil properties that most strongly influence adsorption irreversibility, the soil characteristics and hysteresis indices for the soils (Table 2) were correlated. In the soil, hysteresis in the competitive adsorption of Cd^{2+} and Pb^{2+} (Table 2) was found to depend on; pH, OM, CEC, AM and clay fraction. Based on the foregoing, not all soils can efficiently fix the two metals under the same conditions. In fact, the characteristics of each soil have a crucial influence on its ability to retain metal separately and jointly.

TABLE 4. Correlation coefficients between soil characteristics and hysteresis indices (HI), for competitive adsorption and retention of Cd^{2+} and Pb^{2+}.

Soil characteristics	HI for Pb^{2+}	HI for Cd^{2+}
pH	-1.00**	-0.73
OM	-0.99**	-0.84*
TAM	-0.98**	-0.72
CEC	-0.98**	-0.86*
Clay	-0.99**	-0.78

HI: hysteresis index; OM: organic matter; CEC: cation exchange capacity; TAM: total amorphous material. *, **Significant at *P* = 0.05 and *P* = 0.01 levels, respectively.

For the soils low clay content, The average percentage of the sorbed metals released from S_{10} after desorption steps, were 14% and 60% for Pb^{2+} and Cd^{2+}, respectively. Since a relatively high proportion of sorbed Cd^{2+} was released, it indicates that the adsorption of Cd^{2+} by S_{10} was likely reversible and less specific. This suggests that ion exchange (outer-sphere complexation) is the dominant mechanism of adsorption reaction between Cd^{2+} and S_{10} (Businelle *et al.*, 2003).

As can be seen from Fig. 1, the desorption isotherms for Cd^{2+} onto S_{10} did not deviate strongly from the corresponding adsorption isotherm indicating a reversible adsorption. The amounts of desorbed Cd^{2+} were larger than would be predicted from the adsorption isotherms. This is a case of negative hysteresis ($n_{desorb}>n_{sorb}$), that is, when the sorbate is desorbed more easily than it is sorbed. Barriuso *et al.* (1994) reported negative hysteresis for the adsorption-desorption of atrazine by montmorillonite (Wyoming bentonite).They attributed this phenomenon either to (i) enhanced desorption as a result of temporarily high solid/solution ratio after centrifugation, or (ii) removal of only external water in the desorption experiments while the interlayer water is fixed (Barriuso *et al.*, 1994). In any case, this phenomenon is only observed when the adsorption desorption process is highly reversible.

In the case of Pb^{2+}, the amount of desorbed Pb^{2+} was smaller than the amount that would be predicted from the adsorption isotherm indicating some reactions involved in the adsorption processes may be irreversible or slow reversible. Since preliminarily kinetic studies showed that both the adsorption and desorption rates of Cd^{2+} and Pb^{2+} leveled within about 24 hr, non-equilibrium state of the system can be ruled out as an explanation. Similar findings have been reported by Businelle *et al.* (2003) for adsorption of Pb^{2+} onto montmorillonite. They concluded that irreversibility of Pb^{2+} adsorption by montmorillonite was due to the inner-sphere binding of Pb^{2+} to the mineral edges and its precipitation at pH values higher than hydrolysis point of Pb^{2+} (Businelle *et al.*, 2003).

Based on the estimates obtained by Visual MINTEQ, the species Cd^{2+} and Pb^{2+} were the dominant species present in the equilibrium solutions and none of the systems were supersaturated with regard to Cd^{2+} and Pb^{2+}containing minerals. However, according to McBride (2000), under saturation state of the systems does not exclude the possibility of metal surface precipitation or co-precipitation processes. It is known that the presence of suspended colloids can trigger the nucleation of elements on the surfaces even in diluted solutions under-saturated with regard to individual minerals (McBride, 2000). However, it should be considered that the precipitation reactions are often much slower than chemiadsorption reactions to soil constituents (Strawn & Sparks, 1999 and McBride, 2000).

The gap between adsorption and desorption isotherms was evaluated by the hysteresis index (HI). For both metal ions, the HI increased with decreasing of clay content on the S_{10} (Fig. 4). This is expected, because there were only limited number of high energy adsorption sites available on the sorbent, therefore the metal ions were preferentially sorbed at those high energy adsorption sites first, and the sorbed metals at those sites was difficult to desorb (Singh *et al.*, 2006). At high initial concentrations of the metals, the limited high-energy sites (resistant fraction) were first saturated by Cd^{2+} or Pb^{2+}. The rest of metal ions sorbed at the low energy adsorption sites and hence were more easily desorbed than those at high energy adsorption sites. Thus, overall desorption was easier, and the hysteresis index (HI) was higher at lower clay content.

On the other hand, for the soils high clay content, The average amounts of 10 and 36% of the initially sorbed Pb^{2+} and Cd^{2+} were desorbed from S_{50} after desorption steps, respectively. Release of such a relatively low proportion of sorbed Cd^{2+} and particularly Pb^{2+}indicates that some reactions involved in the adsorption processes may be irreversible or very slowly reversible which may be attributed to diffusion of metal ions into the layer clay minerals and the strong bonding to the high affinity sites (inner-sphere complexation) (Mozgawa, 2004). Infrared spectroscopic studies by Mozgawa (2004) revealed that Pb^{2+} formed inner-sphere surface complexes with zeolite. These sorbed metal ions are relatively difficult to desorb (Brown *et al.*, 1999).

The desorption isotherms of Cd^{2+} and Pb^{2+} onto S_{50} deviated significantly from the corresponding adsorption isotherms (Fig. 1). The amounts of desorbed Cd^{2+} and Pb^{2+} were considerably smaller than the amount that would be predicted from adsorption isotherm. This shows a normal or positive hysteresis ($n_{desorb}<n_{sorb}$) and suggests that a portion of the sorbed metal ion was tightly bonded to the mineral surfaces and was not readily desorbable. Effects of clay content on the hysteresis index are shown in Fig. 4, the apparent hysteresis index (HI) was greatly dependent on the percentage of clay content in soils. For Pb^{2+}-S_{50} systems, the HI decreased with increase of the clay content. But, in the case of Cd^{2+}, the HI increased with decreasing the clay content.

Compared to Cd^{2+}-sorbent systems, higher irreversibility, as reflected by low HI values, was obtained for Pb^{2+}-sorbent systems (especially Pb^{2+}-S_{50}) (Fig. 4). This is usually attributed to differences in metal ion characteristics and resultant affinity for adsorption sites (McBride, 2000 and Apple & Ma, 2002). The hydrated Pb^{2+} (5.2 A◦ diameter) and Cd^{2+} (5.5 A◦ diameter) cations have 6.1 and 7.6 water molecules in their hydration shells, respectively (Marcus, 1999). The hydration energy of $Pb^{2+}$is 1425 kJ mol^{-1} and that of Cd^{2+} is 1755 kJ mol^{-1} (Marcus, 1999). The lower hydration energy of Pb^{2+} means that it loses its hydration shell more easily than Cd^{2+}. This could explain the stronger adsorption of Pb^{2+} than Cd^{2+} (Inglezakis *et al.*, 2003).

The Freundlich binding constants (K_f sorb) of Pb^{2+} adsorption onto soils were greater than those of Cd^{2+} (Fig. 3), which confirms that $Pb^{2+}$was retained stronger by the sorbents. Many studies considering the adsorption-desorption of Cd^{2+} and Pb^{2+} on soils and clay minerals have indicated that Pb^{2+} was much less desorbable than Cd^{2+} (Apple & Ma, 2002, Wingenfelder 2005; Hamidpour *et al.*, 2010).

Conclusions

Adsorption and desorption of Cd^{2+} and Pb^{2+} results were well described by the Langmuir and Freundlich models. The results revealed that the desorption isotherms of Cd^{2+} and Pb^{2+} from S_{50} deviated from adsorption data indicating irreversible or very slowly reversible adsorption, while, for S_{10}adsorption/ deadsorption isotherms showed little deviation indicating reversible adsorption. The parameter n proved to be an accurate choice for comparing the adsorption capacity and competitive retention of Cd^{2+} and Pb^{2+} in different soils, and also for calculating adsorption hysteresis. The soils with the highest pH, OM, CEC, AM and mineral variety in the clay fraction exhibited the highest competitive adsorption capacity for Cd^{2+} and Pb^{2+}. Most of the soils exhibited a high affinity for Pb^{2+}. Also, Pb^{2+} exhibited lower adsorption hysteresis than Cd^{2+}. Based on the hysteresis index, Pb^{2+} was strongly adsorbed compared with Cd^{2+}. The S_{50} was the soil most strongly retaining Pb^{2+} and Cd^{2+}. The amount of Cd^{2+} or Pb^{2+} desorbed from S_{10} was more than that of S_{50}, indicating that S_{50} is a more efficient immobilizer of Pb^{2+} and Cd^{2+} from polluted soil or waste water. Irreversible adsorption would be advantageous for pollutant immobilization in the remediation of already contaminated soils.

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تباطؤ ادمصاص وانطلاق الكادميوم والرصاص على أراضي رسوبية مختلفة المحتوى الطيني

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تباطؤ الادمصاص على أسطح الادمصاص داخل التربة له آثار بيئية هامة في نقل الملوثات. كان الهدف من الدراسة هو تقييم ومقارنة ادمصاص وانطلاق عنصري الرصاص والكادميوم على أربعة أنواع من الأراضي الرسوبية مختلفة القوام بنسب طين (10، 20، 40، 50٪)، تم تطبيق نموذج معادلة لانجمير وفروندليش. أظهرت النتائج أن كمية الرصاص المدمصة كانت اعلى من الكمية المدمصة من الكادميوم في جميع عينات التربة. كما أنه بناءا على قيمة دليل التباطؤ فان حركة عنصر الرصاص داخل التربة كانت أقل من حركة عنصر الكادميوم. كما أظهرت النتائج أن كل من pH ، CEC ، TAM%، TOC% ونسبة الطين كان لها أثر كبير على الكمية المدمصة والمنطلقة من عنصري الرصاص والكادميوم.