ISSN : 0974 - 7451 Volume 6 Issue 6

Trade Science Inc.

Environmental Science
An Indian Journal

Current Research Paper

ESAIJ, 6(6), 2011 [313-319]

The behaviour of cadmium adsorption on some Egyptian surface soils

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Received: 22th July, 2011; Accepted: 22th August, 2011

ABSTRACT

Adsorption of cadmium on two different soils from Egypt (clays and sandy loam soils) was studied. Data on adsorption isotherms, competitive effects and/or inorganic complex formation of NaCl and Na_2SO_4 are presented. The adsorption was described by a Langmuir or a Frendlich equation. The maximum adsorption derived from the Langmuir equation was taken to measure the adsorption capacity, while the Langmuir parameter was taken to point out the relative degree of affinity or energy at different cadmium adsorption conditions. In particular, the clay soil had higher adsorption capacities in all cases than the sandy loam soil. The higher clay content, CEC, OM and the surface area of the clay soil may account for the higher capacity. It appears likely that the existence of NaCl decreases the maximum adsorption of cadmium in both soils and also reduces the bonding energy coefficients less than those in presence of Na_2SO_4 apparently favoring the dissociation of adsorbed Cd complex. Due to this behavior, cadmium adsorption in case of NaCl salt matrix was about three times less than for Na_2SO_4. This effect is important since relatively moderate concentration of Cl in soil solution will greatly reduce the adsorption of Cd on soil surface. Thereby relatively high Cd concentrations in soil solutions will be maintained especially under surface irrigation conditions, which increase the probability for ground water pollution with this harmful and toxic metal.
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KEYWORDS

Cadmium;
NaCl, Na_2SO_4;
Langmuir;
Freundlich;
Egyptian soils.

INTRODUCTION

Cadmium is probably the heavy metal of most concern associated with soil pollutants. It is a potentially dangerous inorganic pollutant ion. The major question here is the ability of the soil to act as an attenuate and perhaps even a sink for cadmium. The answer of this question could be through knowledge concerning cad-

mium adsorption as well as cadmium binding on soil surfaces[14].

The knowledge of the mobility mechanisms of cadmium is an important parameter for the risk assessment of polluted soils. Mobility is highly dependent on the way and the strength of the fixation of the cadmium ions by the soil components. For risk assessment purposes statements have to be made about the mobility (migration, transport) and about the retardation (adsorption and bonding forms)[12].

The occurrence of heavy metals in the soils can theoretically include the following fractions[13]:

1. As free ions or complexed in the pore water
2. Adsorptive or exchangeable bound on soil component surfaces, mainly on iron and manganese oxides and hydroxides, clay minerals and organic matter.
3. Precipitated as chemical compounds (hydroxides, carbonates and sulfides)
4. Co-precipitated on iron and manganese oxides and hydroxides, and on carbonate, sulfide and phosphate minerals
5. Organically complexed (on organic soild phases)
6. Residual, occluded in especially into silicates

The objective of this study was to investigate the behavior of the cadmium ions in some Egyptian soils, to describe the type of adsorption under different levels of some electrolytes. The aspects of its mobility and the thermodynamic free energy of adsorption will be determined. These together might contribute our knowledge for better understanding metal-binding in soils and the factors that govern that behavior. The quantitative informations about the soil adsorption mechanism of cadmium ions will involve:

1. Determination of adsorption isotherms,
2. Competitive effects of sodium ions,
3. The specific adsorption sites available for cadmium on different soil surfaces, and
4. The effect of the counter ions associated with the salt matrix (Cl^- or SO_4^{2-}) on the cadmium complex formation.

MATERIALS AND METHODS

Two soil samples from Egypt were used in this study, the first was alluvial and the second was calcareous. TABLE 1 represents chemical and physical characteristics and the mineralogical analysis of the experimental soils.

Adsorption isotherms

The adsorption isotherms were constructed at pH 7.8. Duplicate samples of each soil was applied. To 100 ml polyethylene tubes containing 2 g samples of each soil, 50 ml of 0.05 NaCl as an indifferent electrolyte, were added. An amount of a stock solution containing 500 mg Cd/L was added to obtain initial cadmium concentrations of 1-15 μg/ml in each tube. The tubes were shaken in an end-over end shaker for 24 hours at room temperature. The pH was adjusted three times to be 7.8 during this period. The slurry was separated by centrifugation. The supernatant was removed. The adsorbed cadmium was calculated be the difference between the concentration of Cd in the original solution and the equilibrium solution.

The effect of NaCl concentration on cadmium adsorption

The competitive effect of sodium on cadmium adsorption was examined. This was evaluated by constructing other cadmium adsorption isotherms at 0.15 N NaCl. The experiments were conducted as described above in the first one, except that 0.15 N NaCl salt matrix was added.

Effect of counter ions

To study the influence of the counter ion of the indifferent electrolyte and its inorganic complex formation on cadmium adsorption, Na_2SO_4 as indifferent electrolyte was used instead of NaCl. Two different concentrations of this salt (0.05 and 0.15 N) were prepared. The experimental procedures were also the same as for NaCl. Cadmium concentration was measured by the atomic absorption.

RESULTS AND DISCUSSION

Two soils from different regions of Egypt were selected for this investigation. This first one is an alluvial and the second is a calcareous soil. Some soil properties which are relevant to the adsorption of Cd ions are presented in TABLE 1.

The wide range of Cd concentration used through-

TABLE 1 : Characteristics and mineralogical analysis of the experimental soils.

Parameters	Alluvial soil	Calcareous soil
Texture of < 0.5 mm		
% Sand (0.02-0.5 mm)	12.10	62.70
% Silt (0-20 μm)	31.60	25.60
% Clay (2 μm)	56.30	11.70
% Calcium carbonate	2.14	21.80
% Organic matter	1.75	0.30
CEC (meq/100 g soil)	48.20	8.70
Specific surface area (m^2/g), O.P. method	233.80	87.60
Cd content (μg/g), hot 1:1 HNO_3 for 6 hrs; [17]	0.36	0.06
Mineralogical analysis		
% Montmorillonite	51.50	14.20
% Kaolinite	15.00	17.20
% Mica	7.50	26.30
% Vermiculite	5.00	-
% Attapulgite	-	22.00
% Quartz	4.00	4.00
% Feldspar	3.00	3.50
% Free oxides	14.00	12.80

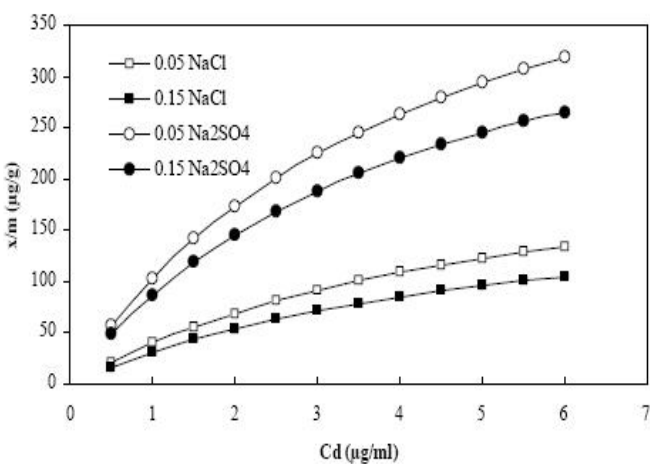

Figure 1 : Cadmium adsorption isotherm in alluvial soil at different concentrations of NaCl and Na_2SO_4 as salt matrices.

out this study produced curvilinear adsorption isotherms. The ability of theses two soils to adsorb Cd was found to be different. This ability was compared by reference to the "Cd adsorption Isotherm Gradients", calculated from the first linear parts of Figures 1 and 2. The values of the gradients were given for all of the soils in TABLE 2. On the basis of these results it can be seen that the Cd concentration in the alluvial soil is influenced more by its constituents than the calcareous soil[10].

The formation of uncharged ion pairs and/or nega-

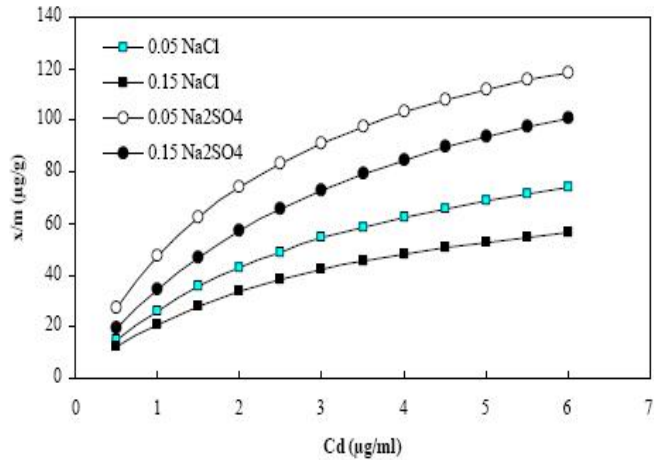

Figure 2 : Cadmium adsorption isotherm in calcareous soil at different concentrations of NaCl and Na_2SO_4 as salt matrices.

tively charged complex can be observed from the comparison between the adsorption isotherms of NaCl and those of Na_2SO_4 as indifferent electrolyte. Figures 1 and 2 show that, for the same Cd ions concentration in solution, the amounts of adsorbed Cd are appreciably lower in chloride systems. The difference in the amounts ranged between two to three times less in NaCl systems as compared with Na_2SO_4 systems this observation can be attributed to the formation of complexes of Cd^{2+} with Cl^- ligands like ($CdCl_2°$, $CdCl_3^-$ and $CdCl_4^{-2}$) where the Cl^- ion may coordinate with a surface ligand and be treated as an inner sphere complex with the surface[5]. On the other hand from the solution chemistry studies, Na_2SO_4 dose not form in these conditions of concentrations, since the formation of this species would decrease the amount of Cd adsorption on the soil surfaces i.e., sulfate ion form an outer sphere complex in the alkaline conditions[5]. This observation tends to confirm the conclusions of the electrolyte effect on heavy metal adsorption. For instance, cations such as the alkali metals and earth alkali metals may compete for low-energy adsorption sites on the soil and hence reduce the sorption of cadmium when these ions are present in substantial amounts. This effect is important since relatively moderate amount of NaCl in soil solution will greatly reduce the adsorption of Cd on soil surfaces and thereby tend to maintain relatively high concentrations of Cd in soil solution[8].

The adsorption of Cd on these soils conformed to the linear form of Langmuir equation:

$$C/(x/m) = 1/(a.b) + [C/a] \quad (1)$$

TABLE 2 : The Langmuir and Freundlich coefficients for the two examined soils under different conditions of salt matrix and concentration.

Soil type	Salt matrix	Salt matrix Conc. N	Langmuir parameters		a x 100 / CEC	Freundlich parameters	
			a (µg/g)	b (ml/µg)		k (ml/µg)	n
Alluvial	Na_2SO_4	0.05	544	0.232	2.05	16.51	1.270
		0.15	448	0.242	1.69	14.09	1.297
	NaCl	0.05	255	0.137	0.96	k_1 5.62 k_2 27.03	n_1 1.077 n_2 2.333
		0.15	198	0.190	0.75	k_1 5.21 k_2 13.74	n_1 1.296 n_2 2.188
Calcareous	Na_2SO_4	0.05	170	0.368	3.12	15.31	2.026
		0.15	163	0.272	2.99	12.92	1.984
	NaCl	0.05	116	0.294	2.13	k_1 5.63 k_2 17.93	n_1 1.591 n_2 2.494
		0.15	85	0.330	1.56	k_1 5.63 k_2 16.58	n_1 1.732 n_2 3.778

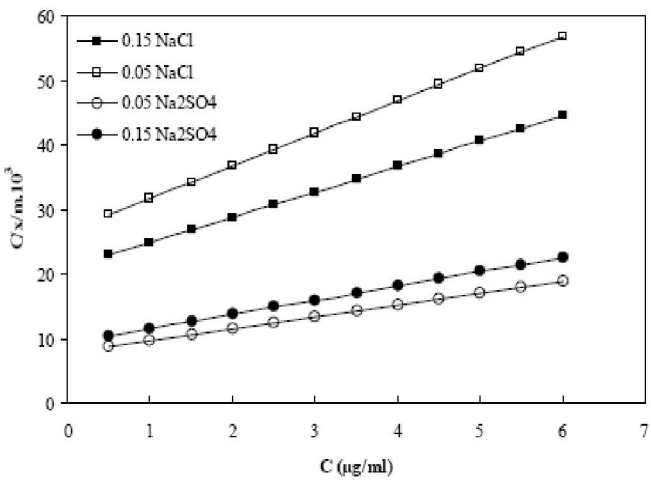

Figure 3 : Langmuir isotherm for cadmium adsorption by alluvial soil

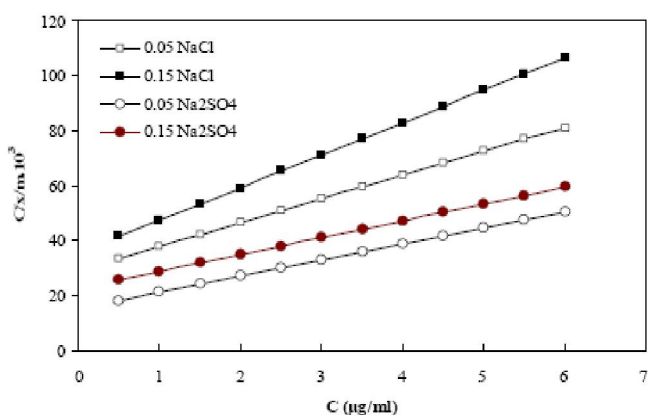

Figure 4 : Langmuir isotherm for cadmium adsorption by calcareous soil

Where (x/m) is the amount of Cd adsorbed by unit weight soil (μg/g), C is equilibrium Cd concentration in solution (μg/ml), A is the Langmuir adsorption maximum (μg/g), and b is the Lagmuir "bonding term" related to bonding energy. To find out the maximum adsorption, a and the bonding term, b for these soils under different salt matrix conditions and different ionic strengths; C/(x/m) was plotted against C (see Figures 3 and 4); which gave a straight line. The variability in surface hydroxyls, notably the variation in point of zero charge and surface charge density, the calcium carbonate, the variations in clay mineral composition and the presence of organic matter combined with the different affinities of the cations for sites, might be responsible for the differentiation in the specifically adsorbed Cd, and to obtained differences of Langmuir parameters.

At the diluted indifferent electrolyte (0.05 N), the cadmium ions will be adsorbed at the diffused parts of the double layer, Where they are in a fully hydrated or partially hydrated forms. On the other hand, at the high level of the electrolyte (0.15N) the double layer of the clay minerals will be compacted and the adsorbed ions would be partially or fully un-hydrated. So the adsorbed cadmium under this condition would occupy the specific surface charged sites[5]. The differences between the maximum adsorption, b, at 0.05 and 0.15 N of the indifferent electrolyte might represent the non-specific adsorbed cadmium (see TABLE 2). It appears from the data of TABLE 2 that the specifically adsorbed cadmium represents about 80% from the total adsorbed amount in these soils. Moreover, this total adsorbed cadmium represents less than 3% from the total surface charges (CEC) in these two soils. It means that the total adsorption of cadmium is very low and consequently most of the cadmium will be free into the soil solution,

causing a harmful condition on the environment in the case of the alluvial soil, while in the case of calcareous soil many authors have reported that the mechanism corresponds to surface precipitation, coprecipitation or diffusion into the existing minerals which may lead to a solid solution formation[3, 11, 15, 16].

The mineral composition of the calcareous soil (see TABLE 1) and its lower content of the organic matter may be the reason to exhibited lower cadmium adsorption than the alluvial soil[1, 7, 10].

Thermodynamic free energy of cadmium adsorption

An attempt was made to calculate the free energy of cadmium adsorption under different conditions of sodium ionic strength and/or the co-ion. In this method the fractional surface coverage, θ, was fixed at 5×10^{-10} meq of cadmium adsorbed per cm^2 of the surface area to provide the rational basis of comparing the surface of these soils. By combining the knowledge of surface area (see TABLE 1) and the adsorption isotherm, θ was calculated through the values of *x*/m per gram taken from the adsorption isotherm at a level reaches to all the adsorption isotherms. Thereby the principle of this method depends on keeping constant θ value for a rational comparison between soils under their different experimental conditions. Finally, the corresponding values for *x*/m divided by surface area of the indifferent electrolyte will be taken to calculate the free energy of adsorption ΔG^o_θ.

The standard free energy of adsorption at fixed θ, ΔG^o_θ is determined from following equation:

$$\Delta Go_\theta = -RT\ln[m_{Cdeq} \cdot \gamma_{Cdeq}] = -RT\ln a_{Cdeq} \quad (2)$$

Where eq, m, γ, and a_{Cdeq} refer to the equilibrium conditions, molality, activity coefficient and activity respectively of aqueous cadmium ions. The activity coefficient, γ, of Cd ions will be calculated from the equilibrium concentration and from the EC values by using Debye-Huckel theory eventually Cd activity, a, can be calculated.

The negative values of the standard free energy of adsorption ΔG^o_θ, indicates that the reaction proceeds spontaneously. These negative values of ΔG^o_θ (see TABLE 3) can provide a measure for cadmium binding on the soils surfaces. The stronger the cadmium binding, the more is the negative value of ΔG^o_θ.

TABLE 3 : Free energy of cadmium adsorption for the two examined soils under different conditions of salt matrix and concentration.

Salts		Free energy ΔG°, KCal./mole	
		Alluvial Soil	Calcareous Soil
NaCl	(0.05 mole)	-6.70	-7140
	(0.15 mole)	-6.62	-6.91
Na_2SO_4	(0.05 mole)	-7.59	-8.00
	(0.15 mole)	-7.44	-7.72

There is a general behavior for ΔG^o_θ values in these experiments. It was found that the values of free energy of adsorption in calcareous soil had higher values than in the alluvial soil; however, the maximum adsorptions for the first soil were lower than the second one as shown in TABLE 2. It means that the calcareous soil exhibited stronger surfaces to bind cadmium ions than the alluvial soil. The mineral composition of the calcareous soil (see TABLE 1) may have been the reason to exhibit the higher free energy of adsorption. The mica and attapulgite contents are high in this soil. It has been found by many authors that these clay minerals have a higher tendency to adsorb cadmium and this tendency dose not changes by changing the electrolyte concentration concentration[4, 9]. The Freundlich equation,

$$\text{Log } (x/m) = \text{Log } K + (1/n) \text{ Log } C \quad (3)$$

was also used to evaluate the data. It is expressed in terms of soil equilibrium concentration (μg/g), *x*/m, adsorption parameter (ml/g), K and adsorption parameter, dimensionless, n.

The correlation coefficients for the linearized Freundlich equation were also fairly high. The n-values obtained were comparable with those reported in the literature, 1.00-1.70. The K-values are not comparable to literature values as mentioned previously for Langmuir a-values. From the statistical analysis it was found that the fit of the Freundlich equation to represent the adsorption data, in the presence of NaCl as salt matrix was excellent when these curves were resolved into two linear portions (Figures 5 and 6). The two portions of the curve were considered separately where the lower six points (referred to as part 1) in the most instances had an obviously different slopes from the upper six points (referred to as part 2).

This behavior may be due to the existence of two energy level sites for Cd adsorption in the presence of NaCl. In the case of Na_2SO_4 the isotherms have one

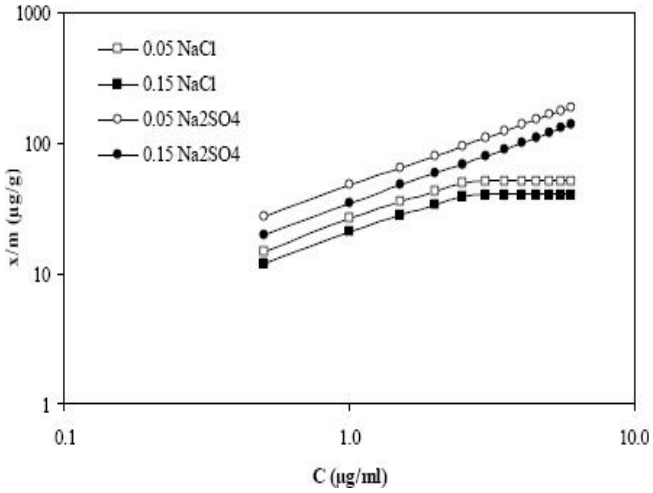

Figure 5 : Freundlich plots of cadmium adsorption by alluvial soil.

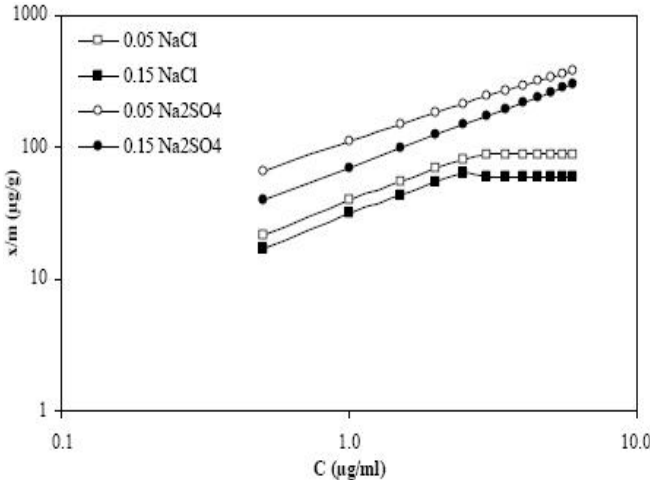

Figure 6 : Freundlich plots of cadmium adsorption by calcareous soil.

slope allover the Cd adsorption points, indicating homogeneity in the sites of cadmium adsorption. The ability of NaCl to produce such behavior could be attributed to the competition between Na^+ in NaCl and Cd ions, to occupy some specific sites, where Cl^- have a tendency to make complex ions with Cd^{2+}[5]. Thus Na^+ in that electrolyte could have higher probability to compete for some of the specific Cd^{2+} sites. This type of sites is not accessible for Na^+ in Na_2SO_4. It may be possible to suggest that this type of sites belongs to the low energy level sites, since Cd^{2+} adsorption increased by increasing the salt content from 0.05 to 0.15 N.

Several soil constituents are able to adsorb cadmium; it is probable that high contents of clay, silt, organic matter, iron and manganese oxides, calcium carbonate and high soil pH indicate a high capacity for adsorbing cadmium. However, no simple linear relationship should be expected. For example, the alluvial soil of this study exhibited three times higher capacity than the calcareous soil (see TABLE 2), although it contained five times more clay and six times more cation exchange capacity than the calcareous soil (see TABLE 1). The higher capacity of the alluvial soil for Cd^{2+} adsorption is likely due in part to the formation of an organo-clay complex with a higher affinity for Cd^{2+} or to the formation of a clay-Cd, organo-Cd bridge that increased the adsorption capacity of the system[6, 7].

CONCLUSIONS

It appears likely that the existence of NaCl as a salt matrix decreases the maximum adsorption, a and reduces the bonding energy coefficient, b, apparently favoring the dissociation of adsorbent-Cd complex. Under semiarid and arid zones, soil where higher Cl^- concentrations are common, Cd^{2+} might be leached more readily in the soil profile, especially under surface irrigation systems. This removal or leaching might result in pollution of the ground water with this toxic heavy metal. The higher, a, values were for the alluvial soil, whereas, the higher, b, values were for the calcareous soil. Thus it seems that the alluvial soil has higher adsorption capacities and the calcareous soil has a higher bonding energy sites; due may be to its higher $CaCO_3$ content and this conclusion is conformed by the free energy of cadmium adsorption. According to the ΔG^o_θ behavior it can be concluded that calcareous soil exhibited stronger surfaces to bind cadmium ions than the alluvial soil. However, the maximum adsorptions for the alluvial soil were higher than those of calcareous soil.

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