
Cadmium Sorption as Influenced by Carbonate Forms of Clay Fraction of Some Calcareous Soils in Al-Hassa

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Abstract:

The different carbonate forms were determined in the fine (< 0.2 μm) and coarse (2 - 0.2 μm) clay fraction of the three representative soil profiles in Al-Hassa Oasis at Saudi Arabia. The results indicate that the total calcium carbonate (C_c) is high (9.40 - 28.10%) and relatively higher in fine than coarse clay. The calcite ranges from 0.35 to 9.55 %, Mg calcite is found to range from 0.00 to 10.20 % and the other carbonate varies 0.24 to 17.70 %. Mg calcite is relatively higher in the fine than the coarse clay fraction.

Data of cadmium sorption by clay fraction indicate two populations of sites, (I and II) having different affinity for cadmium sorption, were present and fit the binary Langmuir equation. The constants related to the bonding energy in part I (K_1^I) were higher in fine clay than the coarse clay and correlated significantly with Mg-calcite content while the maximum adsorption values of part I were higher in the fine clay and correlated significantly with Mg-carbonate content. On the other hand, K_1 and K_2 for part II have no regular trend and no correlation with calcium carbonate forms.

Introduction:

The increasing consumption, production, and exploitation of the earth's raw materials (fossil fuels and minerals), coupled with the exponential growth of the world's population over the past 200 years, have resulted in environmental buildup of waste products, of which heavy metals are of particular concern (Adriano, 1986; Purves, 1977). Soils are an important sink for these metals due to soils' high metal retention capacities. Cadmium pollution in soils has increased during the last decades, mainly due to the large application of farmyard manure, sewage sludges, mining waters or fertilizers obtained from phosphorites of usually very high Cd content (Mortvedt 1987; Vanni *et al.*, 1994).

The major factors affecting the chemistry of Cd in solution are complexation reactions, pH, ionic strength, competing ions, precipitation and the bonding power to the adsorbent (Gerritse and Van Driel 1984; Christensen, 1989). Cadmium sorbed on soil is strongly influenced by soil pH, cation exchange capacity (CEC) and organic content (Basta *et al.*, 1993). However, direct cause-and-effect relationships between soil

composition and metal adsorption are difficult to determine because soil components are often intercorrelated. Thus, the clay particle aggregates, as well as the clay-humic and metal-humic interactions that are usually present in soil solutions, are influenced by the ionic strength and the solution pH in a different way than in suspensions containing only the clay or the humic acid (Taylor and Theng, 1995). However, good correlation has been observed between Cd adsorption on soil and their clay content (Navrot *et al.*, 1978; Basta *et al.*, 1993).

Estimation of the potential toxicity of Cd content in soils requires information on both the adsorption and desorption reactions. A comparison between adsorption and desorption results frequently reveals a hysteretic phenomenon. Although this apparent partial irreversibility has been described very early in the literature (Hisschemsller, 1921), a satisfactory explanation is still missing. In the case of 2:1 clay minerals, various mechanisms have been proposed: heterogeneity of sites at the surface of the exchanger; differential hydration of the exchanging cations; dehydration of the clay; crystalline swelling hysteresis; and inaccessibility of sites caused by domain or quasi-crystal formation (Peigneur, *et al.*, 1975; Kool *et al.*, 1987). In these articles, results of Cd adsorption on and desorption from montmorillonite are presented, and it is shown that both can be explained consistently by the application of a general model for cation adsorption in a closed system (Nir 1984, 1986), which was further developed for Cd adsorption by explicitly accounting for Cd complexation in solution (Hirsch *et al.*, 1989).

Cadmium is more available than other heavy metals to migrate to deeper soil layers or to underground water by leaching (Breslin, 1999). The modeling of the migration of Cd in soil has been studied in relation to soil properties and adsorption isotherms (Filius *et al.*, 1998; Seuntjens *et al.*, 2001) but few published reports deal with the prediction of Cd leaching with a simple test to achieve an estimate of the contamination risk (Garrabrants and Kosson, 2000).

The mechanisms governing the retention and release of Cd in two soils, a loam and a loamy sand, pretreated with anaerobically digested sewage sludges or with chemical fertilizers, were studied using batch equilibration in 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution containing up to 6 μg Cd/ml (Soon, 1981). He found that adsorption rather than precipitation as $\text{Cd}_3(\text{PO}_4)_2$ limited solution Cd^{2+} concentration and with the addition of 50 μg Cd/g, however, precipitation as CdCO_3 was likely at $\text{pH} > 7.6$. Moreover, Cd adsorption increased with increasing soil pH.

Carbonate minerals is usually present in soil in different forms; mainly calcite, Mg-bearing calcite and other forms of carbonate such as dolomite, magnesite and aragonite (Watts, 1980). Carbonate minerals play a major role in the effect on the soil properties and fixation of the metals in soil (McFadden *et al.*, 1991). In Al-Hassa oasis, carbonate is dominating the whole oasis due to its laying on marly parent material (Al-Hawas, 1998). The total carbonate of some soils ranged from 3.0 to 52.0 % (Al-Hawas, 2001), calcite ranged from 0.35 to 11.60%, Mg-calcite was found to range from 1.77 to 11.80% and other carbonate (non Ca and Mg carbonate) ranged 0.0 to 10.70% (El-Garawany, 1996).

The objectives of this study are:

- 1- To determine carbonate forms in two clay fractions of some soil from Al-Hassa, Saudi Arabia.
- 2- To determine the relation between cadmium sorption and the carbonate forms.

Material and methods:

Surface and subsurface soil sample from three soil profiles were selected from private farm on Qatar road (sample 1) and from the station for training & agricultural and veterinary research (samples 2&3) in Al-Hassa Oasis at Saudi Arabia, based on CaCO_3 content in the soil. The following analyses were carried out:

- (1) Samples were analyzed for pH, EC, CEC, organic carbon, CaCO_3 content, particle size distribution, by standard procedure in Page (1982).
- (2) Clay ($<2\mu\text{m}$) fraction was separated by decantation from the selected samples.
- (3) Total calcium carbonate (T_{CaCO_3}), Calcite form (calcite), Magnesium calcite form (Mg-CaCO_3), and other carbonate form ($O_{\text{carbonate}}$) were determined in the separated clay fractions as reported by El-Garawany (1996).
- (4) Duplicate 1.00 g of clay fractions were shaken with series of 50 ml CdCl_2 solutions containing varying amounts (0.445, 0.890, 1.335, and 1.780 mmol/L of inorganic Cd in 0.01 M KCl as electrocute to prevent the interference of soil salts) for one hour at room temperature in 60 ml polyethylene centrifuge tubes. The tubes were then centrifuged and filtrated. Cadmium was determined in the filtrate by AAS. Data were then used to construct Cd sorption isotherm. Available Cd (ppm) was determined in soil samples according to the method of (Lakanen and ErviÖ, 1971).

Cadmium sorption isotherm:

Two linear relationships were obtained when the sorption data were plotted according to the conventional Langmuir equation (Fig. 1). This is indicating the presence of two populations of sites which have widely differing affinity for Cd. At low Cd concentration, the less reactive sites could also sorb Cd through the same mechanism of Langmuir. However, this sorption data were analyzed assuming two types of sites and applying the bonding Langmuir equation in the next form as report by Syers *et al.* (1973).

$$x/m = \frac{K_1^I K_2^I C}{1 + K_1^I C} + \frac{K_1^{II} K_2^{II} C}{1 + K_1^{II} C}$$

Where X/m is the amount of Cd sorbed per weight unit of soil, K_1 is a constant related to the bonding energy, K_2 is the adsorption maximum, C is the equilibrium Cd concentration, and superscript I and II refer to part I and II (straight lines corresponding to lower and higher C values in the isotherm, respectively).

Results and Discussion:

Table (1)
General Soil Properties of the three profiles

Profile No.	Soil depth (cm)	Soil property								
		Clay %	Silt %	Sand %	Texture	EC dSm ⁻¹	pH	O.M%	CEC Cmol _c kg ⁻¹	Ava. Cd
1	0-80	13	6	81	LS	1.92	7.00	0.22	9.87	0.48
	80-120	12	11	77	SL	5.25	7.78	0.50	9.12	0.25
	120-200	25	19	56	SCL	7.80	7.21	0.92	18.45	0.99
2	0-60	24	9	67	SCL	1.60	7.65	0.15	18.73	1.00
	60-120	12	10	78	SL	1.77	8.00	0.42	8.75	0.25
	120-200	2	8	90	S	2.35	7.45	0.46	2.34	0.57
3	0-40	8	2	90	S	3.73	7.36	0.18	6.49	0.89
	40-120	10	3	87	LS	5.95	7.32	0.25	8.43	0.91
	120-200	8	2	90	LS	5.44	7.99	0.15	6.83	0.78

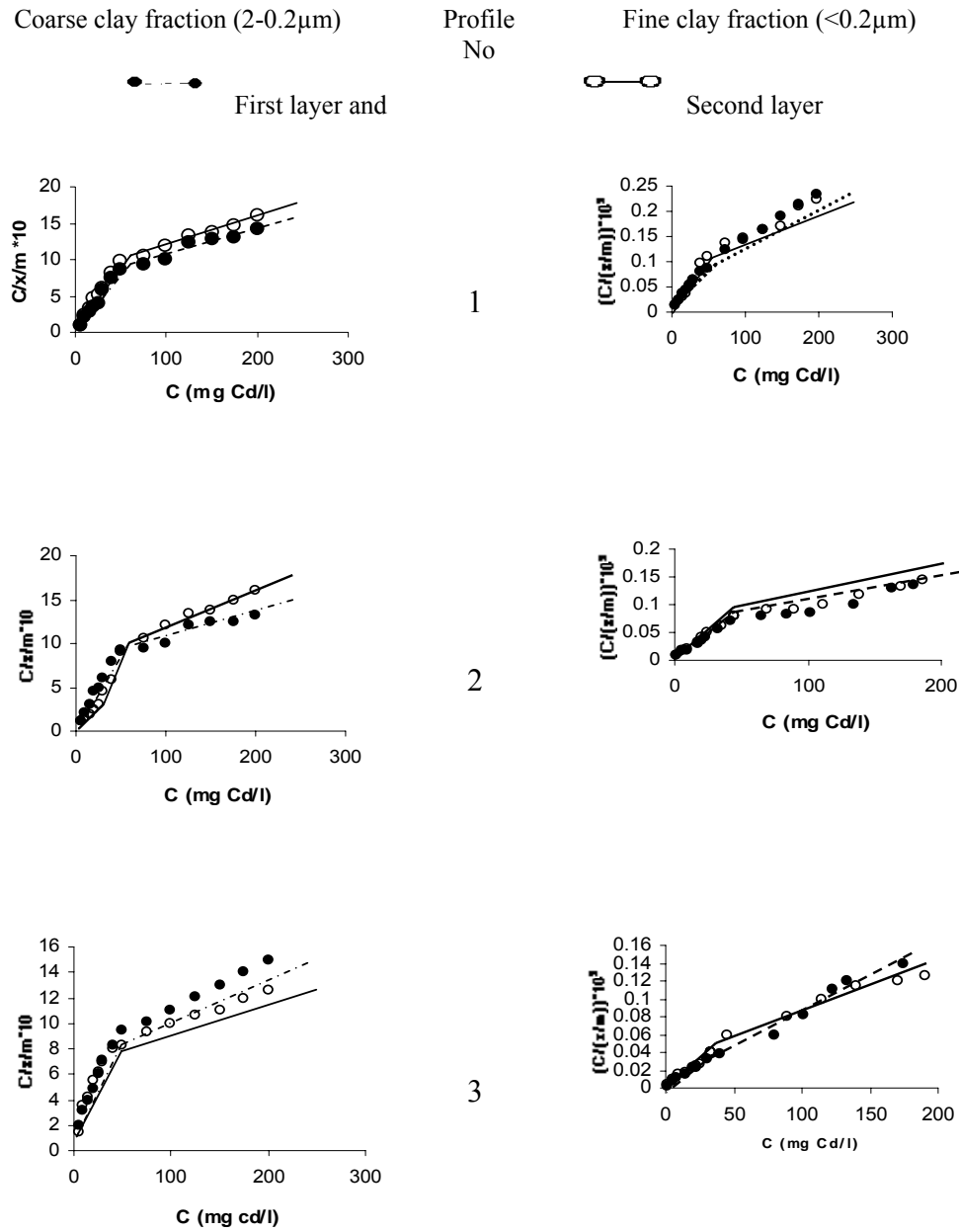


Fig. (1) : Isotherms for adsorption of added Cd by the clay fractions using the Conventional Longmuir equation.

The data in table (1) show that the content of clay, silt and sand ranged between 2-25 %, 2 - 19 % and 56 - 90 %, respectively and therefore the texture varied between sand to sand clay loam. The EC values generally increased with depth and ranged between 1.6 and 7.8 dS m⁻¹. The organic matter (%) in the studied soil samples ranged between 0.15 - 0.92 %. The CEC values varied from 2.34 to 18.73 cmolc kg⁻¹. Available Cd of the soil was ranging between 0.25-1.00 ppm. No trend was found between depth and both CEC and the available Cd.

The dissolution and fractionation of carbonate:

Data of different carbonate forms are summarized in Table (2). The results show that total carbonate and calcite are relatively high and ranges between 9.40 - 28.10 % and from 0.35 to 9.55 % respectively, and both increased with depth. However, the former show higher content in fine clay than the coarse clay. The ratio of calcite/total calcium carbonate differs largely from 0.03 to 0.56 and it is higher in the second layer than others layer. However, the ratio of calcite/Mg-calcite differs largely from 0.05 to 3.79 and generally higher in second layer due to the marly parent material. The genesis and morphology of calcareous soils in which pedogenic calcite is accumulating vary considerably in relation to such variables as the type of parent material, slope position relative to groundwater, internal drainage characteristics, climatic setting, and duration or time of soil development (Keren, 1983; Abdou *et al.*, 1984).

In surface layer, higher values of total carbonate, calcite, Mg-calcite and other carbonate forms were found in fine clay as compared to coarse clay fractions (Table 2). Concerning the Mg-calcite, data exhibited no pattern distribution with the depth but the total carbonate and calcite has pattern distribution where it increased with depth (Table 2).

Table (2)

Percentage and quotient of the different carbonate forms in clay fractions.

Profile No.	Sample depth, cm.	Total carbonate %	Calcite %	Mg-Calcite %	Other carbonate %	Ratio from total carbonate			Calcite/Mg-calcite
						Calcite	Mg-Calcite	Other carbonate	
(A) fine clay (<0.2µm)									
1	0-80	15.30	3.23	4.44	7.63	0.21	0.29	0.5	0.72
	80-120	15.00	6.00	5.00	4	0.40	0.33	0.27	1.21
	120-200	24.40	9.00	3.30	12.1	0.37	0.14	0.5	2.64
2	0-80	16.90	4.15	5.50	7.25	0.25	0.33	0.43	0.75
	80-160	17.00	8.90	6.40	1.7	0.52	0.38	0.1	1.37
	160-200	24.40	9.55	6.12	8.73	0.39	0.25	0.36	1.56
3	0-40	15.00	2.60	9.20	3.2	0.17	0.61	0.21	0.28
	40-120	24.40	8.61	6.76	9.03	0.35	0.28	0.37	1.25
	120-200	28.10	7.30	3.10	17.7	0.26	0.11	0.63	2.36
(B) Coarse clay (2-0.2µm)									
1	0-80	13.13	0.35	8.39	4.39	0.03	0.64	0.33	0.05
	80-160	15.00	8.41	4.95	1.64	0.56	0.33	0.11	1.70
	120-200	16.90	8.86	3.86	4.18	0.52	0.23	0.25	2.26
2	0-80	11.25	3.94	4.90	2.41	0.35	0.44	0.21	0.80
	80-160	13.10	5.85	7.01	0.24	0.45	0.54	0.02	0.83
	160-200	18.30	7.50	10.20	0.6	0.41	0.56	0.03	0.73
3	0-40	9.40	3.90	2.00	3.5	0.41	0.21	0.37	1.95
	40-120	15.00	8.00	2.14	4.86	0.53	0.14	0.32	3.79
	120-200	26.30	9.13	0.00	17.17	0.35	0	0.65	∞

The calculated K_1 and K_2 showed that the ability and affinity of studied clay sample to sorbs Cd in part I are much differ than in part II since K_1 and sorptivity (K_1K_2) values are relatively higher in part I while K_2 values of part II are much higher than in part I as shown in Table (3). The data exhibited also that the fine clay fraction have higher K_1 of part I than coarse clay fraction while the opposite of these results were found in part II. This means that the sites corresponding for sorption in part I are more active in

coarse clay than fine clay. Osman *et al.*, (1999) reported that CaCO_3 in the clay fraction play an important in adsorption of heavy metals. The statistical analysis revealed a positive correlation between K_1^1 and both of total carbonate and other carbonate forms while in the part II it was between K_2^1 and total carbonate, calcite, Mg calcite and other carbonate. On contrary, the maximum adsorption (K_2^1) values are higher in fine clay than coarse clay fraction. A positive significant relationships were found between K_2^1 and total calcium carbonate percentage ($r = + 0.755$) where significant negative correlation was found between bonding energy (K_1^1) and calcite percentage ($r = -0.844$). But with Mg-calcite it was weak significant positive correlation ($r = 0.625$). In addition, non significant correlations was found between K_1^1 and other forms of carbonate ($r = 0.447$). These results show that the different types of carbonates in coarse clay play a good role in Cd adsorption, but it is absent in fine clay fraction. No significant correlations was found between K_1^1 and all forms of carbonate which probably depend on some other soil constituents, i. e. clay minerals which have relatively more activity sites. On the other hand, no regular trend was recorded for the K_1 and K_2 values of part II and a relation was observed only between these values and total carbonate percent.

Conclusions:

It could be concluded that in part I, where Cd concentration is low, most of the sorption take place on the carbonate forms surface which have more active sites. The ability of clay in this part to sorb Cd depends on the carbonate forms content while the maximum adsorption was correlated significantly with the calcite and Mg-calcite and total carbonate. In contrast, carbonate forms in clay fraction work as a sink for the sorption of Cd and prevent the movement through the soil to ground water. Hence, further studies are needed to study the impact of calcareous soil on the Cd movement and accumulation in plants.

Table (3)
Langmuir constants* developed from Cd sorption isotherms for the studied clay fraction

Prof. No	Depth. cm	Part I						Part II					
		K ₁		K ₂		K ₁ K ₂		K ₁		K ₂		K ₁ K ₂	
		Coarse Clay	Fine Clay	Coarse Clay	Fine Clay	Coarse Clay	Fine Clay	Coarse Clay	Fine Clay	Coarse Clay	Fine Clay	Coarse Clay	Fine Clay
1	0-80	1.685	7.67	5.65	434.78	9.52	3333	0.0619	0.009	26.3	1429	1.63	12.71
	80-120	0.0054	0.24	24.39	526.3	9.52	126.6	0.5287	0.023	5.22	1000	2.76	22.68
2	0-60	0.5632	0.26	5.38	625	9.52	163.9	0.0063	0.009	22.2	2000	0.139	18.05
	60-120	0.0882	0.268	4.42	666.6	0.39	178.6	0.0057	0.011	24.39	2000	0.139	22.62
3	0-140	0.1434	0.42	5.46	909.1	0.783	384.6	0.0055	0.016	25.64	2000	0.141	31.15
	140-200	0.209	0.57	4.81	1000	1.007	555.6	0.0047	0.364	32.25	1250	0.151	454.5

* data of part I were calculated by regression analysis of the data plotted in fig. 1 while data of part II were calculated according to syers *et al.* (1973)

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تأثر إدمصاص الكاديوم بأشكال الكربونات المختلفة في الجزء الطيني لبعض الترب الجيرية بالأحساء

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الملخص :

تم تحديد أشكال متنوعة من الكربونات في الجزء الناعم الأقل من ٠,٢ ميكرومتر وفي الجزء الخشن (٠,٢ - ٢,٠ ميكرومتر) في عينات ثلاث قطاعات تربة من واحة الأحساء بالمملكة العربية السعودية. وأشارت النتائج إلى أن كربونات الكالسيوم الكلية (C_1) في الطين الناعم تعتبر مرتفعة عن الموجودة في الطين الخشن حيث أنها تتراوح ما بين ٩,٤٠ و ٢٨,١٠٪. بينما وجد معدن الكالسيت ما بين ٠,٣٥ إلى ٩,٥٥٪، والمغنيسيوم كالسيت ٠٠٠ إلى ١٠,٧٠٪ وقد وجد الأخير في الطين الناعم أكثر من الطين الخشن أما الكربونات الأخرى فتتمثل ما بين ٠,٢٤ إلى ١٧,٧٠٪.

كما تشير النتائج إلى أن إدمصاص الكاديوم في المجموعتين (١ و ٢) جاءت بقدرات مختلفة طبقاً لمعادلة لانجمير. كما تشير الثوابت المتعلقة بطاقة الربط في الجزء الأول (K_1^1) إنها كانت أعلى في الطين الخشن منه في الطين الناعم وأن علاقة الارتباط مع محتوى مغنيسيوم- كالسيت تعتبر معنوية. بينما قيم الإدمصاص الكلي للجزء الأول كانت أعلى في الطين الناعم بينما علاقة الارتباط مع محتوى كربونات المغنيسيوم جاءت معنوية. وفي المقابل فإن K_2 و K_1 في الجزء الثاني لا يوجد إتجاه معين إضافة أنه لا توجد علاقة معنوية مع أشكال الكربونات المختلفة.