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Comparison of Cadmium Adsorption Behavior in Selected Calcareous and Acid Soils

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ABSTRACT- Cadmium (Cd) concentration in soil solution and its bioavailability is controlled by sorption-desorption reactions. The objective of this research was to compare Cd adsorption behavior in six calcareous and four acid soils. Soil samples were equilibrated with 0.01 M $Ca(NO_3)_2$ containing 25 to 3200 mg Cd L^{-1}. Results showed that the tendency for adsorption was high at low Cd concentrations (0-400 mg L^{-1}), but decreased as the Cd increased (400-3200 mg L^{-1}). Among five equations evaluated, Freundlich, Langmuir, and Gunary equations best described Cd adsorption in both calcareous and acid soils as indicated by high values for coefficient of determination (R^2) and low values for standard error of estimate (SE). Stepwise regression equations between constants of the best-fitted models and soil properties revealed that cation exchange capacity (CEC) and clay content were the most important soil properties affecting Cd adsorption behavior in calcareous soils, whereas in acid soils Cd adsorption was mainly affected by soil pH. Constants of the best fitted models showed good correlations with pH, clay, and calcium carbonate equivalent (CCE) in combined calcareous and acid soils. Our tentative conclusion is that higher pH in calcareous soils resulted in greater negative exchange sites available for Cd sorption, therefore Cd adsorption in these soils is greater compared to that of acid soils.

Keywords: Adsorption Equations, Cadmium, Calcareous and Acid Soils, Soil Properties

INTRODUCTION

Excess heavy metals can cause health issues and environmental degradation. Cadmium (Cd) is one of the heavy metals that have received considerable attention because of its association with various human health problems (16). Cadmium has no essential biological function, and is highly toxic to plants and animals (3). Sources of soil Cd contamination are the mining and smelting of Pb and Zn, the disposal of wastes containing Cd, sewage sludge application to land, and the burning of fossil fuels (3). Because of the passage of Cd from environment to animals and human beings, recognizing and characterizing its behavior in soils is essential. There are three main processes that control the fate and bioavailability of metals, including Cd,

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in soils (36), removal of metals from soil solution by sorption onto soil particles (adsorption), release of metals from soil particles to soil solution (desorption), and precipitation–dissolution of metals as an independent phase in the soil matrix. Among these processes, adsorption is a major factor responsible for accumulation of heavy metals in soils. Therefore, the study of sorption process and mechanism is essential for the assessment of the Cd contamination in soils (31), and its bioavailability, and toxicity in plants (25). Adsorption of Cd by soils has been studied by several researchers (8, 9, 1). Cadmium sorption and desorption is affected by several factors including pH (5, 8), organic matter (OM) (26, 41), amount and type of clay (8), cation exchange capacity (CEC) (1), and the total soil Cd (20). These soil parameters could be used to model sorption phenomenon.

Several equations have been used for the analysis of Cd adsorption on soil surfaces, including Freundlich, Langmuir, Temkin, Gunary, and Edie-Hofstee equations.

Harter (14) concluded that adsorption isotherms have provided the majority of information regarding micronutrient adsorption by soils; and that equation coefficients can be used to compare data sets.

Cd adsorption behavior of some calcareous soils in Iran, have been reported (24). However, data on acid soils and the comparison between calcareous and acid soils in Iran are scarce. In the present experiment, the adsorption behavior of Cd in calcareous and acid soils from southern and northern parts of Iran with varying physico-chemical characteristics was examined using different adsorption isotherms. The objectives of this study were to: i) characterize and compare sorption behavior of Cd in six calcareous and four acid soils, ii) to evaluate the adsorption isotherms of Cd using different equations and iii) to determine major soil physico-chemical properties affecting Cd adsorption behavior in calcareous and acid soils.

MATERIALS AND METHODS

Surface soil samples (0-30 cm) were collected from different sites with a wide range of physico-chemical properties including six calcareous soils and four acid soils from southern and northern parts of Iran, respectively (Table 1). The samples were air dried, passed through a 2-mm sieve, and used for laboratory analyses. Soil analysis included pH (38), texture (11), OM (28), electrical conductivity of saturation extract (ECe) (30), CCE (22), CEC (37), and diethylenetriamine pentaacetic acid (DTPA) extractable Cd (21). Classification and selected properties of studied soils are given in Tables 1 and 2. Cadmium sorption was studied by a batch experiment: Two-g of air-dried soil sample was placed in 100 mL polypropylene centrifuge tubes, and 20 mL of 0.01 M $Ca(NO_3)_2$ containing different levels of Cd (25, 50, 100, 200, 400, 600, 800, 1200, 1800, 2400, 2800, and 3200 mg L^{-1}) as $Cd(NO_3)_2$ was added to each tube in three replicates. The soil suspension was shaken for 24 h at 25 °C. Our preliminary studies showed that an equilibrium period of 24 h and a soil-solution ratio of 1:10 was optimum beyond which no significant changes occurred in the amount of Cd sorbed by the soil. The suspension was centrifuged for 15 min at relative centrifuge force of 2053 G, filtered through Whatman no.390 filiter paper. Cadmium concentration in the clear extract solution was determined using atomic absorption spectrophotometry (Shimadzo AA-670). The amount of Cd adsorbed by the soils was determined by calculating the difference between the initial and final concentrations of Cd in the equilibrium solution (41, 1).

Table 1. Sampling locations and classification of studied soils

Soil no.	Sampling location	Classification
	Calcareous soils	
1	**Jooyom, Larestan, Fars**	**Typic Torrifluvents**
2	**Asatid, bajgah, Fars**	**Typic Xerorthents**
3	**Kamfirooz, Marvdasht, Fars**	**Calcic Haploxerepts**
4	**Chitgar, Sarvestan, Fars**	**Typic Calcixerepts**
5	**Badjgah, bajgah, Fars**	**Typic Calcixerepts**
6	**Sepidan, Sepidan, Fars**	**Typic Haploxererts**
	Acid soils	
7	**Rasht, Guilan**	**Typic Sulfaquents**
8	**Rasht, Guilan**	**Typic Epiaquepts**
9	**Lielakoh, Guilan**	**Typic Dystrudepts**
10	**Lahijan, Guilan**	**Typic Dystrudepts**

Table 2. Selected physico-chemical properties of the studied soils

Soil no.¥	Clay (g kg^{-1})	Silt (g kg^{-1})	Texture	pH	ECe (dS m^{-1})	OM (g kg^{-1})	CCE (g kg^{-1})	CEC (cmol$_c$ kg^{-1})	DTPA-Cd (mg kg^{-1})
					Calcareous soils				
1	**50.0**	**160.0**	**Loamy sand**	**7.78**	**2.00**	**0.30**	**740.0**	**3.0**	**0.83**
2	**212.8**	**500.0**	**Loam**	**7.55**	**0.79**	**5.04**	**445.5**	**12.6**	**0.36**
3	**241.6**	**600.0**	**Silt loam**	**7.70**	**0.35**	**13.40**	**308.7**	**18.7**	**0.13**
4	**148.8**	**472.8**	**Loam**	**7.75**	**0.48**	**2.02**	**595.8**	**9.1**	**0.12**
5	**241.6**	**465.6**	**Loam**	**7.79**	**0.28**	**6.72**	**484.9**	**12.6**	**0.18**
6	**430.0**	**320.0**	**Clay**	**7.39**	**0.59**	**29.20**	**270.0**	**24.0**	**0.14**
					Acid soils				
7	**101.6**	**245.6**	**Sandy loam**	**5.70**	**0.47**	**25.5**	**32.29**	**12.2**	**1.20**
8	**141.6**	**345.6**	**Loam**	**5.39**	**0.54**	**40.3**	**55.94**	**15.6**	**0.55**
9	**88.8**	**145.6**	**Sandy loam**	**5.05**	**0.54**	**53.8**	**69.45**	**16.5**	**0.52**
10	**408.8**	**332.8**	**Clay**	**4.93**	**0.29**	**9.75**	**81.27**	**20.9**	**0.11**

Note: ¥ Numbers relate to soils described in Table 1

The experimental data were fitted to Temkin, Gunary, Edie-Hofstee, and linear forms of Freundlich and Langmuir equations (Table 3). To asses the pattern of Cd adsorption, these equations were tested for goodness of fit by least-square regression analysis and standard error of estimate (SE). A relatively high value of the coefficient of determination (R^2) and a low SE were used as criteria for the best fit (15). Constants of the best fitted models were calculated for all soils. The standard error of estimate was calculated using the following equation:

Equation (1)

$$\left[SE = \frac{\sum(q-q')}{(N-2)}\right]^{0.5}$$

Where q and q' are measured and calculated amounts of sorbed Cd, and N is the number of measurements.

Table 3. Equations used to study Cd adsorption in calcareous and acid Iranian soils

Model	equation	Description
Linear form of Freundlich	**$\text{Log } X = \text{Log } K_F + (1/n) \text{ Log } C$**	**K_F, distribution coefficient (L kg^{-1}), and 1/n, Freundlich constant**
Linear form of Langmuir	**$C/X = [1/ (K_L\ b)] + (1/b)C$** **$Kd = K_L b$**	**K_L, Langmuir coefficient (L kg^{-1}), b, the maximum amount of Cd adsorbed on soil solids as a monolayer (mg kg^{-1}) and Kd, distribution coefficient**
Temkin	**$X= K_{1T} + K_{2T} \text{ Ln}C$**	**K_{1T} and K_{2T}, Temkin sorption constants**
Gunary	**$C/X = K_{1G} +K_{2G}\ C +K_{3G}\ C^{1/2}$**	**K_{1G}, K_{2G} and K_{3G}, Gunary sorption constants**
Edie-Hofstee	**$X= b_E – X/K_EC$**	**b_E, Edie-Hofstee adsorption maximum, and K_E, Edie-Hofstee sorption constant**

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg $^{-1}$), and C is the concentration of Cd in equilibrium solution (mg L^{-1})

RESULTS AND DISCUSSION

Cadmium concentration in equilibrium (C; mg L^{-1}) vs. Cd adsorbed (X; mg kg^{-1}) was plotted for calcareous soils (Figure 1). The adsorption isotherm for most soil samples was similar; the amount of adsorbed Cd increased with an increase in equilibrium Cd concentration and appeared to approach a plateau maximum, with the entire curve being described by a typical L-shaped isotherm. The L-shaped isotherm is characterized by a decreasing slope as concentration increases, presumably because the number of vacant adsorption sites decreases as the adsorbent becomes covered. These observations showed that the tendency for adsorption was high at low Cd concentrations (0-400 mg L^{-1}), but decreased as the concentration increased (400-3200 mg L^{-1}). This type of isotherm is the result of a relatively high affinity of soil particles for the adsorbate at low surface coverage mitigated by a decreasing amount of adsorbing surface remaining available as the surface excess increases (35). Similar results were reported by Gao et al. (10), and Sparks (34). Holford et al. (17) assumed that in forty one soils (pH>5.0) from southern England and eastern Australia, soil phosphorous adsorption occurs on two types of surfaces with contrasting bonding energies. They showed that more than 90 percent of the native adsorbed P occurs on the high-energy surface in most soils. Ajwa and Tabatabai (2) evaluated one and two-surface Langmuir equations to study the effect of metal concentration on SO_4^{2-} adsorption by four diverse soils from Iowa, Chile and Costa Rica. Two bonding constants were found, suggesting the presence of two different adsorption sites or different mechanisms, each with a different bonding energy. The results provide evidence that SO_4^{2-} adsorption by soils is caused by more than one mechanism and that the associated metal ion significantly affects SO_4^{2-} adsorption, regardless of the mechanism involved.

Shuman (32) indicated that Zinc adsorption conformed to the Langmuir isotherm and two linear portions of the curve were found.

The relationship between final Cd concentration in equilibrium solutions and Cd adsorbed by acid soils is shown in Figure 2. Cadmium adsorption in acid soils followed a C-shaped isotherm. In this type of isotherm the initial slope remains independent of adsorbate concentration until a maximum adsorption is achieved. This kind of isotherm is usually observed when a constant partitioning of an adsorbate between the interfacial region and the soil solution has occurred, or when a proportionate increase in the amount of adsorbing surface takes place as the surface excess increases (35). Two distinct regions of the curve might have been observed, if greater initial Cd solution concentrations were used. It appears that L-shape curve would be present with greater initial Cd in the solution.

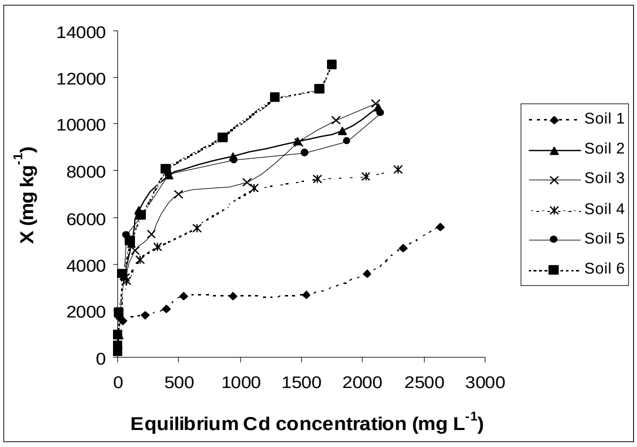

Fig. 1. Relationship between final Cd concentration in equilibrium solution (mg L^{-1}) and Cd adsorbed (mg kg^{-1}) by calcareous soils

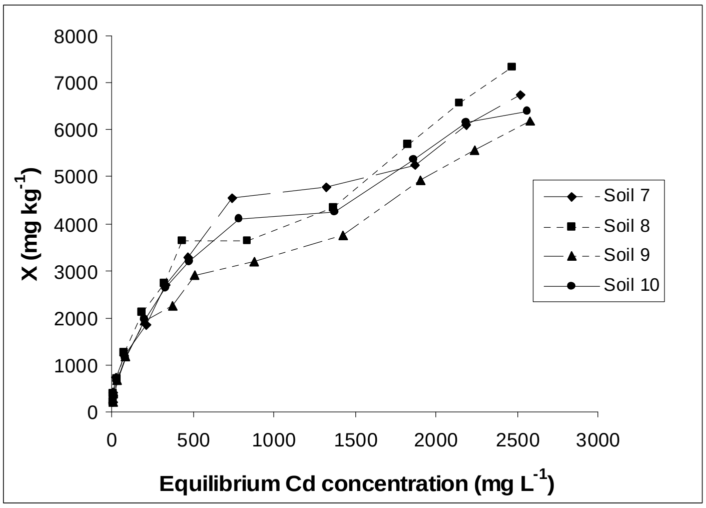

Fig. 2. Relationship between final Cd concentration in equilibrium solution (mgL^{-1}) and Cd adsorbed (mg kg^{-1}) by acid soils

The sorption equilibrium of Cd onto the soils was described by five equations including Freundlich (Table 4), Langmuir (Table 5), Temkin (Table 6), Gunary (Table 7) and Edie-Hofstee (Table 8). These equations were tested for goodness of fit by least-square regression analysis (R^2) and standard error of estimate (SE). Coefficient of determination and standard error of estimate for adsorption isotherms obtained in this study are given in Table 9. The data conformed better to the Freundlich, Langmuir, and Gunary equations as indicated by high coefficient of determination (R^2) values and low standard error of estimate (SE) values. Although R^2 value of Temkin equation was high, the standard error of estimate was also high, and it was therefore not selected for description of Cd adsorption.

Table 4. Freundlich equation isotherm ($\mathrm{Log}X = \mathrm{Log}K_F + 1/n\ \mathrm{Log}C$), coefficient of determination (R^2) and standard error of estimate (SE) for calcareous and acid soils

Soil no.	Equation	R^2	SE	n
	Calcareous soils			
1	$\mathrm{Log}X=2.75+0.25\mathrm{Log}C$	0.941^{***}	0.100	12
2	$\mathrm{Log}X=2.7+0.428\mathrm{Log}C$	0.971^{***}	0.099	12
3	$\mathrm{Log}\ X=2.82+0.37\mathrm{Log}C$	0.991^{***}	0.056	12
4	$\mathrm{Log}X=2.8148+0.34\mathrm{Log}C$	0.987^{***}	0.060	12
5	$\mathrm{Log}X=2.715+0.4183\mathrm{Log}C$	0.957^{***}	0.120	12
6	$\mathrm{Log}X=2.789+0.4221\mathrm{Log}C$	0.982^{***}	0.080	12
	Acid soils			
7	$\mathrm{Log}X=2.04+0.534\mathrm{Log}C$	0.985^{***}	0.063	12
8	$\mathrm{Log}X=2.01+0.5464\mathrm{Log}C$	0.984^{***}	0.070	12
9	$\mathrm{Log}X=2.04+0.5092\mathrm{Log}C$	0.992^{***}	0.045	12
10	$\mathrm{Log}X=1.783+0.6141\mathrm{Log}C$	0.975^{***}	0.087	12

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1}), and C is the concentration of Cd in equilibrium solution (mg L^{-1})

*** Significant at $P \leq 0.001$

Table 5. Langmuir equation isotherm ($C/X = 1/K_L b + C/b$), coefficient of determination (R^2) and standard error of estimate (SE) for calcareous and acid soils

Soil no.	Equation	R^2	SE	n
	Calcareous soils			
1	$C/X= 0.06 + 2\times10^{-4}\ C$	0.840^{***}	0.097	12
2	$C/X= 0.009 + 1\times10^{-4}\ C$	0.991^{***}	0.007	12
3	$C/X= 0.012 + 1\times10^{-4}\ C$	0.968^{***}	0.014	12
4	$C/X= 0.012 + 1\times10^{-4}\ C$	0.985^{***}	0.014	12
5	$C/X= 0.008 + 1\times10^{-4}\ C$	0.989^{***}	0.009	12
6	$C/X= 0.008 + 8\times10^{-5}\ C$	0.981^{***}	0.011	12
	Acid soils			
7	$C/X= 0.055 + 1\times10^{-4}\ C$	0.959^{***}	0.030	12
8	$C/X= 0.059 + 1\times10^{-4}\ C$	0.916^{***}	0.040	12
9	$C/X= 0.07 + 2\times10^{-4}\ C$	0.916^{***}	0.048	12
10	$C/X= 0.07 +1\times10^{-4}\ C$	0.966^{***}	0.026	12

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1}), and C is the concentration of Cd in equilibrium solution (mg L^{-1})

*** Significant at $P \leq 0.001$.

Table 6. Temkin equation isotherm ($X=K_{1T} + K_{2T}\ \mathrm{Ln}C$), coefficient of determination (R^2) and standard error of estimate (SE) for calcareous and acid soils

Soil no.	Equation	R^2	SE	n
	Calcareous soils			
1	$X=609.3+380.69\ \mathrm{Ln}C$	0.710^{***}	906.6	12
2	$X= -207.44+1266.9\ \mathrm{Ln}C$	0.933^{***}	1056.0	12
3	$X= 645.27+1066.1\ \mathrm{Ln}C$	0.883^{***}	1371.4	12
4	$X= 747.18+829.33\ \mathrm{Ln}C$	0.919^{***}	886.5	12
5	$X= -43.53+1212\ \mathrm{Ln}C$	0.930^{***}	1037.3	12
6	$X= 127.1+1440.2\ \mathrm{Ln}C$	0.881^{***}	1741.9	12
	Acid soils			
7	$X= -2429.5 +1017.8\ \mathrm{Ln}C$	0.895^{***}	783.8	12
8	$X= -2640.8 + 1067\ \mathrm{Ln}C$	0.868^{***}	923.6	12
9	$X= -2103.7 + 877.2\ \mathrm{Ln}C$	0.857^{***}	807.1	12
10	$X= -3156.9 +1101.3\ \mathrm{Ln}C$	0.921^{***}	661.7	12

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1}), and C is the concentration of Cd in equilibrium solution (mg L^{-1})

*** Significant at $P \leq 0.001$

Table 7. Gunary equation isotherm ($C/X = K_{1G} + K_{2G}C + K_{3G}C^{1/2}$), coefficient of determination (R^2) and standard error of estimate (SE) for calcareous and acid soils

Soil no.	Equation	R^2	SE	n
	Calcareous soils			
1	$C/X= -0.02+6.96\times10^{-5}C+0.009C^{1/2}$	0.995^{***}	0.03	12
2	$C/X= 0.0005+6.5\times10^{-5}C+0.002C^{1/2}$	0.998^{***}	0.004	12
3	$C/X= -0.003+3.4\times10^{-5}C+0.003C^{1/2}$	0.997^{***}	0.006	12
4	$C/X= -0.001+8.2\times10^{-5}C+0.002C^{1/2}$	0.997^{***}	0.009	12
5	$C/X= 0.0002+7.1\times10^{-5}C+0.001C^{1/2}$	0.997^{***}	0.007	12
6	$C/X= -0.002+2.6\times10^{-5}C+0.002C^{1/2}$	0.993^{***}	0.007	12
	Acid soils			
7	$C/X= 0.01+4.5\times10^{-5}C+0.005C^{1/2}$	0.991^{***}	0.02	12
8	$C/X= -0.001-3.5\times10^{-5}C+0.007C^{1/2}$	0.988^{***}	0.02	12
9	$C/X= -0.01-2.9\times10^{-5}C+0.01C^{1/2}$	0.993^{***}	0.02	12
10	$C/X= 0.03+5.8\times10^{-5}C+0.005C^{1/2}$	0.990^{***}	0.017	12

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1}), and C is the concentration of Cd in equilibrium solution (mg L^{-1})
*** Significant at $P\leq0.001$

Wong et al. (40) indicated that the Cd sorption isotherm conformed better to the Freundlich equation as indicated by the high value for the coefficient of determination (R^2= 0.984-0.998). Hooda and Alloway (18), in five semi-arid soils of India and five acid soils of England, showed that Cd and Pb sorption were best-fitted to Freundlich equation. According to Hanafi and Sjiaola (13), adsorption of Cd and Zn by Malaysia soils were best described by Freundlich equation (R^2= 0.83-0.97).

However, several researchers have utilized the Langmuir equation to describe heavy metal sorption. Singh et al. (33) evaluated heavy metals sorption (Cd, Pb, and Zn) onto phosphatic clay. Experimental data of the single metal sorption in their study fitted to Langmuir equation. They stated that most sorption isotherms were characterized by decreasing slopes as aqueous metal concentration increased beyond the threshold, indicating a high affinity of the adsorbent for high concentrations of the adsorbate. Wan Zuhairi and Abdul Rahim (39) reported that in different acid soils of Malaysia, heavy metal adsoption fitted to the Langmuir adsorption model (R2>0.6). Cavallaro and McBride (9) indicated that adsorption of Cd in acid and neutral soils of New York also fitted to the Langmuir adsorption model (R^2= 0.95 to 0.99). Maftoun et al. (24) reported that Cd sorption fitted well to Langmuir (R^2= 0.94 to 1) as well as the Freundlich (R^2= 0.87-0.99) and Temkin (R^2= 0.65-0.98) adsorption isotherms.

Table 8. Edie-Hofstee equation isotherm ($X= b - X/K_EC$), Coefficient of determination (R^2) and standard error of estimate (SE) for calcareous and acid soils

Soil no.	Equation	R^2	SE	n
	Calcareous soils			
1	X= 2898.2 – 1.5 X/C	0.410^{**}	1293.7	12
2	X= 7170.5 – 13.4 X/C	0.555^{**}	2714.5	12
3	X= 6480.2 – 4.4 X/C	0.446^{*}	2980.0	12
4	X= 5288.8 – 3.23 X/C	0.483^{*}	2183.8	12
5	X= 6873.2 – 11.15 X/C	0.519^{**}	2723.1	12
6	X= 8424.8 – 10.95 X/C	0.551^{**}	3390.8	12
	Acid soils			
7	X= 5051.7 – 139.6 X/C	0.710^{**}	1301.6	12
8	X= 5333.4 – 161.62 X/C	0.706^{**}	1377.7	12
9	X= 4131.4 – 111.2 X/C	0.600^{**}	1346.6	12
10	X= 6025.7 – 333.5 X/C	0.890^{***}	778.4	12

Note: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1}), and C is the concentration of Cd in equilibrium solution (mg L^{-1})
***Significant at $P\leq0.05$; ** Significant at $P\leq0.01$; *** Significant at $P\leq0.001$

The constants of the best fitted equations for the Langmuir, Freundlich, and Gunary isotherms are given in Table 10. Coefficients varied widely among the soils, indicating large variations in Cd adsorption behavior of soils evaluated.

At very low equilibrium concentration, the term $1+K_LC$, in Langmuir adsorption isotherm approaches 1 and the equation is rearranged to the form $X/C=K_Lb$. Since X/C represents the amount of Cd adsorbed by unit weight of the solid phase relative to that remained in unit volume of the solution phase, it is termed the "distribution coefficient" and is designated by K_d (7). This term can also be called the "maximum buffering capacity" (19). Thus, $K_d = K_Lb$. Distribution coefficients (K_d) represent the sorption affinity of metal cations in a solution for the soil solid phase, and can be used as a valuable tool to study metal-cation mobility and retention in soil systems. According to Anderson and Christensen (4), relatively high values of K_d indicate that the metal has been retained by the solid phase through sorption reactions, while relatively low values of K_d indicate that a large fraction of the metal remains in solution. The calculated K_d values ranged from 14.24 to 121.95 mg kg^{-1}. Soil no. 6 presented the highest K_d value, showing that this soil had a high sorption affinity for Cd. In Figure 1, Soil no. 6 also has a greater Cd sorption capacity than other soils, which could be related to high pH and clay content. K_d value in clay soil (soil no. 6) was greater than Loamy sand soil (soil no. 1).

Table 9. Coefficient of determination (R^2) and standard error of estimate (SE) of adsorption isotherms used to describe Cd adsorption in calcareous and acid soils

	Freundlich		**Langmuir**		**Temkin**		**Edie-Hofstee**		**Gunary**	
Soil no.	**R^2**	**SE**	**R^2**	**SE**	**R^2**	**SE**	**R^2**	**SE**	**R^2**	**SE**
					Calcareous soils					
1	0.941^{***}	0.100	0.841^{***}	0.097	0.710^{***}	906.6	0.410^{**}	1293.7	0.995^{***}	0.03
2	0.971^{***}	0.099	0.991^{***}	0.007	0.933^{***}	1056.0	0.555^{**}	2714.5	0.998^{***}	0.004
3	0.991^{***}	0.056	0.968^{***}	0.014	0.883^{***}	1371.4	0.446^{*}	2980.0	0.997^{***}	0.006
4	0.987^{***}	0.060	0.985^{***}	0.014	0.919^{***}	886.5	0.483^{*}	2183.8	0.997^{***}	0.009
5	0.957^{***}	0.120	0.989^{***}	0.009	0.930^{***}	1037.3	0.519^{**}	2723.1	0.997^{***}	0.007
6	0.982^{***}	0.080	0.981^{***}	0.011	0.881^{***}	1741.9	0.551^{**}	3390.8	0.993^{***}	0.007
					Acid soils					
7	0.985^{***}	0.063	0.959^{***}	0.030	0.895^{***}	783.8	0.710^{**}	1301.6	0.991^{***}	0.02
8	0.984^{***}	0.070	0.916^{***}	0.040	0.868^{***}	923.6	0.706^{**}	1377.7	0.988^{***}	0.02
9	0.992^{***}	0.045	0.916^{***}	0.048	0.857^{***}	807.1	0.600^{**}	1346.6	0.993^{***}	0.02
10	0.975^{***}	0.087	0.966^{***}	0.026	0.921^{***}	661.7	0.890^{***}	778.4	0.990^{***}	0.017

Note: * Significant at $P \le 0.05$; ** Significant at $P \le 0.01$; *** Significant at $P \le 0.001$

Moreover, K_d was higher in calcareous soils as compared to acid soils (Table 10). Therefore, among the studied soils, those having high pH and CEC values and clay content adsorbed higher amounts of Cd than those with low values. According to Cavallaro and McBride (9) acid soils demonstrated much less ability to retain the heavy metals than neutral soils.

Freundlich adsorption isotherm constants differed widely among the studied soils (Table 10). Generally, the higher the Freundlich constant (1/n) the lower the binding affinity of soil with metal (40). Freundlich constants (1/n) range between 0 and 1. Furthermore, the equilibrium partition coefficient (K_F) is positively related to the metal sorption capacity of soils (12), and it may be used to compare adsorption properties of different soils. Our results revealed that values for 1/n were in the range of 0.25-0.42 in calcareous soils and 0.51-0.61 in acid soils. This indicates that acid soils have a lower bonding affinity for Cd than calcareous soils. Wong et al. (40) noted that based on the K and 1/n values of three soils studied, the sorption capacities of Cd followed the order: calcareous clay loam > calcareous sandy loam > acid lateritic sandy loam at the same equilibrium Cd concentration.

Table 10. Constants of the best-fitted Cd adsorption equations in calcareous and acid soils

	Langmuir			**Freundlich**		**Gunary**		
Soil no.¥	**K_d ($L\ kg^{-1}$)**	**b ($mg\ kg^{-1}$)**	**K_L ($L\ kg^{-1}$)**	**K_F ($L\ kg^{-1}$)**	**1/n**	**K_{3G} ($L\ kg^{-1}$)**	**$K_{2G\times10^{-5}}$ ($L\ kg^{-1}$)**	**K_{1G} ($L\ kg^{-1}$)**
				Calcareous soils				
1	16.13	5000	0.003	549.54	0.25	0.009	6.96	-0.02
2	114.94	10000	0.01	498.65	0.43	0.002	6.5	0.0005
3	83.33	10000	0.008	660.70	0.37	0.003	3.4	-0.003
4	83.33	10000	0.008	652.83	0.34	0.002	8.2	-0.001
5	121.95	10000	0.01	518.32	0.42	0.001	7.1	0.0002
6	125.00	12500	0.009	614.89	0.42	0.002	2.6	-0.002
				Acid soils				
7	18.10	10000	0.002	109.75	0.53	0.005	4.5	0.01
8	16.98	10000	0.0017	102.33	0.55	0.007	-3.5	-0.001
9	14.28	5000	0.003	109.65	0.51	0.01	-2.9	-0.01
10	14.24	10000	0.0014	60.67	0.61	0.005	5.8	0.03

Note: ¥Numbers relate to soils described in Table 1

Regression equations were constructed between constants of the best fitted models and soil properties for acid and calcareous soils separately, using a forward stepwise procedure (Table 11). Clay and CEC were the most influential soil properties that affected constants of the best-fitted models in calcareous soils, but in acid soils, pH was the most relevant soil characteristic for predicting the constant.

Table 11. Regression equations between soil properties and constants of the best-fitted models in calcareous and acid soils

models	**Regression equation**	**R^2**	**n**
	calcareous soils		
Langmuir	**b= 5737.1 +17.4 Clay**	**0.79^{**}**	**6**
Langmuir	**b=5660.4+13.3 Clay+73.2 CEC**	**0.80^{**}**	**6**
	acid soils		
Freundlich	**K_d = -12.9 + 5.5 pH**	**0.96^{**}**	**4**

Note: ** Significant at $P\leq0.01$

Table 12 shows the regression equations between the constants of the best-fitted equations and soil properties for all 10 soils combined, regardless of soil acidity or basicity. Based on these equations, high pH and an increase in clay content increased sorption of Cd by soils. In general, heavy metal adsorption is supposed to be low at low pH values (6). These results suggest that calcareous soils have a greater sorption capacity than acid soils, which might be due to higher pH, clay, and CCE. Bradl (6) reported that fine soil particles with large surface reactivity and large surface areas, such as clays, enhance adsorption properties.

Table 12. Stepwise regression equations between soil properties and constants of the best- fitted models in combined calcareous and acid soils

models	Regression equation	R^2	n
Langmuir	b = 6596.8+12.85 Clay	0.49^{*}	10
Langmuir	$K_L = -0.012 + 0.003$ pH	0.64^{**}	10
Langmuir	$K_d = -131.2 + 28.4$ pH	0.57^{*}	10
Freundlich	$K_F = -935.7 + 197.4$ pH	0.93^{***}	10
Freundlich	$K_F = 135.6 + 0.82$ CCE	0.64^{**}	10
Freundlich	1/n = 0.95 – 0.08 pH	0.76^{***}	10

Note: * Significant at P≤0.05; ** Significant at P≤0.01; *** Significant at P≤0.001

Wong et al. (40) indicated that an acid sandy soil demonstrated a reduced ability to retain Cd as compared to a calcareous clay loam and sandy loam soils, due to the lower pH even though clay contents were similar between soils. Furthermore, the calcareous sandy loam soil exhibited a lower ability to adsorb Cd as compared to the calcareous clay loam soil, due to less clay content even though soil pH was similar between the two soils. Type of clay mineral also can explain the differences in metal sorption in different soils. Calcareous soils are usually high in 2:1 clay minerals which explain their higher adsorption capacity for Cd. In contrast, acid soils are typically strongly weathered and tend to contain 1:1 type clay minerals, thus they adsorb only small amounts of Cd (42, 27). Similar to our findings, Maftoun et al. (24) observed that the distribution coefficient (K_F) or maximum buffering capacity of Cd increased with an increase in clay, CEC, and CCE content in 20 calcareous soils. Ramachandran and D’Souza (29) concluded that the adsorption capacity of soils for Cd increased with an increase in pH or alkalinity of the soils. Adhikari and Singh (1) observed that K_F was related to pH, clay and CEC of selected soils of India and increased with increasing pH and CEC.

CONCLUSION

Freundlich, Langmuir, and Gunary equations best described Cd adsorption both in calcareous and acid soils. The best-fitted isotherm adsorption coefficients were significantly correlated with CEC and clay content in calcareous soils, whereas in acid soils the best-fitted isotherm adsorption coefficients were correlated with soil pH. Cadmium sorption onto calcareous soils appeared to follow L-shaped adsorption while acid soils followed C-shaped sorption. The greater Cd adsorption capacity in calcareous soils as compared to acid soils suggests a lower availability to plants and could lead to a lower probability of Cd toxicity in such soils. Further research is recommended to evaluate the relationship between constants of the best-fitted models and plant Cd uptake in calcareous and acid soils.

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مقایسه جذب سطحی کادمیم در برخی خاک های آهکی و اسیدی

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چکیده - غلظت کادمیم در محلول خاک و قابلیت استفاده زیستی آن بوسیله واکنش های جذب و واجذبی کنترل می شود. هدف از تحقیق حاضر مقایسه جذب سطحی کادمیم در ۶ خاک آهکی و ٤ خاک اسیدی بود. نمونه های خاک با محلول ۰/۰۱ مولار $Ca(NO_3)_2$ که حاوی ۲۵ تا ۳۲۰۰ میلی گرم کادمیم در لیتر بود، به تعادل رسیدند. نتایج نشان داد که تمایل برای جذب سطحی در غلظت های پایین کادمیم (۰ تا ٤۰۰ میلی گرم در لیتر) زیاد بوده، اما با افزایش غلظت کادمیم (٤۰۰ تا ۳۲۰۰ میلی گرم در لیتر) کاهش می یابد. در بین ۵ معادله ارزیابی شده، معادله های فروندلیچ، لانگ مویر، و گوناری به دلیل ضریب تبیین (R^2) بالا و خطای استاندارد پایین (SE) جذب سطحی کادمیم را در خاک های اسیدی و آهکی بهتر توصیف کردند. معادله های رگرسیونی گام به گام بین ضرایب بهترین مدل های برازش داده شده و ویژگی های خاک نشان داد که ظرفیت تبادل کاتیونی (CEC) و مقدار رس جزو مهمترین ویژگی های خاک هستند که بر جذب سطحی کادمیم در خاک های آهکی اثر دارند، در حالیکه در خاک های اسیدی، جذب سطحی کادمیم عمدتا تحت تاثیر پ- هاش خاک قرار گرفت. هنگامی که هر دو دسته خاک با هم در نظر گرفته شد، ضرایب ثابت بهترین مدل های برازش داده شده با پ- هاش، رس، و کربنات کلسیم معادل (CCE) همبستگی خوبی نشان داد. نتایج اولیه نشان داد که پ- هاش بالاتر در خاک های آهکی مکان های تبادلی منفی بیشتری برای جذب سطحی کادمیم در دسترس قرار می دهند، بنابراین جذب سطحی کادمیم در این خاک ها نسبت به خاک های اسیدی بیشتر می باشد.

واژه های کلیدی: خاک های آهکی و اسیدی، کادمیم، معادله های جذب، ویژگی های خاک

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**مکاتبه کننده