

The Role of CEC and pH in Cd Retention from Soils of North of Iran

Author

Esfandbod, M, Forghani, A, Adhami, E, Rashti, M Rezaei

Published

2011

Journal Title

Soil and Sediment Contamination: An International Journal

Version

Accepted Manuscript (AM)

DOI

[10.1080/15320383.2011.620044](https://doi.org/10.1080/15320383.2011.620044)

Downloaded from

<http://hdl.handle.net/10072/165816>

Griffith Research Online

<https://research-repository.griffith.edu.au>

The role of CEC and pH in Cd retention from soils of North of Iran

M. Esfandbod^A , A. Forghani^B , E. Adhami^C and M. Rezaei Rashti^D

^A Soil Science Department, Guilan University, Rasht, Iran, Email maryam.esfandbod@gmail.com

^B Faculty of Soil Science, Guilan University, Rasht, Iran, Email forghani@guilan.ac.ir

^C Faculty of Soil Science, College of Agriculture, Yasouj University, Yasouj, Iran, Email eadhami@mail.yu.ac.ir

^D Soil Science Department, Guilan University, Rasht, Iran, Email m.rezaei.rashti@gmail.com

Address correspondence to M. Esfandbod, Soil Science Department, Guilan University, Rasht, Iran.

Email: maryam.esfandbod@gmail.com , maryam.esfandbod@griffithuni.edu.au

Abstract:

Cadmium (Cd) is a critical environmental chemical in which sorption reactions control its entry into soil solution. The aim of the present study was to evaluate Cd sorption characteristics of some soils of the northern part of Iran with a wide range of physicochemical properties. Duplicates of each sample were equilibrated with solutions containing 5 to 500 mg Cd L⁻¹ with 0.01 M CaCl₂ as background solution. The quantity of Cd retention was calculated as the difference between initial and equilibrated Cd concentration. Sorption isotherms including Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, and Redlich-Peterson were used to evaluate the behavior of Cd sorption. Cadmium sorption data were well fitted to Langmuir, Freundlich, and Redlich-Peterson isotherms. The constant of Freundlich equation (k_F) and adsorption maxima (b_L) of Langmuir equation were related to pH and cation exchange capacity (CEC). The maximum buffering capacity (K_d) was significantly correlated with pH ($R^2=0.52$, $p\leq 0.001$) and calcium carbonate equivalent (CCE) ($R^2=0.63$, $p\leq 0.001$). Redlich-Peterson constants (k_{RP} and a_{RP}) were significantly correlated with pH ($R^2 k_{RP} = 0.30$, $p\leq 0.007$) and ($R^2 a_{RP} = 0.27$, $p\leq 0.012$). It seemed that pH, CEC, and CCE were the main soil properties regulating Cd retention behavior of the studied soils.

Key Words

Isotherm, Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Redlich-Peterson

Introduction:

Environmental pollution is an important ecological problem. In particular, heavy metals (*i.e.* cadmium, mercury and lead) constitute a serious threat not only to plants and animals, but

also to human lives because of their toxicity and non-biodegradability (Martin-Garin et al., 2002). Among heavy metals often found contaminating soil and groundwater, Cd is both readily available and highly toxic. Cadmium pollution has increased in recent years due to increase of its use (Alloway, 1990).

Cadmium enters the environment as the result of both natural and anthropogenic activities. The natural processes include mineral breakdown, dust storms, volcanic eruptions, and forest fires. Anthropogenic sources comprise all mankind contributions including industrial processes, mining and metallurgy, urban and industrial wastes and sewage and fertilizer applications (Adriano, 1986; Tiller, 1989). It is believed that anthropogenic sources are more hazardous because, their metal forms are environmentally unstable and consequently more soluble and bioavailable (Naidu et al., 1997). Cadmium exists as soluble; adsorbed by various inorganic and organic components of soils and as residual forms in soils (Adriano, 1986; Chlopecka et al., 1996). Cadmium has a potential to transfer through "soil plant" barrier, and concentrate through the food chain in levels that could potentially threat consumers (Chaney and Ryan, 1994; Chaney et al., 1999a, 1999b).

Cadmium adsorption and desorption are the main factors controlling its bioavailability in soil (Singh and Nayyar, 1993). Sorption isotherms have been widely used to assess the heavy metal retention characteristics of soil particles (Shirvani et al., 2006). Soil properties, such as pH (Yuan and Lavkulich, 1997; Boekhold et al., 1993), calcium carbonate concentration (Singh and Nayyar, 1993), clay content (Singh and Nayyar, 1993; Bolton and Evans, 1996), organic matter (Yuan and Lavkulich, 1997), cation exchange capacity (Sanches-Martin and Sanches-Camazano, 1993; Hanafi and Sjaola, 1998), and amorphous hydrous oxide content

(McBride, 1989) have the strong influences on Cd adsorption behavior. Appel and Ma (2002) observed that Cd sorption was more affected by pH than lead. Maftoun et al. (2004) observed that Cd sorption of selected calcareous soils from southern part of Iran was significantly correlated with cation exchange capacity (CEC), calcium carbonate equivalent (CCE), and clay.

Climate and soils of Guilan province, in northern part of Iran are obviously different from those of other parts of Iran. The rainfall in the area is very high (1500 mm annually) which is distributed evenly throughout the year, and the underground water table is shallow there. In this situation, the ability of soils to adsorb Cd is crucial in controlling Cd mobility and transport in the environment. The aims of the present study were to evaluate (i) the trend of Cd sorption by soils from this area, and (ii), the relationship between soil sorption and properties of these soils.

Materials and Methods:

Twenty surface soil samples (0-30 cm) were collected from acidic, alkaline and neutral soils of Guilan province in northern part of Iran. The samples were air dried and passed through a 2-mm sieve. Some physico-chemical properties of the soil including pH in a 1:2.5 soil to 0.01M CaCl₂ solution; organic matter (OM) by the method of Walkley and Black (Allison, 1965); CEC by replacing exchangeable cations with sodium acetate (Summer and Miller, 1996); CCE by neutralization with hydrochloric acid (Loeppert and Suarez, 1996), oxalate extractable Fe (Fe_o) (Houba et al., 1989), and sand, silt and clay by hydrometer method (Gee and Bauder, 1986) were determined.

Sorption Experiments

Two-gram subsamples of each soil were placed in centrifuge tubes and mixed with 40ml CaCl₂ 0.01M solution containing 5, 10, 20, 50, 100, 200, 300, and 500 mg Cd L⁻¹. Cadmium chloride solutions were prepared in 0.01M CaCl₂ to adjust the ionic strength of solutions to approximately the same level and to provide a constant background electrolyte. Three replications per concentration were used for each soil. Two drops of toluene were added to each tube to inhibit microbial growth. The tubes were shaken for 1h on a mechanical shaker at room temperature and allowed to equilibrate at 25±2°C for 24h. The suspensions were then shaken for additional 30 min and subsequently centrifuged for 10 min. The supernatants were filtered through Whatman No. 42 filter paper, and Cd concentration in the clear equilibrium solution was determined by atomic absorption spectrophotometry (SpectrAA 220Z AAS, Varian Model 2002). Detection limit for Cd analysis at 228.8nm was 0.02mgL⁻¹. The quantity of Cd retained by soils was calculated as the difference between Cd concentrations in initial and equilibrated solution.

Sorption Equations

Cadmium sorption data were fitted by Freundlich, Langmuir, Temkin and Dubinin-Radushkevich equations (Table 1). A trial and error procedure was to obtain constants “n” of the Dubinin-Radushkevich isotherm at which R² was the highest.

Statistical Analysis

All data were processed by Microsoft Excel 2007, and by means of that, coefficient of determination (R^2), standard error of estimate (SE) and isotherm coefficients were determined. Coefficient of determination and SE were used to evaluate the suitability of various isotherms. A relatively high R^2 and low SE were used as criteria for the best fit (Havlin et al., 1985). The multiple stepwise regression procedures, processed by SPSS version 11.5 software, were used to study the relationship between the isotherm coefficients and the physicochemical properties of the soils.

Results and Discussion:

Soil Properties

The physical and chemical characteristics of the soils used in this study were widely varying (Table 2). The clay contents ranged from 8.00 to 52.00 %, while pH values ranged from 4.21 to 7.61. The lowest pH was acidic and the highest one was weak alkaline. Values of 1.53 to 9.77 % were obtained for OM and CCE values ranged from 1.59 to 16.51 %. CEC values varied from 14.18 to 51.94 $\text{cmol}_c \text{kg}^{-1}$ and Fe_o was in the range of 582 to 9348 mg kg^{-1} .

Coefficient of Determination and Standard Error

Coefficient of determination and SE of various equations (Table 3) showed that Redlich-Peterson, Langmuir, and Freundlich equations have predicted the pattern of Cd sorption in these soils better than the other equations. The least R^2 belonged to Dubinin-Radushkevich

and Temkin equations. Temkin isotherm produced the maximum SE. Maftoun et al. (2004) showed that Cd adsorption was well fitted to Langmuir, Freundlich, and Temkin equations. The study of Adhami et al. (2008) on nickel adsorption of some southern and northern soils of Iran, indicated that Freundlich, Langmuir, and Redlich-Peterson equations were suitable for describing the trend of Ni adsorption.

Freundlich Isotherm

The " k_F " and " n_F " values of Freundlich isotherm presented in Table 4 were used to evaluate the effect of soil properties on Cd retention. k_F value could be assumed as the amount of Cd adsorption when equilibrium concentration (C) is equal to 1 mg kg⁻¹. (Karimian and Cox, 1978; Maftoun et al., 2002), and could be used to compare the adsorption characteristics of different soils (Karimian and Moafpouryan, 1999). In the present study, the average value of k_F was 504.52 mg kg⁻¹. The maximum " n_F " was 0.72, which was belonged to the soil with the minimum value of k_F (29.71 mg kg⁻¹). This is in accordance with the findings of Ramachandran and Souza (1999), who observed that soils with the maximum value of n_F had the minimum value of k_F . They reported that the Freundlich adsorption parameters " k_F ", shows the adsorption capacity, and " n_F " shows the rate of adsorption. Rattan and Sehgal (1989) showed that cadmium adsorption capacity " k_F " had significant positive correlations with pH, CEC and CaCO₃ content, but significant negative correlations were also obtained between rate of adsorption " n_F " and the above mentioned soil properties. These findings are in the agreement with the present finding, which shows that the adsorption capacity of soils for cadmium increase with the increased of the pH and CEC.

Stepwise multiple regression analysis between soils properties and “ k_F ” indicated that pH was the dominant soil property affecting k_F (Fig. 1), while 68% of variation in k_F was due to the combined effects of pH and CEC (Eq. 1). Appel and Ma (2002) observed that cadmium sorption is related to pH and CEC. They also reported that the soil CEC variation is related to the soil organic matter contents, clay contents, and pH.

McBride et al. (1981) reported that in calcareous or alkaline soils, CdCO_3 precipitation or chemisorption on carbonates may also be responsible for the high adsorption of Cd by soils. Soon (1981) reported that with increasing soil pH, the surface charge and potential become more negative, thereby increasing the adsorption of metals such as Cd^{2+} . Frost and Griffin (1977), reported that the high pH, high CEC and high CaCO_3 content of soils may have favored the conditions for high adsorption of cadmium. Rattan and Sehgal (1989) reported that in soils with the pH ranging from 4.8 to 8.5, the adsorption capacity of cadmium have shown a high significant positive correlation with soil properties, such as pH, CEC and CaCO_3 content. In the present study, based on the solubility diagram of Cavallaro and McBride (1978), there is a possibility of CdCO_3 precipitation in soils with pH above 7 in the presence of high initial Cd concentration. Whereas, in the soils with pH below 7, probably the surface charge and potential might become more negative by increasing of the soil pH, thereby, increasing the adsorption of Cd^{2+} .

$$k_F = - 2163.45 + 342.58 \text{ pH} + 11.17 \text{ CEC} \quad R^2 = 0.68 \quad p \leq 0.001 \quad (1)$$

This equation clearly indicates that increase of pH and CEC caused increased amounts of sorbed Cd. Appel and Ma (2002) observed a positive effect of pH on Cd sorption. Ramachandran and Souza (1999) found a positive significant correlation between Freundlich adsorption constant (k_F) with CEC, pH and CCE. Yuan and Lavkulich (1997) stated that the

Freundlich parameter (k_F) would be affected by the pH and OM content of soil. Although, clay and OM surfaces are the principal sorbent of Cd, in the present study, there was no direct significant correlation between k_F with both clay and OM. However, the results of regression analysis between CEC with other soil properties showed a significant relation between CEC with clay, OM, and pH:

$$\text{CEC} = - 11.73 + 0.44 \text{ clay} + 2.72 \text{ OM} + 2.99 \text{ pH} \quad R^2 = 0.72 \quad p \leq 0.001 \quad (2)$$

According to Eq. (2), it can be concluded that clay and OM contents have indirect effects on Cd sorption by means of CEC. Maftoun et al. (2004) and Naidu et al. (1997) reported that Cd adsorption by soils could be more affected by the kind of clay and OM than the contents of them. There is no physical definition for n_F . It simply shows magnitude of Cd retention as Cd concentration increases. According to the figure 2 and Eq. (3), there was a negative significant correlation between n_F and pH.

$$n_F = 1.76 - 0.19 \text{ pH} - 0.003 \text{ CEC} \quad R^2 = 0.88 \quad p \leq 0.001 \quad (3)$$

Ramachandran and Souza (1999) reported that there was a significant negative correlation between n_F and CEC, pH and CCE; however, those soil properties had a significant positive correlation with k_F . The results of Freundlich isotherm in the present study are similar to the findings of Adhikari and Singh (2003), and Hanafi and Sjaola (1998).

Langmuir Isotherm

The slope of Langmuir equation, b_L , is considered as maximum adsorption (Karimian and Moafpouryan, 1999), and K_L is related to bonding energy (Maftoun et al., 2002). The calculated Langmuir K_L and b_L are presented in Table 5. Maximum adsorption (b_L) ranged from 1105 to 5001 (mg kg^{-1}). The relatively high b_L values in this study indicated that the soil

removed a large amount of Cd from solution. Stepwise regression analysis (Eqs. 4-7) indicated important effects of CEC, pH, and CCE on b_L and K_L :

$$b_L = 1133.05 + 63.80 \text{ CEC} \quad R^2 = 0.48 \quad p \leq 0.001 \quad (4)$$

$$b_L = -2482.02 + 68.79 \text{ CEC} + 521.62 \text{ pH} \quad R^2 = 0.75 \quad p \leq 0.001 \quad (5)$$

$$K_L = -0.210 + 0.042 \text{ pH} \quad R^2 = 0.56 \quad p \leq 0.001 \quad (6)$$

$$K_L = 0.001 + 0.009 \text{ CCE} \quad R^2 = 0.63 \quad p \leq 0.001 \quad (7)$$

$$K_L = -0.123 + 0.006 \text{ CCE} + 0.022 \text{ pH} \quad R^2 = 0.71 \quad p \leq 0.001 \quad (8)$$

Among soil properties, CEC and pH had the most influential effect on maximum adsorption (b_L) (Eqs. 4 and 5). The relationship between b_L and both CEC and pH indicated the presence of Cd as a cation in the soil, and showed that maximum retention of Cd was a function of CEC and pH. In the present study, as has been explained in the subsection of Freundlich Isotherm, and according to Eq. (2), clay and OM contents have indirect effects on Cd sorption by means of CEC. An increase in Langmuir b_L coefficient with pH and CEC has been reported by Ramachandran and Souza (1999), and Singh (1979).

Multiple regression analysis showed that CEC could explain 63% of K_L variation (Eq. 6); inclusion of pH (Eq. 7) increased R^2 to 0.71 (Eq. 8). This is in accordance with the findings of Adhikari and Singh (2003) who observed that the bonding energy constant (K_L) showed a significant positive correlations with pH, CCE, CEC, OM, and clay. Levi-Minzi et al. (1976) observed a significant correlation between K_L and CCE, CEC, and OM.

At a very low equilibrium concentration, it is believed that the term $1+K_L C$ of Langmuir equation ($X = (K_L b_L C)/(1+K_L C)$) approaches $1(\text{mg L}^{-1})$ and therefore, will result in $X/C = K_L b_L$; termed as distribution coefficient (K_d), (Bolt and Bruggenwert, 1976), and defined as “maximum buffering capacity” by Iyengar and Raja (1983). Multiple regression analysis

between K_d and soil properties indicated that in the selected soils K_d was mostly dependent on pH and CCE:

$$K_d = -786.83 + 155.66 \text{ pH} \quad R^2 = 0.52 \quad p \leq 0.001 \quad (9)$$

$$K_d = -6.710 + 33.01 \text{ CCE} \quad R^2 = 0.63 \quad p \leq 0.001 \quad (10)$$

$$K_d = -435.31 + 23.03 \text{ CCE} + 76.38 \text{ pH} \quad R^2 = 0.70 \quad p \leq 0.001 \quad (11)$$

Almost, 52 and 63 percent of K_d variation could be explained by pH and CCE, respectively (Eqs. 9 through 11), while 70% of its variations was predicted by the combination of pH and CEC.

Naidu et al. (1997) stated that pH increment leads to deprotonation and a rapid increase in net negative surface charge that may explain the enhanced affinity for Cd ions. This is also consistent with the studies of Sukreeyapongse et al. (2002). In the present study, according to the high pH value of some soils, elevated initial Cd concentration, and solubility diagram of Cavallaro and McBride (1978), the precipitation of the octavite (CdCO_3) as solid soil phase is probable. These findings are similar to the results reported by Hirsch and Banin (1990). Moreover, the results of correlation between soil properties indicated that pH was significantly correlated with CCE ($R^2=0.67$) and it can be inferred that besides the direct effect of pH on Cd sorption, it also has an indirect effect on Cd sorption. Singh and Nayyar (1993) observed that Cd sorption had significant correlation with the content of CCE. Ramachandran and Souza (1999) found that the high pH, high CEC, and high CCE of soils might be favored conditions for high adsorption of Cd.

Redlich-Peterson Isotherm

The Redlich–Peterson isotherm has three parameters and includes the features of both Langmuir and Freundlich isotherms (Redlich and Peterson, 1959). Adhami et al. (2008) observed that a Redlich-Peterson isotherm would better explain nickel adsorption data of soils. In addition, they used this equation to study the relationships of the parameters of this equation with soil properties. The authors are unaware of such study for retention of Cd by soil. The Redlich-Peterson equation coefficients (n , k_{RP} and a_{RP}) are shown in Table 6.

In the present study, n was determined with the use of “solver” of Excel software for a pseudo-linear form of the Redlich-Peterson equation ($\frac{C}{X} = \frac{1}{k_{RP}} + \frac{a_{RP}}{k_{RP}} C^n$) to obtain values for the isotherm constant. Stepwise multiple regression analysis between k_{RP} and a_{RP} (as dependent variables) and soil properties indicated that in these soils k_{RP} and a_{RP} were dependent to pH:

$$k_{RP} = - 2430.88 + 467.63 \text{ pH} \quad R^2 = 0.30 \quad p \leq 0.007 \quad (12)$$

$$a_{RP} = - 1.928 + 0.453 \text{ pH} \quad R^2 = 0.27 \quad p \leq 0.012 \quad (13)$$

It can be inferred from Eqs. 12 and 13 that pH property had a minor effect on both k_{RP} and a_{RP} . Studies of Adhami et al. (2008) on nickel adsorption of some northern soils of Iran, indicated no significant relationship between the constants of Redlich-Peterson isotherm with soil properties.

Conclusion:

From results reported herein, it is concluded that the sorption of Cd increased with increasing solution Cd concentration, and the soils had different Cd sorption capacity. The results

showed that Redlich-Peterson, Langmuir, and Freundlich equations are respectively suitable for describing Cd retention in the soils studied. Although, the Cd sorption data showed a highly significant fit to Redlich-Peterson, there was a less significant correlation between the coefficients of Redlich-Peterson and soil properties than those of the other two equations. Stepwise multiple regression analysis indicated that pH, CEC, and CCE were the most important soil properties affecting Cd sorption in these soils. Alkaline soils favoured high sorption of Cd, and possibly precipitation as CdCO_3 , which may lead to less bioavailability of Cd; whereas, acidic soils adsorbed less Cd, and more Cd was present in solution, which may result in high bioavailability. It seemed that organic matter and clay contents affected Cd retention indirectly by the means of CEC.

References:

- Adhami, E., Salmanpour, A., Omidi, A., Khosravi, N., Ghasemi-Fasaei, R., and Maftoun, M. 2008. Nickel adsorption characteristics of selected soils as related to some soil properties, *Soil and Sediment Contamination*. **17**, 643-653.
- Adhikari, T., and Singh, M.V. 2003. Sorption characteristics of lead and cadmium in some soils of India, *Geoderma*. **114**, 81-92.
- Adriano, D.C. 1986. *Trace elements in the terrestrial environment*, Springer-Verlag, New York.
- Allison, L.E. 1965. Organic carbon. In: *Methods of soil analysis, Part 2*, pp. 1372-1376 (Black, C.A., Ed.), Am. Soc. Agron., Madison, WI.
- Alloway, B.J. 1990. Cadmium. In: *Heavy metals in soils*, pp. 100-124 (Alloway, B.J., Ed.) Halsted. New York.
- Appel, C., and Ma, L. 2002. Concentration, pH and surface charge effects on cadmium and lead sorption in three tropical soils, *J. Environ. Qual.* **31**, 581-589.
- Boekhold, A.E., Temminghoff, E.J.M., and Vand der Zee, S.E.A.T.M. 1993. Influence of electrolyte composition, pH and cadmium sorption by an acid sandy soil, *J. Soil Sci.* **44**, 85-86.
- Bolt, G.H., and Bruggenwert, M.G.M. 1976. *Soil chemistry, Part A: Basic elements*, Elsevier Scientific Publishing Co: Amsterdam. the Netherlands.
- Bolton, K.A., and Evans, L.J. 1996. Cadmium adsorption capacity of selected Ontario soils, *Can. J. Soil Sci.* **76**, 183-189.

- Cavallaro, N., and McBride, M.B. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils, *Soil Sci. Soc. Am. J.* **42**, 550-556.
- Chaney, R.L., and Ryan, J.A. 1994. *Risk based standards for arsenic, lead and cadmium in urban soils*, DECHEMA, Frankfurt, Germany.
- Chaney, R.L., Ryan, J.A., and Brown, S.L. 1999a. Environmentally acceptable endpoints for soil metals, In: *Environmental availability in soils: Chlorinated organics, explosives, metals*, pp. 111-154 (Anderson, W.C., et al. Eds.), Am. Acad. Environ. Eng., Annapolis, MD.
- Chaney, R.L., Ryan, J.A., Li, Y.M., and Brown, S.L. 1999b. Soil cadmium as a threat to human health, In: *Cadmium in soils and plants*, pp. 219-256 (McLaughlin, M.J., and Singh, B.R., et al. Eds.), Kluwer Academic Publ. Dordrecht, the Netherlands.
- Chlopecka, A., Bacon, J.R., Wilson, M.J., and Kay, J. 1996. Forms of cadmium, lead, and zinc in contaminated soils from southwest Poland, *J. Environ. Qual.* **25**, 69-79.
- Frost, R.R. and Griffin, R.A. 1977. Effect of pH on adsorption of copper, zinc, and cadmium from landfill leachate by clay minerals, *J. Environ. Sci. Health.* **A12**, 139-156
- Gee, G.W. and Bauder, J.W. 1986. Particle-size analysis. In: *Methods of soil analysis, Part 1. Physical and Mineralogical Methods*, (Klute, A., Ed.), Am. Soc. Agron., Inc. Soil Sci. Am. Madison, WI.
- Hanafi M.M. and Sjaola, J. 1998. Cadmium and zinc in acid tropical soils, 1. Soil physical properties effect on their adsorption, *Commun. Soil Sci. Plant Anal.* **29**, 1919-1931.
- Havlin, J.L., Westfall, D.G., and Olsen, S.R. 1985. Mathematical models for potassium release kinetics in calcareous soils, *Soil Sci. Soc. Am. J.* **49**, 371-376.

- Hirsch, D., and Banin, A. 1990. Cadmium speciation in soil solution, *J. Environ. Qual.* **19**, Banin. 366-372.
- Ho, Y.S., Porter, J.F., and McKay, G. 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel, and lead single component system, *Water Air Soil Pollut.* **141**, 1–33.
- Houba, V.J., Van der lee, G., Navozamasky, I., and Walgina, L. 1989. *Soil and plant analysis, Part 5, a series of syllabi*, Wageningen agriculture university, Wageningen, The Netherlands.
- Iyengar, B.R.V., and Raja, M.E. 1983. Zinc adsorption as related to its availability in some soils of Karnataka, *J. Indian Soc. Soil Sci.* **31**, 432-438.
- Karimian, N., and Cox, F.R. 1978. Adsorption and extractability of molybdenum in relation to some chemical properties of soil, *Soil Sci. Soc. Am. J.* **42**, 757–761.
- Karimian, N., and Moafpouryan, G.R. 1999. Zinc adsorption characteristics of selected calcareous soils of Iran and their relationships with soil properties, *Commun. Soil Sci. Plant Anal.* **30**, 1721-1731.
- Levi-Minzi, R., Soldatini, G.F., and Riffaldi, R. 1976. Cadmium adsorption by soils, *J. Soil Sci.* **27**, 10-15.
- Loeppert, R.H., and Suarez, D.L. 1996. Carbonate and gypsum, In: *Methods of soil analysis, Part 3* (Sparks, D.L., Ed.), Am. Soc. Agron., Madison, WI.
- Maftoun, M., Karimian, N., and Moshiri, F. 2002. Sorption characteristics of copper (II) in selected calcareous soils of Iran in relation to soil properties, *Commun. Soil Sci. Plant Anal.* **33**, 2279–2289.

- Maftoun, M., Rassooli, F., Ali-Nejad, Z., and Karimian, N. 2004. Cadmium sorption behavior in some highly calcareous soils of Iran, *Commun. Soil Sci. Plant Anal.* **35**, 1271-1282.
- Martin-Garin, A., Gaudet, J.P., Charlet, L., and Vitart, X. 2002. A dynamic study of the sorption and the transport processes of cadmium in calcareous sandy soils, *Waste Management.* **22**, 201-207.
- McBride, M.B., Tyler, L.D., and Hovde, D.A. 1981. Cadmium adsorption by soils and uptake by plants, *Soil Sci. Soc. Am. J.* **45**, 739-744.
- McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils, *Adv. Soil Sci.* **10**, 1-56.
- Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D., and Tiller, K.G. 1997. Cadmium sorption and transport in variable charge soils: A review, *J. Environ. Qual.* **26**, 602-617.
- Ramachandran, V., and Souza, T.J.D. 1999. Adsorption of cadmium by Indian soils, *Water Air Soil Pollut.* **111**, 225-234.
- Rattan, R.K., and Sehgal D. 1989. Investigations on cadmium adsorption on soils, *J. Indian Soc. Soil Sci.* **37**, 284-289.
- Redlich, O., and Peterson, D.L. 1959. A useful adsorption isotherm, *J. Phys. Chem.* **63**, 1024.
- Sanches-Martin, M.J., and Sanches-Camazano, M. 1993. Adsorption and mobility of cadmium in natural uncultivated soils, *J. Environ. Qual.* **22**, 737-742.
- Shirvani, M., Kalbasi, M., Shariatmadari, H., Nourbakhsh, F., and Najafi, B. 2006. Sorption-desorption of cadmium in aqueous palygorskite, sepolite and calcite suspension: Isotherm hysteresis, *Chemosphere.* **65**, 2178-2184.

- Singh, S.P., and Nayyar, V.K. 1993. Adsorption of cadmium on alkaline and calcareous soils, *J. Indian Soc. Soil Sci.* **41**, 270-273.
- Singh, S.S. 1979. Sorption and release of cadmium in some Canadian soils, *Can. J. Soil Sci.* **59**, 119-130.
- Soon, Y. K. 1981. Solubility and sorption of cadmium in soils amended with sewage-sludge. *J. Soil Sci.* **32**, 85-95.
- Sukreeyapongse, O., Holm, P.E., Strobel, B.W., Panichsakpatana, S., Magid, J., and Hansen, H.C.H.C.B. 2002. pH-dependent release of cadmium, copper and lead from natural and sludge-amended soils, *J. Environ. Qual.* **31**, 1901-1909.
- Summer, M.E., and Miller, W.P. 1996. Cation exchange capacity and exchange coefficients, In: *Methods of soil analysis, Part 3* (Sparks, D.L., Ed.). Am. Soc. Agron., Madison, WI.
- Tiller, K.G. 1989. Heavy metals in soils and their environmental significance, *Adv. Soil Sci.* **9**, 113-142.
- Yuan, G., and Lavkulich, L.M. 1997. Sorption behavior of copper, zinc and cadmium in response to simulated changes in soil properties, *Commun. Soil Sci. Plant Anal.* **28**, 571-578.

Table 1. Equations used to study Cd sorption

Isotherm	Equation	Description	Reference
Freundlich	$\text{Log } X^a = \log k_F + n_F \log C^b$	k_F is Cd adsorption capacity (mg kg^{-1} soil), n_F is rate of Cd adsorption	Ramachandran and Souza (1999); Maftoun et al.(2004)
Langmuir	$C / X = [1 / (K_L b_L)] + (1 / b_L) C$	b_L is Cd adsorption maxima (mg kg^{-1} soil), K_L is a coefficient related to Cd bonding energy (L mg^{-1})	Ramachandran and Souza (1999); Maftoun et al.(2004)
Temkin	$X = k_{T1} + k_{T2} \ln C$	k_{T1} and k_{T2} are Cd adsorption coefficients	Maftoun et al.(2004)
Dubinin-Radushkevich	$X = k_{DR} \exp (-b_{DR} [RT \ln (1 + 1/C)]^2)$	k_{DR} (mg kg^{-1}) and b_{DR} are constants	Ho et al.(2002)
Redlich-Peterson	$X = k_{RP} C / (1 + a_{RP} C^n)$	n , k_{RP} (L kg^{-1}), and a_{RP} (kg mg^{-1}) are constants	Ho et al.(2002)

a: X is the amount of Cd adsorbed per unit weight of soil (mg kg^{-1})

b: C is Cd concentration in equilibrium solution (mg L^{-1}).

Table 2. Some physical and chemical characteristics of the selected soils

Soil no.	clay (%)	pH	OM (%)	CCE (%)	CEC (cmol _c kg ⁻¹)	Fe _o (mg kg ⁻¹)
1	8.00	7.35	1.53	9.89	14.18	582
2	17.00	7.28	5.52	12.16	27.07	1090
3	19.00	4.21	9.49	1.59	32.58	2980
4	20.00	7.42	7.02	16.51	37.01	7072
5	20.00	5.83	3.03	2.88	20.01	5440
6	21.00	7.34	2.84	11.80	29.23	4834
7	24.00	4.88	5.33	5.92	35.96	3067
8	28.00	7.08	5.22	3.43	36.85	4106
9	28.00	6.03	4.24	2.39	28.42	6931
10	28.00	7.22	4.83	6.30	42.32	6403
11	35.00	5.98	7.97	4.02	42.70	4784
12	35.00	5.37	4.53	1.86	28.07	5386
13	36.00	7.16	3.95	7.81	44.18	5593
14	38.00	5.94	9.77	7.97	51.94	9348
15	40.00	6.58	3.41	5.10	41.24	7840
16	44.00	7.34	6.05	13.97	45.15	4334
17	47.00	7.18	2.71	2.85	37.14	4586
18	48.00	7.34	4.45	12.36	42.84	3609
19	50.00	7.61	2.78	16.00	38.30	3593
20	52.00	6.36	5.05	2.58	36.30	7920

Table 3. Coefficient of determination (R^2) and standard error of estimate (SE) of different equations

Soil no.	Freundlich		Langmuir		Temkin		Dubinin- Radushkevich		Redlich- Peterson	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
1	0.89	0.17	0.93	0.042	0.65	406.03	0.34	0.94	0.97	0.029
2	0.87	0.24	0.99	0.002	0.64	1016.04	0.52	1.04	1.00	0.002
3	0.95	0.14	0.86	0.030	0.81	339.45	0.52	1.01	0.86	0.030
4	0.92	0.18	1.00	0.001	0.73	915.25	0.73	0.78	1.00	0.001
5	0.96	0.12	0.91	0.023	0.84	312.09	0.46	1.00	0.91	0.023
6	0.94	0.16	0.98	0.004	0.72	848.30	0.77	0.71	1.00	0.001
7	0.98	0.10	0.94	0.010	0.87	438.82	0.51	1.04	0.94	0.010
8	0.91	0.19	0.99	0.004	0.72	733.69	0.47	1.04	0.99	0.003
9	0.97	0.11	0.96	0.012	0.87	339.42	0.46	1.02	0.96	0.012
10	0.93	0.18	0.98	0.003	0.70	1120.74	0.74	0.79	1.00	0.001
11	0.97	0.11	0.98	0.004	0.88	501.56	0.46	1.08	0.99	0.004
12	0.97	0.10	0.97	0.010	0.89	306.32	0.50	1.00	0.98	0.010
13	0.88	0.22	0.97	0.006	0.61	992.25	0.53	0.99	0.99	0.003
14	0.98	0.09	0.97	0.005	0.86	601.94	0.49	1.07	0.98	0.004
15	0.84	0.26	0.99	0.003	0.60	1114.11	0.48	1.09	0.99	0.002
16	0.92	0.19	1.00	0.002	0.71	1060.58	0.72	0.81	1.00	0.001
17	0.93	0.17	0.98	0.004	0.70	956.34	0.75	0.75	1.00	0.001
18	0.91	0.20	0.99	0.002	0.68	998.88	0.61	0.94	1.00	0.002
19	0.93	0.17	0.99	0.002	0.74	803.56	0.75	0.73	1.00	0.001
20	0.97	0.11	0.98	0.005	0.83	540.37	0.47	1.03	0.99	0.005
Min.	0.84	0.09	0.86	0.001	0.60	306.32	0.34	0.71	0.86	0.001
Max.	0.98	0.26	1.00	0.042	0.89	1120.74	0.77	1.09	1.00	0.030
Ave.	0.93	0.16	0.97	0.009	0.75	717.29	0.56	0.94	0.98	0.007

Table 4. Freundlich adsorption isotherm parameters

Soil no.	k_F ($mg\ kg^{-1}\ soil$)	n_F
1	142.67	0.40
2	701.91	0.27
3	29.71	0.72
4	1001.26	0.23
5	48.31	0.64
6	923.36	0.22
7	58.54	0.71
8	396.14	0.35
9	69.48	0.63
10	1069.70	0.23
11	152.20	0.58
12	58.58	0.65
13	633.66	0.26
14	188.03	0.56
15	683.77	0.27
16	1072.90	0.23
17	948.07	0.22
18	753.68	0.27
19	933.81	0.22
20	224.62	0.48
Minimum	29.71	0.22
Maximum	1072.90	0.72
Average	504.52	0.40

Table 5. Langmuir sorption isotherm parameters

Soil no.	$K_L(L\ mg^{-1})$	$b_L(mg\ kg^{-1}\ soil)$	$K_d = M^a$
1	0.17	1105	186.62
2	0.09	3940	368.44
3	0.01	2166	17.09
4	0.18	3902	702.07
5	0.01	2099	23.78
6	0.08	3933	305.23
7	0.01	3594	35.60
8	0.04	3369	149.34
9	0.01	2553	36.93
10	0.09	5001	442.67
11	0.02	3676	89.35
12	0.01	2415	34.41
13	0.04	4007	167.56
14	0.03	4153	104.64
15	0.06	4304	250.54
16	0.14	4524	634.27
17	0.07	4292	295.70
18	0.08	4172	353.40
19	0.11	3690	421.59
20	0.03	3233	112.77
Minimum	0.01	1105	17.09
Maximum	0.18	5001	702.07
Average	0.07	3506.47	236.60

^a $K_d = M = K_L b_L$

Table 6. Redlich-Peterson sorption isotherm parameters

Soil no.	n	$k_{RP}(L\ kg^{-1})$	$a_{RP}(kg\ mg^{-1})$
1	1.70	36.45	0.0005
2	0.93	480.47	0.9518
3	1.13	16.04	0.4756
4	0.97	836.98	1.1852
5	0.92	25.57	0.5932
6	0.75	1916.15	2.7509
7	1.02	35.22	0.3467
8	0.85	231.29	0.7665
9	0.96	38.31	0.4697
10	0.74	2629.54	1.7995
11	0.94	96.59	0.4236
12	1.13	31.05	0.3061
13	0.67	854.01	2.1443
14	0.81	145.60	0.6351
15	0.84	419.56	0.8605
16	0.91	1047.81	1.2708
17	0.71	2117.13	2.8417
18	0.85	705.58	1.1540
19	0.86	1068.29	1.3631
20	0.88	144.80	0.7345
Minimum	0.67	16.04	0.0005
Maximum	1.70	2629.54	2.8417
Average	0.93	643.82	1.0537

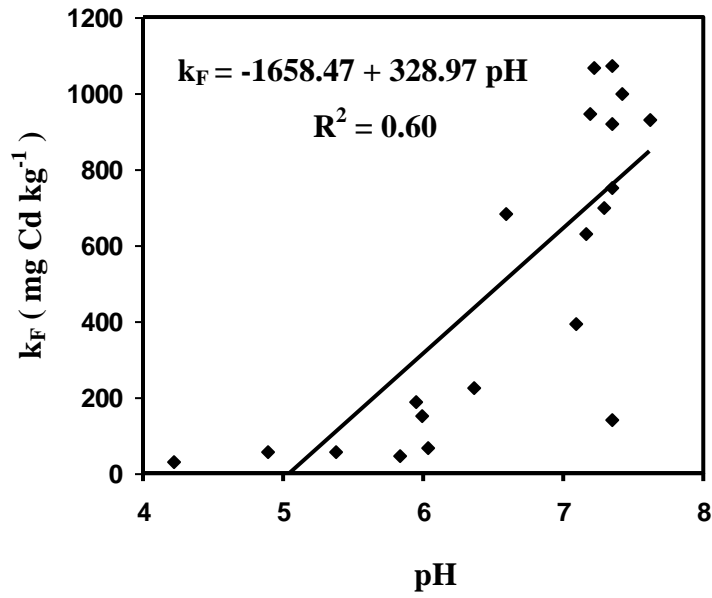


Figure 1. Relationship between Cd adsorption capacity (k_F) and pH.

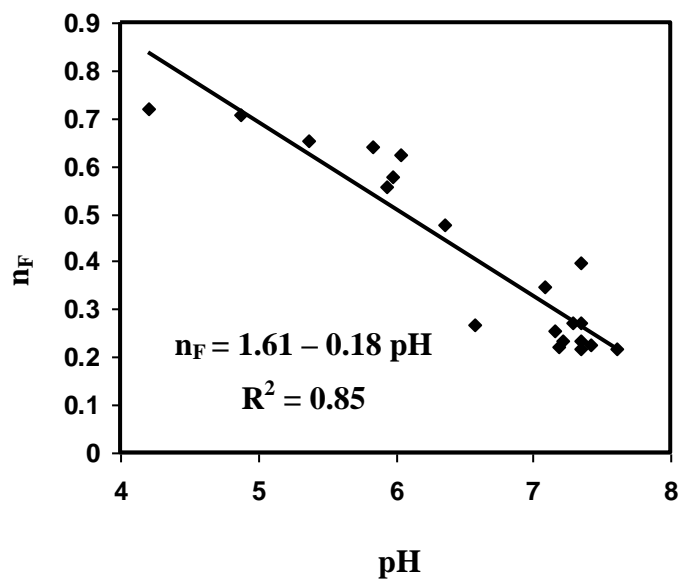


Figure 2. Relationship between rate of Cd adsorption (n_F) and pH.