Cadmium adsorption behavior of some soils from northern of Iran

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Abstract

Cadmium adsorption behavior (Cd) of soils is an important process which exerts a major influence on its uptake by plant roots. Cadmium (Cd) sorption characteristics of 20 surface soils (0-30 cm) with a wide range of soil physicochemical properties, was investigated. Two grams of each sample were equilibrated for 24h at laboratory temperature (25 ± 2°C) with 40ml, 0.01M $CaCl_2$ containing 5 to 500 mg Cd/L. Langmuir, Freundlich and Temkin adsorption isotherms were used to evaluate the trend of Cd adsorption. The data of Cd adsorption was well fitted to Langmuir and Freundlich adsorption isotherms. However, the fit to Langmuir adsorption model was closer than that of Freundlich. Multiple stepwise regression analysis indicated that, the adsorption capacity of the soils for Cd increased with an increase in pH, CEC and calcium carbonate equivalent (CCE).

Key Words

Adsorption, Cadmium, Freundlich, Isotherm, Langmuir, Temkin.

Introduction

Cadmium (Cd) contamination imposes an adverse effect on environmental quality and constitutes a serious threat not only to plants and animals but also to human lives (Martin-Garin *et al.* 2002). Cadmium adsorption and desorption by soils is one of the factors that control its bioavailabilty and transfer in the environment (Singh and Nayyar 1993). Langmuir (Ramachandran and Souza 1999; Singh and Nayyar 1993), Freundlich (Ramachandran and Souza 1999), and Temkin (Maftoun *et al.* 2004) equations have been commonly used to to assess the pattern of heavy metals adsorption by soils. The objectives of the present study were to (1) evaluate the pattern of Cd adsorption of some soils from Guilan province, and (2) and to determine the effect of soil properties on Cd adsorption.

Methods

Twenty surface soil samples (0-30 cm) varying widely in physicochemical properties (Table 1) from Guilan province in northern part of Iran, were used in the present study. 2g subsample of each soil was placed in centrifuge tubes and 40ml of 0.01M $CaCl_2$ containing different concentrations of Cd (ranging from 5 to 500 mg Cd/L) was added and shaken for 1h at room temperature and allowed to equilibrate at 25±2ºC for 24h. The suspensions were then shaken for additional 30 min. Samples were centrifuged for 10 min and the supernatant was analysed for Cd by atomic absorption spectrophotometry. The amount of Cd adsorbed was calculated as the difference between initial and final Cd concentrations. The adsorption data were fitted to Freundlich, Langmuir, and Temkin adsorption isotherms. The stepwise multiple regression procedure was used to study the relationship between the Cd sorption coefficients and the physicochemical properties of the soils.

Table 1. Range of physicochemical characteristics of the soils.

	Clay (%)	pH	OM (%)	CCE (%)	CEC ($cmol_c$/kg)
Min.	8.00	4.21	1.53	1.59	14.18
Max.	52.00	7.61	9.77	16.51	58.46
Ave.	31.92	6.58	4.99	7.37	37.20

Equations

Freundlich $$\text{Log } X = \log k_F + n_F \log C \qquad (1)$$

Langmuir $$C / X = [1 / (K_L b_L)] + (1 / b_L) C \qquad (2)$$

In Langmuir equation, (X / C) is termed the distribution coefficient (K_d) (Bolt and Bruggenwert 1976):

$X / C = K b = K_d$ (3)

Temkin $X = k_{T1} + k_{T2} \ln C$ (4)

Where X is the amount of Cd sorbed per unit weight of soil (mg/kg soil), C is Cd concentration in equilibrium solution (mg/L), b_L is Cd adsorption maxima (mg/kg soil), K_L is a coefficient related to Cd bonding energy (L/mg), K_d is Cd distribution coefficient (L/kg soil), k_F is Cd adsorption capacity (mg/kg soil), n_F is rate of Cd adsorption, k_{T1} and k_{T2} are Cd adsorption coefficients.

Results

Langmuir and Freundlich isotherms were well fitted to the adsorption data (Table 2).

Table 2. Freundlich and Langmuir adsorption isotherm parameters and coefficients of determination (r^2).

	Freundlich Eq.			Langmuir Eq.			
	r^2	k_F	n_F	r^2	K_L	b_L	K_d
Min.	0.82[a]	29.7	0.22	0.86[a]	0.01	1105	17.10
Max.	0.98[a]	1072.9	0.72	1.00[a]	0.18	5000	702.10
Ave.	0.92[a]	504.5	0.41	0.97[a]	0.07	3506	236.60

[a] Significant at $p \leq 0.001$

k_F value ranged from 29.7 to 1072. The K_F value indicates the quantity of adsorption when the equilibrium concentration is 1 mg/L (Kariman and Cox, 1978). Multiple linear regression analysis between K_F and soil properties (Eq. (5) and Eq.(6)) indicated that 68 percent of K_F variation could be explained by cation exchange capacity (CEC) and pH. As it can be clearly seen from these equations, adsorbed Cd increased linearly with increase in pH and CEC. However these properties showed significant negative correlation with n_F coefficient, similar result has been reported by Ramachandran and Souza (1999).

$k_F = -1658.47 + 328.97$ pH $r^2 = 0.60$ $p \leq 0.001$ (5)

$k_F = - 2163.45 + 342.58$ pH $+ 11.17$ CEC $r^2 = 0.68$ $p \leq 0.001$ (6)

Clay and OM surfaces are the main sorbent of Cd; however, the nonsignificant correlation found between k_F with clay and OM might be due to the fact that the adsorption of Cd by tested soils could be more affected by the kind of clay and OM than the amount of clay and OM.

K_L coefficient was correlated with some soil properties. Multiple stepwise regression analysis showed that the simple regression equation could adequately describe such relations:

$K_L = 0.001 + 0.009$ CCE $r^2 = 0.63$ $p \leq 0.001$ (7)

$K_L = - 0.21 + 0.04$ pH $r^2 = 0.56$ $p \leq 0.001$ (8)

$K_L = - 0.123 + 0.006$ CCE $+ 0.022$ pH $r^2 = 0.71$ $p \leq 0.001$ (9)

These findings are similar to those reported by Maftoun *et al.* (2004) and Ramachandran and Souza (1999). In the present study, based on soil pH, and initial Cd concentration, the Cavallaro and McBride solubility diagram (Cavallaro and McBride 1978) indicates the possibility of solid phase Octavite ($CdCO_3$) precipitation in some soils. The calculated Langmuir b_L, ranged from 1105 to 5000 (Table 2). The relatively high b_L values in the present study revealed that the soil removed a large amount of Cd from solution. Stepwise regression analysis between b_L and soil properties showed the following relationships:

$b_L = 1133.05 + 63.80$ CEC $r^2 = 0.48$ $p \leq 0.001$ (10)

$b_L = - 2482.02 + 68.79$ CEC $+ 521.62$ pH $r^2 = 0.75$ $p \leq 0.001$ (11)

which, indicates that CEC and pH are the main soil properties controlling maximum Cd adsorption in the studied soils.

The distribution coefficient, K_d shows the ratio of the Cd concentration in the soil to the concentration of Cd^{+2} in the solution phase. K_d values varied greatly between soils, ranging from 17.10 to 702.10 (L/kg soil) and showed a highly significant correlation with CCE ($r^2 = 0.63$, $p \leq 0.001$) and pH ($r^2 = 0.52$, $p \leq 0.001$). These results clearly demonstrate that pH and, to a greater extent CCE, contribute to the variation of K_d in the soils studied (Eq. (12)). A portion of the removal of Cd from the solution phase may have been a result of precipitation of $CdCO_3$. Similar results have been reported by Yin *et al.* (2002) and Sauve *et al.* (2000).

$K_d = - 435.31 + 23.03$ CCE $+ 76.38$ pH $r^2 = 0.70$ $p \leq 0.001$ (12)

Conclusion

From results reported herein, it is concluded that the adsorption of Cd increased with increasing solution Cd concentration and the soils varied in Cd sorption capacity. The results showed that CEC and pH were the most important soil properties affecting Cd adsorption in these soils. Alkaline soils favoured high adsorption of Cd and possibly precipitation as $CdCO_3$, which may lead to less bioavailability of Cd; whereas, acid soils adsorbed less Cd, and more Cd was present in solution, which may result in high availability. Although, the Cd adsorption data showed a highly significant fit to Freundlich and Langmuir isotherms, Comparison of coefficients of determination of Langmuir and Freundlich equation demonstrated that Langmuir adsorption isotherm has a better fit than Freundlich.

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