Cadmium sorption by some alkaline soils of North-West India

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Abstract

Cadmium adsorption on five alkaline soils of north-west India followed Langmuir equation. The analogues shape of Linear Langmuir plot in each soils at 298 and 313^0K elucidate that temperature does not change the nature of reaction but influence the bonding energy constant and adsorption maxima for Cd ion. The magnitude of adsorption maxima enhanced with increase in $CaCO_3$ and organic content in soils. The positive and constant value of differential isosteric heat of adsorption (ΔH) on each soil between 298 and 313^oK elucidate that adsorption of Cd is an endothermic process which leads to precipitation of Cd rather than physical adsorption. However, the variation of ΔH within different soils might be due to variation in their physico-chemical characteristics. Solubility isotherm diagram revealed that $CdCO_3$ reaction product formed in equilibrated soil-Cd system used for adsorption study. It was concluded from Linear Langmuir plots, differential isosteric heat of adsorption ΔH and solubility isotherm studies that adsorption of Cd in alkaline soils occurred due to precipitation of $CdCO_3$ mineral.

Additional keywords: Cadmium adsorption isotherm, solubility isotherm, differential isosteric heat of adsorption

Introduction

Cadmium is a potentially toxic pollutant in environment and the excessive accumulation of cadmium in man causes bronchitis (Lewis et al. 1969), hypertension (Schroeder 1965), cardiovascular (Page and Bingham 1975) and "ouch - ouch" (Tsuchiya 1969) diseases. Cadmium contamination of the environment has been attributed to Industrial activities like smelting and electroplating of metals, combustion of lubricating oils, vulcanization of rubber for motor vehicle tires and use of cadmium compounds as fungicide sprays (John 1972; Lengerwerff and Specht 1970; Ross and Stewart 1969). The divalent Cd is slightly soluble in an aqueous solution when associated with carbonate anions and in alkaline soils and therefore their leaching must be limited. Thus higher Cd status of surface soils entails its accumulation in plants and eventually in food stuffs (Hundal and Arora 1993). Hodgson (1970) found that cadmium content in plants depends primarily on soil adsorption capacity which, in turn, is governed by the physico-chemical characteristics of the soils concerned.Therefore, the present investigation was undertaken to study cadmium adsorption by alkaline soils of north-west India.

Material and methods

Surface samples of alkaline soils representing alluvial plains in north -west India were collected from different locations in Punjab. Their physico-chemical characteristics are listed in Table 1. For adsorption study, 1 g of soil in duplicate was equilibrated for 24 hours in polyethylene bottles containing 50 ml of 0.01 M $NaNO_3$ solution of different Cd (added as Cd $(NO_3)_2$) concentrations ranging from 0.25 to 1.35 µmol Cd cm^{-3}. Adsorption isotherms were determined by equilibrating the soil solution suspension at 20^0C and 40^0C. A clear solution was separated from soil-solution suspension with Whatman no.42 filter paper. The pH and EC was determined of the filtrate solutions at 25^0C by pH meter and conductivity bridge, respectively. The Langmuir equation was used to interpret the equilibrium adsorption data. The linear form of the Langmuir equation is:

$$C/x/m = 1/Kb + C/b$$

where, C is the equilibrium Cd concentration (µmol Cd cm^{-3}); x/m is the amount of Cd adsorbed (µ mol Cd g^{-1} soil) ; b is the adsorption maxima (µmolCd g^{-1} soil) and k is the constant related to the bonding energy of the soil for Cd (Cm^{-3} µmol Cd).

Table 1. Characteristics of soils used for cadmium adsorption study

Soils	Taxonomic classification	Texture			pH	$CaCO_3$ (g kg^{-1})	CEC (c mol(+)kg^{-1})	O.C. g kg^{-1}
		Sand (%)	Silt (%)	Clay (%)				
1	Fluventic Haplustept	75.8	15.0	9.2	7.8	10.0	4.7	1.9
2	Typic Ustorthent	82.4	6.0	11.6	7.8	-	5.5	5.7
3	Typic Haplustept	51.0	29	20	7.9	5.0	8.0	4.2
4	Typic Haplustept	58.0	24	18	7.9	-	7.2	2.0
5	Vertic Ustochrept	11.8	29.9	58.2	8.6	3.8	26.3	6.9

The differential isosteric heat of Cd adsorption, ΔH, was obtained by collecting adsorption data at 293 and 313^0K and applying the Clausius-Chlapeyron equation to the system. For a given surface coverage θ,

$$\log(C_2/C_1)_\theta = \Delta H_{ads}/2.303R\ (1/T_1 - 1/T_2)$$

Where C_1 and C_2 are the equilibrium concentration (µmol Cd cm^{-3}) at temperature T_1 (293^0K) and T_2 (313^0K), respectively and R is the molar gas constant (Kcal mol^{-1}). The differential isosteric heat of adsorption (ΔH) is related to heat adsorbed or liberated during adsorption reaction at constant surface coverage but at different temperatures (Hayward and Trapnel, 1964). By convention, it is equal but opposite in sign to that portion of the change in enthalpy of the system attributable to adsorption.

$$\Delta H = -\Delta H_{ads}$$

For solubility isotherms, pCd values, the negative logarithm of the cadmium activities were calculated for soils equilibrated with 0.01M $NaNO_3$ solution containing no initial Cd and with the equilibrated initial Cd concentrations of 40, 70, 90 and 140 μmol Cd cm^{-3}. For study of solubility of cadmium minerals, equilibrium reaction of octavite ($CdCO_3$) and cadmium hydroxide ($Cd(OH)_2$ phase was considered at 0.003 atmospheric pressure of CO_2.. Corrections for the following ion-pairs were made: $CdHCO_3^+$, $CdCO_3^0$, $CaNO_3^+$, $Cd(NO_3)^0_2$ and $CdHPO^0_4$.

Results and discussion

Adsorption of cadmium by alkaline soils of north-west India at 298 and 313°K temperature showed single linear Langmuir plots. (Fig.1). Thus Cd adsorption on these soils as adsorbent are described by the Langmuir equation. The bonding energy for Cd adsorption was high in Fluventic Haplustept (S1) and Typic Ustorthent (S2), while it declined in both the Typic Haplustept (S3 and S4) and Vertic Ustochrept with increase in temperature of the soil solution suspension for equilibration from 298 to 313°K (Table 2). K in S2 was lower than that in S3 and S4 at both the temperatures of study (Table 2).

Table 2. Langmuir parameters for Cd adsorption on alkaline soils of Punjab determined at 293 and 313°K

Soils	293°K		313°K		Δ H (kcal mol^{-1})
	K (ml μmol^{-1}Cd)	b (μmol Cd g^{-1} soil)	K (ml μmol^{-1}Cd)	b (μmol Cdg^{-1} soil)	
1. Fluventic Haplustept	11.3	22.2	18.7	31.6	3.24
2. Typic Ustorthent	1.3	30.9	1.3	36.5	1.52
3. Typic Haplustept	1.9	21.6	1.4	32.9	3.74
4.Typic Haplustept	1.7	20.5	1.5	27.3	2.58
5.Vertic Ustochrept	1.1	41.7	0.9	52.1	2.00

The adsorption maxima for Cd adsorption on all these soils enhanced with an increase in temperature of the soil solution suspension for equilibration from 298 to 313°K suspension. Fluventic Haplustept (S1) has got the highest magnitude of bonding energy for Cd adsorption as 11.3 ml μmol $^{-1}$Cd at 293°K and 18.6 ml μmol $^{-1}$Cd at 313°K as compared to the other soils. This might be due to presence of higher amount of $CaCO_3$(1%) as compared to other soils.(Table 1) The highest amount of Cd adsorption maxima of 41.7 μmol Cd g^{-1} soil at 293°K and 52.1 μmol Cd g^{-1} soil at 313°K were observed for the Vertic Ustochrept soil (Table 2). This might be due to high clay content (58.2 %) as well as high CEC (26.3 cmol (+)kg^{-1}) of the Vertic Ustochrept as compared to the other soils studied. The heat released or

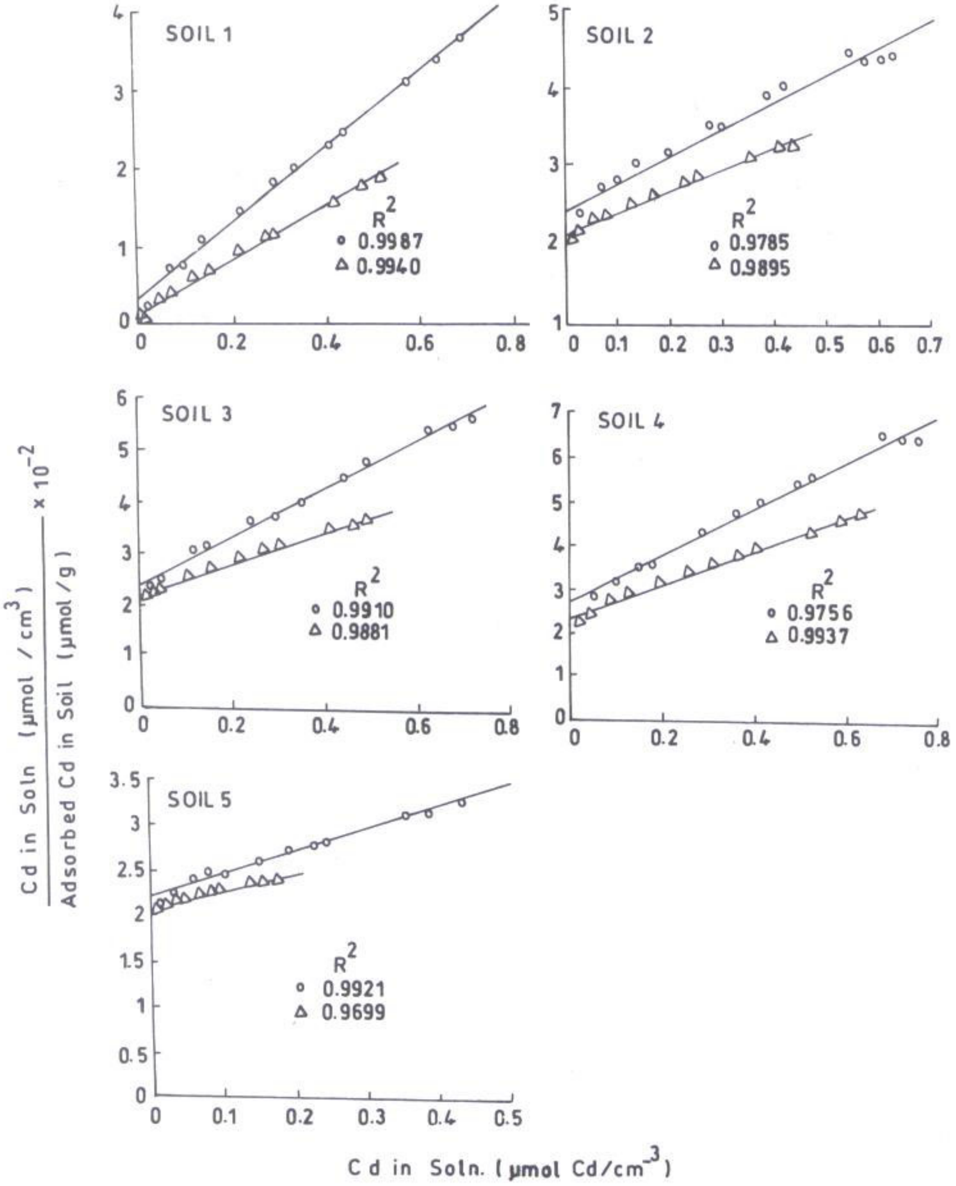

Fig.1. Langmuir isotherm for cadmium adsorption at 293°K(O) and 313°K (Δ) by alkaline soils

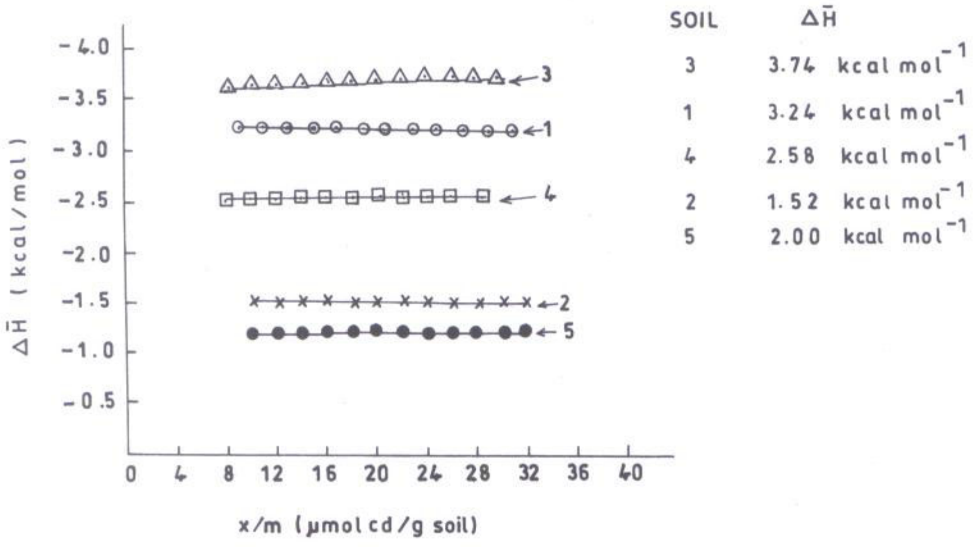

Fig.2. The isothermal differential heat of adsorption ΔH, as a function of Cd Adsorbed x/cm (μmol Cd g^{-1} soil) on alkaline soils of Punjab

absorbed during adsorption of Cd is the differential isosteric heat of adsorption, ΔH. The values of ΔH over the temperature range of 298^0K to 313^0K were computed using the Clausius-Clapeyron equation and are plotted as a function of cadmium adsorbed in Fig 2. This shows that Cd adsorption process is energy consuming (endothermic), with positive and constant ΔH values for each soil, but it varies with different soils due to their different physico-chemical characteristics. The ΔH values were 3.24, 1.52, 3.74, 2.58 and 2.00 k cal mol^{-1} for Fluventic Haplustept, Typic Ustorthent, calcareous Typic Haplustept, non-calcareous Typic Haplustept and Vertic Ustochrept soils, respectively. The constant ΔH values as a function of cadmium adsorbed elucidated that mechanism for cadmium-soil surface interaction remained essentially the same, even with increasing amount of cadmium adsorbed.

Since the adsorption of Cd in all these five soils was endothermic, it elucidate the adsorption occurs, due to the chemisorption precipitation of cadmium solid phase minerals. Physical adsorption on the other hand is always characterized by exothermic reaction and thus an increase in temperature eventually would leads to decrease in adsorption. Since the values of differential isosteric heat of cadmium adsorption remained constant in different soils, it suggests that precipitation of cadmium occur only in single form of Cd solid phase mineral. While admitting that a true thermodynamic equilibrium condition does not exist in soil system and that solubility criteria are thus often not strictly applicable, it is nevertheless, worthwhile to apply these relationship criteria to the equilibrated soil systems containing no initial Cd to 1.13 μmol Cd cm^{-3} in 0.01M $NaNO_3$ electrolytic solution. The solubility relationships in the equilibrated soil systems are plotted as the negative logarithm of activities of Cd ion in relation to pH (Fig. 3). The equilibrated soil-systems for different soils containing no initial Cd were undersaturated with respect to octavite ($CdCO_3$) mineral. All the equilibrated soil systems containing 0.34 to 1.13 μM Cd cm^{-3} in 0.01M $NaNO_3$ remained undersaturated with respect to ß-$Cd(OH)_2$, but supersaturated with respect to $CdCO_3$ (octavite) mineral. This suggests that at these levels of Cd concentration, adsorption of Cd in different soils occurred due to precipitation of $CdCO_3$ (octavite) mineral.

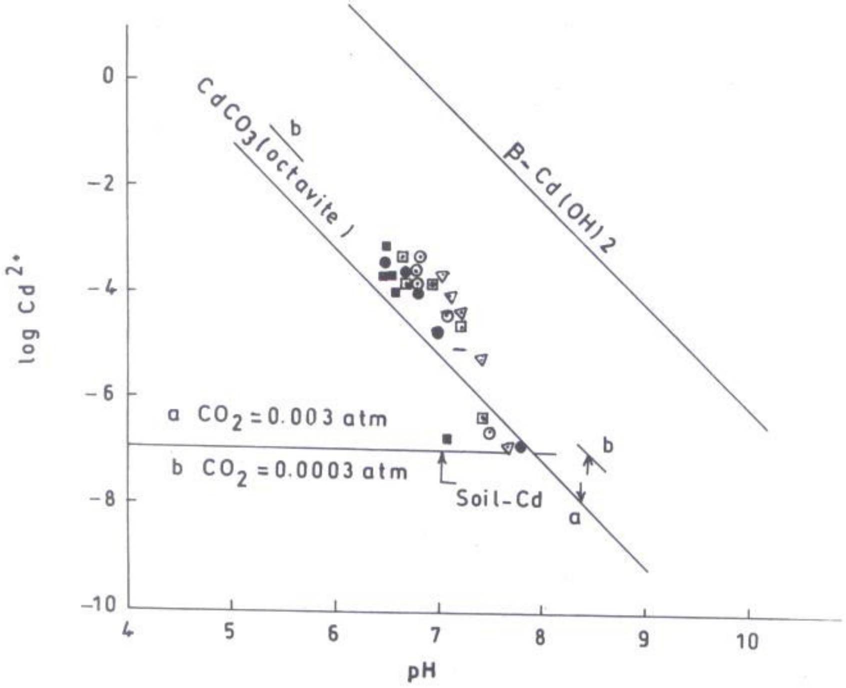

Fig.3. Identification of Cd solid phase formed in soil equilibrated with 0.01 M $NaNO_3$ solution containing no initial Cd and with equilibrated initial Cd Concentration of 40, 70, 90 and 140 μmol Cd cm^{-3} Soil 1 (○), Soil 2 (●), Soil 3 (□), Soil 4 (■), Soil 5 (▽).

The linear Langmuir isotherm plot and constant differential isosteric heat of adsorption (ΔH) as a function of Cd adsorbed revealed that Cd adsorption in alkaline soils of these alluvial plains was mainly due to single adsorption mechanism. Since the reaction is endothermic, precipitation is the likely process for Cd adsorption in these soils. Solubility criteria used to identify the solid phase formed inferred the precipitation of Cd as $CdCO_3$ phase in all the soil equilibrated system used for adsorption study.

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