



ISSN (E): 2277-7695
 ISSN (P): 2349-8242
 NAAS Rating: 5.23
 TPI 2023; 12(4): 2724-2728
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www.thepharmajournal.com

Received: 20-02-2023

Accepted: 05-03-2023

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Thermodynamic parameters (ΔG° , ΔH° , ΔS°) of cadmium sorption in sludge treated calcareous soils

Dr. SN Suman, Dr. SK Thakur, Dr. Vipin Kumar, Dr. Mukesh Kumar and Dr. AP Rakesh

Abstract

Laboratory investigations were carried out to study thermodynamic parameters (ΔG° , ΔH° , ΔS°) of cadmium sorption in calcareous soils. Ten soils varying in clay, organic carbon and CaCO_3 content were used for sorption study. Each soil was treated with sewage sludge @ 25 and 50 g kg^{-1} and incubated for 30 days at $25 \pm 2^\circ\text{C}$ giving four wetting and drying cycles. These untreated and treated soils were used for Cd sorption. The Cd sorption was determined by equilibrating 2 g of soils with 20 ml of CdCl_2 solution containing 5 to 750 $\mu\text{mol Cd}^{2+} \text{L}^{-1}$ at 20 ± 2 and $40 \pm 2^\circ\text{C}$. The ionic strength of the solution was kept constant with background electrolyte, KNO_3 containing ambient concentration of 0.01 mol L^{-1} . The sorption was calculated by depletion of Cd concentration in equilibrium solution. The Cd sorption data were fitted into different equations and the thermodynamic parameters were calculated on the basis of sorption data. The thermodynamic parameters indicated that retention of Cd by soils was governed by spontaneous reaction as the value of ΔG° was negative for both untreated and treated soils. The spontaneity of the reaction of Cd^{2+} with soils increased with rise in temperature. The value of ΔH° are positive and negative indicating both exothermic and endothermic reactions are operating in retention of Cd by soils. The value of ΔS° decreased progressively with enrichment of soils with sludge at different levels. This may be due to decrease in randomness of the system as Cd^{2+} present in the solution phase shifted to adsorption phase.

Keywords: Cadmium, sewage sludge, sorption, free-energy change (ΔG°), enthalpy change (ΔH°), entropy change (ΔS°)

Introduction

Cadmium toxicity can be observed in minute concentration and highly mobile in the soil–plant system and availability in soil is mainly governed by various physio-chemical properties of the soil (Dutta *et al.*, 2020)^[1]. Suman *et al.* (2018)^[16] reported that the amount of Cd sorbed (x/m) by untreated and treated soils increased while, per cent of added Cd sorbed (X_{Ad}) and distribution coefficient (K_d) decreased with increasing Cd concentration in solution indicating that affinity of soils for Cd decreased with increasing Cd concentration in solution indicating that affinity of soils for Cd decreased with fractional surface coverage or increase in concentration of Cd in solution phase.

Thermodynamic principles have been used to characterize the exchange equilibria and metal retention on clay and soil surface which gives insight into the sorption process and its mechanism (Sposito, 1980)^[15]. The thermodynamic approach predicts the final state of a soil system from an initial non-equilibrium state. Evaluation of the free energy change corresponding to the transfer of cadmium from the bulk solution into the appropriate parts of the double layer or lattice helps to express the adsorption in a quantitative way. Free-energy change (ΔG°), accompanying an isothermal sorption process is determined by two contributions: one is enthalpy change (ΔH°) related to the chemical forces, the other is the entropy change (ΔS°), primarily related to the geometric freedom of the particles. However, studies on thermodynamic parameters for the adsorption of the cations and anions by soils have so far, been a neglected. Temperature is one of the most important environmental factors which influences the Cd sorption and it has been found that Cd sorption increased with increase in temperature (Echeverria, 2002)^[14]. Pandeya (1991)^[4] determined the thermodynamic parameters for iron fulvic acid (FA) complexes on fine soils at two temperatures. He reported that the adsorption of Fe-FA in soil surfaces seems to be a complex phenomenon involving physical and electrostatic forces.

The process is essentially spontaneous and endothermic. A large increase in entropy of the system on the formation of clay humus complex may involve release of water molecules from the surface of the adsorbent and partial dehydration of the fulvic acid macromolecules. Hundal *et al.* (2003) [13] studied cadmium adsorption by some alkaline soils of Punjab and found that the analogue shape of the linear Langmuir plot in each soils at 293 and 313 °K elucidated that temperature did not change the nature of reaction but influenced the bonding energy constant and adsorption maxima for Cd ion. They also found that the positive and constant value of differential isosteric heat of adsorption (ΔH) on each soil between 298 and 313°K indicate that adsorption of Cd is an endothermic process which leads to precipitation of Cd rather than physical adsorption. The kinetic and thermodynamic characteristics of cadmium adsorption on humic acid were studied by Li Guanglin *et al.* (2004) [12] using ion selective electrode and found that the increase of temperature resulted in a decrease in the cadmium adsorption amount on humic acid, suggesting a heat release reaction between humic acid and cadmium ions. The adsorption heat was pH relevant with an increased adsorption heat at higher medium pH. Deka *et al.* (1997) [8] reported that the standard free energy of Cd sorption (δG°) increased from -3.86 to -2.97 KJ/mol in the alkaline soil and decreased from 5.22 to 1.71 KJ/mol and 5.78 to 2.42 KJ/mol in alfisol and oxisol respectively on FYM treatment. The negative δG° in the alkaline soil suggested thermodynamic preferences for Cd over Ca and positive δG° in the acidic soils for Ca over Cd. Srivastav *et al.* (1999) [11] reported that values of ΔS° and ΔH° under neutral and acidic condition are negative indicating that nature of process being largely of adsorption at low pH. However, at high pH when the process becomes dominantly one of precipitation, both ΔS° and ΔH° are positive. Thus, the calculation of thermodynamic parameters also suggests that adsorption and precipitation are two main processes that determine the fate of the externally added Cd^{2+} ions in an aqueous system in presence of fine suspended soil particles. Chorom and Jafari (2003) [10] reported that with increase in temperature from 25 °C to 40 °C, cation exchange capacity decreases from 34.3 c.mol (P⁺) kg⁻¹ to 32.5 c.mol (P⁺) kg⁻¹. They also reported that Cd with an ionic radius of 0.97 Å, apparently does not migrate into lattice sites on thermal treatment and remains exchangeable. Adhikari and Rattan ((2002) [9] found that zinc sorption and the values of thermodynamic parameters like K^0 , ΔG° , ΔH° and ΔS° , increased at elevated temperature. They also found that the zinc sorption in the soil is endothermic and spontaneous.

Materials and Methods

Ten soils varying in clay, organic carbon and CaCO₃ content were used for sorption study. Each soil was treated with sewage sludge @ 25 and 50 g kg⁻¹ and incubated for 30 days at 25 ± 2 °C giving four wetting and drying cycles. These untreated and treated soils were used for Cd sorption. The Cd sorption was determined by equilibrating 2g of soils with 20 ml of CdCl₂ solution containing 5 to 750 μ mol Cd²⁺ L⁻¹ at 20 ± 2 and 40 ± 2 °C. The ionic strength of the solution was kept constant with background electrolyte, KNO₃ containing ambient concentration of 0.01 mol L⁻¹. The sorption was calculated by depletion of Cd concentration in equilibrium

solution. The Cd sorption data were fitted into different equations and the thermodynamic parameters were calculated on the basis of sorption data.

Thermodynamic Parameters of Cd sorption

On the basis of sorption data the following dynamic parameter were calculated.

Change in Free energy (ΔG°)

(a) ΔG° (Change in free energy at standard state)

$$\Delta G^\circ = -RT \ln K$$

Where,

R = Universal gas constant (8.314 Jmol⁻¹ K⁻¹)

T = Absolute temperature

ln K = Natural logarithm of equilibrium constant obtained from two surface Langmuir equation

(b) Change in enthalpy (ΔH°)

Change in enthalpy (ΔH°) was calculated by Clausius clapeyron's equation as follows

$$\Delta H^\circ = \frac{-RT_1T_2 (\ln k_1 - \ln k_2)}{T_1 - T_2}$$

Where,

R = Universal Gas constant (8.314 Jmol⁻¹ k⁻¹)

T₁ and T₂ are two absolute temperature of incubation and k₁ and k₂ are the corresponding equilibrium constants.

(c) Change of Entropy (ΔS°)

Change in the entropy of the system was calculated from the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Cadmium adsorption by soils was investigated at two temperature (20 and 40 °C) The thermodynamic parameters (ΔG° , ΔH° , ΔS°) of reaction of Cd²⁺ with soils at equilibrium state of reaction were calculated and are presented in Table 3.

Change in free energy (ΔG°)

The free energy change (ΔG°) due to adsorption of Cd by untreated and sludge treated soils is negative, suggesting that reaction was spontaneous. ΔG° values ranged from -29.34 to 38.05 KJ mol⁻¹ in region-I and -31.56 to -50.89 KJ mol⁻¹ in region-II at 20 °C while at 40 °C it varied from -18.51 to -21.49 in region-I and -20.25 to -22.68 KJ mol⁻¹ in region-II.

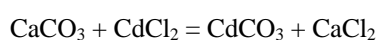
The free energy of adsorption is measure of how much the concentration of Cd²⁺ must diminish starting with activity ($a_{Cd^{2+}} = 1$) before reaching equilibrium. In all the soils, free energy of Cd adsorption become increasingly negative with rise in temperature. This suggests that spontaneity of process increases with rise in temperature. An increase in temperature favours the activation of ions in the solution to pass into an adsorbed phase (Pandeya, 1991) [4]. Levi-Minzi *et al.* (1976) [7] indicating that higher temperature increases the number of adsorption sites and reduces the bonding energy coefficient, apparently favouring the dissociation of adsorbent Cd complex. These result are also consistent with previous

findings of Kumar (2005) [5]. Enrichment of the soils with sewage sludge at different levels progressively increased the value of ΔG° (Table 1) may be due to increase in organic carbon of the soil which provide sites for Cd sorption. Deka *et al.* (1997) [8] reported that the standard free energy of Cd sorption (δG°) increased from -3.86 to -2.97 KJ/mol in the alkaline soil on FYM treatment. The present result supports the above findings. Relatively higher value of ΔG° in Repura soil (S₆) may be attributed to the fact that manifestation of higher organic carbon content of the soil. Similar findings was also reported by Adhikari and Rattan (2002) [9] in the study of Zn sorption by soils.

Change in enthalpy (ΔH°)

The change in enthalpy (ΔH°) is a measure of heat energy gained or lost in the transfer of Cd²⁺ from solution phase to site of adsorption. The value of ΔH° were both positive and negative in the soil system. The positive value of ΔH° of the reaction indicate the universal endothermic nature of reaction while its negative value indicates exothermic nature of reaction. In endothermic reaction, the energy consumed may be required for disruption of water film around the adsorbent, partial dehydration of adsorbent and lateral interaction between adsorbate and adsorbent (Pandeya, 1991) [4].

In contrast, in the present study, ΔH° is negative in the most of the soil indicating exothermic nature of reactions may be attributed to the fact that CaCO₃ is major components of calcareous soils and represents potential adsorptive surfaces for heavy toxic metals. The presence of carbonate minerals in soils directly affects its mobility and reactivity of heavy metal through surface interaction and indirectly through their effect on soil pH. The high affinity of calcite surface for cadmium was attributed to similarities between ionic radii of the Cd²⁺ (0.095 nm) and Ca²⁺ (0.100 nm) (McBride, 1980) [6]. Thus, the mechanism involved in the chemisorption of Cd on calcite surface is the exchange reaction between Ca²⁺ and Cd²⁺ owing to their similar ionic radii.



Thus, it is reasonable to expect that heat is released during chemical reaction due to ease of replacement of Ca²⁺ by Cd²⁺ in calcareous soils. Therefore, reaction is exothermic. Jurinak and Bauer, (1956) [2] also reported that adsorption of zinc on calcite is exothermic. The positive and negative value of ΔH° in Cd sorption by soils were also reported by Singh (1989) [3]. The result further indicated that Cd²⁺ adsorption by soil at a surface may have either a positive or negative heat of adsorption (ΔH°) indicating both endothermic and exothermic reactions are operating in retention of Cd by soils.

Change in entropy (ΔS°)

The driving force for spontaneous reaction is decrease in free energy which is composed of enthalpy and entropy contribution according to the relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Change in entropy of a system, ΔS° is sensitive to any structural changes that may occur in a system and can be regarded as a measure of the order or disorder produced in a systems during a given reaction. The positive value of ΔS° recorded in present investigation indicate that stability of sorption of cadmium in soils system. Higher ΔS° value are indicative of more disorderness in the adsorption process. The value of ΔS° decreased progressively with increasing temperature and enrichment of soils with sludge at different levels, respectively. This may be due to decrease in randomness of the system as Cd²⁺ present in the solution phase shifted to adsorbed phase. As expected, standard entropy of adsorption in the calcareous soils, CaCO₃ system showing positive entropy change indicating that the Cd²⁺ is actually incorporated onto crystal lattice of CaCO₃. The exothermic and endothermic adsorption in the present study, occurred spontaneously as suggested by their respective negative free energy change. It is well supported by favourable entropy values which are of sufficient magnitude to produce necessary negative free energy change. The results are in agreement with the findings of various workers (Jurinak and Bauer, 1956; Singh 1989; Pandeya, 1991 and Kumar, 2005) [2, 3, 4, 5].

Table 1: Initial physico-chemical properties of soils

Soils	Pusa	Patepur	Kalyanpur	Malinagar	Karua	Repura	Jatmalpur	Ladaura	Berheta	Gorai
Properties	(S ₁)	(S ₂)	(S ₃)	(S ₄)	(S ₅)	(S ₆)	(S ₇)	(S ₈)	(S ₉)	(S ₁₀)
pH	8.01	8.15	8.20	8.16	8.25	8.12	7.95	8.20	8.28	8.08
EC (dSm ⁻¹)	0.35	0.28	0.24	0.25	0.15	0.70	0.22	0.46	0.17	0.16
Organic Carbon (g kg ⁻¹)	4.80	7.35	6.75	8.10	4.95	12.60	9.01	6.95	6.61	3.15
CaCO ₃ (g kg ⁻¹)	345	370	295	225	425	410	35	420	80	300
CEC [c mol (P ⁺) kg ⁻¹]	10.35	15.38	17.28	21.04	10.69	22.20	17.20	19.25	14.42	9.82
Sand (%)	51.40	46.44	45.81	48.02	45.86	33.00	45.21	30.72	45.80	58.91
Silt (%)	38.02	40.20	33.82	25.30	43.51	47.80	35.82	44.20	39.92	31.90
Clay (%)	10.52	13.30	20.26	26.62	10.59	19.15	18.90	25.30	14.21	9.12
Texture	Loam	Loam	Loam	Sandy clay loam	Loam	Loam	Loam	Loam	Loam	Sandy loam
DTPA extractable Cd (mg kg ⁻¹)	0.07	0.05	0.06	0.08	0.05	0.09	0.07	0.08	0.06	0.04

Table 2: Physico-chemical properties of sludge enriched soils

Soils Properties	Pusa	Patepur	Kalyanpur	Malinagar	Karua	Repura	Jatmalpur	Ladaura	Berheta	Gorai
	(S ₁)	(S ₂)	(S ₃)	(S ₄)	(S ₅)	(S ₆)	(S ₇)	(S ₈)	(S ₉)	(S ₁₀)
Sludge application @ 25 g kg⁻¹										
pH	7.85	8.03	8.05	7.92	7.93	7.81	7.87	7.93	8.08	7.89
EC (dSm ⁻¹)	0.45	0.51	0.43	0.43	0.35	0.81	0.45	0.77	0.42	0.37
Organic Carbon (g kg ⁻¹)	7.15	10.50	8.81	10.20	7.20	14.06	11.20	8.70	8.40	5.41
CEC [c mol (P ⁺) kg ⁻¹]	10.85	15.72	17.97	21.87	10.98	22.87	17.87	20.06	15.03	10.32
DTPA extractable Cd (mg kg ⁻¹)	0.12	0.08	0.12	0.09	0.09	0.12	0.10	0.09	0.11	0.10
Sludge application @ 50 g kg⁻¹										
pH	7.77	7.85	7.88	7.72	7.75	7.71	7.69	7.86	7.87	7.75
EC (dSm ⁻¹)	0.62	0.59	0.66	0.71	0.58	0.93	0.65	0.81	0.64	0.66
Organic Carbon (g kg ⁻¹)	8.26	12.10	9.80	11.30	8.10	15.41	11.80	10.10	9.20	6.72
CEC [c mol (P ⁺) kg ⁻¹]	11.05	16.03	18.32	22.20	11.12	23.14	18.15	20.41	15.36	10.48
DTPA extractable Cd (mg kg ⁻¹)	0.14	0.13	0.11	0.14	0.11	0.13	0.12	0.10	0.14	0.10

Table 3: Thermodynamic parameters (ΔG° , ΔH° , ΔS°) of cadmium sorption in sludge treated calcareous soils

		ΔG° (KJ mol ⁻¹ at 20 °C)		ΔG° (KJ mol ⁻¹ at 40 °C)		ΔH° (KJ mol ⁻¹)		ΔS° (KJ mol ⁻¹)
		I	II	I	II	I	II	
S ₁	1	-34.67	-19.66	-37.98	-21.10	7.09	1.40	3.44
	2	-33.77	-19.58	-35.90	-21.08	-2.63	2.38	2.65
	3	-33.70	-19.50	-36.22	-20.79	-5.73	-0.51	2.40
S ₂	1	-38.05	-21.27	-40.61	-22.55	-0.63	-2.48	2.87
	2	-37.61	-21.06	-39.79	-22.50	-5.58	-0.07	2.55
	3	-36.49	-20.93	-38.75	-22.41	-3.36	0.78	2.74
S ₃	1	-37.15	-21.39	-41.45	-22.60	25.83	-3.56	4.04
	2	-36.96	-21.19	-37.83	-22.39	-24.23	-3.53	1.52
	3	-34.83	-20.93	-36.13	-22.13	-14.62	-3.39	1.89
S ₄	1	-34.75	-20.84	-36.38	-22.12	-10.89	-2.11	2.13
	2	-33.84	-20.79	-35.92	-22.07	-3.32	-2.07	2.46
	3	-33.08	-20.54	-35.62	-21.77	4.11	-2.57	2.76
S ₅	1	-37.00	-21.19	-41.33	-22.60	26.38	0.51	4.25
	2	-36.83	-21.02	-39.31	-22.45	-5.20	-0.07	2.86
	3	-36.64	-20.79	-38.77	-22.34	-5.38	1.81	2.78
S ₆	1	-34.99	-20.89	-36.82	-22.20	-8.34	-1.62	2.38
	2	-33.91	-20.54	-34.43	-21.60	-26.22	-5.04	1.16
	3	-32.95	-20.20	-34.28	-21.13	-13.45	-6.65	1.65
S ₇	1	-36.91	-21.42	-50.89	-22.68	0.10	-3.04	2.77
	2	-34.89	-21.31	-38.42	-22.45	16.81	-4.56	3.42
	3	-33.84	-20.84	-35.37	-22.37	-11.39	1.51	2.15
S ₈	1	-36.75	-21.02	-38.35	-22.39	-13.43	-1.04	2.22
	2	-35.15	-20.89	-37.31	-22.21	-3.45	-1.47	2.62
	3	-33.95	-20.75	-35.72	-21.86	-8.05	-4.44	2.19
S ₉	1	-37.69	-21.49	-41.67	-22.73	20.63	-3.34	3.82
	2	-37.01	-21.23	-38.98	-22.55	-8.22	-1.86	2.41
	3	-35.18	-21.02	-37.29	-22.23	-4.31	-3.34	2.43
S ₁₀	1	-34.12	-19.06	-36.08	-20.92	-5.41	8.20	2.80
	2	-30.34	-18.96	-33.13	-20.46	10.55	3.05	2.09
	3	-29.34	-18.51	-31.56	-20.25	1.90	6.95	2.79

1 = Untreated Soil 2 = Sludge treated soil @ 25 g kg⁻¹3 = Sludge treated soil @ 50 g kg⁻¹**References**

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