

Thermodynamics of Manganese Adsorption on Some Soils

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Adsorption reactions are of utmost importance to understand the availability of nutrients to the plants. The thermodynamic parameters (ΔG° , ΔH° and ΔS°) of the adsorption of manganese on six soils were calculated at two temperatures, *i.e.*, 25 and 35°C. The adsorption data, fitted into the linear form of the Langmuir equation, made it possible to evaluate the adsorption maxima and binding energy. The values of ΔG° , ΔH° and ΔS° were found to be negative in all the soils indicating the exothermic and spontaneous nature of the adsorption reaction.

Key Words: Mn adsorption, Thermodynamic parameters (ΔG° , ΔH° and ΔS°), Soils.

INTRODUCTION

Surface chemistry plays a significant role in agriculture. Manganese is the essential micronutrient required by the plants for their normal functioning. The adsorption and desorption mechanisms of micronutrients in the soils control the availability of these micronutrients to the plants and hence affect the growth of plants. The most important processes affecting the behaviour and bioavailability of micronutrients in soils are those concerned with the adsorption of these ions from liquid phase on the solid phase. The various species present in the soil solution are involved in the different reactions taking place in the soil and soil-plant root system like adsorption-desorption reactions, surface chemical bonding, ligand exchange, coordinate bonding through polyvalent metal ion bridging and weak physical bonding through van der Waals forces¹⁻³. The thermodynamic approach predicts the final state of a soil system from an initial non-equilibrium state⁴. However, there is lack of thermodynamic data in the literature on surface reactions of micronutrients in soils. An attempt was made to study the adsorption behaviour of manganese, one of the essential micronutrients, on soils varying in physical and chemical characteristics. The objectives of the present investigation were:

- (1) To obtain the adsorption parameters of Mn on soils.
- (2) To evaluate changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) during the interaction of Mn with soils.

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EXPERIMENTAL

Six surface soil samples (0–15 cm) from benchmark soils series were used in the present investigation. Their site of collection, physical and chemical characteristics along with their classification are presented in Table-1. The soil samples after drying in air were crushed and passed through 2-mm sieve. The samples were stored in sealed containers.

TABLE-1
CLASSIFICATION AND PHYSICAL AND CHEMICAL CHARACTERISTICS
OF SOIL SAMPLES

Soil	Classification	Sand Silt Clay			Texture	pH*	EC			
		(dS m ⁻¹)					CaCO ₃	OC	CEC	(cmol kg ⁻¹)
Dasuya (S ₁)	Typic ustifluvent	54.9	36.6	8.5	sl	8.54	0.17	0.90	0.21	5.65
Gahri Bhagi (S ₂)	Typic ustochreptic camborthids	51.2	32.2	16.6	1	8.20	0.24	1.45	0.39	7.05
Kanjli (S ₃)	Typic Ustochrept	62.5	23.3	14.2	sl	8.50	0.28	1.80	0.66	7.91
Lahulspiti (S ₄)	Typic Udorthents	45.8	42.4	11.8	1	6.46	0.24	nil	0.99	12.60
Dalhousie (S ₅)	Typic Udorthents	36.6	32.1	31.6	cl	4.90	0.60	nil	0.45	16.15
Sirmour (S ₆)	Typic Udorthents	78.9	2.8	18.3	sl	5.70	0.07	nil	0.62	12.80

*1 : 2 soil : water suspension.

The adsorption of manganese was studied by equilibrating 1 g of each of the soil containing graded levels of Mn ranging from 0–250 µg mL⁻¹ in the form of MnSO₄. A preliminary experiment was performed and it was observed that equilibrium was attained in less than 24 h. The aliquots of the stock solution of Mn (250 µg mL⁻¹) were added in different reagent bottles so that the concentration of Mn in these ranged from 500–5000 µg). The volume was made to 20 mL by adding double distilled water. These reagent bottles along with contents were incubated at the desired temperature (25 or 35°C) with frequent shaking for 24 h. After equilibration, different suspensions were centrifuged and the supernatant solution was filtered off. The amount of Mn in the extract was determined volumetrically using EDTA method⁵. The amount of Mn adsorbed was determined from the difference in the initial concentration of Mn and the concentration in the equilibrium solution. The data obtained for Mn adsorption at two temperatures were fitted to the following form of the Langmuir adsorption isotherm:

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b}$$

where C = concentration of Mn in the equilibrium solution

x/m = amount of Mn adsorbed per unit weight of adsorbent

K = constant related to equilibrium constant or bonding energy

b = adsorption maximum

The change in Gibbs free energy (ΔG°) was calculated as^{6, 7}:

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

where K is constant obtained from the Langmuir equation

The standard change in enthalpy (ΔH°) was calculated from the K values at 25 and 35°C by using the Vant Hoff equation (the integrated form)

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The standard change in entropy (ΔS°) was calculated from the equation

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

RESULTS AND DISCUSSION

The adsorption data for Mn on the soils at both the temperatures conformed to the linear form of Langmuir equation. The values of bonding energy constant (K), adsorption maxima (b) and coefficients of determination of regression equations for the Langmuir plot are given in Table-2. The Langmuir adsorption isotherm plot of one of the representative soils is depicted in Fig. 1. The binding energy values (K) decreased with the increase in temperature whereas the adsorption maxima (b) values increased with increase in temperature in all the soils. The binding energy values were higher for soils S₄, S₅ and S₆ which may be attributed to the combined effect of high organic matter and high clay content of these soils. The high K values reveal that manganese adsorbed is retained at sites having high affinity. The reciprocal relation seems to exist between b and K values in S₄, S₅ and S₆ soils.

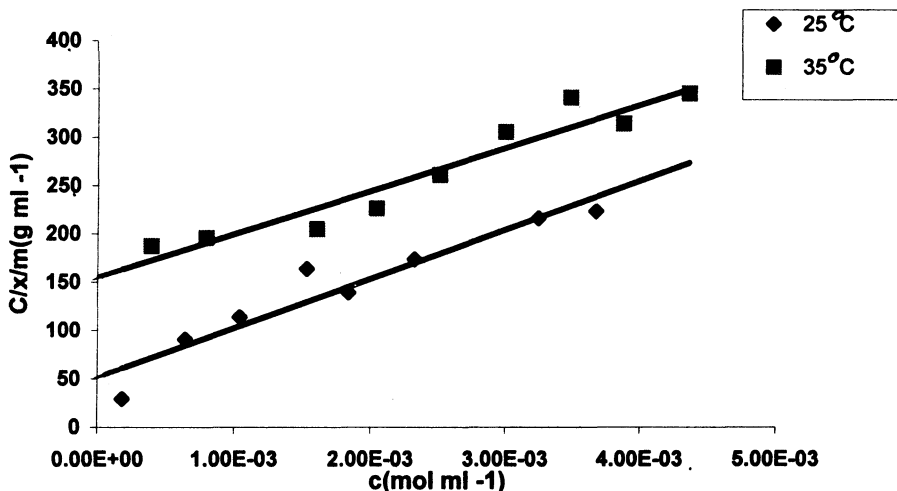


Fig. 1. The Langmuir isotherm for manganese adsorption on S₅ soil at 25° and 35°C

TABLE-2
VALUES OF LANGMUIR CONSTANTS (K AND b) AND CORRELATION COEFFICIENT (r) FOR MANGANESE ADSORPTION BY DIFFERENT SOILS AT 25 AND 35°C

Soil	$K \times 10^{-5} (\text{mL g}^{-1})$		$b \times 10^5 (\mu\text{g g}^{-1})$		r	
	25°C	35°C	25°C	35°C	25°C	35°C
S ₁	2.35	0.62	3.65	8.37	0.74	NS
S ₂	0.82	0.53	0.14	0.14	0.72	0.62
S ₃	3.95	0.89	3.96	6.39	0.92	0.74
S ₄	11.41	6.88	1.82	1.99	0.98	0.95
S ₅	9.89	2.87	1.97	2.24	0.95	0.95
S ₆	6.16	2.35	2.34	3.35	0.93	0.87

The data of adsorption of Mn on soils were used to calculate the thermodynamic parameters, viz., standard free energy change (ΔG°), change in standard enthalpy (ΔH°) and change in standard entropy (ΔS°). The values of ΔG° , ΔH° and ΔS° are given in Table-3. The standard free energy change due to adsorption of Mn by soils is negative revealing the spontaneous nature of reaction. Decrease in free energy change ($-\Delta G^\circ$) gives a measure of decrease of concentration of the adsorbate in the solution phase and exhibits the change in free energy involved in the transformation of Mn from free state to adsorbed state. The standard free energy change values ($-\Delta G^\circ$) are relatively higher in S₄, S₅ and S₆ soils. The higher values of ΔG° may be attributed to the combined effect of high clay content, high OC and low pH of these soils as compared to that of other soils.

The standard enthalpy change of adsorption (ΔH°) which is a measure of the heat of adsorption involved in passing Mn from solution phase to adsorbed state gave negative values in all the soils (Table-3). So adsorption of manganese in all the soils is an exothermic reaction. Higher value of ($-\Delta H^\circ$) in S₁ and S₃ soils imply the involvement of strong forces in the adsorption of manganese in these soils.

TABLE-3
VALUES OF ΔG° , ΔH° AND ΔS° ASSOCIATED WITH THE ADSORPTION OF MANGANESE BY SOILS

Soil	$-\Delta G^\circ (\text{kJ mol}^{-1})$		$-\Delta H^\circ (\text{kJ mol}^{-1})$	$-\Delta S^\circ (\text{J mole}^{-1} \text{ per degree})$
	25°C	35°C		
S ₁	30.65	28.27	101.50	237.70
S ₂	28.05	27.84	34.30	21.11
S ₃	31.94	29.17	114.50	286.17
S ₄	34.56	34.42	38.92	15.10
S ₅	34.19	32.19	93.92	200.00
S ₆	33.03	31.68	73.34	135.00

The change in the entropy of a system (ΔS°) is sensitive to any structural change that occurs in a system and is a measure of the order or disorder produced in a system during a given reaction. The standard entropy change (ΔS°) is negative in all the soils. The adsorption of manganese from solution produces more order in a given system as the random motion of the ionic species in solution is subjected to the restraining forces of the surface causing a decrease in entropy change. This justifies the negative values of ΔS° . The negative values of the entropy change are indicative of the stability of the adsorption complexes formed. Adsorption results in the loss of degrees of freedom producing negative entropy effects. The higher value of entropy change of Mn adsorption in S_3 suggests that Mn is incorporated to a greater extent in the crystal lattice of clay in this soil as compared to that of other soils.

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