Studies on Adsorption of Manganese by Soils in the Presence of Electrolyte (Na_2SO_4)

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Adsorption of manganese in the presence of Na_2SO_4 has been studied on nine soil samples from Punjab (S_1 to S_6) and Himachal Pradesh (S_7 to S_9) at 25° and 35°C. Adsorption of manganese increases with increase in concentration of adsorbate; adsorption isotherms being L-shaped. The adsorption of manganese decreases with increase in temperature. The averaged values of partial molar free enegy change ($\Delta\overline{G}$) and apparent heats of adsorption ΔH have been calculated. The data conform to the Freundlich and the Langmuir equations.

INTRODUCTION

Scientific interest in manganese in soils is primarily related to its role in plants. Widespread deficiency of manganese has been reported in arid and semi-arid tracts of Punjab in north-west India[1]. In India, the deficiency of Mn has been observed in coarse-textured, calcareous soils low in organic carbon and high in pH[2]. The availability of manganese to the plants depends upon a number of factors which are influenced directly or indirectly by adsorption-desorption processes. The present investigation, therefore, was intended to study the adsorption of manganese in the presence of electrolyte (Na_2SO_4).

EXPERIMENTAL

Surface soil samples (0–15 cm) from nine benchmark soil series *i.e.* six from Punjab (designated as S_1, S_2, S_3, S_4, S_5 and S_6) and three from Himachal Pradesh (designated as S_7, S_8 and S_9) were collected. Their place of collection and physico-chemical characteristics have been presented in Table 1. A preliminary experiment was performed and it was seen that equilibrium was achieved after 20 h. Adsorption of manganese was studied by equilibrating 1 g of soil sample with 20 mL of solution for 24 h at 25° and 35°C containing known amounts of Mn as $MnSO_4$ ranging from 550–5500 μg in 0.01 M Na_2SO_4 with frequent shaking. The suspensions were centrifuged and the supernatant solution was filtered off. Manganese in the filtrate was estimated volumetrically using EDTA method[3]. The difference between amount of manganese added initially and that in solution after equilibrium was taken as amount of Mn adsorbed by the soil sample.

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RESULTS AND DISCUSSON

It is evident from the data obtained for Mn adsorption that manganese is adsorbed by all the soils used in the present investigation. The amounts of manganese adsorbed, μg per g of soil at 25° and 35°C are plotted against equilibrium concentration (Fig. 1) to understand the effect of concentration and temepraturee on adsorption. The adsorption isotherms provide evidence that the adsorption of manganese increases with the increase in concentration of the adsorbate. The adsorption isotherms are of L-shape[4] for all the soils at both the temperatures, *i.e.*, 25° and 35°C. These isotherms reveal that the adsorbed molecules are most likely to be adsorbed flat or they suffer little solvent competition.

Adsorption capacity of each soil towards manganese is different. Soils of Punjab are showing relatively greater adsorption capacity as compared to that of soils of Himachal Pradesh. The order of adsorption in the soils of Punjab at 35°C is $S_4 > S_6 > S_3 > S_5 > S_2 > S_1$ at higher concentrations. This order of adsorption appears to be due to the combined effect of clay content and calcium carbonate content of these soils. The order of extent of adsorption in the case of soils of Himachal Pradesh at 35°C is $S_8 > S_7 > S_9$ at equilibrium concentration > 5 μg mL^{-1}.

On comparing the data of manganese adsorption from aqueous solution with that of manganese adsorption in the presence of Na_2SO_4 (Fig. 2), it is evident that adsorption of manganese increases in the presence of Na_2SO_4. Increase in adsorption may be attributed to the dispersion behaviour of sodium ions towards soils. When sodium ions become prominent on the exchange complex, they result in the dispersed condition of the soil colloids[5]. Thus it appears that presence of Na_2SO_4 causes the dispersion of soil to a greater extent generating more adsorption sites for manganese.

The partial molar free energy change ($\Delta\overline{G}$) which results due to adsorption is highly useful to know the extent of adsorption process. Average values of partial molar free energy change ($\Delta\overline{G}$) for manganese adsorption in the presence of Na_2SO_4 have been evaluated using the following relationship:

$$\Delta\overline{G} = -RT \ln \frac{C_0}{C}$$

where C is the equilibrium concentration and C_0 is the initial concentration of the adsorbate. The average values of $\Delta\overline{G}$ have been recorded in Table-2. The average value of $\Delta\overline{G}$ is maximum for S_4 and minimum for S_2 at 25°C. The highest value of $\Delta\overline{G}$ for S_4 indicates the involvement of greater driving force in the adsorption of manganese in this soil.

Temperature plays a significant role in adsorption as this process is exothermic in nature. Amount of manganese adsorbed on all the soils decreases with increase in temperature (Fig. 1). The values of apparent heats of adsorption (ΔH) have been calculated in the manner as suggested by Giles *et al.*[6] The magnitude of the

TABLE-1
LOCATION, CLASSIFICATION AND PHYSICO-CHEMICAL CHARACTERISTICS OF SOILS

Location	Soil classification	Sand	Silt	Clay	Texture	pH*	EC* mmhos cm^{-1}	O.C.	$CaCO_3$	CEC cmol kg^{-1}	Total Mn mg kg^{-1}
		—%—						—%—			
PAU Farm, Ludhiana (S_1)	Typic Ustipsamments	85.0	7.4	7.6	ls	7.58	0.13	0.21	Nil	3.82	352
Dhar, Gurdaspur (S_2)	Typic Eutrochrepts	74.8	15.7	9.5	sl	7.83	0.24	0.20	Nil	5.65	863
Dasuya, Hoshiarpur (S_3)	Typic Ustifluvents	54.9	36.6	8.5	sl	8.54	0.17	0.21	0.90	5.65	368
Gahri Bhagi, Bhatinda (S_4)	Typic Ustochreptic Camborthids	51.2	32.2	16.6	l	8.20	0.24	0.39	1.45	7.05	412
Naura, Jalandhar (S_5)	Typic Haplustalfs	53.5	34.7	11.8	sl	8.61	0.22	0.53	0.55	6.52	560
Kanjli, Kapurthala (S_6)	Typic Ustochrepts	62.5	23.3	14.2	sl	8.50	0.28	0.66	1.80	7.91	683
Kukumseri, Lahulspiti (S_7)	Typic Udorthents	45.8	42.4	11.8	l	6.46	0.24	0.99	Nil	12.60	662
Dalhousie, Dalhousie (S_8)	Typic Udorthents	36.3	32.1	31.6	cl	4.90	0.60	0.45	Nil	16.15	865
Rohali, Sirmour (S_9)	Typic Udorthents	78.9	2.8	18.3	sl	5.70	0.07	0.62	Nil	12.80	552

*1 : 2 soil : water suspension.

values of ΔH is low (*i.e.* < 40 kJ mol^{-1}) in most of the soils indicating involvement of weak forces in the adsorption of manganese.

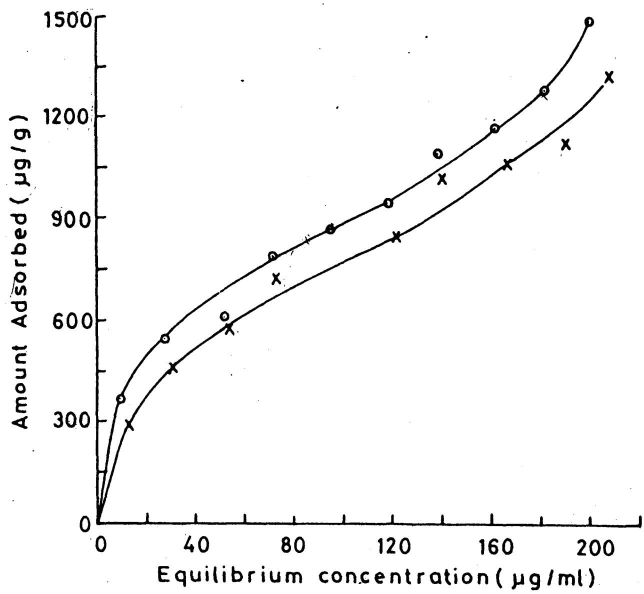

Fig. 1 Adsorption isotherms for manganese on rohali soil (Sg) in the presence of Na_2SO_4 at 25° ⊙——⊙ and 35°C ×——×

TABLE-2
AVERAGED $\Delta\bar{G}$ (PARTIAL MOLAR FREE ENERGY CHANGE) VALUES FOR MANGANESE ADSORPTION BY SOILS IN THE PRESENCE OF Na_2SO_4 AT 25°C

Soil	$-\Delta\bar{G}$ (J mol^{-1})
S_1	916.8
S_2	872.1
S_3	1229.2
S_4	1414.3
S_5	1075.3
S_6	1368.3
S_7	1209.9
S_8	1212.9
S_9	1176.1

The data obtained for the adsorption of Mn at 25° and 35°C were fitted to the Freundlich equation ($x/m = KC^{1/n}$). The data conform to the Freundlich equation. The values of K and n at 25°C have been recorded in Table-3. The values of n which represent the degree of non-linearity of adsorption are greater than unity indicating L-type of isotherms. The value of K corresponds to the adsorption

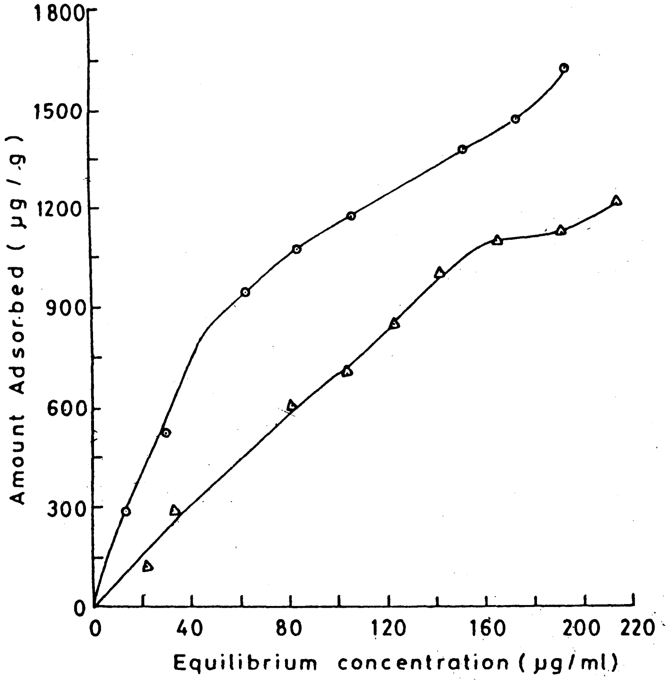

Fig. 2 Adsorption isotherms for manganese on gahri bhagi soil (S_4) at 35°C with Na_2SO_4 O——O ; without Na_2SO_4 Δ——Δ

capacity at unit equilibrium concentration. The value of K is maximum for S_9 and minimum for S_2 at 25°C.

TABLE-3

THE VALUES OF FREUNDLICH CONSTANTS (K AND n), LANGMUIR CONSTANTS (K AND b) AND CORRELATION COEFFICENT (r) FOR MANGANESE ADSORPTION BY DIFFERENT SOILS IN THE PRESENCE OF Na_2SO_4 AT 25°C

Soil	Freundlich constants			Langmuir constants		
	k	n	r	$K \times 10^{-3}$ (mL g^{-1})	$b \times 10^{-3}$ (µg g^{-1})	r
S_1	34.90	1.44	0.99	4.80	2.70	0.88
S_2	15.77	1.17	0.87	25.00	1.33	0.91
S_3	83.37	1.79.	0.97	12.90	2.04	0.98
S_4	105.19	1.85	0.98	13.40	2.34	0.97
S_5	44.77	1.49	0.91	6.39	2.56	0.84
S_6	46.20	1.37	0.99	3.90	4.72	0.84
S_7	121.81	2.11	0.97	11.00	2.04	0.88
S_8	73.45	1.73	0.98	12.10	2.00	0.97
S_9	130.30	2.33	0.97	13.90	1.75	0.94

The data obtained have also been tested in terms of the Langmuir equation (C/X/m = C/b + 1/Kb) where b is the adsorption maxima and K is a constant related to binding energy. The data conform to the Langmuir equation at both the temperatures in the case of all the soils and the values of K and b at 25°C have been recorded in Table-3. The value of K is maximum for S_2 suggesting the highest binding energy for manganese with this soil. S_6 has the highest adsorption maxima value while S_2 has the minimum adsorption maxima value.

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