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Boron Adsorption on Benchmark Soils of Punjab

HARSH ARORA*, S.S. BHARDWAJ and B.D. SHARMA†
Department of Biochemistry and Chemistry
Punjab Agricultural University, Ludhiana-141 004, India

The adsorption reactions of boron in soils strongly influence the release and fixation of applied boron and, thus, decide the efficiency of boron fertilization. Adsorption behaviour of B was investigated for six soil series of Punjab varying in physical and chemical characteristics. Results reveal that, in general, the adsorption of B increased with increase in concentration of boron and decreased with increase in temperature. Adsorption data for boron fitted well to the Freundlich isotherm and K values were positively correlated with clay and calcium carbonate content and negatively correlated with electrical conductivity and organic carbon content of the soil. Boron adsorption data also fitted well to the Langmuir equation. The values of distribution coefficient K_d, partial molar free energy ($\overline{\Delta G}$) change and supply parameter were also calculated.

Key Words: **Boron, Adsorption, Soils, Punjab.**

INTRODUCTION

Boron is one of the essential micronutrients required for the normal growth of plants. Deficiency of boron is the most widespread in a variety of plant species throughout the world[1]. The concentration range between plant deficiency and toxicity is narrow. Both deficient and toxic levels of boron can be encountered by a crop in a single growing season . On the other hand, boron is toxic to many plant species in soil solutions at concentrations only slightly greater than the optimal concentrations[3]. An equilibrium exists between boron in solid and liquid phases[4]. Sorption sites in soil may act as a source or sink for soil solution boron, depending on the changes in concentration in the soil solution and on the soil affinity. Since plants respond only to the boron activity in soil solution, the boron sorption capacity of the soil is an important sink for attenuating phytotoxic concentrations of boron in irrigation water[5]. The amount of boron sorbed by soils varies greatly with changes in important factors determining the release and fixation of applied boron and thus deciding the efficiency of boron fertilization. Therefore it is necessary to understand the mechanism of boron adsorption on soil materials. Hence, the present investigation was undertaken to study boron adsorption in some benchmark soils of Punjab.

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†Department of Soils, Panjab Agricultural University, Ludhiana-141 004, India.

EXPERIMENTAL

Boron adsorption was studied on six soil series varying in physical and chemical characteristics. Soil samples from Ap horizon representing three agro-climatic zones comprising the major soil series of Punjab were collected. The sites of collection, as well as the physical and chemical characteristics and the USDA classification of the studied soils are given in Table-1. The samples were air dried and passed through 2.0 mm sieve. Electrical conductance and pH of the soils in 1 : 2 soil : water suspensions were determined with a solubridge and a glass-electrode pH-meter. Samples were analyzed for cation exchange capacity, organic carbon and particle size distribution by following the standard procedures[6]. Calcium carbonate equivalent was determined by the rapid titration method[7]. For the extraction of total boron, a modified procedure developed by Gupta[8] was followed.

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})
		(%)						(%)		
Gurdaspur	Typic Haplustalfs	56.2	27.2	16.6	l	7.50	0.32	Nil	0.40	10.32
Naura	Typic Haplustalf	23.0	58.7	18.3	sl	8.16	0.35	11.5	0.40	10.52
Bhanger	Natraquic Ustochrept	79.6	10.4	10.0	sl	9.29	0.56	4.1	0.24	5.53
Kaoni	Natric Ustochrep	83.6	2.4	14.0	sl	9.00	0.35	1.9	0.41	8.10
Chamror	Typic Dystochrept	42.0	43.4	14.6	l	7.13	0.37	Nil	0.92	8.30
Dhar	Typic Eutrochrept	46.8	42.0	11.2	l	7.40	0.29	0.5	0.60	7.60

*1 : 2 soil : water suspension

Adsorption studies

A preliminary experiment was performed and it was observed that equilibrium was achieved within 48 h. 1 g of each of the soil samples was equilibrated with 10 mL of solution containing graded amount of boron ranging from 0 to 50 μg mL^{-1} in the form of H_3BO_3 for 48 h at 25 and 35°C with frequent shaking. After equilibrium the samples were centrifuged, the supernatant solution was filtered and analyzed for boron concentration spectrophotometrically using azomethine-H method[9]. The amount of boron adsorbed was determined from the difference between the amount of boron added initially and that which remained in the equilibrium solution.

Modeling

Data pertaining to adsorption of boron were fitted to the Langmuir equation as follows:

$$\frac{C}{x/m} = \frac{C}{b} + \frac{1}{Kb} \qquad \text{(i)}$$

where 'x/m' is the amount of boron adsorbed ($\mu g\ g^{-1}$ of soil), 'C' is the equilibrium concentration of boron, 'K' is the binding energy constant and 'b' is the adsorption maxima. From a linear plot of C/(x/m) *vs.* C, adsorption maxima was calculated as the inverse of the slope and the constant related to bonding energy was determined as slope/intercept.

Boron adsorption data were also fitted to the following form of the Freundlich equation:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C \qquad \text{(ii)}$$

where 'x/m' is the amount of boron adsorbed ($\mu g\ g^{-1}$ of soil), 'C' is the equilibrium concentration of boron, 'K' and '1/n' are Freundlich constants. Plot of log x/m *vs.* log C turns out to be a straight line with slope 1/n and intercept log K. Values for K represent the amount of boron adsorbed at unit equilibrium concentration and 1/n indicates the degree of linearity between solution equilibrium concentration and adsorption[10].

Calculation of the distribution coefficient (K_d)

The values of distribution coefficient (K_d) for the adsorption of boron at 25° and 35°C have been calculated as:

$$K_d\ (mL/g) = \frac{x}{m}\ ((\mu g\ g^{-1})/C\ (\mu g\ mL^{-1}))$$

Evaluation of partial molar free energy change ($\overline{\Delta G}$)

The change in partial molar free energy ($\overline{\Delta G}$) of a system has been evaluated using the following thermodynamic relationship[11]:

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

where R is molar gas constant, T is absolute temperature, C is the equilibrium concentration and C_0 is the initial concentration of boron.

RESULTS AND DISCUSSION

Boron adsorption by soils

The data obtained for boron adsorption were used to develop sorption isotherms of different soils at two different temperatures (Fig. 1). Results reveal that irrespective of the soil, increasing amounts of boron were adsorbed with increasing concentration of boron in the equilibrium solution at both the temperatures. The adsorption isotherms were of similar nature, *i.e.*, L-shaped[12], suggesting thereby that similar mechanism for boron retention is operative in all the soils under study. The initial curvature of L-shaped isotherms indicates that as more sites in the substrate are filled, then bombarding solute molecules face greater difficulty to find a vacant site available. This leads to a suggestion that either the adsorbed molecule is not vertically oriented or that there is no strong competition from the solvent[12, 13]. While comparing the adsorption capacity of all the six soils, it is observed that it is different for each soil. The data obtained for boron adsorption at 25°C reveal that the highest amount of boron is adsorbed in Naura soil followed by Gurdaspur, Kaoni, Chamror, Bhanger and Dhar soils. At 35°C maximum amount of boron is also adsorbed by Naura soil, followed by Gurdaspur, Chamror, Kaoni, Bhanger and Dhar soils. Adsorption behavior of these soils can be explained on the basis of their physical and chemical characteristics (Table-1). The adsorption of boron in these soils is positively and significantly correlated with clay content ($r = 0.82$ to 0.92) and CEC ($r = 0.71$ to 0.90) of these soils. The amount of adsorbed boron is dependent on soil texture and increases with increasing clay content. Several workers reported that adsorbed boron was significantly positively correlated with per cent clay for ten new Mexico soils[14, 15]. The adsorption of boron in these soils was not significantly correlated with $CaCO_3$ content.

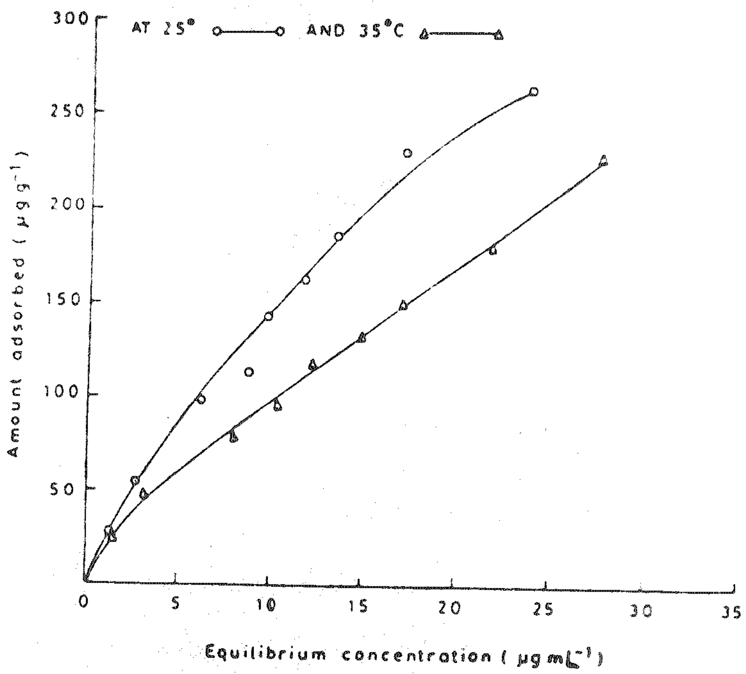

Fig. 1. The adsorption isotherms for boron on Gurdaspur soil at 25 and 35°C

Boron adsorption in terms of theoretical adsorption isotherms

(a) Langmuir Adsorption Equation: In general, the Langmuir plots of $C/(x/m)$ *vs.* C yielded a good straight line ($r = 0.70$ to 0.95) in all the soils at both the temperatures (Fig. 2). The values of Langmuir constant K decreased with increase in temperature. The highest value of K was obtained for Naura soil and the lowest for Dhar soil at 25°C . The values of K are positively correlated with clay content and CEC of the soil. Results suggest that sorbed boron was mainly held on the surface of clay minerals in soils. The adsorption maxima b value is the highest for Dhar soil and the lowest for Bhanger soil at 25°C but b values do not show any correlation with physical and chemical properties of the soils.

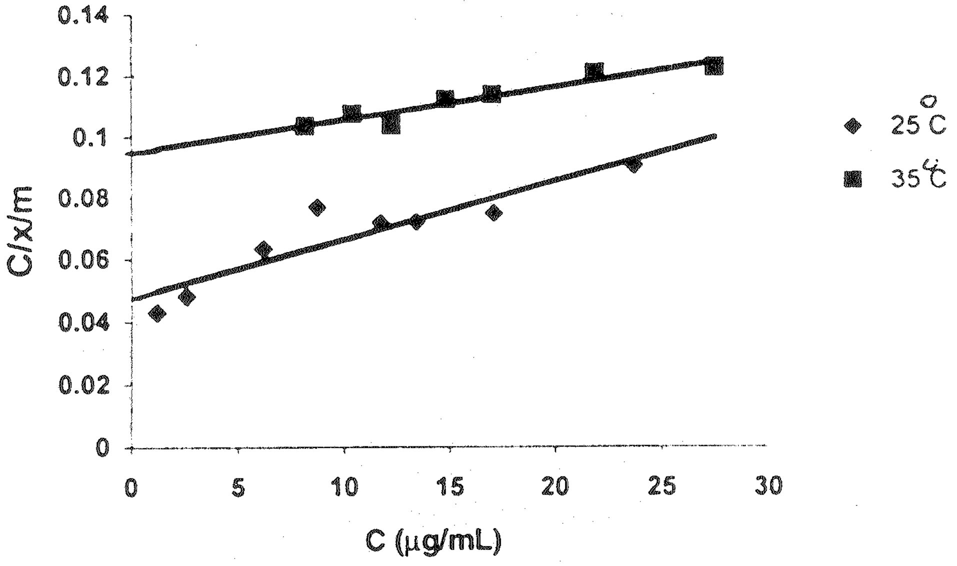

Fig. 2. Langmuir adsorption isotherms for boron adsorption on Gurdaspur soil at 25 and 35°C

(b) Freundlich Adsorption Equation: The boron adsorption data fitted well to the Freundlich equation. Plots of log x/m *vs.* log C depicted a linear relationship (Fig. 3). Values for log K (intercept) indicating the amount of boron adsorbed at unit concentration and that of 1/n are represented in Table-2. The values of K decrease with increase in temperature indicating that sorption capacity of a soil increases with decrease in temperature.

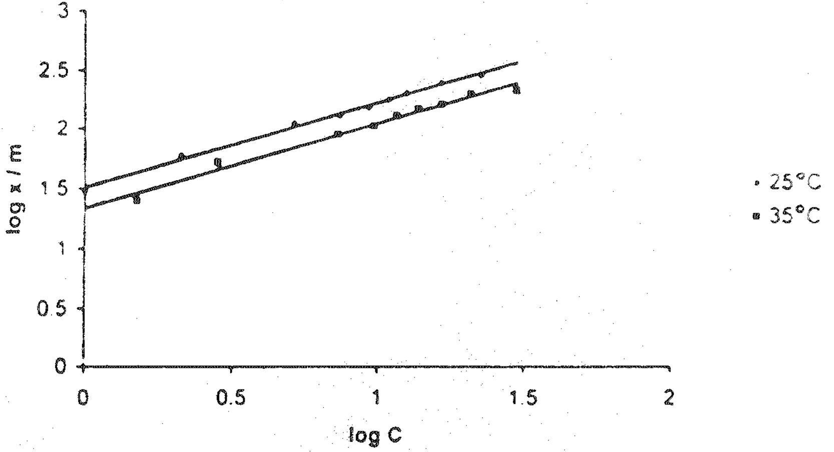

Fig. 3. Freundlich isotherms for boron adsorption on Naura soil at 25 and 35°C

The value of K is the highest for Naura soil and the lowest for Dhar soil at both the temperatures revealing that Naura soil has the highest adsorption capacity whereas Dhar soil has the lowest adsorption capacity. Statistical analysis reveals that the values of Freundlich K are positive and significantly correlated with clay (r = 0.80 and 0.83) and calcium carbonate content (r = 0.81) at both the temperatures. K values are positively correlated with CEC but show a negative correlation with electrical conductivity and organic carbon. The values of 1/n are less than unity in all the cases indicating L-type isotherms. The values of

Freundlich constant 1/n, which reflect the intensity of adsorption, are less than unity because only a small portion of the theoretically available soil surface is available for adsorption[16] at 35°C for each soil.

TABLE-2
THE VALUES OF LANGMUIR CONSTANTS (K AND b) AND FREUNDLICH CONSTANTS (K AND 1/n) FOR BORON ADSORPTION BY DIFFERENT SOILS AT 25 AND 35°C

Soil	Langmuir constants				Freundlich constants			
	25°C		35°C		25°C		35°C	
	K (mL μg^{-1})	b ($\mu g\ g^{-1}$)	K (mL μg^{-1}	b ($\mu g\ g^{-1}$)	K	1/n	K	1/n
Gurdaspur	0.039	526	0.030	454	25.18	0.75	17.62	0.75
Naura	0.061	454	0.053	333	43.25	0.66	31.77	0.58
Bhanger	0.029	344	0.010	666	12.85	0.76	6.98	0.89
Kaoni	0.019	588	0.019	500	12.36	0.86	9.57	0.83
Chamror	0.011	769	0.003	2000	9.44	0.90	5.36	0.99
Dhar	0.007	1000	0.005	1000	7.39	0.93	4.34	0.98

Distribution Coefficients of Adsorbed B (K_d)

The use of K values of the Freundlich equation is not appropriate for comparing the adsorption capacities of different soils as these values correspond to the adsorption at unit equilibrium concentration. This, in fact, is a single point on the isotherm and exhibits adsorption at low concentration of adsorbate. Adsorption measurement in this range is associated with uncertainty which can lead to cause errors in determining the values of K. Therefore K_d values are considered to be more useful for better comparison of adsorption capacity of different adsorbents[17, 18].

The averaged values of distribution coefficient K_d have been recorded in Table-3. When the averaged values for various soils were taken into consideration, then the order of K_d values were highest for Naura soil followed by Gurdaspur, Kaoni, Bhanger, Chamror and Dhar at two temperatures. The K_d values were positive and significantly correlated with clay ($r = 0.88$) and CEC ($r = 0.85$) of the soil, but negatively correlated with EC and organic carbon content of the soil.

Evaluation of Partial Molar Free Energy Change ($\overline{\Delta G}$)

The partial molar free energy change ($\overline{\Delta G}$) as a result of adsorption can be used as a measure of the extent or driving force of the adsorption reaction. Greater magnitude of $\overline{\Delta G}$ value indicates the greater extent to which adsorption reaction takes place. The calculated averaged values of partial molar free energy change ($\overline{\Delta G}$) for boron adsorption are highest in the case of Naura soil at both the temperatures (Table-3) indicating that the driving force of boron adsorption reaction is greater in this soil. The averaged values of $\overline{\Delta G}$ are greater at 25°C than at 35°C for each soil.

TABLE-3

AVERAGED $\overline{\Delta G}$ (PARTIAL MOLAR FREE ENERGY CHANGE) AND AVERAGED K_d (DISTRIBUTION COEFFICIENT) VALUES FOR BORON ADSORPTION ON DIFFERENT SOILS

Soil	Averaged distribution coefficient (K_d) (mL g^{-1})		Averaged partial molar free energy change ($\overline{\Delta G}$) (J $mole^{-1}$)	
	25°C	35°C	25°C	35°C
Gurdaspur	15.52	10.27	2296	1791
Naura	18.88	11.55	2582	1935
Bhanger	7.33	5.56	1353	1130
Kaoni	9.12	7.59	1601	1442
Chamror	7.39	5.17	1372	1066
Dhar	6.27	4.13	1205	884

Supply Parameter

The supply parameter of B which indicates the ability of soil to supply boron to the growing plants in terms of quantity, intensity and buffering capacity was computed according to the equation proposed by Khasawneh and Copeland[19].

$$\text{Supply parameter} = \frac{\sqrt{qC}}{\sqrt{K_1 - K_2}}$$

where q = quantity (boron adsorbed in μg g^{-1})

C = intensity (boron concentration in soil solution in (μg mL^{-1}))

K_1 = adsorption maximum constant

K_2 = constant related to the energy of adsorption

The values of K_1 and K_2 were calculated from the equation[20]

$$q = \frac{K_1 C}{K_2} + C$$

The transformation of above equation in its linear form gives the following relation:

$$\frac{1}{q} = \frac{1}{K_1} + \frac{K_2}{K_1 C}$$

A plot between 1/q and 1/C gives a straight line (r = 0.93 to 0.99). The values of constants K_1 and K_2 can be obtained from the slope and intercept.

$$\text{Slope} = \frac{K_2}{K_1}$$

$$\text{Intercept} = \frac{1}{K_1}$$

The value of K_1 decreases with increase in temperature while the value of K_2 increases with increase in temperature in most of the soils taken in the present investigation. Khasawneh and Copeland[19] have suggested that $\sqrt{Cq}/\sqrt{K_1K_2}$ describes soil phosphorus status in terms of intensity, quantity and buffering capacity over the entire range of supply and observed that this parameter would provide a better measure of soil phosphorus than either quantity or intensity alone. Therefore, it was considered to calculate this parameter for boron adsorption so that the rate of boron uptake could be understood in different soils. The value of $(Cq/(K_1K_2))^{1/2}$ is related only to per cent saturation of the adsorption capacity of the soil because per cent saturation is given by $(q/K_1) \times 100$. The average value of per cent saturation of adsorption capacity is highest in case of Naura soil and lowest in Dhar soil at 25°C. The order of values of per cent saturation of the adsorption capacity is almost the same as that of supply parameter indicating that these quantities are related to each other. The value of supply parameter is maximum for Naura and minimum for Dhar soil indicating that rate of boron uptake will be highest in the Naura soil and lowest in the Dhar soil.

REFERENCES

1. R. Keren and F.T. Bingham, *Adv. Soil Sci.*, **1**, 229 (1985).
2. H.M. Reisenauer, H.M. Walsh and R.G. Hoeft, in: L.M. Walsh and J.D. Beaton (Eds.), Soil Testing and Plant Analysis, Soil Science Society of America, Madison, pp. 177–200 (1973).
3. U. Yermiyaho, R. Keren and Y. Chen, *Soil Sci. Soc. Am. J.*, **52**, 1309 (1988).
4. F.J. Hingston, *Aust J. Soil Res.*, **2**, 83 (1964).
5. R. Keren, F.T. Bingham and J.D. Rhoades. *Soil Sci. Soc. Am. J.*, **49**, 297 (1985).
6. Soil Conservation Service, Laboratory Procedures for Collection and Analysis of Soil Samples, USDA, Washington (1972).
7. A.N. Puri, *Imp. Agric. Res. Pusa Bull.*, **206**, 7 (1930).
8. U.C. Gupta, *Soil Sci. Soc. Am. Proc.*, **30**, 655 (1966).
9. B. Wolf, *Commun. Soil Sci. Plant Anal.*, **5**, 39 (1974).
10. R. Haqu, in: R. Haque and V.H. Freed (Eds.), Environmental Dynamics of Pesticides, Plenum Press, N.Y., p. 97 (1975).
11. M.I. Aly, N. Bakry, F. Kishk and A.H.El-Sebae, *Soil Sci. Soc. Am. J.*, **44**, 1213 (1980).
12. C.H. Giles, T.H. Macewan, S.N. Nakhwa and D. Smith, *J. Chem. Soc.*, 3973 (1960).
13. R. Krishnasamy, J. Jaisankar and M. Suresh, *J. Indian Soc. Soil Sci.*, **45**, 255 (1997).
14. M.A. Elrashidi and G.A. O'Connor, *Soil Sci. Soc. Am. J.*, **46**, 27 (1982).
15. U. Mezuman and R. Keren, *Soil Sci. Soc. Am. J.*, **45**, 722 (1981).
16. A.K. Rai, P.K. Chhonkar and N.P. Agnihotri, *J. Indian Soc. Soil Sci.*, **48**, 52 (2000).
17. A.K. Mandal and M. Adhikarii, *J. Indian Soc. Soil Sci.*, **43**, 561 (1995).
18. N. Senesi, G. Brunetti, P.L. Cava and T.D. Miano, *Soil Sci.*, **157**, 176 (1994).
19. F.E. Khasawneh and J.P. Copeland, *Soil Sci. Soc. Am. Proc.*, **37**, 250 (1973).
20. P.E. Khasawneh, *Soil Sci. Soc. Am. Proc.*, **35**, 426 (1971).

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