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Adsorption and desorption of boron in cultivated soils of Himachal Pradesh

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Abstract
The boron (B) concentration in the soil solution is generally controlled by B adsorption and desorption reactions. With this background, a study was carried out to know the adsorption and desorption of boron using Freundlich, Langmuir and Temkin isotherms in cultivated soil of Himachal Pradesh. Eighty soil samples (0-0.15 m depth) were collected randomly from different locations across different districts of Himachal Pradesh and their B adsorption-desorption behaviour was studied. Among three different adsorption isotherms *i.e.* Freundlich, Langmuir and Temkin used to determine the B retention capacity of soils, Freundlich and Temkin isotherms represented better fit for fine textured soils, while Langmuir isotherm showed better fit for coarse textured soils. The results emanating from the study revealed that with increase in boron concentration, the boron adsorption by soils increases.

Keywords: Boron, adsorption and desorption

Introduction

Boron is an important micronutrient required for plant health, due to its role in forming and strengthening cell walls. It is essential for plants, with its uptake being controlled by the B concentration in the soil solution, which is buffered by the adsorption and desorption reactions of B adsorbed on mineral surfaces (Majidi *et al.*, 2010) [13]. However, excessive uptake of macro and micro-nutrients under intensive cropping, and neglect of their replenishment in adequate quantities resulted in widespread deficiency of different nutrients including B. Averaged across the states, 33% soils exhibited B deficiency (Shukla *et al.*, 2012) [19].

Adsorption and desorption of B is an important phenomenon in soils that regulate its supply from soils to plant growth. A potential source of B in soil solution is that associated with solid phase in the adsorbed form. The soluble boron remains in dynamic equilibrium with the adsorbed forms and hence cannot be readily removed through leaching. Its deficiency in plants is most widespread in soils, which are coarse in texture, low in organic matter, high in pH and calcareousness (Das 2000) [4]. Boron deficiency is quite widespread throughout the world, including India (Katyal and Agarwal 1982; Das, 2000) [11, 4]. Available B content in Indian soils ranges from traces to 12.2 mg kg^{-1} (Das, 2000) [4]. Based on the hot-water-soluble B < 0.5 mg kg^{-1}, B deficiency is predicted in sixteen out of the fifty-seven benchmark soils of India (Sharma and Katyal 2006) [17]. Boron deficiency has been widely found in highly calcareous soils of Bihar, Tamil Nadu, Eastern Uttar Pradesh and Saurashtra, sandy soils of Haryana and Rajasthan, hill and sub-mountaneous soils of north Himalayan and the NEH states and in red and lateritic soils of Orissa, Karnataka, Andhra Pradesh and Kokan region. In Himachal Pradesh, the extent of B deficiency has been found to be 18 to 50% across different districts.

Boron adsorption surfaces in the soil are oxides, clay minerals, calcium carbonate and organic matter (Goldberg 1997) [8]. The mechanism of B adsorption on these surfaces is considered to be ligand exchange with reactive surface hydroxyl groups leading to strong specific adsorption. In addition to solution pH, other factors affecting the availability of B in soils are: soil texture, soil moisture and soil temperature (Goldberg 1997) [8]. Fine-textured soils usually contain more available B than coarse-textured soils because of their greater content of clay minerals (Gupta 1968) [9]. Boron is generally less available in dry soil and increases with increasing temperature (Fleming 1980) [7]. The adsorption isotherms indicated that the adsorption of boron increased with its increasing concentration in the equilibrium solution (Tamuli, *et al.* 2017) [21]

Boron desorption reactions in soils have been studied less extensively than B adsorption reactions. For some soils, the B-desorption isotherm corresponded closely to the B-adsorption isotherm (Elrashidi and O'Connor 1982) [6]. Other soils exhibited hysteresis; that is, the B-adsorption isotherm did not correspond to the B-adsorption isotherm (Okazaki and Chao 1968; Rhoades, Ingvalson, and Hatcher 1970) [15, 16]. Deficiency of B in alluvium derived arid and semi-arid soils of Punjab was reported by Singh and Nayyar (1999) [20] and Arora and Chahal (2005) [3]. The present study was therefore aimed to assess the adsorption and desorption of boron in cultivated soil of Himachal Pradesh.

Materials and Methods

Eighty soil samples (0-15 cm depth) were collected randomly from different locations across different districts of Himachal Pradesh and used in the present investigation. A predominantly mountainous state located in North – West Himachal Pradesh, India. The state has highly dissected mountain ranges spread with deep gorges and valleys. It is also characterized with diverse climate that varies from semi tropical in lower hills, to semi arctic in the cold deserts areas of Spiti and Kinnaur. Altitude ranges from 350 meters to 6975 meters above mean sea level and is situated between 30º22′40″ N to 33º12′40″ N latitudes and 75º45′55″ E to 79º04′20″ E longitudes. The state has different kinds of soils due to variations in climate, parent material, vegetation and topography etc. and different textured soils have different effect on boron sorption behaviour. Owing to these variations, soil samples from almost all the agro-climatic situations across the state have been used for carrying out the present study. The adsorption-desorption behaviour of B in eighty soil samples was studied using the method outlined by Elrashidi and O'Connor (1982) [6] with few modifications. Ten gram soil sample and 20 ml of 0.01M $CaCl_2$ solution (containing increasing concentration 0, 5, 10, 20, 40 and 50 mg B $^{-1}$ as H_3BO_3) was taken in 50 ml polypropylene centrifuge tubes and the contents were shaken for 23 h on a wrist-action shaker. The suspension was centrifuged and a 10 ml aliquot of the clear supernatant was taken and filtered through Whatman No. 42 filter paper. Boron was determined in the filtrate using azomethine-H method (John *et al*. 1975) [10]. The difference between the amount of B in the initial solution and that in the filtrate (after shaking) was taken as the amount of B adsorbed by soil from the equilibrating solution. The following adsorption equations were used to describe B adsorption in the soil:

1. *Freundlich equation:* $x = a\, c^{1/n}$
2. *Langmuir equation:* $x = k\, b\, c / (1 + kc)$
3. *Temkin equation*: $x = a \log c + b$

Where x is the amount of adsorbed B (mg kg^{-1} soil) and c the equilibrium B concentration (mg l $^{-1}$). Two parameters, a and 1/n were calculated using the linear transformation $\log x = \log a + (1/n) \log c$. The parameters b and k were calculated using the linear transformation $c/x = c/b + 1/(kb)$. The slope, b is the intercept and c the B concentration in the solution (mg l^{-1}). A plot of x against log c should give a straight line if the adsorption energy decreases linearly with an increase in surface coverage (Mead 1981) [14].

The soils with treatment of different added B concentration in the adsorption study were used for desorption of B. Desorption was initiated with removal of 10 ml of supernatant from equilibrated solution and addition of 10 ml of B-free 0.01M $CaCl_2$ solution. The mixtures were re-suspended through vigorous agitation and equilibrated for 23 h. The suspensions were centrifuged, and 10 ml of supernatant was removed for B determination. Amount of B desorbed was calculated from the difference between equilibrium B concentration at desorption step and the equilibrium B concentration previous to the desorption step divided by dilution factor. The amount of boron retained (x/m) by the soil during desorption was calculated as the difference between amount of B retained in the previous step and B desorbed in the present step. The data on the amount of B retained (x/m) by the soil during desorption at the corresponding equilibrium concentrations were fitted into Langmuir type equation (Sharma *et al*. 1995) [18] as given below:

$De/S = 1/Kd\, Dm + De/Dm$

Where S is boron adsorbed (mg kg^{-1}), De is boron desorbed (mg kg^{-1}), Dm is the desorption maxima (mg kg^{-1}), and Kd is a constant related to mobility of boron (l kg^{-1}). The desorption parameters such as desorption maxima (Dm) and constant related to mobility of the solid phase (Kd) were worked out from the linear plots of De vs. De/S according to the Langmuir desorption relationship.

Results and discussion

Boron adsorption parameters

Boron adsorption parameters were calculated by fitting the adsorption data into Freundlich, Langmuir and Temkin equations. It may be concluded from the data in tables 1 that boron adsorption had an excellent fit to Freundlich, Langmuir and Temkin isotherms having R^2 = 0.954 to 0.992, 0.979 to 0.998 and 0.954 to 0.992, respectively. Aggarwal and Nayyar (2001) [1] reported that adsorption data confirmed very well and was an excellent fit for Freundlich, Langmuir and Temkin isotherms. The mean values of prediction coefficient (R^2) for Freundlich, Langmuir and Temkin equations were 0.981, 0.992 and 0.976, respectively. The mean R^2 values of Langmuir were higher than those of Freundlich equation. Higher prediction coefficient (R^2) compared with Freundlich model corroborated the earlier reports suggesting the best fit of Langmuir model over a limited range of B concentration as deviations from Langmuir may occur at high concentrations (Datta and Bhadoria 1999; Arora and Chahal 2010) [5, 2].

Boron sorption (adsorption and desorption)

Adsorption of boron

In order to have the critical examination of the data on boron adsorption, the soil samples have been grouped in three categories as per their texture. Samples possessing coarse texture in one category (39 no.), medium texture in second category (36 no.) and fine texture in third category (5 no.). The results have been presented and discussed under these categories in table 2 and figure 1. Adsorption of boron (B) varied markedly among different soils. Data revealed that adsorbed boron ranged between 1.26- 4.58, 2.01- 8.55, 3.51-13.6, 4.44- 24.2 and 4.54- 26.0 mg B kg^{-1} soil with an average value of 2.68 ± 0.82, 4.78 ± 1.76, 7.75 ± 3.05, 11.6 ± 5.45 and 12.0 ± 5.71 mg B kg^{-1} soil with the incremental doses of boron @ 10, 20, 40, 80 and 100 mg B kg^{-1} soil, respectively. It was found that with the increase of boron concentration in equilibrium solution, the boron adsorption by soils increased. But B adsorption increased with boron concentration in equilibrium up to a limit and thereafter further increment in equilibrium concentration did not affect the boron adsorption. The variation in overall amount of B sorbed depends on variation in mineralogical and chemical properties of soils (Elrashidi and O'Connor 1982) [6]. In acid soils, B adsorption is usually controlled by oxides and oxy-hydroxides of Fe and Al, and soil pH (Keren and Bingham 1985) [12].

Desorption of boron

It was of interest to determine whether the adsorbed boron in soils can be readily released. The boron desorption study was done by using the soil left after adsorption studies and the data so obtained were presented in table 2. The percentage of desorbed boron was higher at higher level of added boron in all the soils irrespective of the texture. The coarse-textured soils tended to desorb higher percentage of boron as compared to fine-textured soils. Results revealed that desorbed boron was less than that of adsorbed boron. A perusal of data in table 2 revealed that the desorbed boron ranged between 0.44 to 0.80, 0.89 to 1.62, 1.60 to 3.33, 2.31 to 6.85 and 2.40 to 8.09 mg B kg^{-1} with an average value of 0.67 ± 0.11, 1.36 ± 0.18, 2.58 ± 0.49, 4.48 ± 1.25 and 4.80 ± 1.54 mg B kg^{-1} with the incremental doses of boron @ 10, 20, 40, 80 and 100 mg B kg^{-1} soil, respectively.

A linear relation was obtained in all the soils when desorbed boron (De) was plotted against B desorbed / B adsorbed (De/S) for different types of soils. The Langmuir desorption parameters such as desorption maxima (Dm) and constant related to mobility of the solid phase (Kd) were worked out from the linear plots of De vs. De/S according to the Langmuir desorption relationship and are presented in table 2 and figure 2. The data indicated a marked reduction in desorption maxima (Dm) value from fine textured (22.2 to 23.3 mg kg^{-1} with an average value of 22.8 ± 0.43 mg kg^{-1}), to medium textured (8.70 to 21.28 mg kg^{-1} with a mean of 14.4 ± 3.42 mg kg^{-1}) and further to coarse textured (4.52 to 13.70 mg kg^{-1} with an average value of 8.30 ± 2.46 mg kg^{-1}). Desorption maxima (Dm) indicate the maximum desorbable capacity of the soils. Higher the 'Dm' value, less potential the soil has to release boron to meet the requirement of the crops. Arora and Chahal (2010) [2] also reported that fine textured soils had higher desorption maxima compared to coarse-textured soils. So, it can be interpreted that in coarse textured soils most of the applied boron remained in soil solution for easy availability to the plants.

Table 1: Freundlich, Langmuir and Temkin adsorption parameters for B adsorption in soils

Category		Freundlich equation				Langmuir equation				Temkin equation		
		a (mg kg^{-1})	1/n	n	R2	b (mg B kg^{-1})	k (l mg^{-1})	MBC (b x k) (l kg-1)	R2	a	b	R2
Coarse textured	Range	0.59-1.52	0.539-0.781	1.28-1.86	0.954-0.989	6.41-20.0	0.051-0.068	0.35-1.04	0.990-0.998	3.58-12.1	(-5.11) – (-1.34)	0.954-0.988
(n = 39)	Mean	1.05	0.645	1.57	0.977	10.9	0.059	0.65	0.994	6.04	-3.30	0.970
	SD(±)	0.26	0.073	0.18	0.008	3.37	0.004	0.19	0.002	2.22	1.21	0.008
Medium textured	Range	1.08-2.19	0.533-0.696	1.44-1.88	0.973-0.991	11.2-37.0	0.045-0.068	0.73-1.67	0.983-0.998	5.09-15.7	(-3.86) - (-1.34)	0.972-0.989
(n = 36)	Mean	1.59	0.616	1.63	0.984	22.2	0.053	1.13	0.991	10.8	-2.10	0.980
	SD(±)	0.29	0.046	0.13	0.005	7.30	0.007	0.27	0.005	3.26	0.61	0.005
Fine textured	Range	2.34-2.56	0.511-0.665	1.50-1.96	0.989-0.992	38.5-43.5	0.045-0.049	1.80-1.95	0.979-0.990	16.5-16.8	(-1.57) – (-1.26)	0.989-0.992
(n = 5)	Mean	2.48	0.587	1.72	0.991	40.4	0.047	1.90	0.985	16.6	-1.43	0.990
	SD(±)	0.09	0.060	0.18	0.001	1.85	0.001	0.06	0.004	0.13	0.12	0.001
Overall	Range	0.59-2.56	0.511-0.781	1.28-1.96	0.954-0.992	6.41-43.5	0.045-0.068	0.35-1.95	0.979-0.998	3.58-16.8	(-5.11) – (-1.26)	0.954-0.992
	Mean	1.39	0.629	1.61	0.981	17.8	0.056	0.94	0.992	8.83	-2.64	0.976
	SD(±)	0.47	0.063	0.16	0.008	9.68	0.007	0.41	0.004	4.06	1.14	0.009

Table 2: Boron adsorption and desorption (mg B kg^{-1}) in different soils and Langmuir desorption parameters for B desorption in soils

Category		Adsorption B added (mg B kg^{-1})					Desorption B added (mg B kg^{-1})					Langmuir desorption		
		10	20	40	80	100	10	20	40	80	100	Dm (mg kg^{-1})	Kd (l kg^{-1})	R^2
Coarse textured	Range	1.26-2.90	2.00-5.56	3.51-9.70	4.34-13.00	4.54-13.4	0.51-0.79	0.89-1.59	1.60-2.90	2.31-5.01	2.40-5.31	4.52-13.7	0.24-0.46	0.993-0.999
(n = 39)	Mean	2.08	3.47	5.60	7.62	7.80	0.71	1.28	2.22	3.52	3.64	8.30	0.32	0.998
	SD(±)	0.46	0.96	1.61	2.28	2.40	0.08	0.20	0.39	0.72	0.79	2.46	0.06	0.002
Medium textured	Range	2.13-4.11	3.54-7.91	5.16-13.1	7.76-22.4	8.01-23.2	0.46-0.80	1.33-1.62	2.32-3.33	3.65-6.79	3.78-7.80	8.70-21.3	0.23-0.43	0.987-0.999
(n = 36)	Mean	3.09	5.69	9.30	14.2	14.7	0.66	1.46	2.91	5.22	5.63	14.4	0.29	0.994
	SD(±)	0.51	1.18	2.48	4.00	4.14	0.11	0.09	0.29	0.87	1.06	3.42	0.04	0.004
Fine textured	Range	4.29-4.58	8.23-8.55	13.0-13.6	23.4-24.2	24.4-26.0	0.44-0.50	1.11-1.32	2.83-3.24	6.37-6.85	7.71-8.09	22.2-23.3	0.22-0.27	0.992-0.995
(n = 5)	Mean	4.45	8.41	13.3	23.9	24.9	0.46	1.20	3.05	6.60	7.87	22.8	0.24	0.994
	SD(±)	0.11	0.12	0.24	0.29	0.63	0.03	0.08	0.17	0.19	0.18	0.43	0.02	0.002
Overall	Range	1.26-4.58	2.01-8.55	3.51-13.6	4.44-24.2	4.54-26.0	0.44-0.80	0.89-1.62	1.60-3.33	2.31-6.85	2.40-8.09	4.52-23.3	0.22-0.46	0.987-0.999
	Mean	2.68	4.78	7.75	11.6	12.0	0.67	1.36	2.58	4.48	4.80	12.0	0.30	0.996

	SD(±)	0.82	1.76	3.05	5.45	5.71	0.11	0.18	0.49	1.25	1.54	4.99	0.06	0.004

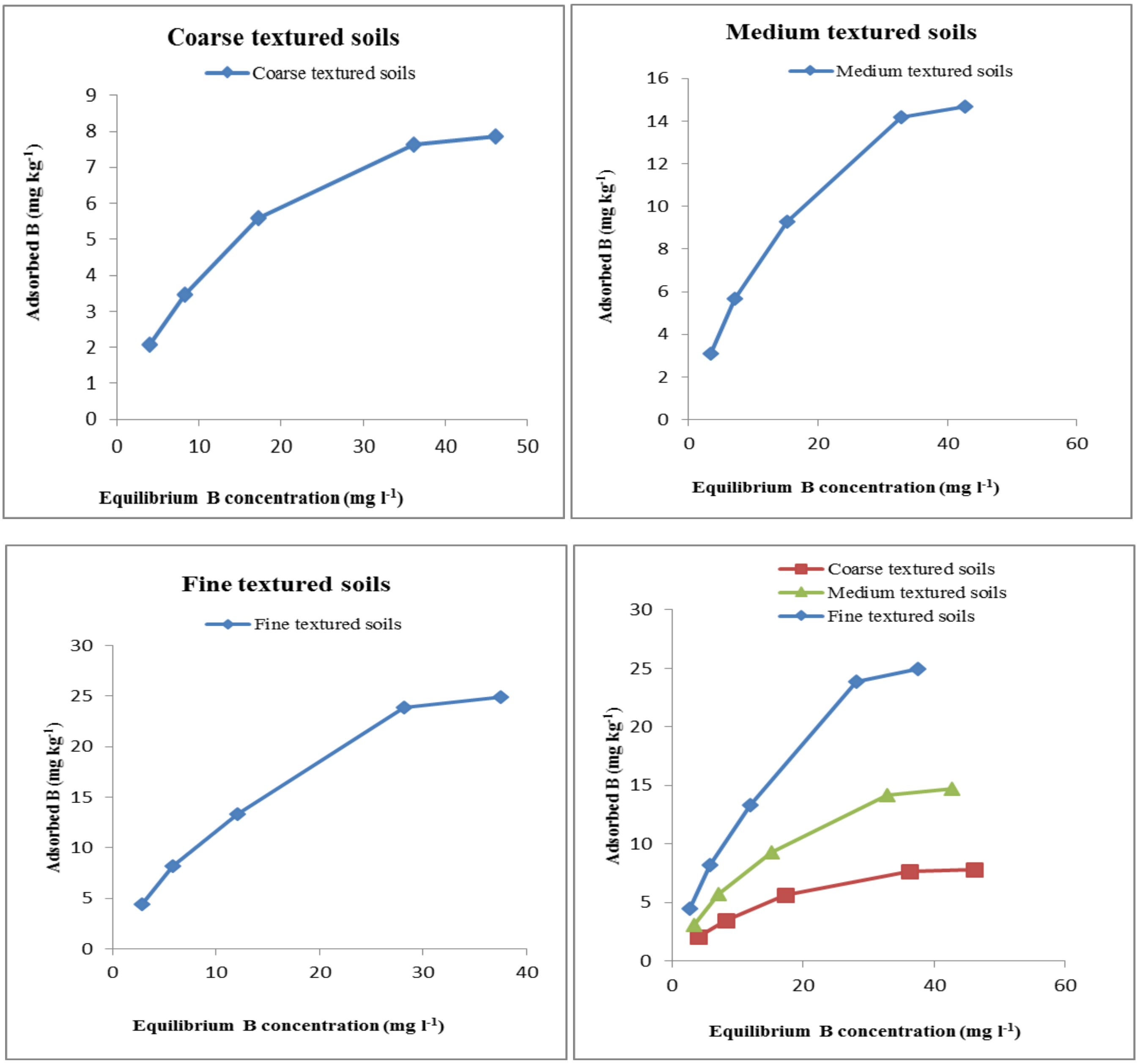
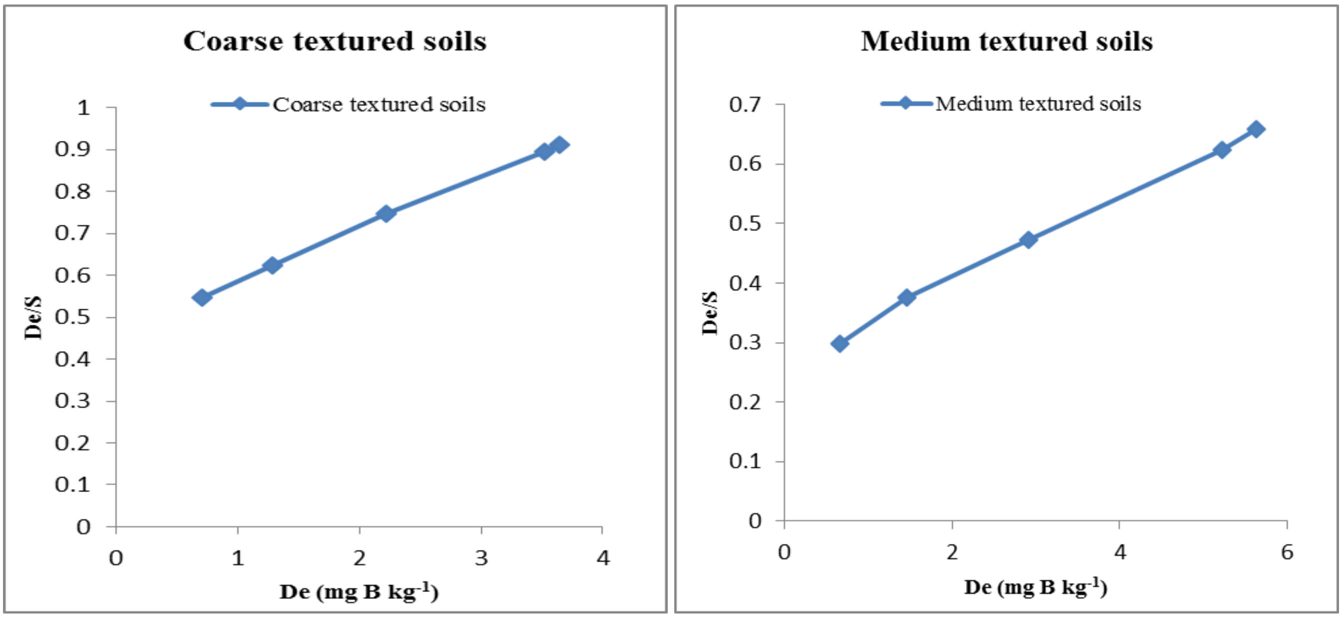


Fig 1: Adsorption of B at varying equilibrium B concentration in soils



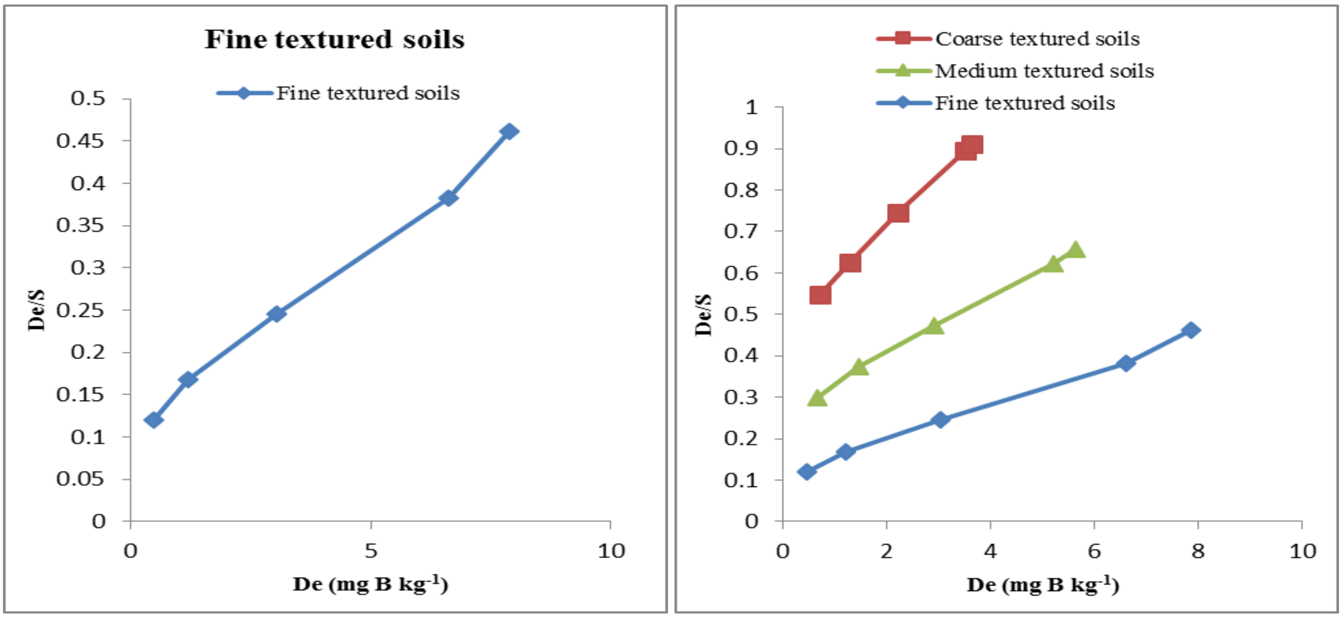


Fig 2: Langmuir isotherm of B desorption in soils

Conclusion

The study indicated that adsorption of B in soil was significantly influenced by organic matter content, pH, CEC, temperature, applied fertilizers in soil and soil texture. Adsorption of B increased with increase pH and temperature levels. Fine textured soils recorded significantly higher adsorption capacities with Freundlich and Temkin equations. Langmuir adsorption isotherm was found better in coarse textured soils. Boron desorption calculated using Langmuir desorption isotherm depicted higher desorption capacity in coarse textured soils.

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