Comparison of Kinetic Models for Boron Adsorption in Major Soil Groups of India

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The aim of present study was to understand the boron (B) adsorption kinetics in soils. Three soils belonging to Alfisol, Vertisol and Inceptisol orders were selected. The soils were widely differed in their properties. Externally applied B content was allowed to equilibrate with intermittent shaking at different temperature levels (25 and 35 °C) for different intervals ranging from 0.5 to 72 h. Boron retention by soils followed decreasing order of: Vertisol > Inceptisol > Alfisol. Five different kinetic models *viz.* zero-order, first-order, parabolic, Elovich and power function were used for describing B adsorption kinetics in soils. The Elovich equation was proved to be the best among the various kinetic equations studied to describe B adsorption kinetics. The equilibrium concentration was achieved at 16 h at 35 °C whereas it takes more time at 25 °C. Adsorption of B decreased with a subsequent increase in temperature level.

Key words: Boron adsorption kinetics, soil order, parabolic, Elovich, power function

Equilibrium rather than kinetics of adsorption reactions in clay and soil system has been received considerable attention over the years (Elrashidi and O'Connor 1982; Datta and Bhadoria 1999; Dey *et al.* 2013). These thermodynamic studies have proved valuable but they do not assist one in understanding the mechanism and rates of reactions in clay minerals and soils, nor are they often applicable to field-conditions. Usually intensively cropped and fertilized agricultural soils are not in equilibrium with regard to ion transformations because equilibrium is precluded by periodic addition of fertilizers. To fully understand and model elemental reactions in soils, knowledge of kinetics is fundamental. Limited information is available on the kinetic reactions of essential plant nutrients in general and B in particular. In view of its narrow range of toxicity and deficiency in soils and plants studying adsorption kinetics of B is of paramount importance.

The kinetics of B adsorption decides the fixation and release of applied B and thus controls the efficiency of B fertilization. Knowledge of the kinetics of adsorption reaction is essential for the sound prediction of B availability to crops (Dey *et al.* 2013,

2014). Elrashidi and O'Connor (1982) reported that B sorption reactions completed in 12 h, however for convenience, a 23 h equilibration period is mostly used in adsorption study (Datta and Bhadoria 1999; Dey *et al.* 2013). Keren and Gast (1983) found that adsorption equilibrium was established in less than 1 h after addition of B. On the other hand, Krishnasamy *et al.* (1997) reported that adsorption of B was almost complete after 24 h in soils of Tamil Nadu. Boron adsorption in these soils was best described by parabolic diffusion and Elovichian kinetics. While working on different soils of Punjab, Arora and Chahal (2007) found that Elovich equation was the best to describe the rate of B adsorption followed by the power function. Working on arid soils of India, Chaudhary and Shukla (2013) tested eight kinetic models to describe B desorption. The comparison of coefficient of determination (R^2) and standard error of estimate (SE) revealed that the order of application to describe B desorption kinetics in these soils was as follows: second approximation > two-constant rate equation > Elovich rate equation > parabolic diffusion rate equation. Similar results were also found by Ranjbar and Jalali (2013) on the calcareous soil of Iran. In the present study, an attempt was made to evaluate the suitability of kinetic equations for describing B sorption in soils.

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Table 1. Important physicochemical characteristics of soils used for kinetics of B adsorption

Soil order	Vertisol	Inceptisol	Alfisol
Location	Raipur	New Delhi	Ranchi
Agro-ecological sub-region (AESR No.)	Chhattisgarh/Mahanadi Basin (AESR 11.0)	North Punjab Plain and Ganga-Yamuna Doab (AESR 4.1)	Chhotanagpur Plateau (AESR 12.3)
pH	6.76	8.28	5.18
EC	0.09	0.38	0.08
Organic C (g kg^{-1})	5.9	4.2	5.0
HWB (mg kg^{-1})*	0.12	0.63	0.17
Free CaCO$_3$ (%)	4.05	2.38	1.9
Free Fe oxides (%)	0.32	0.21	0.59
Free Al oxides (%)	0.64	0.74	1.38
CEC [cmol(p$^+$) kg^{-1}]	41	11.2	6
Sand (%)	18	54	66
Silt (%)	31	17	9
Clay (%)	51	29	25
Texture class	Clay	Sandy clay loam	Sandy clay loam

*HWB: Hot water extractable B

Materials and Methods

Three soil samples representing three major soil orders of India *i.e.,* Alfisol, Vertisol and Inceptisol were selected from the archive of Soil Testing Laboratory, ICAR-Indian Agricultural Research Institute (ICAR-IARI). These samples were collected from cultivators' fields from different places. Details of the soils *viz.* AESR name, state, districts are given in table 1. Soil samples were processed and soil characteristics *viz.* texture (Bouyoucos 1962), pH, electrical conductivity (EC), cation exchange capacity (CEC) (Jackson 1973), organic C (Walkley and Black 1934), free CaCO$_3$ (Piper 1966) and Fe- and Al-oxides (Jackson 1973) were determined as per standard procedures.

A background electrolyte (20 mL; 0.01 M CaCl$_2$) containing 40 mg B L^{-1} as boric acid (H$_3$BO$_3$) was added to 10 g of soil in 50-mL polypropylene centrifuge tubes in triplicate. The contents were allowed to equilibrate with intermittent shaking at two temperature levels (25 and 35 °C) for different intervals ranging from 0.5 to 72 h. At the end of the reaction time, the suspension was centrifuged and filtered. The B concentration in the equilibrium solution was determined colorimetrically using azomethine-H (Wolf 1974). The amount of B adsorbed was calculated from the difference between the concentrations of the initial solution and the equilibration solution. The amount of B adsorbed at various time intervals were fitted to different kinetic models. Five different kinetic models *viz.* zero-order, first-order, parabolic, Elovich and power function were used for describing B adsorption kinetics in soils (Arora and Chahal 2007).

Zero order: $C_t = C_0 + K_0 t$ …(i)

where, K_0 is the zero-order rate constant (mg B kg^{-1} s^{-1}); C_t and C_0 denotes the amount of B adsorbed at time t and zero, respectively.

First order: $\ln C_t = \ln C_0 - k_a t$ …(ii)

where, k_a is the adsorption rate coefficient.

Parabolic diffusion: $C_t = \alpha + K_d t^{1/2}$ …(iii)

where K_d is the diffusion rate constant [(mg B kg^{-1}) s$^{-1/2}$].

Elovich equation: $C_t = C_0 + (1/\beta) \ln \alpha\beta + (1/\beta) \ln t$ …(iv)

where, α is the initial B adsorption rate [(mg B kg^{-1}) h^{-1}] and β is B sorption constant [(mg B kg^{-1}) h^{-1}].

Power function: $\ln y = \ln a + b \ln t$ …(v)

where, y is the quantity of B adsorbed at time t; and a and b are constants.

To determine the suitability of kinetics model for describing B adsorption in soils, a standard error estimate was calculated for each equation. High value of the coefficient of determination (R^2) and low standard error of estimate (SE) were used as criteria for the best fit. The SE was calculated as follows:

$$SE = \left[\frac{\sum (q - q\prime)^2}{N-2} \right]^{0.5} \qquad …(vi)$$

where, q_p and q_o are the predicted and observed amounts of B adsorbed in soil, respectively, at time t; and n is the total number of observation.

Results and Discussion

Soil physicochemical characteristics

The study on soil properties indicated that the Vertisol belongs to textural class clayey with very

high CEC, whereas the Inceptisol and Alfisol fall in sandy clay loam textural class with low CEC (Table 1) respectively. Vertisol had a neutral pH, whereas that of Inceptisol and Alfisol were alkaline and acidic in nature, respectively. Organic C content of these soils ranges from low to medium with value of 5.0, 5.9 and 4.2 g kg^{-1}, respectively. Free $CaCO_3$ content was very high in Vertisol, which was approximately double of that present in Inceptisol and Alfisol. The CEC was higher in Vertisol compared to other two soils. On the contrary, Alfisol contained free Al- and Fe-oxides by 2 to 3 times compared to that in Vertisol and Inceptisol. On the basis of hot water soluble B (HWB) Inceptisol falls in adequate category whereas the other two were deficient (Table 1). Similar results were obtained by Dey *et al.* (2014, 2015, 2017).

Boron adsorption in soils of different orders

Adsorption of B in different soils varied markedly among soil orders. Irrespective of levels of temperature, B adsorption was greater in the Vertisol, followed by Inceptisol and Alfisol (Fig. 1). Relatively greater B adsorption in Vertisol may be ascribed to its high CEC, clay and $CaCO_3$ content which provide major B adsorbing surfaces in soil. Acidic soil reaction in Alfisol might have been responsible for low B adsorption. Boron at low pH exists mainly as

Fig. 1. Boron adsorption as influenced by equilibrium time and temperature in different soil orders at (a) 25 ℃ (b) 35 ℃

boric acid molecule [$B(OH)_3$], which being not adsorbed on clay or other adsorbing surfaces, leading to loss through leaching. This often induces B deficiency especially in coarse-textured soils of high rainfall areas (Goldberg 1997; Datta and Bhadoria 1999; Dey *et al.* 2015). Inceptisol had intermediate adsorbing surface indicated by CEC, clay and $CaCO_3$ with neutral soil reaction. Thus, adsorption of B in Inceptisol was in between Vertisol and Alfisol. In all the soils, the B adsorption was characterized by an initial fast reaction followed by a slow one, which is in agreement with earlier reports (Krishnasamy *et al.* 1997; Arora and Chahal 2007). The first step in mechanism for B sorption is rapid due to chemical adsorption of B in the "frayed edge" of the clay surfaces whereas the second step is a much slower due to diffusion of B into the tetrahedral structural position in the crystal (Krishnasamy *et al.* 1997).

The prolonged time requirement for obtaining equilibrium in B adsorption is probably related to diffusion of B from the outer solution into sites that are not readily accessible for adsorption reactions (Datta and Bhadoria 1999; Dey *et al.* 2013, 2017). Kinetics of B sorption also varied in between thermal regimes. At 25 ℃ in Alfisol and Inceptisol reaction completed in 24 h, whereas in Vertisol it even not completed until 72 h. This may be described on basis of higher amount of clay in Vertisol (51%), which results in higher second step adsorption reaction due to diffusion of B in tetrahedral structural position in the clay crystal (Dey *et al.* 2017). Similar results were found by Dey *et al.* (2013) where adsorption reaction completed in 23 h in Alfisol and Inceptisol, whereas it continues in Vertisol even after 23 h. However, at 35 °C B adsorption equilibrium has been reached earlier (at 16 h) for all three soil types (Fig. 1). Compared to 25 °C, the adsorption of B was of lesser extent at 35 °C. At adsorption equilibrium, the amount of adsorbed B was less compared to that at 25 °C. Goldberg *et al.* (1993) also reported a decrease in B adsorption, as a function of temperature in the range of 10 to 40 °C on soils dominant in crystalline minerals. The reason behind this is that B adsorption is chiefly exothermic in nature.

Kinetics of boron adsorption

Irrespective of soil orders and temperature regimes, zero and first order kinetic equations were found poorly fits for description of B adsorption as evident from lower R^2 and higher SE values compared to other models (Table 2). Parabolic equation had higher R^2 (ranging from 0.75** to 0.86**) and lower
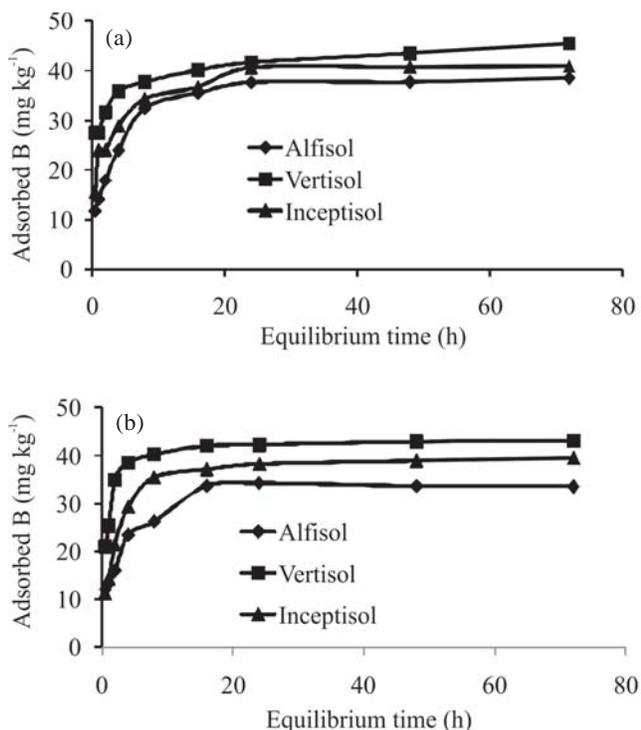
Table 2. Coefficient of determination (R^2) and standard error of estimate (SE) of different kinetic equations for B adsorption

Kinetic model	Soil order	Coefficient of determination (R^2)		Standard error of estimate (SE)	
		25	35	25	35
			Temperature (ºC)		
Zero order	Vertisol	0.68*	0.33	10.7	4.14
	Inceptisol	0.92**	0.36	109	8.92
	Alfisol	0.54*	0.51*	17.4	8.24
First order	Vertisol	0.62*	0.31	5.13	8.37
	Inceptisol	0.46*	0.30	13.9	11.1
	Alfisol	0.47*	0.96**	10.7	14.1
Power function	Vertisol	0.97**	0.77**	2.54	5.17
	Inceptisol	0.89**	0.75**	1.50	17.8
	Alfisol	0.92**	0.91**	5.38	4.71
Parabolic	Vertisol	0.86**	0.53*	3.16	6.24
	Inceptisol	0.75**	0.54*	3.53	7.95
	Alfisol	0.76**	0.73**	6.79	5.51
Elovich	Vertisol	0.98**	0.84**	1.13	4.35
	Inceptisol	0.94**	0.91**	2.72	6.66
	Alfisol	0.95**	0.92**	3.22	2.04

*significant at *P= 0.05*, **significant at *P= 0.01*

SE values (ranging from 3.16 to 6.79), thus can be said to score better than these two equations for describing B adsorption kinetics at 25 °C, however it fails to describe adsorption of B at 35 °C as is evident from comparatively lower R^2 (ranging from 0.53* to 0.73**) and higher SE values (ranging from 5.51 to 7.95). Elovich equation was found to be the best to describe the adsorption kinetics of B irrespective of thermal regime and soil types. Elovich equation scores highest R^2 and lowest SE, the value of which ranged in between 0.84** to 0.98** and 1.13 to 6.66, respectively. Interestingly power function was at par with Elovich equation for describing B adsorption kinetics at 25 °C, registering even lower SE for Inceptisol (1.50) as compared to that of Elovich (2.72). However, Elovich equation was a far better fit for B adsorption data at 35 °C, compared to power function (Table 2). Our results were in concurrence with the earlier findings of Arora and Chahal (2007).

Conclusions

The present study can conclude that Elovich kinetic model can be used to explain B adsorption in all these soils satisfactorily. Adsorption of B was the highest in Vertisol, followed by Inceptisol and Alfisol. For B adsorption studies, temperature is a very important factor. It not only controls amount of absorption but also the time required. A further study on effect of temperature on B adsorption is required for better prediction and modelling.

Acknowledgement

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