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Kinetics of Boron Adsorption in Soils of Assam State, India

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Batch studies were conducted to investigate the adsorption behaviour of boron in four major soil orders of Assam *viz.* entisol, inceptisol, alfisol and ultisol, which had wide variations in physico-chemical properties. Three mathematical models (*viz.*, zero order, first order and parabolic diffusion) were used to describe kinetics of boron adsorption. The boron adsorption pattern was characterized by an initial fast reaction followed by a slow process and the equilibrium was attained in 24 h of equilibration. The boron adsorption with respect to reaction time was positively and significantly correlated with organic carbon content (r = 0.901**), clay (r = 0.964**), free Fe_2O_3 (r = 0.774**), free Al_2O_3 (r = 0.868**) and total free $Fe_2O_3 + Al_2O_3$ (r = 0.882**) of the soils. The parabolic diffusion equation was found to be the best to describe the rate of boron adsorption as indicated by the highest values of coefficient of determination, R^2 (0.980 to 0.985) and lowest values of standard error (SE) (6.56 to 10.76) over the entire time range from 0 to 70 h. This observation leads to the conclusion that the adsorption of boron in soils of Assam was mainly controlled by diffusion.

Keywords: Adsorption, Kinetics, Parabolic diffusion, Boron.

INTRODUCTION

Availability of boron in soils is mainly governed by adsorption process on to soil surface [1] and there exist equilibrium between boron in soil solid and liquid phases [2,3]. Liquid phase boron mostly exist as undissociated H_3BO_3 or as an anion in soil solution. At relatively low concentrations (< 0.1 M) H_3BO_3 dissociates and hydrates to form $B(OH)_4^-$ which is the ionic species present in soil solution. Moreover, it was reported that boron was adsorbed or fixed more easily than it was removed from the soil by leaching [4]. Therefore, the mechanism of adsorption is an important factor of boron nutrition in plants.

Kinetics of adsorption reactions of boron in soils is important for retention and release of boron for plant nutrition. It was reported that boron adsorption reactions were completed in 12 h [5], whereas adsorption equilibrium was established in less than 2 h after boron was added [6]. Adsorption of boron was almost completed after 24 h in agricultural soils of Tamil Nadu (South India) [7]. Six kinetic models had been tested by Some scientists (*viz.* zero order, first order, second order, Elovich, power function and parabolic diffusion) to describe the boron adsorption in benchmark soils of Punjab [8]. It had been observed that boron equilibrium was only attained under conditions of prolonged reaction period. The prolonged time requirement was probably related to diffusion of boron from the outer solution into sites that are not readily accessible for adsorption reactions [9]. With this background information present investigation was carried out in soils of Assam, India to assess the kinetics of boron adsorption. The information on energies of boron retention and kinetics of boron adsorption will be helpful in evolving empirical relationships that predict boron availability to plants in the major groups of soils of Assam, India.

EXPERIMENTAL

Soils: The study was carried out in four surface (0-15 cm) soil samples, belonged to the four major orders of Assam *viz.* entisol, inceptisol, alfisol and ultisol (Table-1). The physical and chemical parameters *i.e.* pH and organic carbon [10], texture [11], cation exchange capacity [12], free oxides of iron [13] and aluminium [14] of the soils were determined by following standard procedures.

Kinetics of boron adsorption: Experiment on kinetics of boron adsorption was conducted by adding 20 mL of 0.01 M $CaCl_2$ background electrolyte containing 40 μg mL^{-1} boron as boric acid (H_3BO_3) to 10 g of soil taken in 100 mL polypropylene centrifuge tubes in duplicate. The soil solution suspensions were allowed to equilibrate with intermittent shaking at constant room temperature 23°C (± 1 °C) for different time intervals

TABLE-1
DETAILS OF THE SOIL SAMPLES

Sample notation	Location	Taxonomic order	Latitude	Longitude
S_1	Majuli	Entisol	26°50'N	94°03'E
S_2	Baghchung	Inceptisol	26°43'N	94°13'E
S_3	Balijan	Alfisol	26°25'N	94°10'E
S_4	Shilonijaan	Ultisol	26°19'N	93°50'E

ranging from 1 to 70 h. At the end of the reaction time, the suspensions were centrifuged at 8000 rpm for 5 min and filtered with Whatman No. 42 filter paper. The filtrate was analyzed for boron concentration spectrophotometrically using azomethine-H method [15]. The amount of boron adsorbed by the soils was calculated as the difference between added boron and boron present in equilibrium solution.

Modelling of rate kinetics: The data on kinetics of boron adsorption were described by following equations:

Zero order equation: The zero order equation used was $q_t = q_0 + K_0t$, where, q_0 and q_t are the amounts of boron adsorbed (μg B g^{-1}) at time zero and t, respectively and K_0 is the zero order constant (μg B g^{-1} h^{-1}).

First order equation: The first order equation was taken as $\ln q_t = \ln q_0 + K_1t$ where, q_0 and q_t are the amounts of boron adsorbed (μg B g^{-1}) at time zero and t, respectively and K_1 is the first-order rate constant (h^{-1}).

Parabolic diffusion equation: The parabolic diffusion equation used was of the form $q_t = \alpha + Kdt^{1/2}$ where, q_t is the amounts of boron adsorbed (μg B g^{-1}) at time t and K_d is the diffusion rate constant [(μg B g^{-1}) $h^{-1/2}$].

Statistical evaluation: Mathematical equations including the zero order, first order and parabolic diffusion were evaluated statistically by calculating co-efficient of determination (R^2) and standard error of the estimate (SE) for each equation. Least square regression analysis for boron adsorption kinetics data of the soils were done to find out the R^2 value of the regression equations. The standard errors of estimate (SE) were calculated by using the following equation [16].

$$SE = \left(\frac{\Sigma(q - q')^2}{(N-2)} \right)^{0.5}$$

where q and q' were the measured and the calculated amounts of boron in soil, respectively, at time t and N is the number of measurements.

RESULTS AND DISCUSSION

Soil properties: The soils of Assam varied in pedogenic development from entisol to ultisol had texture ranged from sandy loam to sandy clay loam, pH ranged from 4.95 to 7.12, organic carbon content from 0.87 to 1.10 %, clay content ranged from 15.30 to 25.6 %, cation exchange capacity from 5.50 to 9.50 c mol (p+) kg^{-1} and free Fe and Al oxides content from 0.43 to 1.12 and 0.34 to 0.71 %, respectively (Table-2).

Kinetics of boron adsorption: The concentration of boron in solution gradually decreased with the increase of equilibration time in all soils till 24 h of reaction time (Table-3). After that boron concentration in solution is almost constant in all the soils. Therefore, it can be inferred from the data that equilibrium of the boron adsorption reaction was attained at 24 h of equilibration time in all the four major soil orders of Assam. The equilibrium concentration of boron for S_1, S_2, S_3 and S_4 soils at 24 h was 23.5, 23.6, 26.9 and 15.4 μg mL^{-1}, respectively. The finer the texture, the higher was the adsorption of boron. Boron adsorption was positively correlated with organic carbon (r = 0.901**), clay content (r = 0.964**), free Fe_2O_3 (r =0.774*), free Al_2O_3 (r = 0.868**) and total free Fe_2O_3 + Al_2O_3 (r = 0.882**) of the soils (Table-4).

TABLE-4
SIMPLE CORRELATION COEFFICIENT OF BORON ADSORPTION (μg g^{-1}) WITH RESPECT OF TIME WITH DIFFERENT SOIL PROPERTIES

Soil properties	B adsorption (μg g^{-1})
pH	-0.413
Organic C	0.901**
Sand	-0.334
Silt	-0.423
Clay	0.964**
CEC	0.559
Free Fe_2O_3	0.774*
Free Al_2O_3	0.868**
Free Fe_2O_3 + Al_2O_3	0.882**

*Significant at 5 % level, **Significant at 1 % level

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF THE SOILS

Sample No.	pH	Organic carbon (%)	Mechanical analysis (%)			Textural class	Cation exchange capacity [c mol (p+) kg^{-1}]	Free Fe_2O_3 (%)	Free Al_2O_3 (%)	Free Fe_2O_3 + Al_2O_3 (%)
			Sand	Silt	Clay					
S_1	7.12	0.98	60.00	22.00	17.60	Sandy loam	9.50	0.75	0.52	1.27
S_2	5.20	1.05	55.00	28.00	17.00	Sandy loam	7.45	0.90	0.41	1.31
S_3	5.40	0.87	62.00	22.50	15.30	Sandy loam	5.50	0.43	0.34	0.77
S_4	4.95	1.10	52.00	22.30	25.60	Sandy clay loam	9.10	1.12	0.71	1.83

TABLE-3
CONCENTRATION OF BORON (μg mL^{-1}) IN SOLUTION WITH RESPECT TO EQUILIBRATION TIME IN SOILS OF ASSAM

Sample No.	Time (h)											Mean
	0	1	4	8	10	12	24	30	40	50	70	
S_1	36.4	30.7	28.4	27.0	26.2	24.8	23.5	23.3	23.2	23.2	23.1	26.35
S_2	35.8	31.6	28.3	27.2	25.1	24.5	23.6	23.5	23.3	23.0	23.0	26.26
S_3	37.4	33.9	32.5	30.8	28.9	27.2	26.9	26.8	26.8	26.7	26.5	29.49
S_4	34.3	27.5	23.0	21.2	19.5	16.5	15.4	15.3	15.2	15.1	15.0	19.82

In all the soils, the boron adsorption was characterized by an initial fast reaction followed by a slow process. The rapid initial rate of adsorption could be attributed to a chemical reaction and the subsequent slow reaction was the diffusion of boron into micro pores of inorganic and organic compounds [17]. Equilibrium of boron adsorption was attained at 24 h of equilibration in all the soils as at 30, 40, 50 and 70 h of equilibration time adsorption of boron was almost similar to that of at 24 h (Table-5). At equilibrium (24 h) the adsorption of boron in S_1, S_2, S_3 and S_4 soils was 33.0, 32.8, 26.2 and 49.2 µg g^{-1}, respectively.

Mathematical equations including zero order, first order and parabolic diffusion equation were tested by least square regression analysis for boron adsorption in all the soils to determine the best equation for describing the data (Figs. 1-3). The coefficient of determination (R^2) and the standard error of estimate (SE) were calculated for each equation (Table-6). The equations that had the highest coefficient of determination (R^2) and the lowest standard error of estimate (SE) values were considered to be the best fit [18].

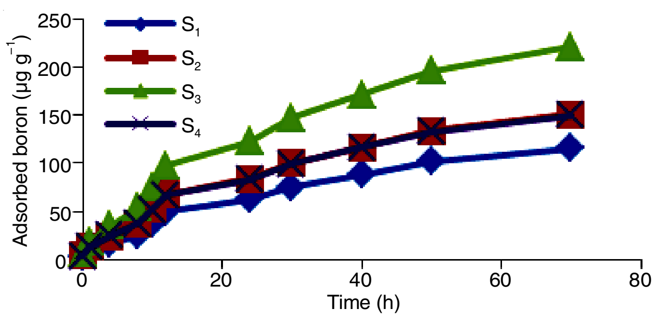

Fig. 1. Plot of zero order boron adsorption kinetic in soils of Assam

It was evident from the Table-6 that, among the three kinetic models, the parabolic diffusion equation was the best fit because of the overall highest values of R^2 (0.980 to 0.985) and the lowest values of standard error of estimate (6.56 to 10.76). In the zero order kinetic equation, the R^2 values ranged

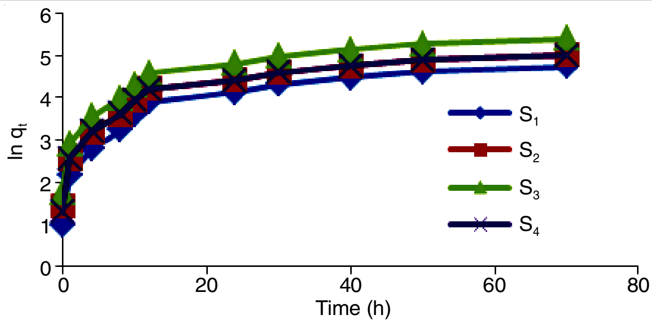

Fig. 2. Plot of first order boron adsorption kinetic in soils of Assam

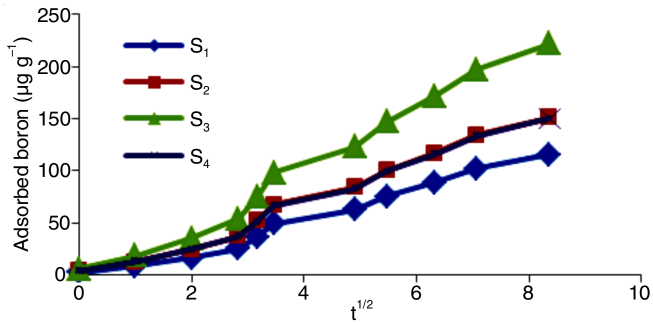

Fig. 3. Plot of parabolic diffusion of boron adsorption kinetic in soils of Assam

from 0.928 to 0.936, but could not describe the adsorption of boron because of high error of estimate value (9.15 to 19.48). The first-order kinetic equation also did not describe boron adsorption sufficiently in all the soils studied, as is evident from lower values of R^2 (0.609 to 0.629) and very high error of estimate values (395.25 to 788.96). These observations further emphasize the conjecture that the adsorption kinetics of boron in these soils was mainly diffusion controlled.

Conclusion can be drawn from above discussion that the equilibrium of boron adsorption is attained at 24 h in all the four soils of Assam, India *viz*., entisol, inceptisol, alfisol and ultisol. Therefore, 24 h of equilibration could be taken as standard to study the boron-adsorption characteristics in these soils. Soil characteristics that directly controlled the kinetics

TABLE-5
AMOUNT OF BORON ADSORBED (µg g^{-1}) BY SOIL WITH RESPECT TO REACTION TIME IN SOILS OF ASSAM

Sample No.	Time (h)											Mean
	0	1	4	8	10	12	24	30	40	50	70	
S_1	7.2	18.6	23.2	26.0	27.6	30.4	33.0	33.4	33.6	33.6	33.8	27.30
S_3	8.4	16.8	23.4	25.6	29.8	31.0	32.8	33.0	33.4	34.0	34.0	27.47
S_5	5.2	12.2	15.0	18.4	22.2	25.6	26.2	26.4	26.4	26.6	27.0	21.02
S_7	11.4	25.0	34.0	37.6	41.0	47.0	49.2	49.4	49.6	49.8	50.0	40.36

TABLE-6
COEFFICIENT OF DETERMINATION (R^2) AND STANDARD ERROR OF ESTIMATE (SE) OF KINETIC EQUATIONS FOR BORON ADSORPTION IN SOILS OF ASSAM

Sample No.	Equations					
	Parabolic diffusion: $q_t = \alpha + Kdt^{1/2}$		Zero order: $q_t = q_0 + K_0t$		First order: $\ln q_t = \ln q_0 + K_1t$	
	SE	R^2	SE	R^2	SE	R^2
S_1	6.72	0.985**	13.72	0.929**	531.87	0.609
S_2	7.12	0.984**	13.42	0.928**	535.15	0.625
S_3	6.56	0.980**	9.15	0.936**	395.25	0.629
S_4	10.76	0.984**	19.48	0.929**	788.96	0.621

* Significant at 5 % level, ** Significant at 1 % level

of boron adsorption were organic carbon, clay content and free oxides of iron and aluminium. The adsorption kinetics of boron in these soils was the best fit in the parabolic diffusion equation, hence the process of boron adsorption was diffusion controlled and the diffusion coefficients of the equation of the respective soils could be used to predict the rate of boron adsorption of the soil.

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