Boron Desorption Kinetic in Calcareous Soils

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Abstract

Boron release (desorption) is one of the important factors use in estimating fertilizers use efficiency and management of boron in agricultural soils and correlation soil properties with it availability to plant. Chemical kinetics for boron desorption experiment was carried out of boric acid (source for boron fertilizer) under controlled conditions in three calcareous soils (clay, loamy and sandy loam) from central Iraq at three temperatures (278, 298 and 308 Kelvin), by using six mathematical and empirical equations viz. Zero order, First order, Second order, Parabolic diffusion, Power function and Elovich equation were used to study kinetic behavior of boron in calcareous soils.

Elovich equation was the best for predication and describing boron released with highest correlation r = 0.942 and t value (9.004), and lowest SE.e (0.530) where boron release rate constant (K) was positively correlated with temperature (r = 0.978). Released rate constant (K) was increased from 0.329 to 0.561 hrs^{-1} as increasing incubation temperature from 278 to 308 K. Soils texture effect in boron release activation energy (Ea) in three soils under study. The overall average of boron release activation energy of three soils was 15.284 and the highest was 20.923 in clay soil and the lowest amount was 4.596 in sandy loam while loamy soil gave 20.332 KJ mol^{-1}.

Keywords: boron release, kinetic models, texture

1. Introduction

Growth, development and completion life of most economic plants depends mainly on the availability and release of ions in soil system. Fried and Broeshart (1967) explained that the process of ion interaction in the soil and its transfer to plant root system can be described according to the following equation:

$$A \longleftrightarrow B \longleftrightarrow C$$

where, A: amount of ions in soil solution; B: amount of adsorption ion; C: represents the amount of ion retention in the form of limited and low-solubility compounds.

When equilibrium occurrence between A and B is fast reaction and this reaction determines the initial adsorption surface (t = 0) while the interaction between the two components (B and C), which is type of forward reaction, is generally slow, because strength bond of ion in component C is relatively high. Boron quantities in soil solution are usually controlled by adsorption-desorption reactions.

Two types of equations have been used to describe the relationship between path and speed of boron release reactions over time, one of which is based on kinetic chemistry as the Zero-order, First and Second-order equations, and the second is based on natural bases such as Parabolic and empirical as Power function and Elovich (Sparks, 1986). The comparison between the two equations is based on statistical parameters, namely correlation coefficient (r), determined coefficient (r^2), SE.e and t value (Al-Ameri, 2001, 2013).

In order to study kinetic behavior of boron in calcareous soil, a laboratory experiment (batch Technic) was conducted under controlled conditions to study the kinetic chemistry of boron release reactions at three different temperatures in three soils from center of Iraq.

2. Materials and Methods

The experiment was conducted to characterize the kinetic behavior of boron with time (using 11 time periods from zero to 720 hour) and temperature 278, 298, and 308 Kelvin implementing different kinetics equations in three calcareous soils from the center of Iraq, chemical and physical soil properties estimate according to Page et al. (1982) (Table 1). For this purpose, 125 gm of plastic pots was used; 100 g of soil was packed in these pots. Adding of boric acid as a source of boron fertilizer in solution of 20 mg kg^{-1} solvent in calcium chloride solution (0.01 molar) and in the form of Bands. Cover the compost with about 15 gm of soil (1 cm deep). Soil moisture was maintained at 80% of field capacity during incubation periods of 0, 0.5, 1.0, 2.0, 4.0, 6.0, 24, 96, 240, 480, 720 hours. Loss of soil moisture was compensated periodically depending on weight throughout the course of the experiment. Samples were taken at the end of each incubation period, dried and sieved with 2.0 mm sieve. Boron was extracted with hot water according to Berger and Truog (1939) and estimated by ICP (Inductivity Couple Plasma Atomic Emission Spectrometer model ICPE-9000 SHIMADZU).

Table 1. Soil chemical and physical properties

Property	Unit	Value		
		Clay	Loam	Sandy loam
EC 1:1	dSm^{-1}	0.72	7.47	0.16
pH 1:1		7.50	6.82	7.69
Calcium carbonite	g kg^{-1} soil	238.3	250.0	256.0
Organic mater		20.0	1.98	4.0
NH$_4$-N	mg N Kg^{-1} soil	40.88	30.92	12.32
NO$_3$-N		14.7	10.42	7.7
Available-P	mg Kg^{-1} soil	18.21	23.51	13.29
Available-Ca		74.49	81.425	46.52
Available-Mg	C mole + kg^{-1} soil	5.48	5.95	1.80
Available-K		7.58	9.83	1.16
Boron (H.W.)	mg Kg^{-1} soil	1.268	3.050	0.147
Sand		162.64	428.7	755.51
Silt	g kg^{-1} soil	378.03	368.7	80.16
Clay		459.33	202.6	164.33
Texture		Clay	Loam	Sandy loam

Several kinetic equations based on kinetic chemistry and mathematical and physical equations have been used to describe boron release in the soil system (Chien et al., 1980; Al-Ameri, 2001; 2013):

➢　Zero order equation: $C_t = C_0 - kt$

➢　First order equation: $LnC_t = LnC_0 - kt$

➢　Second order equation: $1/C_t = 1/C_0 + kt$

➢　Parabolic diffusion equation: $C_t = C_0 - k\sqrt{t}$

➢　Power function equation: $LnC_t = LnC_0 - kLnt$

➢　Elovich equation: $C_t = C_0 - kLnt$

where, C_t: boron desorption at $t > 0$; C_0: boron desorption at $t = 0$; k: Release rate constant; t: time.

3. Results and Discussion

In order to determine relationship between behavior of boron desorption speed reactions with incubation period (reaction time), six equations were used, some of which were based on kinetic chemistry, (Zero, First and Second order) and equations of natural bases, such as Parabolic diffusion equation and mathematical, empirical bases, like Elovich and Power function equation at three temperatures are 5, 25 and 35 °C (278, 298 and 308 Kelvin). Some statistical parameters (r, r^2, and t) and standard error of estimate (SE.e) were used to evaluate the efficiency of these equations in description boron desorption (Tables 2, 3 and 4).

Results showed (Tables 2, 3, 4; Figure 1) that Elovich equation was the most efficient in describing relationship between boron desorption and reaction time (t) and was significantly at ($P \leq 0.01$) in clay, loam and sandy loam soils, with highest correlation coefficient (0.929, 0.923 and 0.974), respectively and highest value of calculated t (7.291, 7.286 and 12.343) compared with other equations that used in the study. The efficiency of these equations in description boron desorption and evaluation release rate were 0.86, 0.85 and 0.95% for clay, loam and sandy loam soils respectively. The equations used in this study can be arranged in the following order: Elovich > Power function > Parabolic diffusion > Second order > First order > Zero order.

Table 2. Efficiency of kinetic and experimental equations in describing relationship between boron desorption and time (n = 11) in Clay soil

Equation	Mathematical model	Temperature degree	r**	r²	Standard error of estimate SE.e	t value
Zero order	$C_t = C_0 - k_t$	5	0.915	0.838	0.873	6.821
		25	0.776	0.602	0.751	3.687
		35	0.763	0.582	1.145	3.541
		Mean	0.818	0.674	0.923	4.683
First order	$LnC_t = LnC_0 - k_t$	5	0.932	0.868	0.059	7.702
		25	0.803	0.645	0.052	4.039
		35	0.796	0.633	0.066	3.941
		Mean	0.844	0.715	0.059	5.227
Second order	$1/C_t = 1/C_0 + k_t$	5	0.945	0.892	0.004	8.622
		25	0.828	0.686	0.004	4.431
		35	0.826	0.682	0.004	4.397
		Mean	0.866	0.753	0.004	5.817
Parabolic diffusion	$C_t = C_0 - kLn_t$	5	0.965	0.932	0.566	11.091
		25	0.892	0.796	0.447	5.593
		35	0.845	0.713	0.949	4.732
		Mean	0.901	0.814	0.654	7.139
Power function	$LnC_t = LnC_0 - kLn_t$	5	0.893	0.798	0.072	5.623
		25	0.931	0.866	0.027	7.177
		35	0.947	0.897	0.030	8.368
		Mean	0.923	0.854	0.043	7.056
Elovich	$C_t = C_0 - kLn_t$	5	0.903	0.815	0.913	5.934
		25	0.935	0.874	0.352	7.452
		35	0.949	0.900	0.474	8.487
		Mean	0.929	0.863	0.580	7.291

Note. ** significant at level 0.01.

Elovich equation success in describing boron desorption corresponds to what Al-Falahi (2000) mentioned when he studied boron release kinetics in a number of soils from central and southern of Iraq. He pointed out that this equation can give a clear picture of the mechanism of boron releasing from these soils; boron release can be considered a complex function of heterogeneous surfaces, binding forces, chemical and physical nature of the reaction system. Al-Ameri (2013) also pointed to the superiority of Elovich equation and Power function in describing boron behavior with time in calcareous soil from central Iraq. These results are consistent with Peryea et al. (1985) when they found that Elovich equation succeeded in describing boron release data successfully in four soils from California.

Table 3. Efficiency of kinetic and experimental equations in describing relationship between boron desorption and time (n = 11) in Loamy soil

Equation	Mathematical model	Temperature degree	r**	r²	Standard error of estimate SE.e	t value
Zero order	$C_t = C_0 - k_t$	5	0.880	0.774	0.945	5.559
		25	0.871	0.759	0.495	5.322
		35	0.710*	0.504	1.246	3.025
		Mean	0.820	0.679	0.895	4.635
First order	$LnC_t = LnC_0 - k_t$	5	0.891	0.793	0.056	5.876
		25	0.883	0.779	0.029	5.630
		35	0.747	0.558	0.072	3.372
		Mean	0.840	0.710	0.052	4.959
Second order	$1/C_t = 1/C_0 + k_t$	5	0.898	0.806	0.003	6.108
		25	0.893	0.798	0.002	5.960
		35	0.782	0.611	0.004	3.763
		Mean	0.858	0.738	0.003	5.277
Parabolic diffusion	$C_t = C_0 - kLn_t$	5	0.935	0.874	0.708	7.887
		25	0.941	0.886	0.340	8.378
		35	0.783	0.613	1.102	3.772
		Mean	0.886	0.791	0.717	6.679
Power function	$LnC_t = LnC_0 - kLn_t$	5	0.810	0.656	0.067	3.902
		25	0.957	0.915	0.017	9.304
		35	0.897	0.805	0.040	5.755
		Mean	0.888	0.792	0.041	6.320
Elovich	$C_t = C_0 - kLn_t$	5	0.912	0.831	0.845	6.280
		25	0.960	0.923	0.261	9.798
		35	0.898	0.807	0.620	5.780
		Mean	0.923	0.854	0.575	7.286

Note. ** significant at level 0.01, * significant at level 0.05.

Results showed (Table 5) that increase in the incubation temperature from 5 to 35 °C increased boron release rate constant from 0.329 to 0.561 mg kg^{-1} hours^{-1} with increase of 70.5%. The results showed a positive correlation between reaction temperature (T) and boron release constant (K) according to the simple linear regression equation: $K = 0.2827 + 7.4286 \times 10^{-3} T$ (r = 0.978). This equation shows that increasing reaction temperature one absolute degree led to an increase boron release rate constant by 7.4286×10^{-3} mg kg^{-1} absolute degree. Increasing reaction temperature led to increases kinetic energy amount of the molecules, which increases the number of collisions between these molecules in time unit, which in turn increases molecules number that have energy equal to or greater than activation energy (Ea), which increases or Double desorption reactions speed (Bohn et al., 1985; Chang, 1977).

Table 4. Efficiency of kinetic and experimental equations in describing relationship between boron desorption and time (n = 11) in Sandy loam soil

Equation	Mathematical model	Temperature degree	r**	r^2	Standard error of estimate S.Ee	t value
Zero order	$C_t = C_0 - k_t$	5	0.753	0.567	1.335	3.431
		25	0.842	0.710	1.053	4.689
		35	0.849	0.721	1.184	4.825
		Mean	0.815	0.666	1.191	4.315
First order	$LnC_t = LnC_0 - k_t$	5	0.783	0.613	0.077	3.772
		25	0.865	0.748	0.067	5.174
		35	0.879	0.773	0.067	5.534
		Mean	0.842	0.711	0.070	4.827
Second order	$1/C_t = 1/C_0 + k_t$	5	0.810	0.657	0.005	4.151
		25	0.886	0.786	0.004	5.745
		35	0.906	0.821	0.004	6.418
		Mean	0.867	0.755	0.004	5.438
Parabolic diffusion	$C_t = C_0 - kLn_t$	5	0.853	0.727	1.059	4.901
		25	0.971	0.942	2.441	11.423
		35	0.926	0.858	0.845	7.372
		Mean	0.917	0.842	1.448	7.899
Power function	$LnC_t = LnC_0 - kLn_t$	5	0.967	0.936	0.028	10.808
		25	0.980	0.960	0.027	13.931
		35	0.966	0.934	0.035	10.609
		Mean	0.971	0.943	0.030	11.783
Elovich	$C_t = C_0 - kLn_t$	5	0.968	0.936	0.441	10.825
		25	0.983	0.965	0.358	14.958
		35	0.971	0.943	0.504	11.518
		Mean	0.974	0.948	0.434	12.434

Note. ** significant at level 0.01.

Number of studies have indicated temperature effect on the speed and path of boron release rate constant (K), Goldberg et al. (1993) pointed out that Boron adsorption decreased with increasing temperature from 10 to 40 °C, Al-Falahi (2000) mentioned that boron releases increased with the increasing of temperature when he studied status and behavior of boron in Iraqi soil, Al-Ameri (2013) pointed out B concentrations increased with temperature.
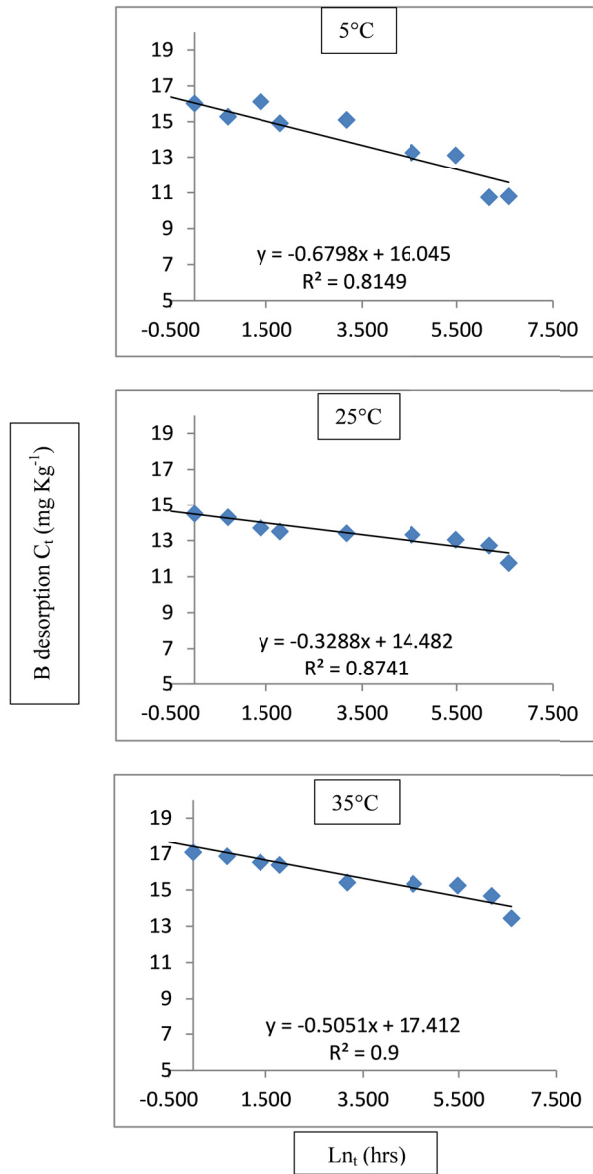
Figure 1. Relationship between boron desorption C_t (mg Kg^{-1}) with time Ln_t (hrs.) according to Elovich equation in clay soil
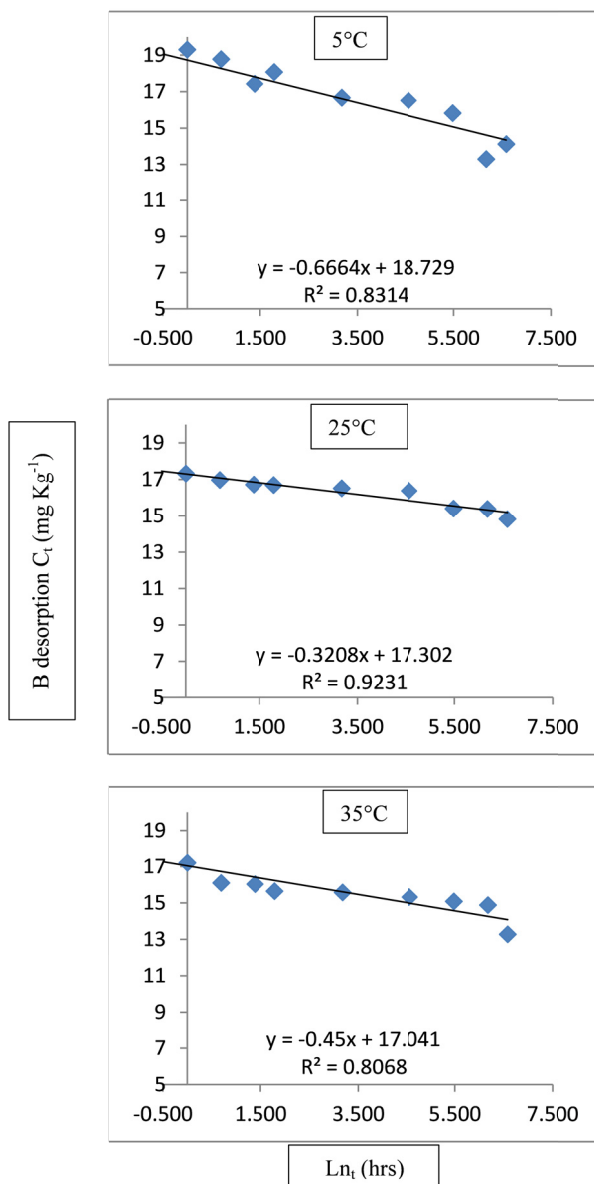
Figure 2. Relationship between boron desorption C_t (mg Kg^{-1}) with time Ln_t (hrs.) according to Elovich equation in loam soil
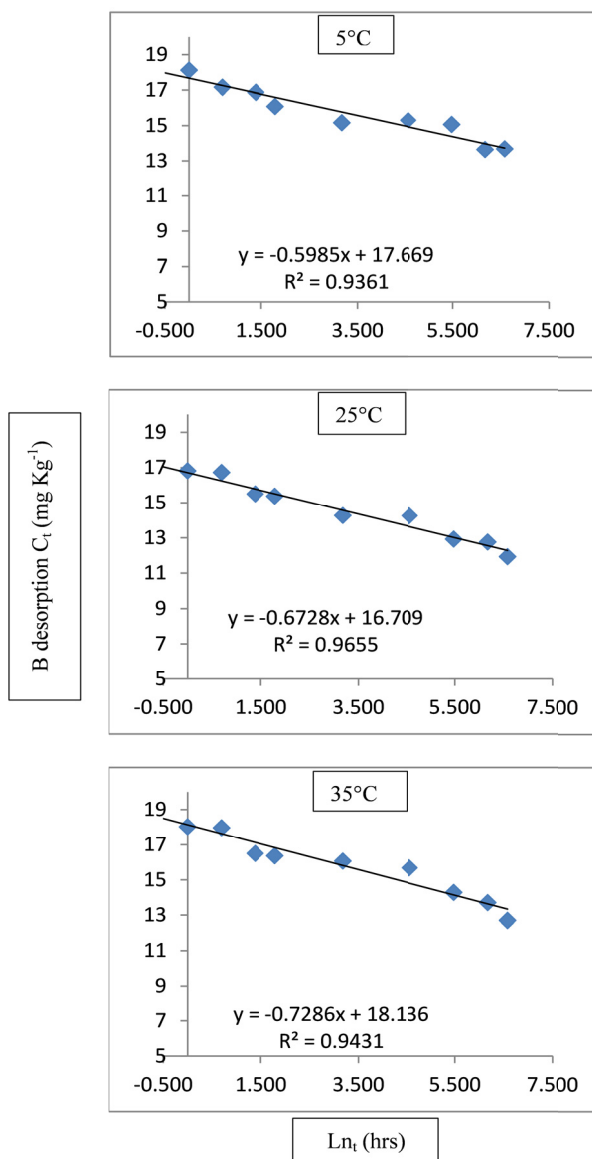
Figure 3. Relationship between boron desorption C_t (mg Kg^{-1}) with time Ln_t (hrs.) according to Elovich equation in sandy loam soil

Table 5. Release rate constant and activation energy of boron at different incubation temperatures and for all incubation periods

| Soil | K release rate B (mg Kg^{-1} $hours^{-1}$) | | | Mean | Activation energy (Ea KJ mol^{-1}) |
| | Incubation temperature | | | | |
	5	25	35		
Clay	0.202	0.329	0.505	0.345	20.923
Loam	0.188	0.321	0.450	0.320	20.332
Sandy loam	0.598	0.673	0.729	0.667	4.596
Mean	0.329	0.441	0.561	0.444	15.284

Soil texture was found to have an effect on the path and boron release rate constant (K), as indicated by the results shown in Table 5. The highest mean of boron release rate constant for all temperatures and incubation periods was in sandy loam soil. The mean release constant for this element was 0.345, 0.320 and 0.667 mg B kg^{-1} hrs^{-1} for clay, loam and sandy loam respectively. Average boron release rate constant in sandy loam soil compared to clay and loam soil was increased due to the chemical and physical soil properties. The low clay

content and electrical conductivity (Table 1) have contributed the faster release of this element and increase of its diffusion coefficient from solid phase to liquid phase (soil solution) compared to clay and loamy soil. This is consistent with several studies that indicated increased boron release by low clay content and electrical conductivity as indicated by Nicholaichuk et al. (1988) that Boron adsorption maxima increased with increasing clay content, Awad and Maki (1990) showed that highest values of adsorption maximum recorded in fine textured soils in another study on calcareous soils of Iraq, soils low in clay adsorb less boron than clay-rich soils (Keren, 1996).

Activation energy of boron release in the three soils was calculated according to the Arrhenius equation (Chang, 1977): $LnK = LnA - Ea/R (1/T)$. This equation shows linear relationship between the boron release rate constant (K) and inverted absolute temperature (1/T) there is a positive correlation between K and absolute temperature.

The results indicated the effect of soils under study in boron release activation energy (Table 5). The overall average of boron release activation energy of three soils was 15.284 and the highest was 20.923 in clay soil and the lowest amount was 4.596 in sandy loam while loamy soil gave 20.332 KJ mol^{-1}. Boron release activation energy in clay soil increased by 2.9 and 355.2% compared to its value in loam and sandy loam soil, respectively. This is due to the high clay and organic matter content, low electrical conductivity values which leads to fact that boron is susceptible to rapid reactions such as retention (adsorption and precipitation) on clay and organic matter surfaces as well as formation complexes with dominant ions in soil which contributed in reducing boron release rate constant in those soils compared to sandy loam soil, this is confirmed by many studies Havlin et al. (2005), Goldberg et al. (1996) and Yermiyaho et al. (1995) which indicated that boron release decreases with increasing clay and organic matter content, low electrical conductivity, this means activation energy for boron release reaction is high as a result.

Boron fertilizer release constant increased by a decrease in activation energy Ea (Table 5). Therefore, soil properties, such as clay and silt content, which contribute to reduction boron release rate constant, increase activation energy, thus reducing its availability. These results are consistent with the finding of Havlin et al. (2005) that plants can take larger amounts of boron from coarse texture compared with fine textured soils at equal concentrations of boron dissolved in water.

5. Conclusion

The Soils vary in their capacity to release boron and in activation energy (Ea) which are affecting by temperature, time and clay content. Elovich equation successfully describes boron release kinetics of three soils. It is clear from this study that a large proportion of added boron is subject to rapid release from loam and sandy loam soil due to their low content of clay and organic matter.Therefore, it is necessary to take advantage of the kinetic chemistry concepts in describing boron behavior in management boron fertilizers.

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