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Boron Adsorption and Desorption in Soils with High Boron Content

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Abstract

Boron is one of the microelements that should be carefully monitored in boron-rich soils. Boron is not engaged in leaching, volatilization, or oxidation-reduction reactions, controlling adsorption-desorption mechanisms. These soils are prone to extra B loading from soil-forming processes and agriculture. This work aims to explain adsorption/desorption in B-rich soils in connection to soil characteristics. The sorption parameters were determined by batch sorption study by subjecting a series of B solutions (0-40 mg L^{-1}) prepared in 0.01 M $CaCl_2$ background solution. The desorption properties were determined by extracting the adsorbed B with 0.01 M $CaCl_2$ solution. Statistical tests compared sorption data to Langmuir and Freundlich models. Spearmen correlation reveals model parameters and soil coherence. Both models characterized soil sorption with high determination coefficients, although Langmuir isotherm was superior. There was a significant correlation between maximum adsorption capacity and sand content (R^2 = -0.882, $p<0.05$). Up to 10 mg kg^{-1}, the experimental sorption capacities of soils are unaffected; there was even a decline in adsorption capacity at this concentration, indicating desorption controlled section. When boron sorption reaches a concentration above 8 mg kg^{-1}, boron mobility increases, and plants can be adversely affected by such concentrations.

Key words

Boron Adsorption, Langmuir isotherm, Freundlich isotherm.

Introduction

Plants need 2-4 mg kg-1 of B. This means plants might develop deficiency and toxicity signs in one season. Boron toxicity is higher in dry, semiarid, and heavy soils (Goldberg, 2004). The high B concentration in some areas of Turkey's soils is attributed to the boron deposits (Kar et al. 2006). This raises B levels in river water, which is utilized for irrigation, and B enrichment in the soil is more dangerous.

Adsorption-desorption processes in soils govern plant B uptake (Goldberg, 1997). It is known that B adsorption rises as a function of pH from 3 to 9 (Van Eynde et al. 2020) and declines at pH 10 and above (Goldberg and Glaubig, 1986). It has been shown that the B adsorption maximum values are highly linked with soil pH (Evans, 1987). Researchers reveal that Fe-Al oxides exhibit strong B sorption (Anuo et al. 2021). Boron adsorption happens through ligand exchange with surface hydroxyl groups (Su and Saurez, 1995). Organic matter is also a significant soil component for B adsorption. There are two conflicting views on the B adsorption of organic matter: organic matter contributes significantly to B adsorption (Tlili et al. 2019), and organic matter reduces B adsorption ability by masking B adsorption sites of clays and/or oxide minerals (Diana et al. 2010). All of these above-mentioned adsorption investigations were done within a B-deficient environment. Natural soil formation processes, notably in Turkey, or agricultural techniques, especially fertilization and irrigation, may improve B-rich settings. Due to the inclusion of B as a conditioner in fertilizers (%) (Pişkin, 2021) and B's high solubility in soil, it may seep into natural continental and/or aquatic habitats.

Therefore, the goal of this work is to obtain knowledge about B adsorption and desorption qualities of soils with genetically high B content and to find out the coherence of adsorption parameters and soil features.

Materials and Methods

This research region is located near the Quaternary and Plio-Quaternary basalt and andesite-formed Great and Little Ağrı Mountains. Along the Aras River, Quaternary sediments are prevalent, and there is a Quaternary alluvial fan, slop debris, and moraine on the mountain's downslope. It acquired sediments during the floods, from which soils were produced and used extensively for agriculture. Therefore, the parent material of the examined soils consists of alluvial sediments from the Aras River that are calcareous, heavy, and have a low organic carbon content. In the studied region, basaltic, alluvial, colluvial, regosol, and brown great soil types are prevalent. Iğdır Plain has different problems, such as salinity, alkalinity, and soil drainage, and it is Türkiye's second-largest wind erosion area. There are saline, alkaline, B toxic soils and their combination soils throughout the Plain. Approximately 45% consists of salinity-alkalinity and B toxicity problems which have a surface area of 83.000 ha (Temel and Simsek, 2011). Iğdır has a continental semiarid climate (BSk) with hot and dry summers and cold and snowy winters. Iğdır has one of the most arid climates in Türkiye, averaging 225 mm of mean precipitation per year. The daily average temperature is 12.9°C (Karaoğlu, 2011).

Soil samples (0-20 cm) were taken from 5 points, representing common soil great groups in the Iğdır plain. These soil samples were dried and homogenized by passing through a 2 mm sieve. Some physicochemical properties of the experimental soils were determined by using the suggested methods for neutral to alkaline soils (Sparks et al. 1996). Fractions of sand, silt, and clay were determined by the Bouyoucos hydrometer (Bouyoucos, 1951). pH and EC were measured in suspensions of 1:2.5 with a combined electrode and EC meter (Richards, 1954). The dichromate wet-oxidation method of Walkley-Black was used for organic matter determination (Nelson and Sommers, 1983). The soil's calcium carbonate equivalent (CCE) was determined by a manometric method using a Scheibler calcimeter (Richards, 1954). Cation exchange capacity (CEC) was determined according to the sodium acetate method (Polemio and Rhoades, 1977). Specific surface areas were determined with the aid of a polar molecule ethylene glycol mono ethylene ether (Carter et al. 1986). The plant-available boron was extracted with 0.01 M $CaCl_2$ + 0.05 M mannitol by shaking at 20°C for 16 h and determined by ICP-OES (Thermo Scientific 7200 ICP-OES

Analyzer) (Kinrade and Van Loon, 1974). The amount of B passing into the solution from the soil sample, which was wet-ashed with a mixture of concentrated nitric acid and perchloric acid (3:1, v/v) was determined by ICP-OES (Thermo Scientific 7200 ICP-OES Analyzer) (Kinrade and Van Loon, 1974).

Adsorption/Desorption Experiments

Adsorption

Scoops of 5 g soil samples were weighed into 50 mL plastic tubes in triplicates. The soil samples were equilibrated with 20 mL solutions containing 0, 1, 2, 3, 5, 10, 20, and 40 mg L^{-1} B prepared in 0.01 M $CaCl_2$ at a constant 24±1 °C on a reciprocal shaker at 150 rpm for 23 hours. The supernatants were separated by sequential centrifugation at 4000 rpm for 10 minutes and filtering through Whatman No 42 filter paper. The B concentration in the supernatant solution was then measured by the ICP-OES at 249.773 nm wavelength.

With the following equation, we were able to determine the quantity of B absorbed by comparing the difference between the initial and equilibrium concentrations. The sorption results were checked against the Langmuir and Freundlich adsorption models described below. The confirmation of the sorption data to the Langmuir and Freundlich adsorption models given below were tested.

$$Ce/Si = Ce/b + 1/kb \text{ (Langmuir, 1918)}$$

Where k and b are the binding energy and the sorption maximum, respectively.

$$Si = Kf\ Cn$$

The Freundlich isotherm above can be linearized as follows:

$$\text{Log } (Si) = \text{Log } Kf + n \log Ce$$

Where Kf and n are coefficients related with distribution coefficient and correction factor respectively.

Desorption

After the adsorption process, 20 mL 0.01 M $CaCl_2$ solution were added, and the indigenous and/or adsorbed boron were extracted by shaking at a constant 24 °C for 23 hours as in the evaluation of B availability in the soil. At the end of the equilibrium period, the solid and liquid phases were separated and analyzed as in the adsorption processes. The desorption ratio was calculated by the following equation:

$$\% \text{ desorption} = 100 - (Si - Sides)/Si * 100$$

Where Sides is the quantity of B extracted by the 0.01 M $CaCl_2$ solution (mg kg^{-1}).

Results and Discussion

The physico-chemical properties of the soils used in the study show that the texture classes of the soils are clay (Table 1.). The natural pH of the soils of the region is strongly alkaline, and their EC is in the slightly saline class. They have a high cation exchange capacity above 29.2 cmol kg^{-1} and a very high specific surface area indicating very high clay content. The experimental soils have a lime (CCE) content below 5% with changing organic matter content due to depth of water table and topography. The occurrence of very high phyto-available B in the range of 7.61-15.4 mg kg^{-1} has been limiting economically feasible cultivation of many crops.

Table 1. Some physical and chemical properties of soil

Soil	N	W	pH	EC (µS cm^{-1})	Sand (%)	Clay (%)	Silt (%)	Texture class
A	39° 52' 23"	44° 31' 54"	8.58	1398	20.8	53.3	25.9	Clay
B	39° 55' 14"	44° 25' 56"	8.58	1398	20.8	53.3	25.9	Clay
C	39° 54' 56"	44° 26' 24"	9.15	1259	12.2	54.0	33.8	Clay
D	39° 58' 17"	44° 21' 15"	9.30	1468	1.8	70.2	28.0	Clay
E	39° 58' 40"	44° 18' 20"	9.52	1045	11.8	40.2	48.0	Silty-Clay

Soil	OM (%)	CCE (%)	SSA (m^2 g^{-1})	CEC (cmol kg^{-1})	Available-B (mg kg^{-1})	Total B (mg kg^{-1})	Availability index (%)
A	3.28	4.20	2682	34.7	13.8	213	15.4
B	3.28	4.20	2822	34.6	16.4	231	14.1
C	2.51	4.90	3052	43.1	31.0	262	8.47
D	1.12	3.01	2956	41.0	26.5	202	7.61
E	0.95	4.97	2958	29.2	13.3	170	12.8

CCE calcium carbonate equivalent, SSA specific surface area, CEC cation exchange capacity

Adsorption Isotherm Parameters

Langmuir and Freundlich adsorption models were applied to the boron adsorption data. From these models, qmax (adsorption maximum), KL (Binding Energy), n (adsorption power), and Kf (Binding Energy) values were calculated as adsorption parameters. The isotherm coefficients obtained from the treatment of solutions containing B with different concentrations with five different soils were formed. Adsorption isotherm parameters are as in Table 2.

It was observed that adsorption increased with increasing concentrations in the investigated soils but deviated at higher concentrations (Figure 1). At high pHs, B tends to form in the $[B(OH)_4]^-$ form (Keren and Bingham 1958). The high pH of the investigated soils probably supports the replacement of clay minerals in the form of borate anion with hydroxyl groups (Keren and Bingham, 1958).

Table 2. Adsorption parameters of soils Langmuir and Freundlich isotherm models

0	**Langmuir**				**Freundlich**		
	q_{max}	K_L	R_L	R^2	**n**	**K$_f$**	**R^2**
A	90.1	1.7	0.1	0.93	3.6	28.3	0.91
B	90.9	0.3	0.2	0.98	4.6	38.7	0.97
C	166.6	0.2	0.1	0.99	4.9	73.9	0.97
D	185.2	0.5	0.1	0.99	6.3	101.6	0.97
E	109.9	0.8	0.1	0.98	8.5	67.8	0.91

Boron adsorption data were calculated according to Langmuir and Freundlich Adsorption models (Figure 1). It was found that the data were at acceptable levels in both models. The high determination coefficient of regression shows that Langmuir isotherm defines adsorption data better than Freundlich isotherm for all soils. Researchers such as Arora and Chahal (2010), Elrashidi and O'Connor (1982) also found similar results to the data we found. It is assumed that single-layer adsorption takes place on the Langmuir isotherm. At increasing doses, B adsorption could occur as a multilayer and/or precipitation reaction. It is also due to the heterogeneity of the Langmuir isotherm monolayer reaction and homogeneity versus high B concentrations (Arora and Chahal, 2010; Hingston, 1964).

In order to determine the suitability of adsorption isotherms, a statistical comparison was made between the adsorption maximum values obtained from the Langmuir isotherm equation and the adsorption maximum values obtained experimentally (Figure 2).

For comparison, correlation analysis was made between the adsorption maximum values obtained from the Langmuir isotherm equation for B and the adsorption maximum values obtained experimentally. In the correlation, a statistically significant relationship ($p < 0.01$) was found between the adsorption maximum values obtained from the Langmuir isotherm equation and the experimental adsorption maximum. This situation implies that the soils are similar in terms of general characteristics and differ from each other in terms of B content.

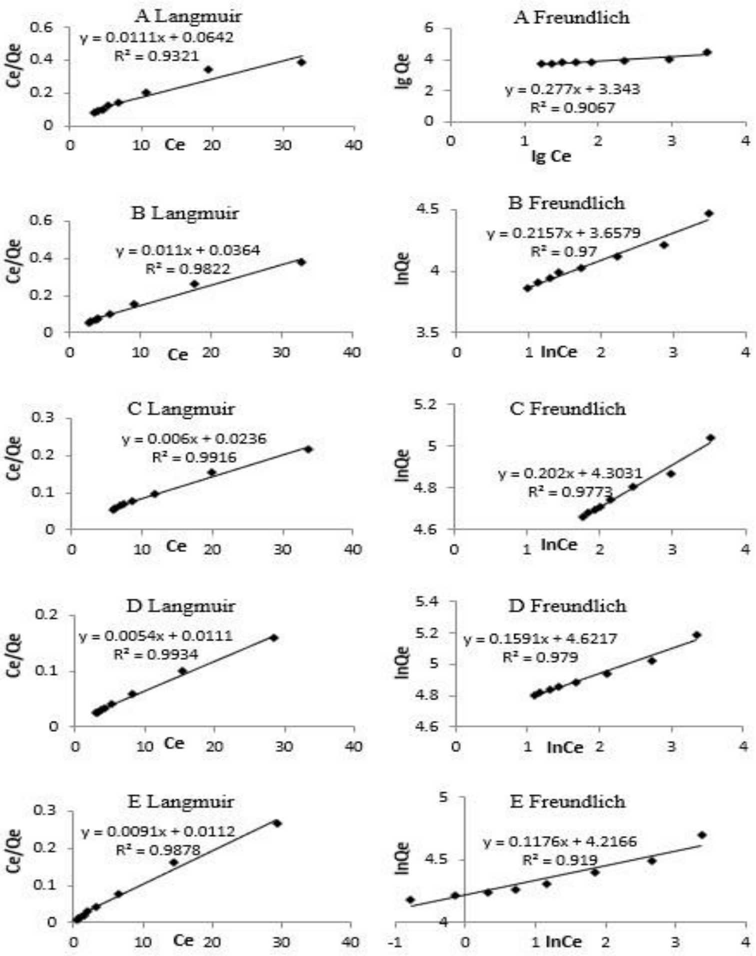

Figure 1. Langmuir and Freundlich isotherms of soils.

There are frequently reported deviations between the experimental data and the ones predicted from the Langmuir model depending on the sorption site heterogeneity, multiple sorption mechanisms, changes in ionic speciation and complexion reactions over a large concentration range, chelate formation, the amount of previously adsorbed sorbate, and desorption. These circumstances in fact result in deviation in the lower and/or upper end of the isotherms leading to the misapplication of the Langmuir equation (Harter and Baker, 1977). Precipitation-derived scavenging mechanism of the sorbate or chelation reactions produces systematically larger sorption maxima with deviation at the upper and lower-end due to apparent decrease and increase in the Ce/Q term, respectively. Since the precipitation reactions were likely to be the main mechanisms in high-loading cases, like the abovementioned case, the calculated sorption maxima were larger than the experimentally observed ones.

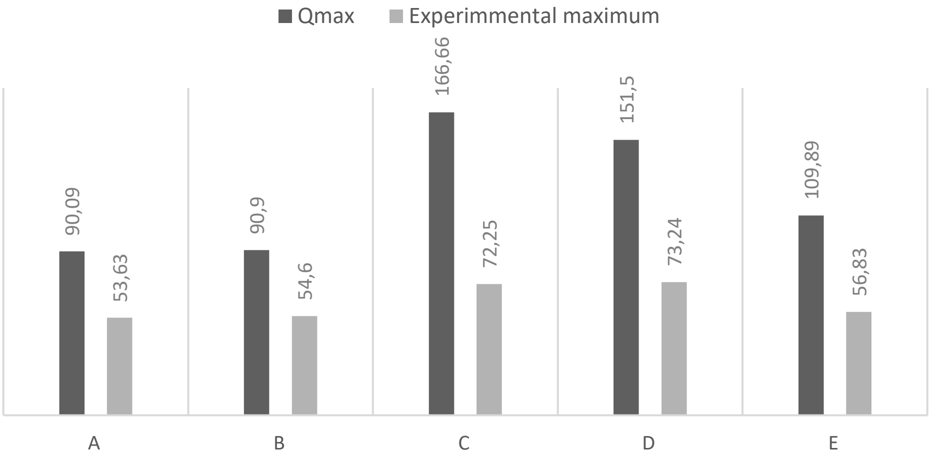

Figure 2. The predicted and experimental B sorption maxima for the soils

Relationships Between the Sorption Parameters and Soil Properties

The correlation analysis between soil properties and coefficients obtained from Langmuir and Freundlich isotherms is given in Table 3. According to these results, the EC value from soil properties is negatively correlated with the RL value obtained from Langmuir isotherms at the level of 0.05. The sand content of soils is negatively correlated with the Kf value obtained from Freundlich isotherms at the level of 0.01.

Table 3. Correlation between soil properties and coefficients obtained from Langmuir and Freundlich isotherms

	K_L	R_L	Qmax	n	K_f
pH	-0.709	0.260	0.342	0.856	0.634
EC	0.408	**-0.879***	0.567	-0.030	0.437
OM	0.552	-0.162	-0.264	-0.834	-0.604
$CaCO_3$	-0.240	0.733	-0.617	-0.059	-0.583
Sand	0.347	0.448	**-0.882***	-0.565	**-0.975****
Clay	-0.156	-0.222	0.703	-0.291	0.536
Silt	-0.128	-0.141	-0.04	0.861	0.244
B	-0.567	-0.120	**0.974****	0.098	0.827
SSA	-0.761	0.097	0.75	0.568	0.802
CEC	-0.431	0.040	0.79	-0.407	0.488
TB	-0.386	0.494	0.23	-0.701	-0.125

* Significant a p≤ 0.05 and ** at p≤ 0.01.

B adsorption is significantly dependent on soil texture. The findings of this study are in line with the results obtained by other studies (Elrashidi and O'Connor, 1982; Mezuman and Keren, 1981; Hatcher et al. 1967; Wild and Mazaheri, 1979) and as clay percentage rises, so does B adsorption maximum (Communar and Keren, 2006). Although there was no statistically significant value, CEC and SSA values were found to be high. As a result, we can say that the soil's clay content and type, pH, specific surface area, and cation exchange capacity are the primary factors influencing boron adsorption. It was found by Keren and Talpaz (1984) that the increased cation exchange capacity of clay was related to the increased B adsorption in smaller clay particles. Contrary to the general knowledge we know about B adsorption, no relationship was found between Qmax and pH, EC, OM, and TB due probably to the similarity of soil properties in many terms.

Boron (B) Desorption

The boron desorption process is related to the amount of B adsorbed. The mechanism of B binding in soils, as well as the type and contact duration of the extraction solution, affect the degree of adsorption and B desorption. It shows that at high saturation of the solid phase matrix, the desorption rate of B is fast, and at high saturation, which indicates that in soils with a capacity of saturated B content, B is rapidly released. In Table 4, the amount of desorbed B was constant at the initial concentrations but decreased after the administration of 10 $mg\ kg^{-1}$ B. In soils with high B content, it is seen that a low concentration of B desorption is constant, B is adsorbed with high energy, and high concentrations have high B desorption due to physical adsorption.

Table 4. Boron desorption rates of soils

B loading ($mg\ kg^{-1}$)	Desorbed %				
	A	**B**	**C**	**D**	**E**
0	96.5	96.3	96.9	95.5	67.6
1	94.7	91.3	94.0	94.7	67.1
2	89.0	87.7	92.2	91.8	66.5
3	89.9	85.7	91.6	88.9	66.8
5	87.0	81.9	87.8	83.5	66.1
10	83.7	78.9	84.0	76.1	68.3
20	80.6	77.9	79.8	71.5	71.8
40	80.0	78.1	77.5	71.1	74.8

Desorption as a Function of Soil Properties

The percentage of desorbed B was found to be lower with a higher amount of B added. Elrashidi and O'Connor also found comparable outcomes (1982). Soils with a greater affinity for boron adsorption are said to desorb less B than those with a lower affinity. In this case, adsorption and desorption of B seemed to be virtually antipodal processes. Consistent with the findings of (Elrashidi and O'Connor 1982).

The contact duration of solution B and the intensity of the B binding in soils determine the amount of the differential between the adsorption and desorption of B. From our data analysis, we learn that when the solid phase matrix is just slightly saturated, B desorbs at a moderate pace, but when it is very saturated, it desorbs quickly. Soil with a greater B adsorption capacity would seem to have a slower B release.

Correlation analysis between soil properties and data obtained from desorption data is given in Table 5. According to these results, sand content and desorption data at high concentrations are positively correlated at p≤0.05. The total B content of soils and desorption data at low initial loadings are positively correlated. A significant correlation was also found in other soil properties. When examining the status of the coefficient in varying concentrations, besides the importance of the relations, there is a constantly increasing positive coefficient in the amounts of lime, sand, and the initial B concentrations. There is a decreasing positive correlation coefficient with an increasing initial concentration of TB content. An increasing positive correlation indicates that these components are not effective in B adsorption. The gradually decreasing negative correlation indicates that the components have a strong B retention, but the decrease indicates that this component moves towards the B sorption saturation; therefore, the energy of the retained B decreases as it approaches saturation (Tlili et al. 2019; Arora and Chahal, 2010; Suganya et al. 2019).

Table 5. The effect of initial B concentration and soil properties on the desorption ratio

	Initial B concertation (mg/L)							
	0	**1**	**2**	**3**	**5**	**10**	**20**	**40**
pH	-0.533	-0.559	-0.532	-0.587	-0.576	-0.569	-0.502	-0.412
EC	-0.202	-0.219	-0.258	-0.246	-0.341	-0.441	-0.549	-0.628
OM	0.703	0.723	0.702	0.753	0.724	0.702	0.633	0.541
$CaCO_3$	0.401	0.422	0.461	0.475	0.547	0.646	0.765	0.844
Sand	0.541	0.584	0.600	0.653	0.731	0.839	**0.923***	**0.953***
Clay	0.070	0.038	0.003	-0.047	-0.121	-0.266	-0.461	-0.607
Silt	-0.576	-0.576	-0.549	-0.536	-0.519	-0.444	-0.288	-0.139
B	0.117	0.065	0.050	-0.019	-0.126	-0.293	-0.460	-0.571
SSA	-0.134	-0.180	-0.168	-0.233	-0.297	-0.389	-0.433	-0.437
CEC	0.518	0.476	0.453	0.393	0.294	0.117	-0.097	-0.264
TB	**0.947***	**0.928***	**0.925***	**0.892***	0.844	0.739	0.593	0.457

* Significant a p≤ 0.05 and ** at p≤ 0.01

It can be concluded that boron desorption is mainly governed by the sand content, but this was actually covering the true effect of sorption sites. As the coefficients of possible B sorption surfaces (e.i. CaCO3, OM, and clay) are considered, this fact can be clearly understood. The OM is likely to mediate B desorption up to 10 mg L-1 loadings, and then the effect of CCE showed a serious support trend to the desorption. The organic compounds are to dissolve at alkaline pH to form high molecular weight organic anions such as humate and fulvate anions which can compete for the sorption sites.

According to Nazir and Wani (2015), B desorption is favourably and strongly linked with sand concentration and negatively connected with clay content and cation exchange capacity. The difference in surface area of sand compared to clay and silt was the main factor governing B desorption. The smaller amount of sand, which had less adsorption capacity, resulted in smaller amounts of saturation capacity (Tlili et al. 2019; Arora and Chahal, 2010; Suganya et al. 2019) which in turn yielded a limited magnitude of desorption.

Conclusions

The sorption of B in B-rich soils can be satisfactorily described by Langmuir and Freundlich models despite possible solid phase formation. The B adsorption-desorption abilities of soils with high B content were elucidated towards understanding possible roles of routinely analyzed soil properties. While there were effects on soil sand content and available B parameters in B adsorption, sand content of soils and total B parameters played an important role in B desorption. Although a statistically significant relationship was not obtained with the clay content, specific surface area, and cation exchange capacity of the soil, they had considerable significant effects on the adsorption maxima. These results from adsorption-desorption show that at boron concentrations over 8 mg kg^{-1}, boron mobility increases, and this can exacerbate the hazards for crop production.

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Conflict of Interest

The authors declare no conflict of interest for this study.

Author's Contributions

The authors contributed equally to this manuscript.

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