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Zinc Adsorption and Desorption Characteristics of Soils in Semi-Arid Region, Turkey

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The purpose of this study was to determine the zinc adsorption and desorption characteristics and their relationships with some soil properties in semi-arid regions of Tokat, Turkey. Zinc adsorption data of the studied soils fitted into the linear form of Langmuir, Freundlich and Temkin isotherms, but the fit to Freundlich and linear Langmuir model were statistically better than the Temkin model. The mean distribution coefficients (K_d) of the soils ranged from 414 to 1001 and the higher K_d values were calculated at soils having higher clay and $CaCO_3$. Similarly, the Zn adsorption maximum exceeds cation exchange capacity values of the soils high in clay and $CaCO_3$. This could be attributed to adsorption on the internal surface of clay and precipitation of the applied Zn to the soils. Besides, recovery values (%) by DTPA of the retained Zn on the soils having higher clay and $CaCO_3$ contents were lower than those of the other soils. According to the observed findings, clay and $CaCO_3$ contents at the soils are the most important soil properties affecting adsorption and desorption of Zn.

Key Words: Adsorption isotherms, Soil, Zinc adsorption and desorption.

INTRODUCTION

The availability of micronutrients, except Mo, is limited in calcareous soils. Experiments on micronutrient availability in calcareous soils are important to determine and explain the behaviour of micronutrients. The concentration of Zn in soil solution and availability of Zn to plants are governed by the adsorption mechanism of Zn on the soil.

Zinc adsorption behaviour depends on soil chemical and mineralogical characteristics such as pH, clay content and mineralogy, organic matter, cation exchange capacity (CEC), carbonates and hydrous oxides[1, 2].

Zinc adsorption characteristics have been described by different equations such as Langmuir adsorption isotherm[3], the modified Langmuir equation[4] and Freundlich equation[5]. Olsen and Watanabe[6] first used Langmuir adsorption isotherm to determine the P adsorption characteristics in soils and later the isotherm was used to evaluate Zn adsorption on soils[3, 4, 7]. From a practical point of view, Langmuir isotherm can be regarded as a phenomenological equation successfully predicting the solid and liquid phases in solis of Zn[8].

Majority of soils in arid and semi-arid regions of Turkey are calcareous and clay contents of the soils are usually high. Zinc deficiency (DTPA-extractable Zn)

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would usually occur in most of the soils in arid and semi-arid regions of Turkey[9]. Zinc adsorption and desorption characteristics of these soils in Tokat region have not been investigated yet. Therefore, the aim of the study was to investigate the Zn adsorption and desorption characteristics and their relationships with some soil properties in semi-arid region (Tokat) of Turkey.

EXPERIMENTAL

Soil samples were taken from 0–20 cm depths of six great soil groups located in semi-arid Tokat region (39°51′–40°55′ N, 35°27′–37°39′ E) of Turkey. These soils were classified as Ustifluvent (1), Ustorthent (2), Haplustalf (3), Ustochrept (4), Haplustoll (5) and Argiustoll (6) as according to soil taxonomy[10].

DTPA-extractable zinc was analyzed by the procedure of Lindsay and Norvell[11]. Soil pH was determined in (1 : 2.5) soil : water (w : v) mixture[12]. Particle size distributions of the soil samples were determined by the hydrometer method, organic matter content (O.M.) by Walkley-Black method, carbonates by clacimeter method and cation exchange capacity (CEC) by sodium acetate method[13].

Zinc adsorption and desorption: 0.4 g air-dried soil samples were placed as duplicate in 33 mL centrifuge tubes and were mixed with 20 mL of 0.01 M $CaCl_2$ solution containing Co (Zn concentrations): 0, 10, 25, 50, 75, 100, 150, 200 μg mL^{-1} Zn as $ZnSO_4{\cdot}H_2O$. Then, the tubes were shaken for 24 h at 25°C until the suspensions reached equilibrium. The samples were centrifuged and the clear supernatant was carefully taken to determine the Zn concentration of the solution phase and filtered through Whatmann filter paper. Zinc contents in the filtrates was analyzed by a flame atomic adsorption spectrophotometer[14] (AAS, Perkin- Elmer Analyst 700 model).

After separation of the solution phase for adsorption, the same soil samples in centrifuge tubes were subjected to desorption sequence to determine the Zn desorption by 0.005 M DTPA extracting solution (20 mL) as explained above. The average value of the duplicate analysis was used to calculate the amount of Zn in solution. The difference between the amount of added Zn and that recovered in the solution was considered as retained Zn by the soil.

Langmuir [non-linear and linear form, eqn. (1) and (2)], Freundlich and Temkin [eqn. (4)] isotherms were used to evaluate Zn adsorption data.

$$x/m = (k \cdot b \cdot C)/(1 + k \cdot C) \qquad (1)$$

$$C/(x/m) = C/b + 1/k \cdot b \qquad (2)$$

$$x/m = K_f \cdot C^{1/n} \qquad (3)$$

$$x/m = k_1 + k_2 \cdot \ln C \qquad (4)$$

where C is equilibrium Zn concentration (μg mL^{-1}); x/m is the amount of Zn adsorbed (μg g^{-1}); adsorption maxima (b), bonding energy coefficient (k), adsorption capacity (K_f), adsorption rate (1/n) and Temkin constant (k_1 and k_2) are coefficients relating with adsorption. The goodness of fit was evaluated by the determination coefficient (R^2) as reported by Mesquita *et al.*[15]

Average distribution coefficient or maximum buffering capacity (K_d) was calculated by the amount of adsorbed Zn divided by equilibrium Zn concentration ($K_d = (x/m)/C$). Correlations among adsorption parameters and soil properties were determined by using Pearson method with Minitab computer program.

RESULTS AND DISCUSSION

Some physical and chemical properties of the studied soils are presented in Table-1. Smectite clay minerals were dominant in the studied soils. All the soils contained different amounts of kaolinite clay minerals[16].

TABLE-1
SOME SELECTED PHYSICAL AND CHEMICAL PROPERTIES OF THE STUDIED SOILS

Soil No.	Sand (%)	Loam (%)	Clay (%)	pH (1 : 2.5)	$CaCO_3$ (%)	O.M. (%)	CEC (cmol kg^{-1})	Zn (μg/mL)
1	32	29	39	7.5	8.6	1.2	22	1.32
2	41	26	33	7.5	2.5	2.4	23	0.53
3	32	16	52	7.6	15.2	2.5	28	0.86
4	33	32	35	7.3	13.4	1.8	17	0.35
5	64	16	20	7.1	2.8	2.6	29	0.15
6	42	17	41	7.3	1.9	2.6	38	0.21

CEC: Cation exchange capacity; O.M.: Organic matter.

Zinc adsorption: The adsorption data of the investigated soils (soils 1, 3 and 4) fitted into the Langmuir adsorption isotherm [$x/m = (k \cdot b \cdot C)/(1 + k \cdot C)$] and the other soil data did not conform to the model [$C/(x/m) = C/b + 1/kb$]. The b and k values varied from 6212 to 9804 and 0.059 to 0.15, respectively (Table-2). Relatively high b values were found at soils 3, 1 and 4 with higher $CaCO_3$ and clay (except soil 6) contents. Conversely, the lower k values were calculated at soil 5 and soil 2 containing higher sand. Similar findings of Langmuir isotherm for Zn in soils were reported previously[2, 3].

TABLE-2
ZINC ADSORPTION MAXIMUM AND BONDING ENERGY PARAMETERS OF LANGMUIR MODELS AND DISTRIBUTION COEFFICIENTS

	Langmuir model			Linear Langmuir model			Distri. coefficient	
Soil No.	k	b	R^2	k	b	R^2	k · b	K_d
1	0.067	10518	0.980‡	0.150	8333	0.890‡	1250	974
2	–2.210	2711	0.460^{ns}	0.079	6250	0.842‡	494	694
3	0.098	10729	0.995‡	0.140	9804	0.926‡	1372	1001
4	0.052	9410	0.970‡	0.120	7692	0.910‡	923	847
5	–1.251	2898	0.460^{ns}	0.059	6493	0.778†	383	414
6	–2.03	2599	0.390^{ns}	0.120	6212	0.53*	745	718

*significant at $p < 0.05$, †siginificant at $p < 0.01$, ‡significant at $p < 0.001$, ns: not significant.

The Zn adsorption maxima (b) exceed CEC values of the soils 1, 3 and 4 with higher $CaCO_3$ and clay content, indicating that the added Zn to the soils is probably adsorbed on the internal surface of clay as Zn-hydroxide and precipitated as Zn-carbonates. Similar phenomenon for copper adsorption was suggested by Maftoun *et al.*[17] and McBride and Boulding[18]. Shuman[7, 19], Kuo and Mikkelsen[5], Gupta *et al.*[20] suggested that precipitation reactions controlled Zn solubility at high pH and concentrations on calcareous soils.

The fit of the data to Freundlich model was highly significant ($P < 0.001$) for all the soils as shown in Table-3. Kuo and Mikkelsen[5], Dhillon and Dhillon[21], Karimian and Moafpouryan[22] also pointed out that Zn adsorption in alkaline and calcareous soils conformed to the Freundlich isotherm at both low and high Zn concentrations. The K_f and 1/n values ranged from 755 to 1230 and 0.438 to 0.672, respectively. The K_f coefficient could be used to represent the amount of Zn adsorbed by unit weight of soil at unit Zn concentration of equilibrium solution[22]. Generally, K_f and 1/n values of soils having high clay and $CaCO_3$ contents were found higher than those of the other soils.

TABLE-3
ZINC ADSORPTION PARAMETERS OF THE FREUNDLICH AND TEMKIN MODELS

Soil No.	Freundlich model			Temkin model		
	K_f	1/n	R^2	k_1	k_2	R^2
1	1257	0.493	0.493‡	1799	1247	0.820†
2	777	0.461	0.970‡	761	970	0.780†
3	1008	0.672	0.963‡	1030	1903	0.959‡
4	1152	0.450	0.980‡	1554	1050	0.803†
5	757	0.438	0.950‡	768	885	0.710*
6	959	0.420	0.850†	1470	1046	0.490^{ns}

*Significant at $p < 0.05$, †significant at $p < 0.01$, ‡significant at $p < 0.001$, ns: not significant

Adsorption energy at the Temkin model decreases linearly when the amount of adsorption increases[17]. Generally, Zn adsorption data (except soil 6) fitted into the Temkin isotherm (Table-3). However, determination coefficient (R^2) between adsorption data was found lower than that of linear Langmiur and Freundlich models. Temkin parameters (k_1 and k_2) ranged from 761 to 179 and, 775 to 1903, respectively.

Although linear Langmuir, Freundlich and Temkin isotherms could describe the Zn adsorption data, the fit of data to Freundlich and Langmuir isotherm were found to be more suitable relative to Temkin isotherm.

Correlations among adsorption parameters and soil properties: Simple correlation analyses were performed to compare the relationships among K_d, adsorption parameters and soil characteristics. The correlation coefficients of adsorption parameter with soil properties are given in Table-4.

TABLE-4
CORRELATIONS AMONG ADSORPTION PARAMETERS AND SOIL PROPERTIES

	k	b	K_f	1/n	k_1	k_2	K_d	k · b	Clay	$CaCO_3$	O.M.	Sand
b	0.718											
K_f	0.912†	0.559										
k/n	0.545	0.859*	0.213									
k_1	0.786	0.330	0.963*	–0.055								
k_2	0.568	0.949*	0.311	0.956†	0.050							
K_d	0.958†	0.956†	0.892*	0.856*	0.744	0.896*						
k · b	0.939†	0.912†	0.802*	0.748	0.615	0.805*	0.965†					
Clay	0.830*	0.838*	0.544	0.803*	0.336	0.719	0.838*	0.833*				
$CaCO_3$	0.646	0.899†	0.593	0.666	0.398	0.796*	0.815*	0.806*	0.591			
O.M.	–0.573	0.342	–0.799*	0.115	–0.831*	–0.108	–0.404	–0.506	–0.0921	–0.376		
Sand	–0.861*	–0.616	0.762	–0.475	–0.630	–0.533	–0.774	–0.506	–0.812*	–0.663	0.547	
Rec. %	–0.935*	–0.753	–0.766	–0.669	–0.616	–0.670	–0.833*	–0.930†	–0.825*	–0.813*	0.480	0.731

Re. %: Zinc recovery by DTPA; * Significant at $P < 0.05$ levels; † Significant at $P < 0.01$ levels.

Highly significant positive correlation was found between Langmuir b values and soil $CaCO_3$ ($P < 0.01$) contents and k values and clay ($P < 0.05$) content, where k values are negatively correlated with sand ($P < 0.05$) contents. These results implied that soils with higher $CaCO_3$ and clay contents adsorbed higher Zn than soils with sand and lower clay and $CaCO_3$ contents. Udo *et al.*[4], Kariman and Moafpouryan[22] also pointed out that the Langmuir adsorption maximum values were positively correlated with soil pH, clay and $CaCO_3$ contents.

Significant correlation ($P < 0.05$) between 1/n and clay content and negative correlation ($P < 0.05$) between K_f and organic matter content were obtained, indicating that clays and $CaCO_3$ had a high affinity for Zn in the solute and organic matter decreased Zn sorption in the studied soils. The lack of significant relationships between Freundlich parameters and the other soil properties could be attributed to the high variability of soil properties and the low degree of freedom of soil samples. Karimian and Moafpouryan[22] also found that clay had pH significantly related to Freundlich A (K_f) and the relationships between Freundlich B (1/n) and soil properties were not significant.

Soils 3, 1 and 4 with higher $CaCO_3$ and clay contents showed higher Temkin k_2 values relative to other soils. The k_2 values were significantly correlated with clay content ($P < 0.05$) and Langmuir b parameter ($P < 0.01$), implying the k_2 values could be used to describe adsorption capacity of soils. Maftoun *et al.*[17] reported that Temkin k_2 was significantly related to $CaCO_3$ and clay content for Cd adsorption data. In general, Zn sorption by the soils was strongly influenced by clay and $CaCO_3$ and sand contents and sorption parameters increased with increasing clay and $CaCO_3$ contents.

Average distribution coefficient (maximum buffering capacity) (K_d): The mean distribution coefficient or maximum buffering capacity over the entire cocentration range was calculated (Table-2). The high K_d values indicate the Zn retained by sorption and the low K_d values indicate that most of the metal remains in the soil solution[23]. Namely, K_d values could be used as an important parameter for the sorbability and availability of Zn in soils.

The K_d values ranged from 414 to 1001 and the higher K_d values were also calculated at soil 3 (1001), 1 (974) and 4 (847) having higher clay and $CaCO_3$. The lowest K_d values was found in soil 5 containing the lower clay and the higher sand contents. This means that for soil 3, one unit concentration of Zn in equilibrium solution corresponds to as high as 1001 units of sorbed Zn by solid phase, whereas the similar value for soil 5 is only 414. Significant positive correlations were found between K_d and $CaCO_3$ ($P < 0.05$) and clay ($P < 0.05$), whereas negative with sand content ($P < 0.01$). The K_d values for Zn increase with increases of clay and $CaCO_3$ contents[22], and similar findings also reported for Cu by Joshi[24].

Bolt and Bruggenwert[25] and Karimian and Moafpouryan[22] reported that at very low equilibrium concentrations the term $1 + k \cdot C$ approaches to 1 and thus, $x/m = (k \cdot b \cdot C)/(1 + k \cdot C)$ converts to $x/m = k \cdot b \cdot C$ and $(x/m)/C = k \cdot b$. Therefore, at very low equilibrium concentration is $K_d = k \cdot b$. However, at higher Zn equilibrium concentrations (at present research is $1 + k \cdot C > 2$), the mean K_d values calculated $[(x/m)/C]$ over the entire concentration range had positive and significant correlation ($P < 0.01$) with $k \cdot b$. Hence, in our study, the $k \cdot b$ values could be used to evaluate and compare to the K_b values of soils at higher equilibrium concentrations. The observed result reveals that sand, clay and $CaCO_3$ content play important roles in the variation of K_d in the soils.

Zinc desorption: The retained Zn by the soils and recovery values (%) by DTPA of the retained Zn are presented in Table-5. The mean retained Zn in the soils ranged from 58.9 to 77.5 $\mu g\ g^{-1}$. As soil samples were subjected to desorption with 0.005 M DTPA extracting solution, Zn recovery (%) by DTPA varied from 37 to 56. Zinc recovery (%) at low concentrations (Co: 10 μg Zn mL^{-1}) was higher than that at high concentrations. Adsorption reactions occurring on solid surfaces are fast with the readily available surface and much slower with crystal lattices[26, 27]. The greater recovery (%) at low concentration could be attributed to zinc to be bounded to classical exchange surfaces and organic matter, namely the non-specific adsorption of Zn below a certain concentration. These would be related to precipitation of Zn at high concentrations as pointed out by Udo *et al.*[4] Dhillon and Dhillon[21] also reported similar observations. Negatively significant correlation ($P < 0.05$) was obtained between the mean Zn recovery (%) and both clay and $CaCO_3$ values. The mean results of recovery values (%) by DTPA of the adsorbed Zn were negatively correlated with both Langmiur affinity coefficient (k) ($P < 0.01$) and K_d ($P < 0.05$) [Langmuir $k \cdot b$, $P < 0.01$).

TABLE-5

RECOVERY VALUES (%)* BY DTPA OF THE ADSORBED ZINC ON THE SOILS

Co	Soil ⇒ 1		2		3		4		5		6	
0	0	(0)	0	(0)	0	(0)	0	(0)	0	(0)	0	(0)
10	9.9	(63)	9.7	(80)	9.5	(47)	9.9	(55)	9.8	(82)	9.9	(61)
25	23.9	(37)	22.5	(62)	23.7	(42)	23.5	(54)	21.3	(48)	22.5	(55)
50	44.8	(33)	41.8	(46)	47.5	(34)	47.7	(50)	37.4	(50)	40.8	(40)
75	68.5	(29)	51.5	(49)	69.9	(34)	61.5	(48)	55.2	(50)	54.2	(37)
100	89.0	(26)	70.1	(57)	92.5	(24)	83.9	(45)	63.0	(56)	76.2	(37)
150	122.5	(35)	110.5	(32)	131.2	(38)	123.0	(49)	100.8	(52)	121.5	(45)
200	161.5	(36)	120.0	(42)	168.0	(49)	139.4	(48)	124.7	(55)	173.8	(43)
Mean	74.3	(37)	60.9	(53)	77.5	(39)	69.4	(50)	58.9	(56)	71.3	(45)

*Recovery values (%) are given in parentheses.

Recovery values (%) by DTPA of the adsorbed Zn on the soils 3 and 1 with both higher clay and $CaCO_3$ and higher K_d $(k \cdot b)$ and k values were lower than those of the other soils (Table-5). Conversely, the higher recovery (%) results would be attributed to greater amount of sand and lower $CaCO_3$ contents on the soils 2, 5 and 6 as also reported by Shuman[3], Uygur and Rimmer[27], Wenming *et al.*[23] These results reveal that while higher clay and $CaCO_3$ content decrease the desorbability of retained Zn, sand content increases the release of adsorbed Zn.

In conclusion, the Zn adsorption data showed a highly significant fit to linear Langmuir and Freundlich isotherms. Adsorption coefficients and the K_d values were significant correlated with clay and $CaCO_3$ contents. According to the observed results, soluble Zn compounds applied to soils with higher clay and $CaCO_3$ contents could be adsorbed highly by the soils. To decrease sorption by the soil and increase the availability of applied Zn to plants in these soils, Zn could be used as a combined with organic matter (manure) or in the form of Zn-chelates, which stay more in the solution phase as also suggested earlier[22].

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