

## Zinc Sorption Characteristics of Some Selected Calcareous Soils of Iran

A. Reyhanitabar<sup>1\*</sup>, M. Ardalan<sup>2</sup>, R. J. Gilkes<sup>3</sup>, and G. Savaghebi<sup>2</sup>

### ABSTRACT

This study was carried out to obtain quantitative relationships between Zn in equilibrium solution and that retained by 20 calcareous soils. Soils were brought into equilibrium with varying solution concentrations of Zn, and the amounts removed from solution were used to check the fit to six adsorption isotherms, namely, Freundlich, Langmuir, Temkin, Gunary, two surface Langmuir and Adjusted Freundlich. Zinc sorption and desorption data showed hysteresis which indicates adsorption and desorption mechanisms not being the same. Fits of adsorption equations showed that Freundlich equation did not describe Zn sorption in most of the soils at low equilibrium concentrations, but after removal of the three first concentration points this equation showed a best fit to the data. The single surface Langmuir equation did not describe Zn sorption data, but a two surface Langmuir equation showed statistically significant fits to the data for some of the selected soils. Temkin equation described data only at low equilibrium concentrations.

**Keywords:** Adsorption, Calcareous soils, Freundlich, Langmuir, Zinc

### INTRODUCTION

Zinc status of selected calcareous soils of Iran has been previously reported (Karimian and Yaserbi, 1995; Maftoun and Karimian, 1989; Karimian and Moafpourian, 1999), according to which most of these soils need supplemental zinc for optimum plant growth, but the recovery by plants of the applied Zn is low. Even in cases where Zn chelate was applied, less than 5% of it was recovered by the first crop (Darjeh *et al.*, 1991; Maftoun and Karimian, 1989). Harter (1991), in a review of the subject, concluded that, adsorption isotherms have provided the majority of information about micronutrient adsorption by soils.

Several adsorption isotherms have been employed to relate the Zn concentration in

solution to that retained by the solid phase (Xie and Mackenzie, 1991).

Freundlich adsorption isotherm [Equation (1)] and Langmuir adsorption isotherm (Equation 2) are those frequently used by investigators:

$$q = Kc^{1/n} \quad (1)$$

$$q = \frac{kcb}{1 + kc} \quad (2)$$

Where  $q$  is the amount of Zn retained by unit weight of soil,  $\text{mg kg}^{-1}$ ,  $c$  is the concentration of Zn in equilibrium solution,  $\text{mg L}^{-1}$ ,  $K$ ,  $n$  are Freundlich adsorption coefficients,  $k$  is the Langmuir adsorption coefficient the magnitude of which is proportional to the binding energy of Zn to the soil, and  $b$  is the adsorption maxima, that is, the maximum amount of Zn retained as a monomolecular layer by the soil,  $\text{mg kg}^{-1}$ .

<sup>1</sup> Department of Soil Science, Faculty of Agriculture, University of Tabriz, Tabriz, Islamic Republic of Iran.

<sup>2</sup> Department of Soil Science, Faculty of Water and Soil, University of Tehran, Karaj, Islamic Republic of Iran.

<sup>3</sup> School of Earth and Geographical Science, Faculty of Natural and Agricultural Science, University of Western Australia, Crawley, WA 6009, Australia.

\* Corresponding author, e-mail: areyhanitabar@yahoo.com



Other mathematical expressions used, although to a lesser extent, are adjusted or modified Freundlich [Equation (3)], Temkin [Equation (4)] and Gurney equation (Equation 5):

$$q = Kc^{1/n} - q_0 \quad (3)$$

$$q = K_1 + K_2 L_n c \quad (4)$$

$$q = K_1 + K_2 c + K_3 c^{0.5} \quad (5)$$

Where  $q$  and  $c$  are the same as those defined for Equations (1) and (2).  $q_0$  is the amount of residual zinc,  $\text{mg kg}^{-1}$ .  $K_1$  and  $K_2$  are Temkin adsorption coefficients,  $L_n$  is the natural logarithm; and  $K_1$ ,  $K_2$  and  $K_3$  are Gurney adsorption coefficients.  $K_1$  and  $K_2$  in Equations (4) and (5) do not bear the same meaning.

Maftoun *et al.* (2000) reported that Zn adsorption in eight calcareous soils from south of Iran followed a Freundlich adsorption isotherm. The two-surface Langmuir adsorption isotherm also showed a significant fit to their data. Therefore, they concluded the presence of two different adsorbing sites for Zn each with their own  $k$  and  $b$  [Equation (6)].

$$q = \frac{k_1 b_1 c}{1 + k_1 c} + \frac{k_2 b_2 c}{1 + k_2 c} \quad (6)$$

Where  $k_1$ ,  $b_1$ ,  $k_2$  and  $b_2$  are Langmuir coefficients for the first and second sites.

Shuman (1975) observed that binding energy and adsorption maxima of soils were dependent on soil texture; both of which increased with the texture becoming finer. Rao *et al.* (1985) also reported the effect of type of clay minerals on Zn adsorption maxima.

It has been demonstrated that Langmuir equation can equally well describe both adsorption and precipitation (Sposito, 1989). Thus mechanistic information can not be derived from a macroscopic model like the Langmuir equation (Sparks, 1995).

The main objectives of this study were:

(1) To compare the suitability of six adsorption isotherms for prediction of soil/solution relations of Zn in some calcareous soils of Iran.

(2) To investigate the relationship between soil properties and the coefficients of these isotherms and

(3) To provide quantitative estimation of Zn retention capacities of calcareous soils from selected routinely measured soil properties.

## MATERIALS AND METHODS

Surface soil samples (0-30 cm) from 20 locations representing 20 soil series in two taxonomic orders, namely, Entisols and Aridisols were collected from the central part of Iran.

Soil samples were air dried, passed through a 2-mm sieve and used for determination of physical and chemical properties through the following procedures:

Clay by the hydrometer method (Day, 1965); pH of 1 to 5 soil to  $\text{CaCl}_2$  0.01M ratio through glass electrode; organic carbon (OC) by the Walkley-Black method (Allison, 1965), cation exchange capacity (CEC) through replacing exchangeable cations with sodium acetate (NaOAC) and determining Na concentration by use of flame photometry (Chapman, 1965);  $\text{CaCO}_3$  equivalent by the acid method (HCl) (Allison and Moodie, 1965). Available phosphorus was determined by sodium bicarbonate application (Olsen *et al.*, 1954). Active  $\text{CaCO}_3$  was determined by the  $\text{NH}_4$ -Oxalate method (Drouineau, 1942). Total Zn by digestion of soils in HF,  $\text{HClO}_4$  and  $\text{HNO}_3$  (Tessier *et al.*, 1979) and available Zn according to the Lindsay and Norvell (1978) method. Specific surface area (SSA) was measured using the  $\text{N}_2$ -BET method (Brunauer *et al.*, 1938) with a micrometrics Gemini III 2375 surface area analyzer.

Preliminary experiments revealed that a 24 hour period was sufficient for complete equilibration of the Zn solutions with the

soils and that a suitable range for Zn solutions was 1 to 160  $\text{mg Zn L}^{-1}$ .

Thirteen 1-g duplicate sub samples of each soil were placed in separate centrifuge tubes, to which were added 20 ml of zinc sulfate containing 1, 2, 5, 8, 10, 15, 20, 40, 60, 80, 100, 120 and 160  $\text{mg Zn L}^{-1}$ , which had been prepared in 0.01M  $\text{CaCl}_2$  to keep the ionic strength almost constant.

The tubes were shaken for 24 hours at  $25\pm 1^\circ\text{C}$  in a constant temperature chamber and at a slow ( $20\text{ rpm min}^{-1}$ ) rate.

At the end of equilibration, the tubes were centrifuged until clear. The supernatant was filtered through a filter paper (Whatman 42 Ashless) and the Zn concentration of filtrates determined by an ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) using a Perkin-Elmer Elan instrument.

The difference between initial and final Zn concentrations was assumed to be the amount of Zn adsorbed by the soil. The results were fitted to Equations (1) through (6), and the coefficients obtained for each isotherm were made related to soil characteristics by constructing regression equations using the stepwise procedure of SPSS (2002). Zn species distribution and SI Values were calculated by use of PhreeqCi software. PhreeqCi is a graphical interface that can be used interactively to perform all the modeling capabilities of geochemical model including speciation, batch-reaction, 1D reactive-transport, and inverse modeling (Parkhurst and Appelo, 1999). PhreeqCi is a computer program for simulating chemical reaction and transport processes in water and in soil solution.

Zinc desorption was assessed with  $\text{CaCl}_2$  0.01M at the end of sorption experiment with the same condition (24 hours at  $25\pm 1^\circ\text{C}$  in a constant temperature chamber at a slow ( $20\text{ rpm min}^{-1}$ ) pace. The results were fit to Equations (1) through (6), and the coefficients obtained for each isotherm were made related to soil characteristics by constructing regression equations using the stepwise procedure of SPSS (2002).

## RESULTS AND DISCUSSION

### Soil Characteristics

As shown in Table 1, soil clay ranged from 106 to  $410\text{ g kg}^{-1}$  with a mean value of  $236\text{ g kg}^{-1}$ . The pH values ranged from 6.7 to 7.95 with a mean of 7.5. The organic carbon content ranged from  $3.2\text{ g kg}^{-1}$  to  $24.7\text{ g kg}^{-1}$

with a mean of  $12.5\text{ g kg}^{-1}$ . Soil surface area (SSA) ranged from  $8.5\text{ m}^2\text{ g}^{-1}$  to  $39\text{ m}^2\text{ g}^{-1}$  with a mean of  $19.7\text{ m}^2\text{ g}^{-1}$ . In general, total and active carbonates varied among the soils. The equivalent carbonate of these soils ranged from  $38\text{ g kg}^{-1}$  to  $228\text{ g kg}^{-1}$  while the active carbonate ranging from  $13.4\text{ g kg}^{-1}$  to  $99.8\text{ g kg}^{-1}$ . X-ray diffraction (XRD) analysis showed that  $\text{CaCO}_3$  is the carbonate most commonly found in the soils studied (XRD patterns not shown). X-ray diffraction patterns of the clay fraction showed that illite, chlorite and smectite are dominant clay minerals occurring in all the soil samples.

### Zinc Sorption Experiment

The processes of sorption and desorption of Zn were found to be hysteretic, which suggest that the desorption mechanism or path is not the exact reverse of the adsorption mechanism or path (Figure 1). Sparks (1995) believes that most of the hysteresis reported by investigators may be unreal hysteresis because of short equilibrium time periods.

This study revealed that at 24 hours, a high percentage of added Zn had been sorbed and so 24 hours is a sufficient time for equilibrium to be reached. The Freundlich equation did not describe data at low equilibrium concentrations, but after removal of the three initial concentrations, namely, 1, 2 and  $5\text{ mg Zn L}^{-1}$ , the fit of data was excellent for most of the soils. This procedure is similar to those of Fitter and Sutton (1975), and Barrow (1978).

Barrow (1978) considered that logarithmic change of data will give greater weight or higher importance to lower concentrations and this may be attributed to the accuracy of data and while a second reason may be cited as due to residual Zn in the soil.

Following removal of the first three concentrations, Freundlich equation was fitted and the relevant coefficients calculated (Table 2). As shown in Table 2, variations in  $\frac{1}{n}$  are smaller than in K. The same result was reported by Shuman (1975).

**Table 1.** Physical and chemical properties of studied soils.

Soil No.	SSA <sup>a</sup>		pH	CEC <sup>b</sup> [cmole(+) kg <sup>-1</sup> ]	CCE <sup>c</sup> g kg <sup>-1</sup>	ACCE <sup>d</sup> g kg <sup>-1</sup>	Olsen-p mg kg <sup>-1</sup>	Zn* mg kg <sup>-1</sup>	Zn** mg kg <sup>-1</sup>
	Clay g kg <sup>-1</sup>	Silt g kg <sup>-1</sup>							
1	325	325	7.63	16.4	80	38	58	2.30	108.5
2	106	238	7.70	12.4	46	19	11	2.20	94.8
3	226	185	7.70	19.2	72	27	20	4.40	104.7
4	308	308	7.80	16.3	136	62	46	2.33	95
5	253	210	7.50	17.7	62	44	42	2.40	98
6	215	225	7.20	15.3	88	16	12	4.81	99.3
7	188	272	7.31	24.6	98	13	19	7.00	129.6
8	134	287	7.56	30.0	125	33	23	2	96.7
9	200	300	7.66	14.2	108	28	43	1.50	104.0
10	307	330	7.77	20.2	228	100	11	2.60	128.8
11	305	375	7.53	25.9	95	22	41	1.50	98.0
12	203	385	7.40	19.8	82	41	14	4.90	129.3
13	165	371	7.66	14.8	38	27	13	2.30	109.7
14	410	340	7.60	19.2	94	41	16	1.90	150.7
15	134	283	7.51	32.0	194	58	13	1.20	99.3
16	200	100	7.52	8.30	170	65	16	8.75	70.0
17	363	406	7.36	19.6	90	23	61	2.60	111.8
18	403	323	6.7	30.0	48	15	14	2.50	169.9
19	142	265	7.66	17.0	108	35	10	0.81	107.6
20	160	156	7.95	16.1	140	31	1	1	80.0
mean	236	284	7.54	19.5	105	37	26	2.5	109.3

<sup>a</sup> Soil Surface Area; <sup>b</sup> Cation Exchange Capacity; <sup>c</sup> Carbonate Calcium Equivalent, <sup>d</sup> Active Calcium Carbonate Equivalent, respectively.  
\* and \*\*, Respectively stand for extractable Zn with DTPA, and total Zn.

**Table 2.** Freundlich adsorption isotherm coefficients and the coefficients of determination ( $R^2$ ) for the fit of data.

Soil No	1/n	K	$R^2$	Soil No	1/n	K	$R^2$
1	0.334	626	99.26	11	0.378	635	99.60
2	0.344	440	99.47	12	0.378	590	99.53
3	0.356	540	98.49	13	0.348	517	99.70
4	0.357	623	97.62	14	0.375	866	99.30
5	0.352	503	99.81	15	0.373	1052	97.90
6	0.384	365	99.73	16	0.346	530	99.70
7	0.395	402	99.74	17	0.417	682	99.40
8	0.365	646	96.81	18	0.473	624	98.81
9	0.348	570	99.42	19	0.371	596	99.52
10	0.358	809	98.54	20	0.345	575	98.91
min	0.334	365	96.81				
max	0.473	1052	99.81				
mean	0.369	610	99.06				

All  $R^2$  values are significant at  $P < 0.01$ . The min, max and mean values are assessed based on data of all the 20 soils.

The Freundlich  $K$  coefficient showed highly significant relationships ( $P < 0.01$ ) with CCE, CEC, silt content and DTPA extractable Zn [Equation (7)].

$K(F) = 185 + 15 \text{ CCE} + 8.9 \text{ CEC} + 6.9 \text{ Silt} - 38.6 \text{ Zn DTPA}$ ,  $R^2 = 0.75$ ,  $P < 0.01$  (7)

Elrashidi and O'Connor (1982) reported a significant relationship between Freundlich coefficients and soil clay, CEC and pH, but not CCE. Their results also indicated a strong positive correlation of pH with Freundlich  $K$ . In our studies we also found a significant relationship between pH and

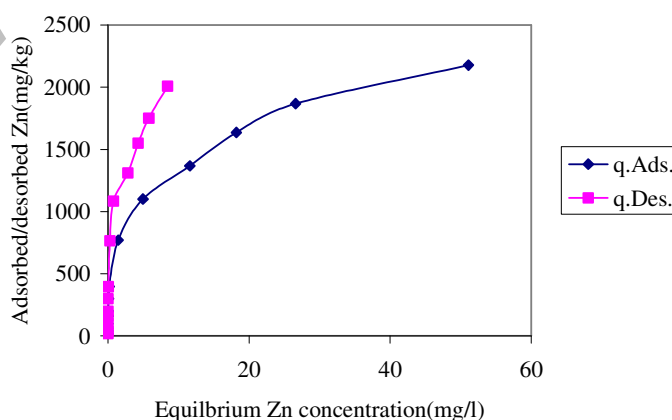
the Freundlich  $\frac{1}{n}$  coefficient.

$$\frac{1}{n} = 1.247 - 0.103 \text{ pH}, R^2 = 0.74, P < 0.01$$

(8)

The statistical significance of the correlation coefficient for  $c/q$  versus  $c$  was the criterion by which the fit of the data to the Langmuir isotherm was tested. The fit was not good and there was a systematic departure from linearity, so it was concluded that the single Langmuir equation did not describe the sorption data.

For an evaluation of the two-site adsorption Langmuir isotherm, the distribution coefficient  $K_d = q/c$ , versus equilibrium concentration ( $c$ ) was plotted (Sposito, 1982), but only 16 soil samples showed a significant fit (Table 3). As

**Figure 1.** Zn sorption and desorption isotherm for calcareous soil No.1

**Table 3.** Soils showing significant fit to two surface Langmuir adsorption along with their coefficients.

Soil No	$k_1$	$k_2$	$b_1$	$b_2$	$k_1/k_2$	$b_1/b_2$	$R^2$ (%)
1	16.81	0.24	484	1580	71	0.30	99.76
2	4.38	0.041	637	1634	100	0.40	99.85
3	4.49	0.092	754	1479	49	0.51	99.95
4	6.33	0.11	794	1650	59	0.48	99.94
5	10.98	0.12	428	1653	92	0.26	99.82
6	5.26	0.062	384	1646	83	0.23	99.91
7	6.55	0.085	382	1802	85	0.22	99.77
8	4.56	0.17	872	1364	26	0.64	99.85
9	12.43	0.20	457	1597	62	0.28	99.80
10	12.64	0.29	748	1725	44	0.44	98.96
11	6.91	0.11	713	1952	63	0.37	99.88
12	5.34	0.10	732	1927	61	0.38	99.83
13	11.89	0.16	424	1568	76	0.27	99.64
16	18.41	0.17	387	1624	111	0.24	99.50
17	12.26	0.33	403	2030	37	0.20	99.91
18	2.46	0.14	820	2162	18	0.38	99.98
min.	2.46	0.041	382	1364	18	0.20	98.96
max.	18.41	0.33	872	2162	111	0.51	99.98
mean	8.86	0.15	589	1712	65	0.35	99.77

All  $R^2$  are significant at  $P < 0.01$ . The min, max and mean values are assessed based on data of all the 20 soils. The slope and intercept for the soils no 14, 15, 19 and 20 were not significant ( $P \leq 0.05$ ) and therefore not included in the table.

indicated in Table 3, on the average  $k_1 = 65 k_2$  and  $b_1 = 0.35 b_2$ . Our finding is in agreement with Shuman (1975) for Zn adsorption and with Holford *et al.* (1974) for phosphorus adsorption. In this study, pH did not show any relationship with  $b_1$  but with  $b_2$  it showed a negative relationship [Equation (12)]. Many investigators have reported that for some ranges of pH, Zn sorption increases with increasing pH (Bart-Tal *et al.*, 1988; Bar-Yousef, 1979; Guadalix and Pardu, 1995). In contrast, some investigators, such as Saeed and Fox (1977) reported that Zn sorption decreased with increasing pH. They also reported that organic matter solubility at high pH might be one of the reasons for the decrease of Zn sorption.

In this study pH had no effect on the Langmuir adsorption maxima,  $b_1$ . This might be due to the narrow range of pH in the soils under study (Table 1).

$k_1 = 13.6 + 0.312 \text{ SSA} - 0.563 \text{ CEC}$ ,  $R^2 = 0.52$ ,  $P < 0.01$  (9)

$k_2 = 0.013 + 0.0071 \text{ SSA}$ ,  $R^2 = 0.41$ ,  $P < 0.05$  (10)

$b_1 = 205 + 231 \text{ CEC} - 0.54 \text{ SSA}$ ,  $R^2 = 0.504$ ,  $P < 0.01$  (11)

$b_2 = 4295 - 381 \text{ pH} + 11.5 \text{ Clay}$ ,  $R^2 = 0.65$ ,  $P < 0.01$  (12)

Native soil Zn extractable with DTPA was not correlated with sorption maxima. This is in agreement with the findings of Udo *et al.* (1970).  $\text{NaHCO}_3$ -extractable P has also been reported to be related to Zn adsorption (Melton *et al.*, 1973). The Olsen-P relationship with Zn sorption was also studied but no statistical relationship found.

In this study no statistical relationship was found out between CCE, ACCE and the Langmuir equation  $b$  coefficient, which is in agreement with the findings of Trehan and Sekhon (1977).

Equations (9) and (10) show that soil surface area (SSA) and cation exchange capacity of soils (CEC) may play important roles in the binding energy of Zn to soil.

Gunary coefficients of soils for Zn adsorption are shown in Table 4. The following equations were found to relate Gunary coefficients with soil characteristics:

**Table 4.** Gunary adsorption isotherm coefficients and the coefficients of determination ( $R^2$ ) for the fit of data.

Soil No	$K_1$	$K_2$	$K_3$	$R^2$	Soil No	$K_1$	$K_2$	$K_3$	$R^2$ (%)
1	83	-29	501	99.02	11	53	-30	564	99.48
2	76	-11	310	99.15	12	46	-29	537	99.51
3	76	-11	315	99.20	13	96	-20	412	99.37
4	70	-32	540	99.12	14	28	-88	950	99.78
5	58	-19	407	99.52	15	75	-103	1066	98.69
6	39	-10	300	99.65	16	61	-25	448	99.40
7	34	-13	350	99.71	17	-30	-62	788	99.87
8	44	-53	699	98.89	18	-30	-44	737	99.76
9	76	-24	461	98.92	19	64	-27	516	99.32
10	71	-68	797	97.97	20	72	-27	479	99.10
min:	-30	-103	300	99.97					
max:	83	-10	1066	99.87					
mean:	53	-36	557	99.3					

The min, max and mean values are belong to all the 20 soils

$k_1 = -598 + 88\text{pH} - 1.35 \text{ Clay} + 0.57 \text{ Olsen-P}$ ,  $R^2 = 0.85$ ,  $P < 0.01$  (13)

$k_2 = 28.6 - 2.31 \text{ CEC} - 0.63 \text{ ACCE}$ ,  $R^2 = 0.52$ ,  $P < 0.01$  (14)

$k_3 = 100 + 20 \text{ CEC} - 49 \text{ DTPA-Zn} + 10 \text{ SSA}$ ,  $R^2 = 0.68$ ,  $P < 0.01$  (15)

Fits of Zn adsorption data to the Temkin equation revealed that in the range of Zn concentrations studied, this equation did not adequately describe the data and for just 9 out of the 20 soils studied, at low equilibrium concentrations, fits of this equation to the data could be justified. The only Temkin coefficient that showed a significant relationship with soil characteristics was  $K_2$  [Equation (16)].

$K_2 = 290 + 21.9 \text{ CCE}$ ,  $R^2 = 0.46$ ,  $P < 0.05$  (16)

The adjusted Freundlich equation fitted to Zn adsorption data and related parameters are shown in Table 5. (Ratkowsky, 1986)

This equation shows excellent fits to the data, but in interpretation of the results there should be caution (Barrow, 1978). The amounts of estimated  $q_0$  are not justified since they are greater than total Zn in some soils (soil No 8, 10, 14, 15 and 19).

A common method used to ensure that an ion has been adsorbed by a soil instead of being precipitated onto soil particle surface is to calculate the saturation index (SI) (Sposito, 1989).

**Table 5.** Adjusted Freundlich adsorption isotherm coefficients and the coefficients of determination ( $R^2$ ) for the fit of data.

Soil No	K	1/n	$q_0^a$	$R^2$	Soil No	K	1/n	$q_0$	$R^2$ (%)
1	733	0.29	87	99.6	11	722	0.34	69	99.81
2	454	0.34	26	99.7	12	694	0.33	75	99.76
3	673	0.29	93	99.6	13	588	0.31	56	99.76
4	757	0.30	96	99.5	14	1117	0.28	163	98.82
5	561	0.33	53	99.7	15	1252	0.30	143	99.38
6	392	0.37	29	99.8	16	637	0.31	77	99.50
7	442	0.37	33	97.7	17	927	0.38	148	99.10
8	954	0.25	21	99.6	18	803	0.33	108	99.72
9	664	0.306	74	99.6	19	686	0.30	64	99.82
10	1041	0.271	162	98.8	20	691	0.27	87	99.63

<sup>a</sup> Residual zinc,  $\text{mg kg}^{-1}$ .

**Table 6.** Zn species distribution and SI values.

Zn species	Molarity	Phase	SI
$Zn^{2+}$	$8.69 \times 10^{-4}$	Zincite (Zno)	-0.2
$Zn(CO_3)_2^{2-}$	$5.34 \times 10^{-4}$	$Zn(OH)_2$	-1.21
$ZnCl^+$	$2.44 \times 10^{-5}$	Smithosonite	-1.35
$ZnOH^+$	$1.86 \times 10^{-5}$	( $ZnCO_3$ )	
$Zn(OH)_2$	$5.68 \times 10^{-6}$	$Zn_2(OH)_3Cl$	-2.1
$ZnCl_2$	$3.61 \times 10^{-7}$	Willemite ( $Zn_2SiO_4$ )	1.28
$ZnCO_3$	$8.54 \times 10^{-7}$		
$ZnCl_3$	$8.11 \times 10^{-9}$		
$Zn(OH)_3$	$6.76 \times 10^{-10}$		
$ZnCl_4^{2-}$	$1.12 \times 10^{-10}$		
$Zn(OH)_4^{2-}$	$5.57 \times 10^{-15}$		

Zn species distribution and SI Values at 60 mg Zn L<sup>-1</sup> as an equilibrium concentration (related to 160 mg Zn L<sup>-1</sup> as an initial concentration) are shown in Table 6. The only SI>0 is for the Willemite phase ( $Zn_2SiO_4$ ); all other phases are under saturated.

Variable pressure scanning electronic microscopy (VPSEM) images at high Zn concentrations (close to a Zn Fertilizer granule, Figure 2) and at low concentration, (Figures 3 and 4) showed Zn precipitation and uniform Zn atom distribution, respectively. At initial concentrations of 50, 100 and 200 mg Zn L<sup>-1</sup> in all studied soils, the map of Zn distribution showed uniform distribution, so the probability of Zn precipitation seemed to be low. At 500 mg Zn L<sup>-1</sup>, an initial high density of Zn atoms may be an indication of Zn precipitation (Figure 3).

## CONCLUSIONS

Some outstanding points of conclusion of the ongoing research could be cited as follows:

(1) The required time for reaching equilibrium for Zn sorption in studied soils is 24 hours.

(2) Because of hysteretic characteristic of Zn sorption and desorption, for modelling of zinc uptake by plants, desorption isotherms should be preferred.

(3) The Freundlich and Gurnary equations show significant fits to Zn sorption data.

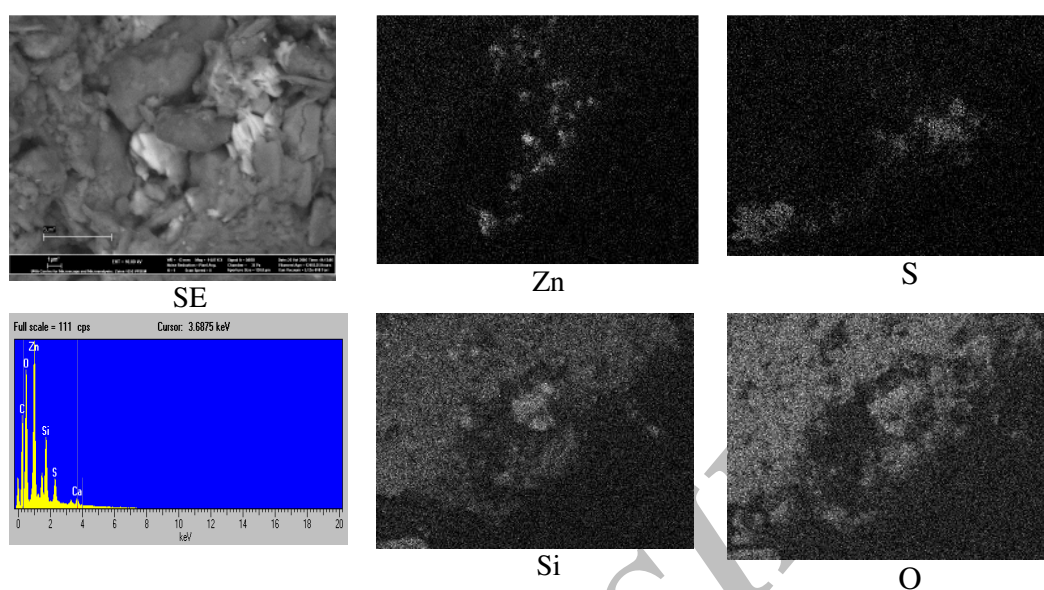
(4) Under the prevailing experimental conditions, the two-surface Langmuir adsorption isotherms showed a significant fit for most of our experimental soils.

(5) The Temkin equation showed significant fits to our experimental data only under low equilibrium concentrations.

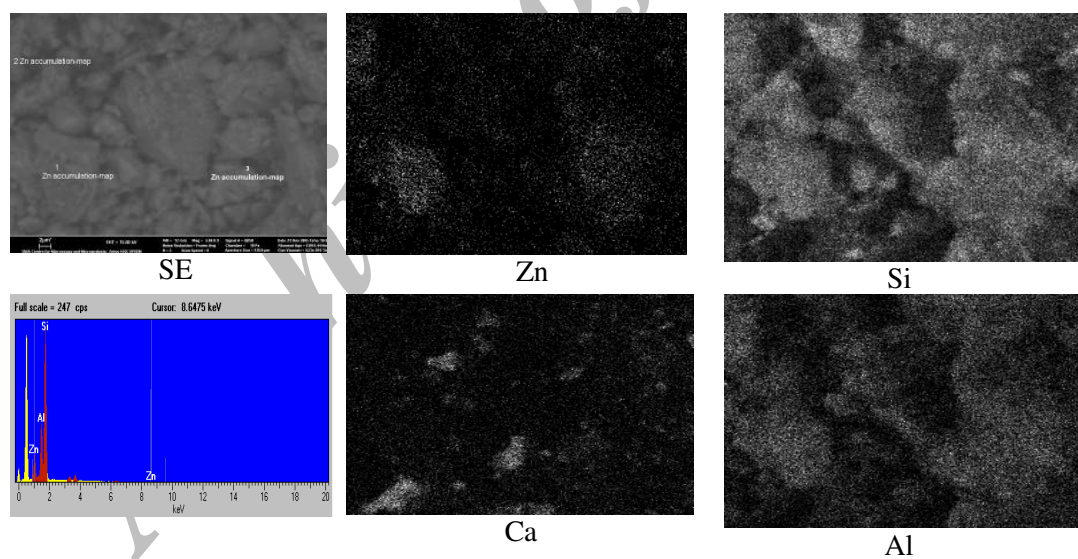
(6) The modified Freundlich equation showed significant fits for most of the obtained experimental data in this experiment but for some soils the predicted residual Zn ( $q_0$ ) was through as unrealistic.

(7) A variable pressure scanning electron microscopy (VPSEM) study showed that Zn was uniformly distributed in the soil matrix up to an initial concentration of 500 mg Zn L<sup>-1</sup> to the limit of the spatial resolution of this technique. There were no local concentrations of Zn or spatial associations of other elements with Zn and as well there was little indication of Zinc precipitation.

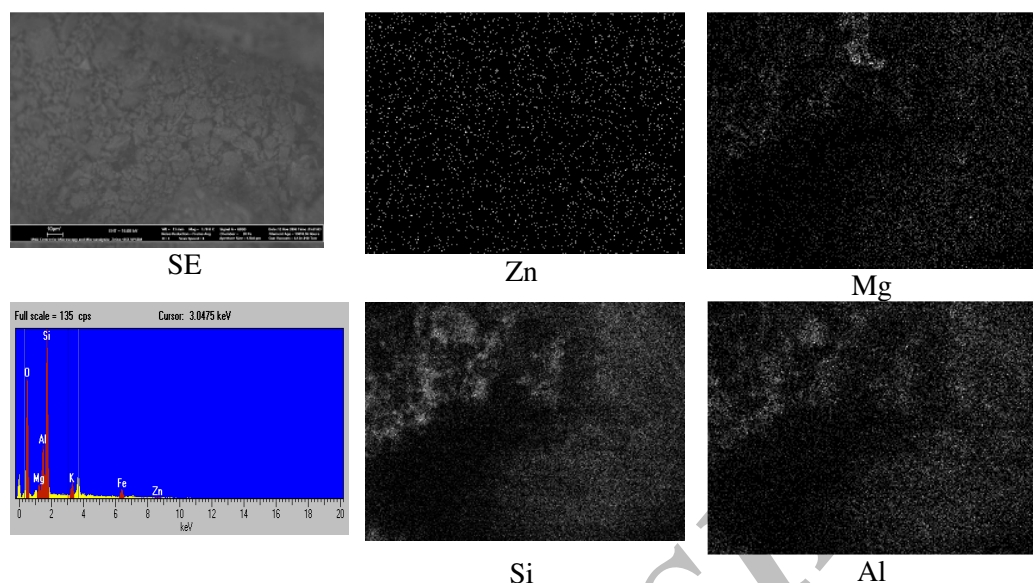




**Figure 2.** VPSEM data for unpolished surface of high concentration Zn treated in calcareous soil No10. Secondary electron image (SE), element distribution maps for Zn, S, Si, O and X-Ray spectrum for whole field of view indicating the presence of a high quantity of precipitated Zn.



**Figure 3.** VPSEM data for unpolished surface of Zn – treated of calcareous soil No 5. Secondary electron image (SE), element distribution maps for Zn, Si, Ca, Al and X-Ray spectrum for whole field of view indicating the presence of minor amounts of Zn. (Initial concentration of Zn was  $500 \text{ mg Zn L}^{-1}$  as  $\text{Zn SO}_4$ .)



**Figure 4.** VPSEM data for unpolished surface of Zn – treated of calcareous soil No.5 Secondary electron image (SE), element distribution maps for Zn, Mg, Si, Al and X-Ray spectrum for whole field of view indicating the presence of minor amounts of Zn. (Initial concentration of Zn was 200 ppm).

## ACKNOWLEDGEMENTS

The authors wish to thank the University of Western Australia and as well, the Ministry of Science and Technology of Iran for funding this research and for providing a research fellowship to the paper's first author. Also the authors wish to extend their sincere thanks to CMM of the University of Western Australia for providing a research facility.

## REFERENCE

- Allison, L. E. 1965. Organic Carbon, In: "Methods of Soil Analysis", Black, C. A. (Ed). Part 2, American Society of Agronomy, Madison, W. I., PP. 1367-1378.
- Allison, L. E. and Moodie, C. D. 1965. Carbonate. In: "Methods of soil Analysis", Black, C. A. (Ed). Part 2, American Society of Agronomy, Madison, W. I., PP. 1379-1396.
- Bar-Tal, A., Bar-Yosef, B. and Chen, Y. 1988. Effects of Fulvic Acid and pH on Zinc Sorption on Montmorillonite. *Soil Sci.*, **146**: 367-373.
- Bar-Yosef, B. 1979. pH-dependent Zinc Adsorption by Soils. *Soil Sci. Soc. Am. J.*, **43**: 1095- 1099.
- Barrow, N. J. 1987. The Effects of Phosphate on Zinc Sorption by a Soil. *J. Soil Sci.*, **38**:453-459.
- Brunauer, S., Emmett, P. H. and Teller, E. 1938. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.*, **60**: 309-319.
- Chapman, H. D. 1965. Cation Exchange Capacity. In: "Methods of Soil Analysis", Part 2, Black, C. A. (Ed), American Society of Agronomy, Madison, W. I., PP. 891-901.
- Darjeh, Z., Karimian, N., Maftoun, M., Abtahi, A. and Razmi, K. 1991. Correlation of Five Zn Extractants with Plant Responses on Highly Calcareous Soil of Doroodzan Dam Area, Iran. *Iran Agric Res.*, **10**: 29-45.
- Day, P. R. 1965. Particle Fractionation and Particle-size Analysis. In: "Methods of Soil Analysis", Black, C. A. (Ed). Part 1, Agron. Monogr. 9. ASA, Madison, W I., PP. 545-567.

10. Drouineau, G. 1942. Dosage Rapid du Calcire Actif du sol, Houvelles Donnness sur Lase Paration et al Nature des Fraction Clacaires. *Am. Agron.*, **12**: 441-450.
11. Elrashidi, M. A. and OConnor, G. A. 1982. Influence of Solution Composition on Sorption of Zinc by Soils. *Soil Sci. Soc. Amer. J.*, **46**:1153-1158.
12. Fitter, A. H. and Sutton, C. D. 1975. The Use of the Freundlich Isotherm for Soil Phosphate Sorption Data. *J. Soil. Sci.*, **26**: 241-246.
13. Guadalix, M. E. and Pardo, M. T. 1995. Zinc Adsorption by Acid Tropical Soils as an Affected by Cultivation. *Europ. J. Soil. Sci.*, **46**: 317-322.
14. Gunary, D. 1970. A new adsorption isotherm for Phosphate in soils. *J. Soil Sci.* , **21**: 72-77
15. Harter, R. D. 1991. Micronutrient Adsorption Desorption Reaction in Soils. In: "Micronutrients in Agriculture", Mortvedt, J. *et al.* (Ed.). 2<sup>nd</sup> Ed., SSSA, Madison, W. I., PP. 59-87.
16. Holford, I. C. R., Wedderburn, R. W. M. and Matingly, G. E. G. 1974 .A Langmuir Two Surface Equation as a Model for Phosphate Adsorption by Soils. *J. Soil Sci.*, **25**: 242-255.
17. Karimian, N. and Moafpurian, G. R. 1999. Zinc Adsorption Characteristics of Selected Calcareous Soils of Iran and Their Relationship with Soil Properties. *Commun. Soil Sci. Plant Anal.*, **30**: 1721-1731
18. Karimian, N. and Yaserbi, J. 1995. Prediction of Residual Effects of Zinc Sulfates on Growth and Zinc Uptake of Corn Plants, Using Three Zinc Soil Tests. *Commun. Soil Sci. Plant Anal.*, **26**: 277-287.
19. Lindsay, W. L. and Norvell, W. A. 1978. Development of a DTPA Soil Test for Zinc, Iron, Manganese and Copper. *Soil Sci. Soc. Am. J.*, **42**: 421-428.
20. Maftoun, M., Haghghat Nia, H. and Karimian, N. 2000. Characterization of Zinc Adsorption in Some Calcareous Paddy Soils from Fars Province. *J. Sci. Technol. Agric. Natur. Res.*, **4**: 71-84(In Persian).
21. Maftoun, M. and Karimian, N. 1989. Relative Efficiency of Two Zinc Sources for Maize (*Zea mays* L.) in Two Calcareous Soils from an Arid Area of Iran. *Agronomie.*, **9**: 771-775.
22. Melton, J. R., Mahtab, S. K. and Swoboda, A. R. 1973. Diffusion of Zinc in Soils as a Function of Applied Zinc, Phosphorus, and Soil pH. *Soil Sci. Soc. Amer. Proc.*, **37**: 379-381
23. Naganma, K., Okazaki, M. and Yonebayashi, K. 1993. Surface Charge and Adsorption Charge and Adsorption Characteristics of Copper and Zinc on Tropical Peat Soils. *Soil Sci. Plant Nutr.*, **39**: 455-462.
24. Olsen, S. R., Cole, C. V., Watanabe, F. S. and Dean, L. A. 1954. Estimation of Available Phosphorous in Soil by Extraction with Sodium Bicarbonate. USDA Circular 939, Government Printing Office. Washinton, DC.
25. Parkhurst, D. L. and Appelo, C. A. J. 1999. *User's Guide to PhreeqCi (Version 2)*. A Computer Program for Speciation, Batch-reaction, One-dimensional Transport and Inverse Geochemical Calculations. Water Resources Investigation Report 99-4259, U.S.A Department of the Interior and U.S.A Geological Survey, Denver, Colorado.
26. Ratkowsky, D. A. 1986. Sorption of Phosphate by Soil. *J. soil Sci.*, **37**: 193-189.
27. Shuman, L. M 1975. The Effect of Soil Properties on Zinc Adsorption by Soils. *Soil Sci. Soc. Amer. Proc.*, **39**: 454-458
28. Rao, P. N., Singh, A. P., Singh, S. and Singh, B. 1985. Effect of Phosphorus and Manganese Application on Available Zinc and Iron in Soil. *J. Indian Soc. Soil Sci.*, **33**: 437-439
29. Saeed, M. and Fox, R. L. 1979. Influence of Phosphate Fertilization on Zinc Adsorption by Tropical Soils. *Soil Sci. Soc. Am. J.*, **43**: 683-686
30. Sposito, G. 1982. On the Use of the Langmuir Equation in the Interpretation of Adsorption Phenomena: II. The Two-surface Langmuir Equation. *Soil Sci. Soc. Am. J.*, **46**: 1147-1152.
31. Sposito, G. 1989. *The Chemistry of Soils*. Oxford University Press. Inc., PP. 127-147.
32. Sparks, D. 1995. *Environmental Soil Chemistry*. Academic Press, San Diego, CA.
33. SPSS, Inc. 2002. SPSS for Windows, Release 9.5 Spss. Inc.
34. Tessier, A., Campbell, P. G. C. and Bisson, M. 1979. Sequential Extraction Procedure for the Speciation of Particular Trace Metal. *Anal. Chem.*, **51**:844-851.
35. Trehan, S. P. and Sekhon, G. T. 1977. Effect of Clay, Organic Matter, and CaCO<sub>3</sub> Content



- on Zinc Adsorption by Soils. *Plant and Soil*, **46**:329-336.
36. Xie, R. J. and A. F. Mackenzie. 1991. Effects of Autoclaving on Surface Properties and Sorption of Phosphate and Zinc in Phosphate-treated Soils. *Soil Sci.*, **152(4)**: 250-258.
37. Udo, E. J., Bohn, H. L. and Tucker, T. C. 1970. Zinc Adsorption by Calcareous Soils. *Soil Sci. Soc. Amer. Proc.*, **34**: 454-407.

## ویژگیهای جذبی روی در تعدادی از خاکهای آهکی ایران

ع. ریحانی تبار، م. اردلان، ر. جلیکس، و غ. ثواقبی

### چکیده

این مطالعه به منظور بدست آوردن رابطه کمی بین روی محلول خاک و روی جذب شده توسط بیست خاک منتخب آهکی انجام گرفت. خاکها با غلظت های گوناگون روی به تعادل رسانده و مقدار روی جذب شده برای برآزش ۶ همدمای جذبی یعنی همدماهای فروندلیچ، لانگ موئیر، تمکین، گانری، لانگ موئیر و مکانی، و فروندلیچ اصلاح شده مورد استفاده قرار گرفت. داده های جذب و واجذب روی بر همدیگر منطبق نشده و پدیده پسماند مشاهده شد که نشاندهنده یکسان نبودن مکانیسم جذب و واجذب روی می باشد. برآزش معادله فروندلیچ به داده های حاصله نشان داد که این معادله قادر به توصیف داده ها نبوده اما پس از حذف سه غلظت ابتدایی این معادله برآزش خوبی به داده ها نشان داد. معادله تک مکانی لانگ موئیر نتوانست بر داده ها برآزش یابد، اما معادله دو مکانی لانگ موئیر در تعدادی از خاکها بطور معنی داری برآزش یافت. معادله تمکین فقط در غلظت های پایین تعادلی بر داده ها برآزش نشان داد.