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Adsorption of Zinc in Some Selected Soils

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Abstract

Eight soils were studied for adsorption reactions of zinc and evaluated for their quantity, intensity and supply parameters for zinc. With the addition of increasing amounts of zinc there was a simultaneous increase in the equilibrium concentration, adsorption, percent saturation of adsorption capacity and supply parameter of zinc. Multiple regression analysis revealed that in all soils quantity, intensity and equilibrium concentration were the main parameters accounting for the supply of zinc. Light loam (1), silty medium loam (6) and silt loam (7 and 8) soils having comparatively higher values for the adsorption maxima, bonding energy constant and differential buffering capacity of the soils will require higher rates of zinc to change in the solution concentration. For an ecological point of view this means a reduction of Zn toxicity.

Keywords: adsorption of Zn, adsorption maxima, bonding energy constant, differential buffering capacity, supply parameter

Introduction

Adsorption and precipitation are known to regulate the concentration of nutrients in soil solutions. The buffering capacity of a soil for adsorption-desorption processes usually affects quantity, intensity and kinetic parameters, which determine the capacity of the soil to supply plant nutrients. The adsorption of zinc by soils is influenced by soil properties including texture, calcium carbonate and organic matter content. Appreciable fractions of total soluble zinc may be in equilibrium with specially adsorbed forms associated with insoluble organic matter [2, 9]. The hydrolysis constant of zinc is $10^{-9.6}$ so at pH greater than 7.0 the hydrolyzed species $Zn(OH)^+$, $ZnHCO_3^+$, $Zn(OH)_3^-$ will be present in sufficient amounts relative to Zn^{2+} to be important in adsorption reactions. In the same way, the hydrolysis process favors chemisorption by allowing zinc to interact with the surface as a monovalent cation [11]. The rate of zinc sorption from solution to solid surfaces is a dynamic factor that directly or indirectly regulates the amounts of Zn in solution and its availability [12].

The present investigation is carried out to characterize texturally different soils for their adsorption reactions with zinc and thereby their quantity, intensity and supply parameters.

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Material and Methods

Eight soil samples were collected from arable areas. They were air-dried and crushed with a wooden pestle and mortar to pass through a 0.5 mm mesh-screen. The textural analysis was performed using the hydrometer method, organic carbon ($C_{org.}$) by Tiurin's method and soils reaction (pH) in 1M KC1 with a 1:2.5 (w/v) ratio using a glass electrode. Cation exchange capacity (CEC) by the Mehlich$_{g2}$ method in Kociałkowski's [8] modification, iron and manganese in their amorphous bonds according to Gupta [4], (Table 1). Extractable (soluble) Zn in 1M HC1 [3], as well as Fe and Mn, were determined by atomic absorption spectrophotometry.

Adsorption Studies

Different concentrations of zinc 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 mmol$_c$/dm^3 were prepared by dissolving $Zn(NO_3)_2$ in 0.1M $Ca(NO_3)_2$ as a background electrolyte. These solutions were added to soils at 1:15 soil/solution ratios in a series of polyethylene centrifuge tubes and shaken for two hours. They were allowed to equilibrate over the night and filtered. The concentration of zinc was determined by atomic absorption spectrophotometry. The amount of zinc adsorbed was calculated as the difference between initial zinc concentration and that rema-

Table 1. Physico chemical properties of the soils.

Textural type of soils	pH in 1 M KCl	Organic C (g/kg)	Clay (g/kg)	Amorphous Fe (g/kg)	Amorphous Mn (g/kg)	CEC ($cmol_c$/kg)	Extractable Zn (mg/kg) 1 M HCl*
1. light loam	7.3	1.16	49	5.12	0.19	9.40	12.32
2. light loamy sand	6.4	1.22	21	2.30	0.37	9.68	33.44
3. light loamy sand	6.5	0.93	29	0.89	0.35	8.53	28.50
4. light loamy sand	4.9	1.10	30	1.17	0.30	5.97	36.08
5. lihgt loamy sand	6.7	1.28	44	1.17	0.40	9.34	43.40
6. silty medium loam	6.9	1.96	74	3.33	0.71	21.29	60.36
7. silt loam	6.9	1.10	70	1.33	0.48	10.13	41.29
8. silt loam	7.0	1.40	66	1.33	0.35	13.18	56.60

* These values were used for S_o calculation

ining in solution after equilibration. The Langmuir one-surface adsorption equation was applied to interpret the reaction of zinc with soil.

$$C_e/S = \frac{1}{a_{max} \cdot b} + \frac{C_e}{a_{max}} \quad [1]$$

where,
C_e - equilibrium concentration of Zn in soil solution ($mmol_c/dm^3$),
S - amount of Zn adsorbed ($mmol_c$/kg),
a_{max} - adsorption maxima ($mmol_c$/kg),
b - bonding energy constant ($dm^3/mmol_c$).
The S value for each measurement was calculated as follows:

$$S = (C_o - C_e) \cdot V/W + S_o \quad [2]$$

where,
C_o - initial equilibrium concentration of Zn in the solution ($mmol_c/dm^3$),
C_e - equilibrium concentration of Zn in soil solution ($mmol_c/dm^3$),
V - volume of the solution (cm^3),
W - weight of soil sample (g),
S_o - initial Zn content in the soil ($mmol_c$/kg),
Correlation coefficients between C_e and S were calculated and lines fitted by regression analysis. The differential buffering capacity was assessed by:

$$DBC = \frac{a_{max} \cdot b}{(1 + bC_e)^2} \quad [3]$$

where,
DBC - differential buffering capacity (dm^3/kg),
a_{max} - adsorption maxima ($mmol_c$/kg),
b - bonding energy constant ($dm^3/mmol_c$),
C_e - equilibrium concentration of Zn in soil solution ($mmol_c/dm^3$).
A supply parameter for Zn in the studied soils was mentioned by the relationship:

$$SP = \sqrt{\frac{S \cdot C_e}{\sqrt{a_{max} \cdot b}}} \quad [4]$$

where,
SP - supply parameter (mmol • $kg^{-1/4}$ • $dm^{-9/4}$),
S — amount of Zn adsorbed ($mmol_c$/kg),
C_e - equilibrium concentration of Zn in soil solution ($mmol_c/dm^3$),
a_{max} - adsorption maxima ($mmol_c$/kg),
b - bonding energy constant ($dm^3/mmol_c$).
In order to assess the capacity of the studied soils for zinc adsorption, the percent saturation was established as:

$$\Theta(\%) = \frac{Amount\ of\ Zn\ adsorbed\ (mmol_c/kg)}{Adsorption\ maxima\ (mmol_c/kg)} \cdot 100 \quad [5]$$

Results and Discussion

Physico chemical properties of the soils reported in Table 1 revealed that the soils vary in their texture from sandy loam to loamy soils with a range of clay content from 21 to 74 g/kg. Most of the soils had neutral reaction (6.4 to 7.3) except one, soil nr 4 (pH 4.9) presenting an acidic reaction. The carbon content varied from 0.93 to 1.96 g/kg, whereas the CEC values ranged from 8.53 to 21.29 $cmol_c$/kg. The content of amorphous iron comprised from 0.89 to 5.12 g/kg and that of manganese between 0.19 and 0.71 g/kg.

With the addition of increasing amounts of zinc to all soils, there was an increase in the equilibrium concentration of zinc (Table 2). Similarly with the increasing equilibrium concentration *(C_e)* an increase in the adsorption of zinc *(S)* was also noted as reported by Narwal [10] and Wada [13]. At the lowest and highest concentration of zinc (0.1 and 1.0 $mmol_c/dm^3$), a noticeable difference in the adsorption of zinc by these texturally different soils occurred. Soils nr 1,2, 3, 4, and 5 adsorbed almost equal quantities of Zn added. The lowest levels were observed in the soil nr 4 (with CEC = 5.97), and the highest in the soil nr 6 (CEC = 21.29). The adsorption maxima did not similarly follow the same tendency (Table 2). The rise in the acidity of the soil nr 4 might be an explanation of its low adsorption parameters for Zn, since H^+ may potentially saturate the soil adsorbing complex. Such a state was pointed out by Boehringer [1]. On the other hand a high a_{max} value (66.5 $mmol_c$/kg) found for soil nr 6 is perhaps related to the higher clay and organic matter content that enhance soil cation exchange capacity. Adsorption maxima was correlated (but not significantly) with clay (r = 0.20), cation

Table 2. Influence of Zn additions on the equilibrium concentration (C_e, mmol$_c$dm^3), adsorption (S, mmol$_c$kg), adsorption maxima (a_{max}, mmol$_c$kg) and bonding energy constant (b, dm^3/ mmol$_c$ for analyzed soils.

Type of soils		Initial Zn concentrations in solution (mmol$_c$/dm^3)										a_{max}	b
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0		
1. light loam	C_e	0.01	0.01	0.01	0.02	0.04	0.06	0.09	0.14	0.17	0.20	26.10	34.40
	S	3.20	6.17	9.02	11.75	14.27	16.43	18.62	20.21	22.25	24.26		
2. light loamy sand	C_e	0.04	0.06	0.07	0.08	0.09	0.24	0.29	0.55	nd	0.97	18.40	13.50
	S	3.39	6.18	8.94	11.85	14.68	15.36	17.67	16.83		16.53		
3. light loamy sand	C_e	0.01	0.03	0.07	0.12	0.18	0.25	0.31	0.37	0.44	0.49	17.30	11.70
	S	3.54	5.91	7.77	9.27	10.56	11.46	12.51	13.77	14.76	16.08		
4. light loamy sand	C_e	0.19	0.27	0.39	0.59	0.77	0.88	1.08	1.21	nd	1.52	6.47	1.33
	S	1.18	2.09	2.69	2.65	2.86	3.50	3.52	4.03		4.70		
5. light loamy sand	C_e	0.01	0.03	0.06	0.10	0.17	0.21	0.28	0.33	0.38	0.46	19.50	12.60
	S	3.94	6.55	8.50	10.33	11.29	13.15	14.02	15.52	16.96	17.50		
6. silty medium loam	C_e	0.02	0.02	0.05	0.09	0.17	0.23	0.38	0.52	nd	0.78	66.50	13.60
	S	11.04	20.74	29.54	37.14	43.54	50.24	52.94	55.84		62.94		
7. silt loam	C_e	0.00	0.01	0.02	0.03	0.04	0.07	0.10	0.13	0.16	0.20	14.10	39.50
	S	2.72	4.15	5.54	6.86	8.11	9.23	10.30	11.38	12.31	13.27		
8. silt loam	C_e	0.01	0.02	0.04	0.09	0.12	0.19	0.25	0.30	0.35	nd	31.20	19.10
	S	6.33	10.83	14.53	17.13	20.53	22.48	24.18	26.93	29.38			

nd: not determined

exchange capacity (r = 0.45), organic carbon (r = 0.58), amorphous iron and manganese (r = 0.24 and 0.31) (Table 3). In soil systems it is difficult to attribute the exchangeability of Zn to any one mechanism. Moreover, at 0.2 and 0.8 mmol$_c$/dm^3, the adsorption of Zn showed a high dependence on CEC, followed by C_{org} and amorphous Mn. The multiple regression analysis revealed that these different soil parameters together accounted for 61% of the variation in the adsorption maxima and the relationship is given by the following equation:

$$a_{max} = 15.18 - 2.31\text{pH} + 38.77\ C_{org} - 0.28\ \text{Clay} + 1.10\ \text{CEC} - 0.003\ Fe_{amor.} - 0.03\ Mn_{amor},\ (R^2 = 0.61)$$

The bonding energy constant values for different soils varied from 1.33 to 39.5 dm^3/mmol$_c$. In acidic soil conditions the CEC may be partly saturated by protons (H^+). This onwards promotes a weak bonding energy (1.33 dm^3/mmol$_c$ for soil 4). Among different soil properties only pH had a higher and significant relationship (r = 0.67, $P < 0.05$) and multiple regression analysis indicated that all properties together accounted for 65 percent of the variation and then:

$$b = -31.88 + 8.0\ \text{pH} - 8.55\ C_{org} + 0.05\ \text{Clay} - 0.48\ \text{CEC} + 0.003\ Fe_{amor.} - 0.03\ Mn_{amor},\ (R^2 = 65\%)$$

As presented in Table 5 the degree of the CEC saturation by zinc was generally low, irrespective of the type of soils. It varied from 10.8 to 31.2%, confirming in the same way the relatively low values of coefficients of determination mentioned above. A value of 23% for a sandy loam soil was reported by Narwal [10].

Nutrients in solution and associated with colloid surfaces are important for plant growth. The solution fraction is readily available while adsorbed fractions may be gradually released as the ions in solution are depleted. The data on the influence of different levels of zinc on the percent saturation, differential buffering capacity and the supply parameter are listed in Table 4 (irrespective of soils). An increase in the percent saturation (from 12.25 to 79.24%) was noted for initial Zn concentrations between 0.1 to 0.5 mmol$_c$/dm^3. A similar tendency was obtained by Joshi [5] with copper sorption. As shown in Table 5, the highly recorded correlation coefficients of zinc added with equilibrium concentration and percent

Table 3. Correlation coefficients of soil properties *vs* adsorption maxima, bonding energy constant, supply parameter and amount of adsorbed zinc

Some soil properties	Adsorption[a] maxima (a_{max})	Bonding[a] energy (b)	Zinc adsorbed (S)[a] at		Supply parameter (SP)[b] at	
			0.2 (mmol$_c$/dm^3)	0.8	0.2 (mmol$_c$/dm^3)	0.8
pH	– 0.36	0.67*	0.43	0.49	– 0.94***	– 0.74*
$C_{org.}$	0.58	– 0.09	0.83*	0.83*	– 0.10	0.28
Clay	0.20	0.57	0.49	0.50	– 0.47	– 0.31
CEC	0.45	– 0.02	0.91**	0.91**	– 0.30	0.16
Amorphous Fe	0.24	0.26	0.32	0.43	– 0.32	– 0.20
Amorphous Mn	0.31	0.05	0.79*	0.76*	– 0.16	0.22

* – significat at $P < 0.05$ ** – $P < 0.005$ *** – $P < 0.0005$

a – for more details, see Table 2; b – (mmol · kg$^{-1/4}$ · dm$^{-9/4}$)

Table 4. Influence of initial Zn concentration in solution on percent saturation (Θ), differential buffering capacity (DBC) and the supply parameter (SP).

Textural type of soils	Initial Zn concentration in solution ($mmol_c/dm^3$)									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Percent saturation (Θ), [%]									
1. light loam	12.25	23.62	34.53	44.98	54.63	62.90	71.28	77.37	85.18	92.87
2. light loamy sand	18.39	33.52	48.49	64.27	79.24	83.31	95.84	91.28	nd	89.65
3. light loamy sand	20.50	34.23	45.01	53.69	61.17	66.38	72.46	79.76	85.49	93.14
4. light loamy sand	18.15	32.29	41.55	40.86	44.10	54.07	54.30	62.18	nd	72.60
5. light loamy sand	20.18	33.55	43.54	52.92	57.83	67.36	71.82	79.50	86.88	89.65
6. silty medium loam	16.61	31.21	44.45	55.89	65.52	75.60	79.66	84.03	nd	94.71
7. silt loam	19.21	29.40	39.16	48.50	57.42	65.27	72.91	80.55	87.13	93.92
8. silt loam	20.26	34.67	46.51	54.83	65.71	71.96	77.40	86.40	94.04	nd
	Differential buffering capacity (DBC), [dm^3/kg]									
1. light loam	654.72	617.88	473.18	315.43	179.32	87.62	52.64	27.18	19.15	14.09
2. light loamy sand	101.35	80.71	64.01	59.06	48.35	13.50	10.31	3.55	nd	1.26
3. light loamy sand	158.72	107.00	61.06	34.94	21.41	13.34	9.33	7.11	5.40	4.40
4. light loamy sand	5.49	4.68	3.75	2.69	2.11	1.83	1.45	1.26	nd	0.94
5. light loamy sand	181.09	139.28	78.60	48.18	25.36	19.06	12.23	9.40	7.39	5.32
6. silty medium loam	609.76	535.55	242.04	174.10	85.16	52.34	23.96	13.87	nd	6.74
7. silt loam	446.25	342.62	220.14	130.73	76.67	40.22	23.92	15.84	10.09	7.11
8. silt loam	448.96	330.42	176.17	78.50	52.59	29.04	17.78	13.48	10.26	nd
	Supply parameter (SP), [$mmol/kg^{1/4} \cdot dm^{9/4}$]									
1. light loam	0.02	0.04	0.06	0.09	0.13	0.19	0.24	0.30	0.36	0.41
2. light loamy sand	0.10	0.15	0.20	0.24	0.30	0.49	0.57	0.76	nd	1.01
3. light loamy sand	0.05	0.12	0.20	0.28	0.36	0.45	0.52	0.60	0.67	0.75
4. light loamy sand	0.28	0.44	0.60	0.73	0.86	1.02	1.14	1.29	nd	1.56
5. light loamy sand	0.06	0.10	0.18	0.26	0.35	0.42	0.50	0.57	0.64	0.72
6. silty medium loam	0.08	0.12	0.21	0.34	0.49	0.62	0.82	0.98	nd	1.28
7. silt loam	0.02	0.04	0.06	0.09	0.12	0.16	0.21	0.25	0.29	0.33
8. silt loam	0.05	0.09	0.16	0.25	0.32	0.41	0.50	0.57	0.65	nd

Table 5. Correlation coefficients (r values)[a] between different adsorption parameters.

	1. Light loam	2. Light loamy sand	3. Light loamy sand	4. Light loamy sand	5. Light loamy sand	6. Silty medium loam	7. Silt loam	8. Silt loam
– Zn added *vs*								
Equilibrium conc.	0.949	0.888	0.995	0.997	0.992	0.954	0.970	0.985
Percent saturation	0.995	0.911	0.990	0.975	0.990	0.975	0.997	0.991
DBC*	– 0.943	– 0.958	– 0.862	– 0.946	– 0.880	– 0.897	– 0.903	– 0.879
Supply parameter	0.986	0.968	0.998	0.999	0.999	0.991	0.992	0.998
– Percent satur. *vs*								
Equilibrium conc.	0.917	0.620	0.917	0.958	0.965	0.864	0.997	0.954
DBC	– 0.965	– 0.950	– 0.921	– 0.938	– 0.930	– 0.968	– 0.932	– 0.928
Supply parameter	0.967	0.781	0.990	0.980	0.986	0.939	0.980	0.982
– Supply parm. *vs*								
Equilibrium conc.	0.987	0.972	0.995	0.993	0.994	0.991	0.994	0.982
DBC	– 0.887	– 0.890	– 0.864	– 0.850	– 0.876	– 0.846	– 0.843	– 0.856
– Equilib. conc. *vs*								
DBC	– 0.806	– 0.761	– 0.809	– 0.939	– 0.820	– 0.732	– 0.775	– 0.790
CEC-Zn (%)**	27.8	19.0	20.3	10.8	20.8	31.2	17.3	23.7

a – r values: $P < 0.005$ at least

* – Differential buffering capacity

** – Degree of cation exchange capacity saturation by zinc [$(a_{max}/CEC) \cdot 100$]

Table 6. Multiple regression equations relating supply parameter (SP) with the adsorption proprieties of zinc.

Textural type of soils	Supply parameter	Intercept Zn	Zn added X_1	Percent saturation X_2	Equilib. conc. X_3	DBC* X_4	R^2
1. light loam	Y	0.069	1.974	– 0.0162	– 0.582	– 0.00006	0.998
2. light loamy sand	Y	0.312	1.755	– 0.0097	– 0.119	– 0.0022	0.997
3. light loamy sand	Y	0.105	0.996	– 0.0038	0.016	– 0.0004	0.999
4. light loamy sand	Y	0.279	2.932	– 0.0047	– 0.857	– 0.0086	0.999
5. light loamy sand	Y	0.115	0.653	– 0.0030	0.429	– 0.0004	0.998
6. silty medium loam	Y	0.207	1.187	– 0.0058	0.580	– 0.0003	0.995
7. silt loam	Y	– 0.252	– 0.064	– 0.0065	0.163	0.0003	0.998
8. silt loam	Y	0.111	1.084	– 0.0055	0.235	– 0.0001	0.999

* – Differential buffering capacity

percent saturation revealed that in all studied soils the addition of Zn increased the amount variable, which was not in equilibrium with the intensity variable.

The differential buffering capacity of soils is an indicator of the resistance to change in ions of the soil solution when they are added to or removed from it. At 0.2 $mmol_c/dm^3$ of applied zinc the differential buffering capacity was higher for soils nr 1 (617.88) and nr 6 (535.55) followed by soils nr 7 and 8 (342.62 and 330.42 respectively), whereas soils nr 5, 3, 2 (from 139.28 to 80.71) were found to have relatively low DBC values. An exception took place for soil nr 4 (4.68). With increasing levels of zinc, the capacity decreased and at 1.0 $mmol_c/dm^3$ the values of differential buffering capacity were in the range of 0.94 to 14.09, irrespective of all soils analyzed. The negative correlation of differential buffering capacity with concentration of added zinc, percent saturation and equilibrium concentration that once the processes controlling the quantity variables are saturated, concentration of Zn in solution phase will increase.

Khasawneh [6] and Khasawneh and Copeland [7] introduced supply parameters to integrate quantity, intensity and buffering capacity. At the 0.5 $mmol_c/dm^3$ level of zinc, the supply parameter was comparatively low for soils nr 7 and I (0.12 and 0.13, respectively) but for soils nr 2, 3, 5, 6 and 8 it ranged between 0.30 to 0.49 and was highest for soil nr 4 (0.86). A gradual increase of the supply parameter values for all soils was observed, so at the level of 1.0 $mmol_c/dm^3$ of Zn added the range varied from 0.33 to 1.56. There was a significant positive correlation (Table 5) of the supply parameter with the concentration of added zinc, equilibrium concentration and percent saturation, and a negative correlation with the differential buffering capacity. The multiple regression analysis relating supply parameters with quantity and intensity in these soils as expressed by equations in Table 6, revealed that in texturally different soils the influence of all the variables is quite similar, even very high coefficients of determination ($R^2 > 0.99$). This is partly in agreement with the findings of Khasawneh and Copeland [7] suggesting that quantity, intensity and buffering capacity of the soils are mainly responsible for the supply of nutrients such as phosphorus, zinc and copper. It is therefore obvious to point out that the relase of these nutrients is partly controlled by soil reaction. This state being revealed by the correlation coefficients, negative and significant (Table 3). For Zn, the lower the soil reaction the higher the Zn supply, leading in such a way to a possible Zn toxicity in soil. From these studies it is apparent that soils nr 1, 6, 7 and 8 with comparatively high adsorption maxima, bonding energy constants and buffering capacities have a greater affinity for added zinc. Thus, for any change in the supply parameter, these soils will require higher rates of **zinc.**

Conclusions

1. Adsorption of zinc increased simultaneously with its rate of application, irrespective of the textural type of soils.
2. Amounts of zinc adsorbed were strongly related to organic carbon content and cation exchange capacity, and weakly related to amorphous manganese level.
3. Results revealed that the lower the soil reaction, the higher the supply parameter values. These conditions are favorable for sufficient Zn concentration in the soil solu tion.
4. The main parameters acting towards zinc supply in all soils were quantity, intensity and equilibrium concent ration.

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