

Zinc Sorption by Acid, Calcareous and Gypsiferous Soils as Related to Soil Mineralogy

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ABSTRACT- Zinc (Zn) availability and mobility in soils is controlled by its interaction with the soil matrix and amendments. Contradicting evidence has been reported for factors influencing Zn behavior in soils. The aim of this study was to investigate the Zn sorption in selected acid, calcareous and gypsiferous soils with different background electrolytes (Na⁺, K⁺ and H₂PO₄, NO₃ and Cl backgrounds). Isotherm curves for Zn sorption were examined on 2 calcareous, 2 acid and 2 gypsiferous soils. Lability of the adsorbed Zn was evaluated by DTPA following sorption. The Zn adsorption data showed a highly significant fit to the Langmuir, Freundlich and Temkin adsorption isotherms. The fit of the present experiment's data to Langmuir isotherm proved to be more suitable as compared with Freundlich or Temkin isotherms. The presence of Na⁺ increased total Zn adsorption as opposed to K⁺ in all soils. Gypsiferous soils exhibited greater Zn adsorption than calcareous and acid soils. The high adsorption of Zn by gypsiferous soils could be related to the presence of a palygorskite mineral with a large surface area, but for acid soils with high contents of kaolonite and illite minerals, minimum Zn sorption was observed. In acid soils, the largest Zn sorption was observed with H₂PO₄, whereas in gypsiferous and calcareous soils, H₂PO₄ decreased Zn sorption. The lability of Zn affected the clay minerals amount and type. The results showed that a large percentage (90 to 98%) of the sorbed Zn was associated with nonlabile pool. It is concluded that other nutrients and clay minerals have significant effect on Zn applied to soils.

Keywords: Acid soil, Calcareous soil, Gypsiferous soil, Zinc

INTRODUCTION

The Zn content of the lithosphere is approximately 80 mg kg⁻¹, and the common range for soils is 10-300 mg kg⁻¹ with an average content of 50 mg kg⁻¹. Zinc is considered a trace element in soils. The specific minerals controlling the activity of Zn²⁺ in soils are not known. The solubility of some Zn minerals is presented below:

Zn(OH)₂ > α-Zn(OH)₂ > β-Zn(OH)₂ > γ-Zn(OH)₂ > ε-Zn(OH)₂ > ZnCO₃ > ZnO > Zn₂SiO₄ > Soil-Zn > ZnFe₂O₄

The solubility of all Zn minerals decreases 100-fold for each unit increase in pH. The Zn content in soil depends on the nature of parent rocks, texture, organic

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matter and pH, and ranges from 10 to 300 mg kg⁻¹ with an estimated global average* of 64 mg kg⁻¹ (24). Different forms of Zn in soil may include: 1- water soluble; 2- exchangeable and extractable from soil colloids; 3- occluded by soil hydrous oxides; 4- precipitates; 5- immobilized in living organisms and biological residues, and 6- constituents in the lattice of primary and secondary minerals. An inverse correlation has been observed between the amount of extractable Zn and free CaCO₃, soil pH and base saturation (24). Since Zn is easily adsorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons (14). Below a 7.5–8.0 pH, Zn occurs predominantly in the Zn²⁺ form. At higher pH values, it forms low solubility complexes with carbonate and hydroxyl ions (24).

Repeated soil application of Zn and other heavy metals to agricultural lands has caused considerable concern about their impacts on soil and water quality (25). Zn is one of the elements which are essential in small amounts, but can be toxic in high concentrations (33). The bioavailability of trace elements including Zn, decrease with the clay mineral content in soils (35). It has been proven by many studies that among soil clay minerals, smectites have the greatest adsorption affinity to Cu and Zn (36, 12). Zn sorption capacity correlates with soil contents of aluminosilicate clays, metal oxides and carbonates (15, 30). The interaction between Zn and Fe or Al oxides through the formation of a covalent bond with surface aqua and/or hydroxy groups have been proved to be the major mechanism of Zn retention by acid soils (4,15, 21). However, Zn sorption by CaCO₃ and precipitation of Zn hydroxide or Zn hydroxyl carbonates are mechanisms controlling Zn solubility in calcareous soils (27). Soil pH (2), organic matter (29), ionic solution strength (37), ionic solution composition (42) and minerals (35) also affected Zn sorption. Increasing soil pH increases the total number of negative sites of clay minerals and organic matter, hence increasing the capacity for Zn sorption (21).

Saha et al., (30) showed that the adsorption of Zn and Cd on the Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite complexes is very strongly pH dependent. Substantial fractions of these two metals were also adsorbed on complexes with a pH below 5. As the pH rose above 5, Cd and Zn adsorption on the complexes steeply increased, reaching plateau levels of almost 100% when the pH was between 6 and 7.

The effect of major cation and ionic strength on the chemistry of Cd, Cu, and Zn in alkaline sodic and acidic soils has been investigated by Fotovat and Naidu (8). Increasing ionic strength was found to decrease Zn retention in acid soils but did not have any significant effect in calcareous soils (37). Additional ionic strength, cation and anion affected in Zn sorption. Wang and Harrell (42) showed that NH₄⁺ and K⁺ equally decreased Zn sorption as opposed to Na⁺ in acid and calcareous soils; NH₄⁺ yielding 4 to 12% more adsorbed Zn in the labile pool as compared to K⁺ in acid soils. They showed that the effect of background ions on the lability of adsorbed Zn varied between acid and calcareous soils. There are few studies that link the relationship of Zn sorption with its lability and cation, anion in soils, and its relationship with soil minerals. The objective of this study was to investigate Zn sorption in selected acid, calcareous and gypsiferous soils in Fars and Mazandaran provinces, Iran and the effect of minerals on Zn sorption.

Material and Methods:

Soil sample and chemical characterization

Surface samples (0–15 cm) selected of two acid soils were collected from Mazandaran and two calcareous and two gypsiferous soils were collected from Fars province, Iran.

The two acid soils included Typic Argiustolls (A₁), and Typic Haplustolls (A₂). The two calcareous soils were Typic Endoaqualfs (C₁) and Typic Calciustepts (C₂), and the two gypsiferous soils were Gypsic Calciustepts (G₁) and Aridic Haplustolls (G₂). The soil samples were air-dried and ground to pass through a 2 mm sieve before laboratory analyses. The chemical characteristics of the soils are presented in Table1.

Gypsum (CaSO₄. 2H₂O) was determined by precipitation with acetone (31). Electrical conductivity (total soluble salts) was determined in a saturation extract (31). Soil particle size distribution was determined by the hydrometer method (5) and soil pH was measured with a glass electrode in a saturated paste (31). Soil exchangeable Ca, Mg and K were determined by 1N NH₄OAC (39) and Calcium carbonate equivalent (CCE) was measured by acid neutralization (31). Analysis of Fe, Mn and Zn by DTPA-TEA [diethylenetriaminepentaaceticacid-triethanolamine: N, N-bis (2-(bis-(carboxymethyl)ethyl)-glycin and 2,2', 2-nitrilotriethanol] were carried on the soil samples (18). Amorphous Fe was determined by ammonium oxalate extraction in the dark (19). Organic carbon was measured by wet oxidation with chromic acid and back titration with ferrous ammonium sulphate (26).

Table1. Some of the chemical characteristics of the soils.

Soil	pH	CaCO ₃ Equival. (%)	Org. carb on (%)	Gypsu m (%)	K ⁺ (solution) (meq/100 g)	Ca ²⁺ (sol.) (meq/100 g)	Mg ²⁺ (sol.) (meq/100)	Ferrous Ferric	Zn-DTPA (mg/k)
Typic Endoaqualfs Calcareous (C ₁)	7.4	52.8	1.57	-	Trace	124	32.5	0.26	0.394
Typic Calciustepts Calcareous(C ₂)	7.4	55	1.14	-	Trace	82	trace	0.04	0.928
Gypsic Calciustepts Gypsiferous (G ₁)	7.45	47.5	0.11	5.62	Trace	18	trace	0.02	0.094
Aridic Haplustolls Gypsiferou (G ₂)	7.75	18	0.7	33.5	Trace	144	trace	0.25	0.26
Typic Argiustolls Acid (A ₁)	6.62	4.77	5.46	-	0.88	4.4	2.2	2.45	14.3
Typic Haplustolls Acid (A ₂)	5.38	2.36	3.08	-	0.05	4.8	1.3	4.03	0.88

Mineralogical analysis

Chemical cementing agents were removed and clay fractions separated according to Mehra and Jakson (23), Kittrick and Hope (16), and Jakson (13). Iron-free samples were centrifuged at 750 RCF for 5.4 min to separate total clay (< 2µm) and at 2700

RCF for 40 minutes to separate fine clay (<0.2 μ m), (16). The mineralogy of fine and coarse-clay fractions was analyzed by X-ray diffractometry (13). Similar concentrations of clay suspensions were used for all samples to give reliable comparisons between relative peak intensities. Two drops of the prepared suspensions were used on each glass slide. 001 reflections were obtained on various treatments of Mg saturation, ethylene glycol salvation and K saturation. The X-ray analyses on treatments of air-dried and heated samples (K-saturated) were carried out in order to identify kaolinite in the presence of tri-octahedral chlorite. Samples were also treated with 1N NH₄Cl at 80° C overnight. Clay minerals were estimated semi quantitatively from the relative X-ray peak areas of glycol-treated samples (20) (Table 2).

Table 2. Clay mineralogy analysis of the soils

Soil	Chlorite (%)	Illite (%)	Smectite (%)	Vermiculite (%)	Palygorskite (%)	Kaolinite (%)	Quartz (%)	Intermediate of clay (%)
Typic Endoaqualfs Calcareous (C ₁)	10-25	10-25	25-40	25-40	<5-10	5-10	5-10	5-10
Typic Calcustepts Calcareous (C ₂)	10-25	5-10	25-40	10-25	5-10	10-25	<5	10-25
Gypsic Calcustepts Gypsiferous (G ₁) Aridic Haplustolls Gypsiferous (G ₂)	10-25	10-25	10-25	--	40-60	--	<5	5-10
Typic Argiustolls Acid (A ₁)	--	10-25	--	5-10	--	10-25	<5	<5
Typic Haplustolls Acid (A ₂)	--	10-25	10-25	5-10	--	10-25	<5	<5

Zn sorption isotherms

Two-gram subsamples of each soil sample were placed in separate centrifuge tubes and mixed with 20mL of a different electrolyte solution containing 0, 0.5, 1, 3, 5, 10 mM of ZnSO₄. The (preweighed) centrifuge tubes were shaken for 24h on a reciprocating shaker. Four 50-mM electrolyte background solutions were used in this study, NaNO₃, KCl, KNO₃ and KH₂PO₄ (42). Various amounts of Zn-sorbed in nitrate and in K-salts could reveal the effect of cations (K⁺ and Na⁺) and anions (NO₃⁻ and H₂PO₄⁻), respectively.

The use of 50-mM background solutions was to ensure that effects of cations and anions were evaluated at a dominant and constant ionic strength. After equilibrium, samples were centrifuged and the supernatant was filtered through a Whitman No. 42 filter paper. Two replicates were used for collecting each data point. Zn concentration in the supernatant was analyzed by ICP–OES (inductively coupled plasma–optical emission spectroscopy) at a wavelength of 213.8 nm. In the equilibrium solution the amount of adsorbed Zn was found by calculating the difference between the initial and the final concentration. Zn sorption parameters were obtained by fitting experimental data to the mathematical equations termed adsorption isotherms. Harter (11) believes that adsorption isotherms have provided a good deal of information about micronutrient adsorption by soil components. Adsorption isotherms most frequently used are Freundlich (7) (Eq.1), Langmuir (17) (Eq.2) and Temkin (1) (Eq.3) equations:

$$X = KC^{1/n} \quad \text{Eq.(1)}$$

$$X = (KbC)/(1+KC) \quad \text{Eq.(2)}$$

$$X = K_1 + K_2 \ln C \quad \text{Eq.(3)}$$

Where X is the amount of sorbed Zn (mg kg^{-1}), C is the Zn concentration in the equilibrium solution (mg L^{-1}), and K, n, b, K_1 and K_2 are adsorption coefficients. However, the linear forms of Freundlich and Langmuir isotherms are usually used for fit of the adsorption data:

$$\log X = \log K + n \log C \quad \text{Eq. (4)} \quad C/X = (1/Kb) + (1/b)C \quad \text{Eq.(5)}$$

(X, n, C, K and b as previously described).

Lability of sorbed Zn

Following the DTPA-TEA extraction the desorbed- and adsorbed- Zn were evaluated at the end of sorption experiments (18). A 20-mL DTPA-TEA solution was added to each centrifuge tube containing Zn-sorbed samples. The tubes were then shaken for 2 h on the reciprocating shaker, the samples were centrifuged, and the supernatant solutions were filtered and analyzed for Zn content by ICP OES (inductively coupled plasma–optical emission spectroscopy). The amount of DTPA extracted-Zn was corrected for Zn concentration in the interstitial solution based on preweighed tubes, soil weight, and solution weight. The corrected DTPA extractable Zn was designated as the labile pool, whereas Zn unextractable by DTPA was considered as the nonlabile Zn.

Results and discussion

All the pH of the initial experimental solutions, and the soil sorption solution mixtures were measured after equilibration (presented in Table3). The linear form of the Langmuir equation significantly described the fit of the data for Zn-adsorption in all soil samples (Eq. 5 and Table 4). The data also showed a highly significant fit to Freundlich and Temkin adsorption isotherms equations (Table 4).

Table 3. Measured range of pH values for initial experimental solutions and for each soil-sorption mixture after 24 h equilibrium in different electrolyte solutions.

	KCl	KNO ₃	NaNO ₃	KH ₂ PO ₄
Experimental solution	5.98-6.5	6.3-6.74	6.2-6.8	4.7-5.5
Typic Endoaqualfs Calcareous Soil (C ₁)	6.63-7.63	6.94-8.35	6.93-8.47	4.56-5.95
Typic Calciustepts Calcareous Soil(C ₂)	6.62-7.64	6.9-8.48	6.9-8.55	4.55-5.9
Gypsic Calciustepts Gypsiferous Soil (G ₁)	6.6-7.74	6.74-8.19	6.95-8.46	4.48-5.89
Aridic Haplustolls Gypsiferous Soil (G ₂)	6.4-7.83	6.82-8.18	6.93-8.01	4.01-5.23
Typic Argiustolls Acid Soil (A ₁)	5.42-6.2	5.45-6.02	5.3-6.4	4.36-5.25
Typic Haplustolls Acid Soil (A ₂)	5.41-6.1	5.17-5.97	5.3-6.18	4.37-5.1

Effect of cations on the total Zn sorption

The data presented in Fig. 1 and 2 showed that both cations and anions had a considerable impact on Zn sorption, especially at high Zn concentrations. The total amount of Zn sorbed within the experimental concentration range was higher in gypsiferous than calcareous and acid soils. In the studied soils, the largest Zn sorption was observed in the Na⁺ background followed by that in the K⁺ background. The differences in total Zn sorption caused by different cations were generally

reflected in Langmuir sorption maxima for all soils (Table 4). Large-sized hydrated ions such as Na^+ caused to form only outer-sphere metal-clay complexes whereas K^+ is able to form inner-sphere complexes with mineral surfaces (38). Similar results have been reported for acid sandy soils and Andepts (44, 28, 2).

Zhu and Alva (44) observed a decrease in adsorption of both Cu and Zn in the presence of K, Mg, and Ca. In contrast, Winistorfer (43) reported that concentration of Cu in acidic soils in the presence of Na was lower than that in water extracts and that the concentration of Zn and Cd were higher in Na extracts. The results of this study (Fig.1) clearly showed that K^+ ions reduce Zn sorption in calcareous soils, although such decrease is relatively small, possibly due to large Zn sorption capacity in calcareous soils. Wang and Harrell (42) showed the large total Zn sorption in the Na^+ background as opposed to that in either K^+ or NH_4^+ backgrounds.

Table 4. Temkin, Freundlich, Langmuir isotherms parameters and coefficients of determination (R^2) for total Zn sorption by different soils

Soil	Background solution	Temkin [†]			Freundlich [†]			Langmuir [†]		
		K_1	K_2	R^2	n	k	R^2	b (mgkg ⁻¹)	K (Lkg ⁻¹)	R^2
Typic	KCl	1574	308	0.97***	1.37	1001.7	0.98***	3333	1	1***
Endoaqualfs	KNO ₃	1300	356	0.97***	2.83	837.1	0.96***	3333	0.25	0.99***
Calcareous	NaNO ₃	466	773	0.96***	2.34	612.1	0.80***	5000	0.33	0.99***
(C ₁)	KH ₂ PO ₄	118	388	0.99***	2.87	354	0.96***	2500	0.064	0.98***
Typic	KCl	284	812	0.98***	0.44	91579.7	0.92***	5000	0.08	0.86***
Calciustepts	KNO ₃	500	316	0.95***	2.91	447.1	0.99***	5000	0.03	0.81***
Calcareous	NaNO ₃	875	633	0.81***	2.69	742.4	0.98***	2500	0.57	0.99***
(C ₂)	KH ₂ PO ₄	36	317	0.90***	3.17	289.7	0.98***	2500	0.02	0.91***
Gypsic	KCl	640	226	0.64**	0.91	718.8	0.97***	5000	0.5	0.97***
Calciustepts	KNO ₃	314	415	0.77***	1.33	77.2	0.97***	2000	0.032	0.74***
Gypsiferous	NaNO ₃	111	472	0.86***	1.93	306.8	0.92***	2000	0.24	0.85***
(G ₁)	KH ₂ PO ₄	93	57	0.55**	0.90	734.5	0.54**	476	0.27	0.99***
Aridic	KCl	186	471	0.69**	1.85	1.1	0.99***	5000	0.04	0.66***
Haplustolls	KNO ₃	1163	684	0.61***	0.55	1.1	0.99***	2500	0.05	0.64***
Gypsiferou	NaNO ₃	1103	746	0.70***	1.52	144.2	0.96***	588	0.02	0.81***
(G ₂)	KH ₂ PO ₄	NS	NS	-	1.02	246.3	0.64**	5000	0.07	0.99***
Typic	KCl	235	593	0.99***	0.52	31535.5	0.92**	3333	0.04	0.99***
Argiustolls	KNO ₃	633	676	0.98***	1.95	216.1	0.95***	3333	0.03	0.99***
Aci (A ₁)	NaNO ₃	511	777	0.94***	1.60	170.8	0.97***	5000	0.02	0.99***
	KH ₂ PO ₄	810	785	0.98***	3.06	7337.1	0.97***	5000	0.8	0.98***
Typic	KCl	2086	411	0.57**	2.7	862.4	0.59**	129	0.04	0.89***
Haplustolls	KNO ₃	143	32	0.95***	1.71	21	0.96***	370	0.06	0.99***
Acid (A ₂)	NaNO ₃	953	490	0.98***	1.81	81.2	0.99***	1666	0.02	0.97***
	KH ₂ PO ₄	720	159	0.64**	1.04	3163.1	0.66**	4168	0.12	0.99***

[†] b = Sorption maximum; K and k = Bonding energy constant. [†]K₁= Adsorption coefficients; K₂ = Adsorption coefficients,

[†] n = Adsorption coefficients; NS, **, ***: Not Significant, Significantly at P ≤ 0.5 and P ≤ 0.1, respectively.

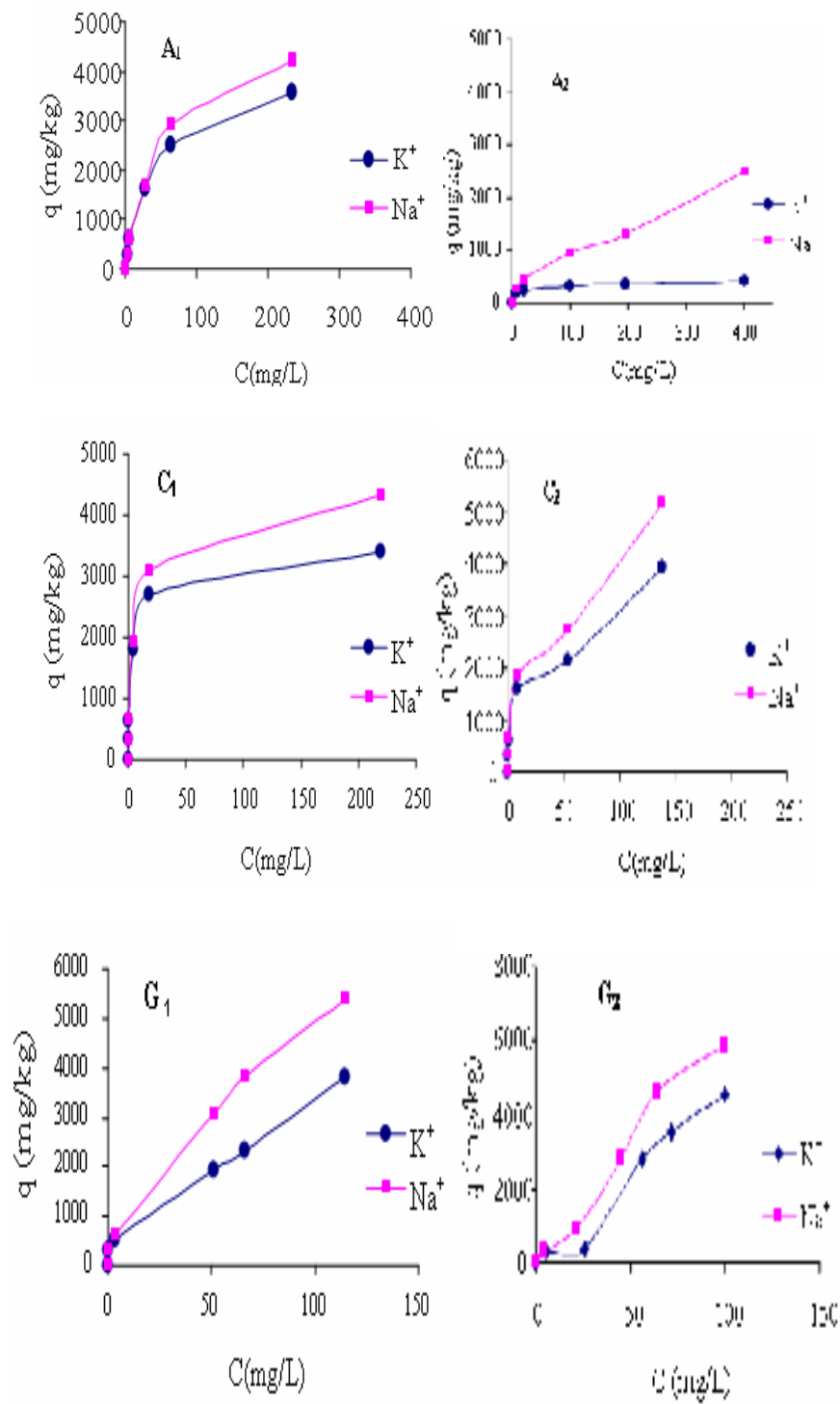


Fig. 1. Zn sorption by two acid (A₁, A₂), two calcareous (C₁, C₂) and two gypsiferous soils (G₁, G₂) as affected by different background cations. C = Equilibrium solution concentration; q = Adsorbed Zn amount

Effects of anions on the total Zn sorption

The effects of anions on the amounts of sorbed Zn were different in acid, gypsiferous and calcareous soils. In acid soils, the largest Zn sorption was observed with H_2PO_4^- followed by Cl^- and NO_3^- , whereas in gypsiferous and calcareous soils, the H_2PO_4^- decreased Zn sorption, with the exception of the G2 soil. In acid soils oxy-anions such as PO_4^{3-} and AsO_4^{3-} can form inner-sphere surface complexes with iron and aluminum oxides that increase negative surface charges (4).

The predominance of Fe and Al oxides in acid soils (Table 1) may explain the greater Zn sorption in the H_2PO_4^- treated in acid soils. In this study, the lower Zn sorption by H_2PO_4^- in gypsiferous and calcareous soils may be due to pH difference between H_2PO_4^- and other background solutions (Table 3). The pH ranges of soil-sorption solution mixtures are shown in table 3. The first three solutions, NaNO_3 , KNO_3 and KCl have similar amounts of PH values and the last one, KH_2PO_4 , has a remarkably lower PH value than the former solutions (Table 3). This especially occurred in gypsiferous and calcareous soils. Strong buffering by KH_2PO_4 maintained relative lower pH ranges in its soil-solution mixtures compared with the other electrolytes. Wang and Harrell (42) state that the strong acidity of H_2PO_4^- could dissolve a certain quantity of CaCO_3 in these soils, which could not only decrease the total carbonated surface for Zn sorption but also release more Ca ions to compete with Zn for surface sites of aluminosilicate clays. Increasing H^+ may also be due to the competition with Zn for clay exchange sites (44). All these could constitute the cause for low total Zn sorption observed for calcareous and gypsiferous soils. Arias et al., (2) showed that the adsorption of copper and Zn in acid soils depends to a significant extent on pH and CEC. Langmuir sorption parameters showed that in acid soils, the presence of H_2PO_4^- increased Zn sorption maxima as well as the bonding energy value (Table 4).

The G₂ soil, which contained lower CaCO_3 and higher amorphous oxide-Fe (Table1) have different behavior from other soils. The relationship between the amount of total Zn sorption and the amorphous Fe have been showed by Wang and Harrell (42). They showed that the regression equation for acid soils with approximately 98.8% of the variation in total sorbed Zn could be explained by amorphous Fe oxide content. Clearly, the integrated effect of very high amorphous Fe oxide content and low CaCO_3 content caused an increase, rather than decrease in Zn sorption in the presence of H_2PO_4^- in the G₂ soil. Regardless of the Cl^- and NO_3^- treatments, similar results observed for the Zn sorption in all soil samples by the Langmuir prediction model (Fig. 2 and Table 4). There was no difference in Zn sorption caused by the presence of Cl^- and NO_3^- (Fig. 2). This result was true for both acid and calcareous soils.

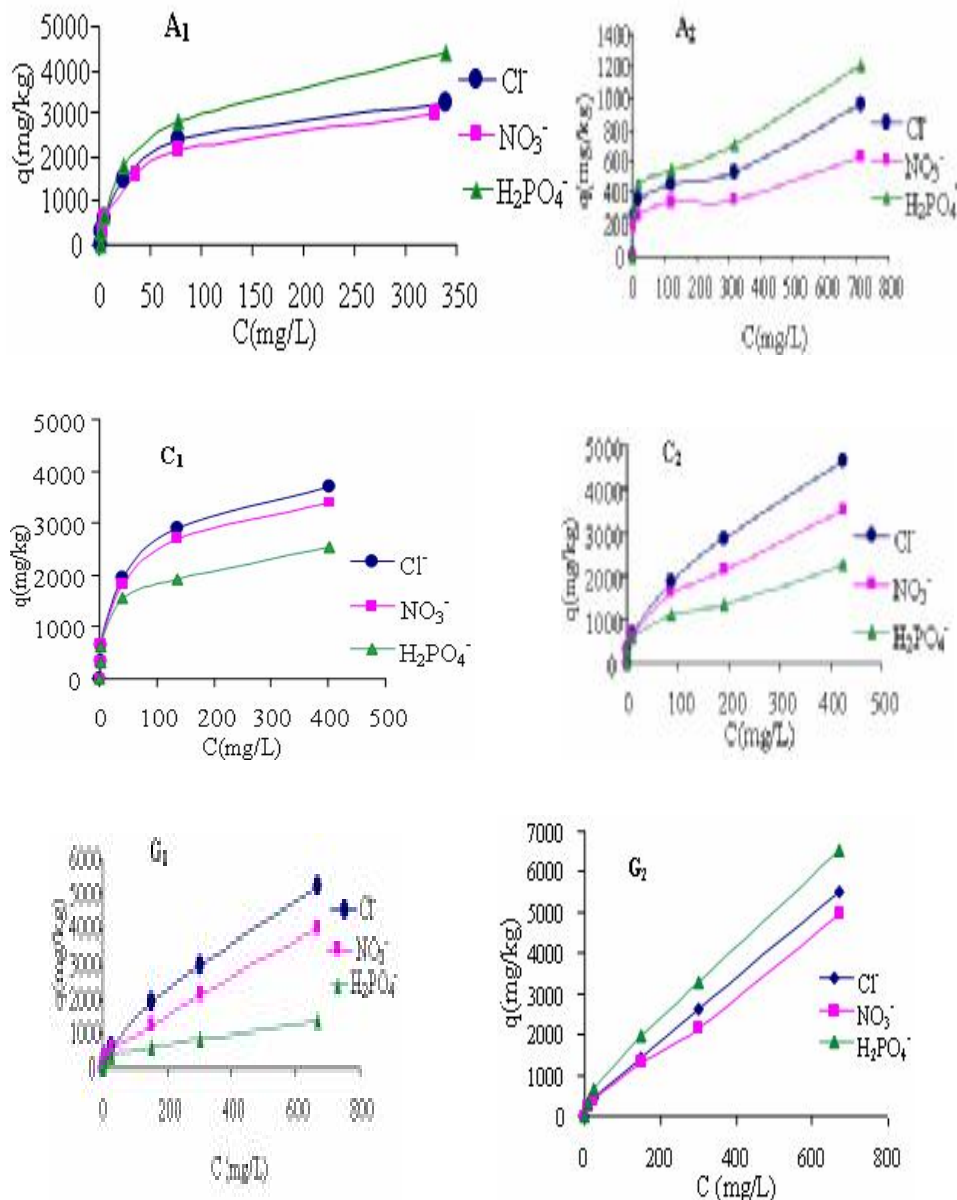


Fig. 2. Zn sorption by two acid (A₁, A₂), two calcareous (C₁, C₂) and two gypsiferous soils (G₁, G₂) as affected by different background anions. C = Equilibrium solution concentration; q = Adsorbed Zn amount

Effect of Minerals on total Zn sorption

The mineralogy of gypsiferous soils showed that Palygorskite has more proportions (Table 2). Highly sorbed Zn by Palygorskite was due to its large surface area (300-600 m²/g) (9). The amount of Zn sorption by calcareous soils, in which smectite and vermiculites are dominant clay minerals, is high but not as much as gypsiferous soils. The acid soils with Illite showed minimum Zn sorption. Freundlich and Elovich equations were found to be the most suitable to characterize the adsorption of heavy metals on the studied mineral i.e. montmorillonite, kaolinite and calcite, and results showed that the adsorption of heavy metals depends mainly on the radius number and electro-negativity of each element. The type of mineral has a great role on the adsorption of heavy metals (41).

Effect on lability of sorbed Zn

By DTPA-TEA extraction of the sorbed-Zn, it partitioned into labile and non-labile Zn. Analysis using isotopic exchange and dilution techniques showed that this extraction was able to characterize the labile pool of Zn in both acid and calcareous soils (34). The results, presented in Fig 3 to 5, show this fractionation in the presence of different background electrolytes for one acid, one calcareous, and one gypsiferous soil respectively in some background electrolytes.

Similar results were also observed for other acid and calcareous soils of different background electrolytes (data not shown).

The results showed that most of the total sorbed Zn is nonlabile (as defined by DTPA-TEA extraction). On average about 90% to 98% of the total sorbed Zn by all soils was nonlabile (Figs 3 to 5). Incorporation of Zn into hydroxyl-Al interlayer phyllosilicates was recently confirmed in an acid subsoil of a contaminated site by x-ray absorption spectroscopy (32).

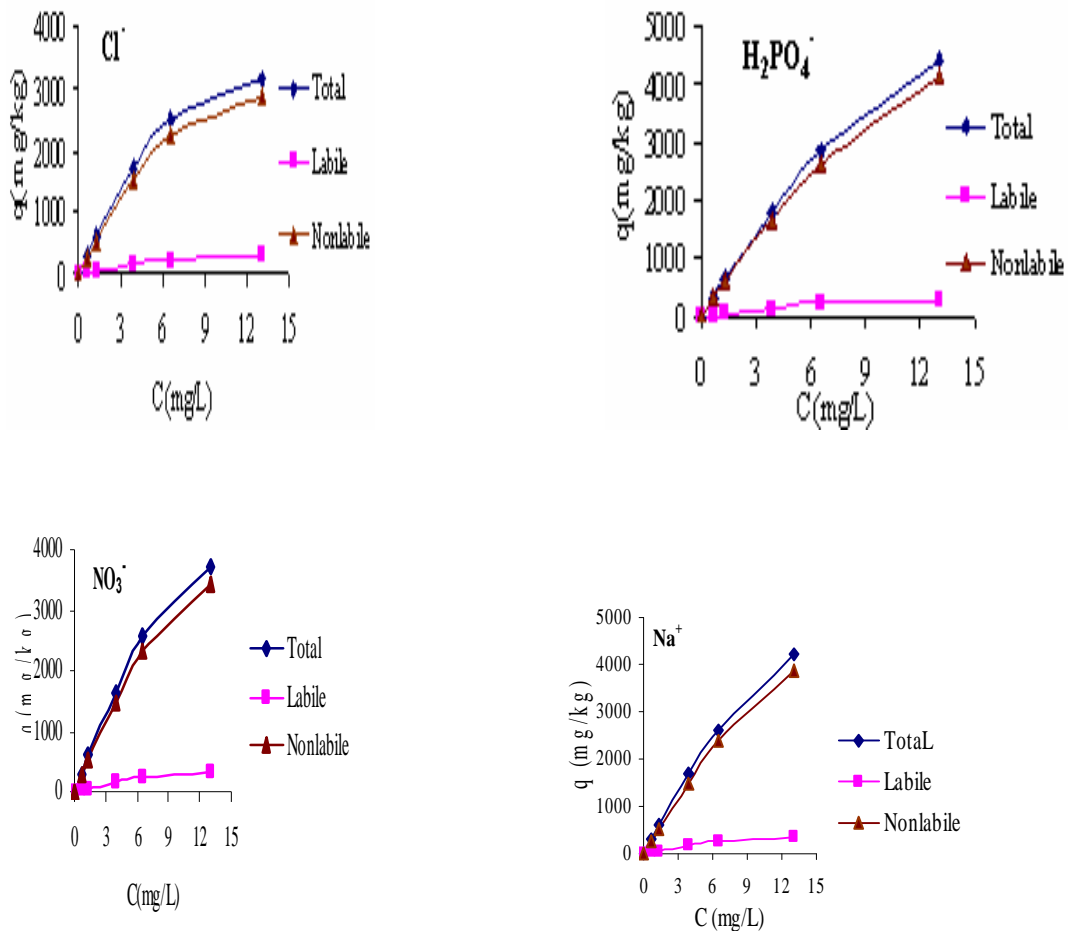


Fig. 3. Sorption isotherms for total, labile, and nonlabile Zn sorption for an acidic soil as affected by different background anionic and cationic species. C = Equilibrium solution concentration; q = Sorbed Zn amount.

The difference among the three anions in influencing the lability of total sorbed Zn in the presence of H_2PO_4^- caused more nonlabile Zn than Cl^- or NO_3^- . Nonlability of a metal ion in the soil has been generally attributed to the entrapment of the metal into small pores of particle aggregates or clay mineral structures, the strong surface adsorption by oxides, and/or the formation of insoluble metal precipitates (10). Wang and Harrell (42) reported that carbonate ions could react with Zn to form ZnCO_3 precipitates in mixtures for calcareous soils with low P concentrations. Other research suggests that the formation of Zn-Fe precipitates such as ZnFe_2O_4 (franklinite) may occur in both acid and calcareous soils (32). Wang and Harrell (42) suggested that the increase in the nonlabile fraction of sorbed Zn in calcareous soils may be largely due to the formation of Zn-phosphate precipitation such as $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Hopeite). More research showed that Zn-contaminated soils may indeed lead to the formation of Hopeite, the addition of KH_2PO_4 (22) and an increase in the nonlabile pool (irreversible sorption) of soil Zn as confirmed by isotopic exchange and dilution technique (10).

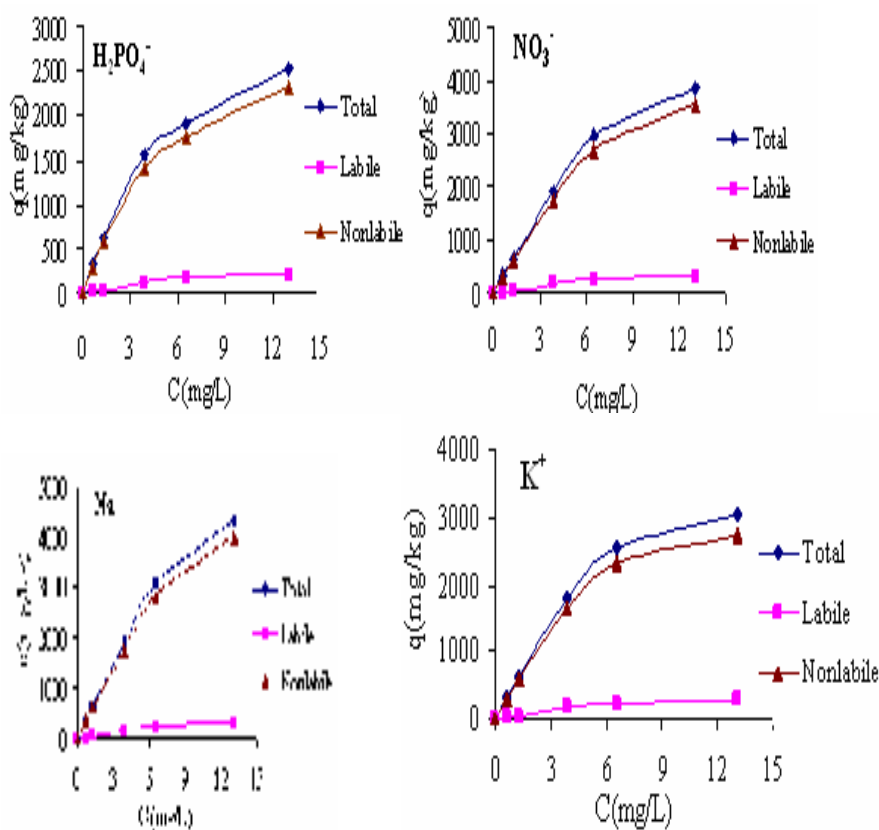


Fig. 4. Sorption isotherms for total, labile, and nonlabile Zn sorption for a calcareous soil as affected by different background anionic and cationic species

CONCLUSIONS

These results clearly demonstrate various effects of background K^+ , Na^+ cations and H_2PO_4^- , Cl^- and NO_3^- anions on Zn sorption characteristics and lability in acid, gypsiferous and calcareous soils. The presence of K^+ reduced total Zn sorption as compared to Na^+ . However, this suggests that in soils, a more efficient application of Zn would occur with the co-application of Na^+ , not K^+ salt fertilization. In

gypsiferous soils the amount of Zn adsorption was greater than that of acid and calcareous soils. In acid soils, total Zn sorption was enhanced by the presence of H_2PO_4^- . In calcareous soils total Zn sorption was decreased by H_2PO_4^- . A large percentage of the sorbed Zn was associated with nonlabile pool. The bioavailability of the Zn decreases with the clay mineral content, referring to the strong retention capacity of clay minerals to Zn. Although the Zn adsorption data showed a high significant fit to Freundlich, Langmuir and Temkin isotherms but Langmuir isotherm results fit better and were more suitable as compared with Freundlich or Temkin isotherms. The presence of various ions and minerals changed both the capacity and specificity characteristics of Zn sorption in all soils. To obtain a thorough investigation of mineral effects, Microprobe & Microscopic studies must be applied.

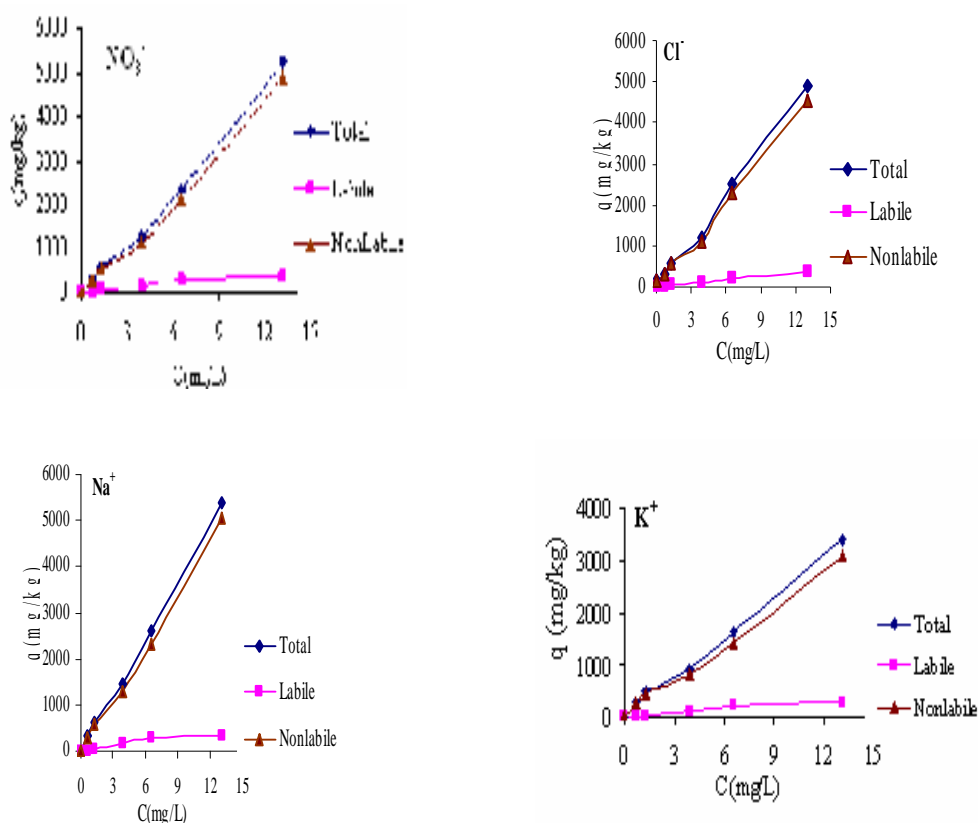


Fig. 5. Sorption isotherms for total, labile, and nonlabile Zn sorption for a gypsiferous soil as affected by different background anionic and cationic species. C = Equilibrium solution concentration; q = Sorbed Zn amount

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جذب روی در خاک های اسیدی، آهکی و گچی و ارتباط آن با مینرالوژی خاک ها

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چکیده - قابلیت دسترسی و تحرک روی بوسیله برهمکنش ماتریکس خاک و بهسازها کنترل می شود. مشاهدات بسیاری در مورد عوامل موثر بر رفتار روی در خاک گزارش شده است. هدف از این مطالعه بررسی جذب روی در خاک های گچی، آهکی و اسیدی با محلول های الکترولیت متفاوت (سدیم، پتاسیم، ارتوفسفات، نترات و کلر) است. منحنی های همدمای جذب روی در دو خاک آهکی، 2 خاک اسیدی و 2 خاک گچی به دست آمد. قابلیت دسترسی روی نیز بوسیله دی تی پی مورد ارزیابی قرار گرفت. داده های جذب روی سطح معنی دار بالائی را در منحنی های جذب لانگمیر، فروندلیچ و تمکین نشان دادند. این داده ها با منحنی همدمای لانگمیر در مقایسه با منحنی های فروندلیچ و تمکین، هماهنگی بیشتری نشان دادند. حضور سدیم بر خلاف پتاسیم جذب روی را در تمامی خاک ها افزایش داد و خاک های گچی بیشترین میزان جذب را نسبت به خاک های اسیدی و آهکی نشان دادند. بالا بودن جذب روی در خاک های گچی بدلیل حضور کانی پالیگورسکایت با سطح ویژه بالا است، اما خاک های اسیدی حاوی کانی های کائولنیت و ایلایت حداقل جذب روی را نشان دادند. در خاک های اسیدی بیشترین میزان جذب در محلول الکترولیت $H_2PO_4^-$ مشاهده شده است در حالی که در خاک های آهکی و گچی، $H_2PO_4^-$ جذب روی را کاهش داد. میزان قابلیت دسترسی روی بوسیله نوع و میزان کانی های رسی کنترل می شود. نتایج نشان داد که درصد بالائی (۹۰ تا ۹۸٪) از کل روی جذب شده در جایگاه غیر قابل دسترس قرار دارد. می توان نتیجه گرفت سایر عناصر غذایی و کانی های رسی اثر معنی دار بر عنصر روی اضافه شده به خاک دارند.

واژه های کلیدی: خاک گچی، خاک آهکی، خاک اسیدی، روی

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**مکاتبه کننده