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Adsorption and Desorption of Zinc by Calcareous Aridisols

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Abstract : Adsorption and desorption of zinc by the calcareous soils of arid Rajasthan were studied. Both the calcareous and non-calcareous soils followed the Langmuir adsorption isotherm. The calcareous soils had low adsorption maxima and high bonding energy constants than the non-calcareous soils. Addition of up to 1000 μg Zn g^{-1} soil did not significantly increase the per cent zinc saturation, differential buffering capacity and supply parameter values. With further addition of Zn there was rapid rise in saturation. In calcareous soils high per cent saturation, low buffering capacity and low supply parameter values indicated that inspite of high zinc application, availability of zinc was limited. Lower desorbed zinc in calcareous soils indicated strong affinity of zinc with $CaCO_3$. However, the zinc potential (pZn + pOH) values in the rage of 17.7 to 20.1 suggested that applied zinc could be retained by the soil as Zn^{2+}. Frequent application of Zn was necessary in calcareous soils to maintain its availability to plants.

Key words : Adsorption, desorption, supply parameters of zinc, calcareous aridisols.

Zinc deficiency is common in plants growing on alkaline soils which have high $CaCO_3$ (Thorne, 1957). In calcareous soils the Zn availability is controlled by the adsorption of zinc on $CaCO_3$ (Jurinak and Bauer, 1956; Khasawneh, 1971) and precipitation as zinc hydroxide or zinc carbonate (Saeed and Fox, 1977).

High $CaCO_3$ content is a characteristic feature of the arid zone soils. Joshi *et al.* (1982, 1983) observed that available zinc was marginal to low in many calcareous soils. In south-eastern arid Rajasthan, the fine textured calcareous alkaline soils are of common occurrence. These soils are placed in better rainfall zone (400 to 450 mm) and ground water is also available for irrigation. This has resulted in higher nutrient uptake due to intensive and regular cropping. Therefore, a study was taken up to characterize the zinc adsorption and desorption processes and the supply parameters in fine textured calcareous soils.

Materials and Methods

Surface soil samples (0-25 cm), representing calcareous and non-calcareous soils, were collected. These were dried, crushed with wooden pestle and mortar, passed through 2 mm sieve and stored in plastic containers. The samples were then analysed for $CaCO_3$ (Calcimeter), organic carbon (Walkly and Black's method) and particle size distribution (Hydrometer method), as described by Piper (1950). The pH and EC (in 1:2.5 soil, water suspension) and the cation exchange capacity (Richard, 1954) were determined. Free oxides (haematite, limonite and amorphous ferric oxide on soil particles as coating) were extracted. Concentration of zinc in the extracts was determined by Varian Techtron Atomic Absorption Spectrophotometer (AAS).

Adsorption studies: Different concentrations of zinc, viz., 5, 10, 25, 50, 100, 250, 400 and 1000 μg mL^{-1} were prepared by dissolving $ZnSO_4$ salt in 0.01 M $CaCl_2$ solution. These solutions are added to soil (10 mL solution per g of soil on dry weight basis) in a number of polythene tubes (50, 100, 250, 500, 1000, 2500, 4000, 5000 and 10000 μg Zn g^{-1} soil). These were vigorously shaken for one hour on a reciprocating shaker and intermittently for 24 hours. Each treatment was replicated thrice. The supernatant solution was separated after centrifugation. In the supernatant solution, concentration of zinc was determined with the help of AAS. Amount of zinc adsorbed (q) was calculated as the difference between zinc concentration in initial solution and that remaining in solution after equilibrium (C). The data were fitted to the Langmuir equation:

$$C/q = (1/K_b) + (C/b) \quad (1)$$

Best fitting regression lines were drawn for the plot C/q vs C. The slope and intercept were derived from the regression line and the following zinc availability parameters were calculated.

Adsorption maxima (b) = 1/slope

Bonding saturation of zinc adsorption capacity = (q/b) x 100

Differential buffering capacity $= a/(a+bC)^2$

Supply parameters for Zn =
$Z\nu = \sqrt{\theta X/(\beta K)^{0.05}}$

Desorption studies

The soils equilibrated with 50, 250, 2500 and 10000 μg Zn g^{-1} soil were saved for desorption studies. These were shaken with 0.01 M $CaCl_2$ solution (10 mL solution g^{-1} soil) for 10 minutes and intermittently for 48 hours. The pH of the soil suspension was recorded. After centrifugation, concentration of zinc in the supernatant solution was determined and electrical conductivity was measured. The zinc ion activity coefficient was calculated by using Debye-Huckel equation:

$$-\log fi = AZ^2 \sqrt{\mu}/1+Bd\sqrt{\mu}$$

where,

A and B : constant,

d : ionic diameter of zinc,

μ : ionic strength (EC in dS m^{-1} x16, Ponnamperuma *et al.*, 1966),

Z : valence of zinc, and

fi : activity coefficient.

The activity of zinc was obtained by multiplication of concentration of desorbed zinc (Mol L^{-1}) with the activity coefficient. The negative log of zinc ion activity (pZn) and

Table 1. Physico-chemical characteristics of soils

Soil	pH	$CaCO_3$ (%)	Organic carbon (%)	Clay (%)	CEC (Cmol kg^{-1})	Free iron (%)	Available Zn (mg kg^{-1})
Calcareous soils							
Pali II	8.1	19.80	0.567	24.2	23.3	0.330	1.08
Asop	8.3	9.20	0.195	32.8	22.1	0.179	0.94
Lilian	8.6	4.33	0.292	35.8	21.4	0.157	0.57
Non-calcareous soils							
Khajwan	8.2	1.91	0.391	16.3	11.4	0.443	0.59
Silgaon	8.0	1.43	0.382	16.8	12.9	0.571	2.36
Pali I	7.7	0.16	0.480	16.8	20.2	0.460	1.35

negative log of OH activity (pOH = 14-pH) were calculated. The zinc hydroxide potential (pZn+2pOH) was obtained.

Results and Discussion

The physico-chemical characteristics of the soils (Table 1) revealed that the soils were alkaline (pH 7.7 to 8.6) and available zinc was marginal to low (0.59 to 2.36 $\mu g\ g^{-1}$). The calcareous soils (fine loamy Typic Haplocalcids) of Pali II, Asop and Lilian contained higher amount of clay (24.2 to 35.8%), $CaCO_3$ (4.3 to 19.8%) and CEC (21.4 to 23.3 C mol kg^{-1}). The non-calcareous (coarse loamy, Typic Haplocambids) contained clay 16.3 to 16.8%, $CaCO_3$ 0.16 to 1.91% and CEC 11.4 to 20.2 C mol kg^{-1}.

Adsorption of Zn

In calcareous soils the values of adsorption maxima were in lower ranges (2.0 to 7.6 mg g^{-1}) than the non-calcareous soils (6.6 to 10.9 mg g^{-1}; Table 2). The bonding energy constant value was in higher ranges in calcareous soils (0.009 to 0.085 mL kg^{-1}) than in non-calcareous (0.001 to 0.02 mL kg^{-1}). However, when compared with the sandy soils (adsorption maxima 1.0 to 5.3 mg g^{-1}, DBC 0.002 to 0.015 mL kg^{-1}; Joshi and Sharma, 1986) the values for both the parameters were higher in the present study. This can be attributed to higher clay and $CaCO_3$ content of the soils.

Table 2. Adsorption maxima and bonding energy constant

Soils	Adsorption maxima (mg g^{-1})	Bonding energy constant (ml kg^{-1})
Calcareous soils		
Pali II	2.03	0.080
Asop	6.85	0.085
Lilian	7.60	0.009
Non-calcareous soils		
Khajwan	8.87	0.004
Silgaon	6.67	0.001
Pali I	10.91	0.020

With the increasing addition of zinc, there was an increase in the per cent saturation, zinc adsorption capacity and supply parameter and a decrease in the differential buffering capacity (Table 3). With the addition of 50 μg Zn g^{-1} soil the saturation of zinc adsorption capacity was low in calcareous (0.26 to 1.0%) than in non-calcareous (0.53 to 2.0%) soils. With increasing addition of Zn, there was increase in the zinc saturation per cent of both the groups of soils. At 10,000 μg Zn g^{-1} soil addition the zinc saturation per cent was higher in calcareous (80 to 140) than in non-calcareous (61 to 140) soils. Higher zinc saturation per cent values are attributed to the specific adsorption of zinc (Wada and Abd-El-Fattah, 1979; Abd-El-Fattah and Wada, 1981).

At 50 μg Zn g^{-1} soil addition the differential buffering capacity (DBC) values of soils were in the range of 0.064 to 0.251 in calcareous and 0.03 to 0.09 in non-calcareous soils. The DBC values decreased with the addition of Zn and at 10,000 μg Zn g^{-1} soil addition the values were very low in calcareous soils (0.00010 to 0.00339) than in the non-calcareous (0.00068 to 0.0021) soils.

Supply parameter combines the quantity, intensity and buffering capacity of soil for assessing ability of soil to supply the nutrient. With the 50 g Zn g^{-1} soil addition the supply parameter was in lower ranges in the calcareous (0.057 to 0.39) than in the non-calcareous (0.09 to 0.59) soils. With increasing addition of Zn the supply parameters increased in both the soil groups and at 10,000 g Zn g^{-1} soil, the values were much lower in calcareous (35 to 96) than in non-calcareous (91 to 117) soils. This indicated that calcareous soils have low ability to maintain zinc supply.

Tab. 3. Per cent saturation, differential buffering capacity and supply parameters of soils treated with different Zn concentrations

Soils	Concentration of Zn added (μg Zn g^{-1} soil)								
	50	100	250	500	1000	2500	4000	5000	10000
					Per cent saturation				
Calcareous soils									
Pali II	2.00	4.40	11.80	24.00	33.40	102.00	123.50	130.0	140.0
Asop	1.00	1.00	4.00	7.30	14.00	36.00	55.00	58.4	102.2
Lilian	0.53	1.02	3.00	6.30	12.00	28.10	39.50	47.9	80.0
Non-calcareous soils									
Khajwan	0.26	0.94	2.68	5.00	8.91	24.00	32.70	36.8	61.0
Silgaon	0.53	1.00	3.58	7.00	13.48	34.49	50.00	54.0	82.0
Pali I	1.00	2.20	5.40	10.50	16.32	38.50	55.00	60.5	104.5
					Differential buffering capacity				
Calcareous soils									
Pali II	0.25	0.25	0.25	0.25	0.01	0.06	57×10^{-5}	13×10^{-5}	10×10^{-5}
Asop	0.57	0.57	0.57	0.56	0.50	0.45	0.05	64×10^{-4}	82×10^{-5}
Lilian	0.06	0.06	0.06	0.06	0.51	0.04	0.02	14×10^{-3}	33×10^{-5}
Non-calcareous soils									
Khajwan	0.03	0.03	0.03	0.03	0.03	0.03	0.02	12×10^{-3}	45×10^{-4}
Silgaon	0.06	0.06	0.06	0.06	0.05	0.04	0.02	11×10^{-3}	21×10^{-5}
Pali I	0.09	0.09	0.09	0.08	0.02	0.02	0.01	30×10^{-4}	68×10^{-5}
					Supply parameter				
Calcareous soils									
Pali II	0.24	0.35	0.57	0.82	6.26	12.59	25.90	32.5	35.0
Asop	0.06	0.08	0.18	0.36	1.08	2.29	9.68	22.9	52.6
Lilian	0.39	0.83	1.07	1.24	6.07	17.53	34.27	44.2	96.7
Non-calcareous soils									
Khajwan	0.59	0.89	1.29	2.81	9.64	20.80	42.3	56.3	117.9
Silgaon	0.45	0.79	1.07	1.81	6.05	13.67	29.6	44.4	98.3
Pali I	0.09	0.13	0.53	1.89	5.93	20.87	35.3	45.3	91.0

The Pali II and Asop soils which contain higher $CaCO_3$ (19.8% and 9.2%) have lower supply parameter values (35 and 52.6). This is perhaps because of the strong affinity of $CaCO_3$ with zinc. Raikhy and Takkar (1983) also observed that higher $CaCO_3$ content depressed zinc supply parameters.

Thus the calcareous soils were characterized by higher saturation of Zn adsorption capacity, higher differential buffering capacity and low zinc supply parameters, in spite of treatment with higher amount of Zn (10,000 μg g^{-1} soil). These observations are in accordance with the reports of Jurinak and Bauer

Table 4. The desorbed zinc and zinc potential in soils treated with varying amount of zinc

Zinc added (μg Zn g^{-1} soil)	Desorbed				Desorbed			
	pH	Zn (mole/L^{-1})	pZn	pZn + 2 pOH	pH	Zn (mole/L^{-1})	pZn	pZn + 2 pOH
	Calcareous soils				Non calcareous soils			
	Pali - II				Khajwan			
50	7.6	11.4×10^{-6}	4.9	17.7	7.3	3.8×10^{-6}	5.4	18.8
250	7.5	11.4×10^{-6}	4.9	17.8	7.4	5.8×10^{-6}	5.2	18.4
2,500	7.3	22.9×10^{-6}	4.6	18.0	7.4	3.8×10^{-6}	2.4	15.6
10,000	7.1	207×10^{-6}	3.7	17.5	7.2	7700×10^{-6}	2.1	15.7
	Asop				Silgaon			
50	7.7	1.5×10^{-6}	6.7	19.4	6.6	3.8×10^{-6}	5.4	18.6
250	7.6	1.5×10^{-6}	6.7	19.6	7.3	5.7×10^{-6}	5.2	18.6
2,500	7.3	161×10^{-6}	4.7	18.2	7.2	14×10^{-6}	2.9	17.6
10,000	7.0	280×10^{-6}	4.5	18.5	7.2	8400×10^{-6}	2.1	15.7
	Lilian				Pali - I			
50	7.7	7.6×10^{-6}	5.1	17.7	7.1	0.8×10^{-6}	6.1	20.1
250	7.6	15.3×10^{-6}	4.8	17.6	7.2	2.2×10^{-6}	6.6	20.3
2,500	7.3	152×10^{-6}	3.8	17.2	6.7	240×10^{-6}	4.5	19.2
10,000	7.0	4500×10^{-6}	2.4	16.2	6.3	1766×10^{-6}	3.7	19.1

(1956). Chawla *et al*. (1985) and Shrivastava and Gangwar (1987) observed that soils with higher saturation of adsorption capacity have low supply parameter values.

Desorption of Zinc

The concentration of zinc desorbed from the soils treated with different concentrations of Zn potential (pZn + 2 pOH) are reported in Table 4. The desorbed Zn from soils treated with 50 g Zn μg^{-1} soils was higher in calcareous (1.5 to 11.4×10^{-6} moles L^{-1}) than in the non-calcareous (0.8 to 3.8×10^{-6} moles L^{-1}) soil. From 10,000 μg Zn g^{-1} treated soils the desorbed Zn was very low in calcareous (207 to 280×10^{-6} moles L^{-1}) than in the non-calcareous (7700 to 8400 moles L^{-1}) soils. These values were much higher than those reported for sandy soils (137.7 to 1606×10^{-6} moles L^{-1}; Joshi and Sharma, 1986). The negative log of the desorbed Zn ion activity (pZn) values in the soils treated with 50 μg Zn varied from 4.9 to 6.7. With the increased Zn treatment, there was a decrease in p Zn values, indicating higher ion activity of the desorbed zinc. The zinc potential values for 50 μg Zn treated soils ranged between 17.7 and 20.1. At 10,000 μg Zn treatment, the zinc potential values were higher than the zinc potential values for $Zn(OH)_2$ and $ZnCO_3$ (16-17), which suggested that the soils, inspite of treatment with higher amount of Zn, are unsaturated with respect to $Zn(OH)_2$ and $ZnCO_3$. The applied zinc could be retained by these soils as Zn^{2+} (Lindsay and Norvell, 1978; Trehan and Sekhon, 1977).

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Refereces

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