ZINC ADSORPTION BEHAVIOR OF DIFFERENT TEXTURED CALCAREOUS SOILS USING FREUNDLICH AND LANGMUIR MODELS

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Zinc adsorption was studied in ten soils varying in texture or calcareousness of Punjab. Adsorption process was executed by equilibrating 2.5g soil in 25 ml of 0.01M $CaCl_2$ solution containing 0, 5, 10, 15, 20, 25, 70, and 120 mg Zn L^{-1}. Sorption data were fitted to Freundlich and Langmuir adsorption models. The data were best fitted in both linearized Freundlich and Langmuir equations as evidenced by higher correlation coefficient values ranging from 0.87 to 0.98. High clay contents ranging from 8 to 32 % and $CaCO_3$ 4.46 to 10.6 % promoted an increase in the amount of adsorbed Zinc in these soils. Adsorption of Zn increased with the increasing level of Zn and also increased with increase in clay, and $CaCO_3$ contents. The maximum adsorption of Zn was observed in the Kotli whereas, the minimum in the Shahdra soil series.
Keywords: Zinc, adsorption model, texture, calcareous soil

INTRODUCTION

One of the first minerals known to be essential for plants, animals, and man is Zn (Kabata-Pendias, 2000). Zn is a nutrient which is required by the plants in smaller quantity (Reed and Martens, 1996). Because plants absorb Zn from soil solution, adequate levels of dissolved Zn are needed for the optimal growth of crops (Reed and Martens, 1996).

The availability of Zn in soil is mostly regulated by adsorption-desorption process and its partitioning between the solution and solid phases (Gaudalix and Pardo, 1995; Catlett *et al.*, 2002). The relationships between Zn adsorption-desorption and soil properties have been extensively studied. Of the soil properties, clay, pH, cation exchange properties, organic matter and pedogenic oxides exert the most significant influence on the adsorption-desorption reactions of Zn in soils and, thus, regulate the amount of Zn dissolved in soil solution (Stahl and James, 1991; Gaudalix and Pardo, 1995). Adsorption isotherms can be used to describe the equilibrium relationship between the amounts of adsorbed and dissolved species at a given temperature. A sorption isotherm takes into account intensity, quantity and capacity factors, which are important for predicting the amount of soil nutrient required for maximum plant growth. As the amounts of nutrients required by a soil are affected by the clay minerals, CEC, organic matter, soil texture, $CaCO_3$ and other properties, which need not to be measured in order to determine soil requirements using sorption technique (Solis and Torrent, 1989). In several studies, Zn adsorption has been described primarily by the Langmuir equation (Udo *et al.*, 1970; Shuman, 1975). None of these workers attempted to explain Zn adsorption by Freundlich equation, although this equation has been used for describing adsorption from dilute solutions. Usually studies on Zn retention have been made using relatively high levels of Zn to show its fixation in soil. No attempt has been made to study the effect of realistic low concentrations of equilibrating Zn solutions on adsorption isotherms. The literature on the subject is limited, and little information is available on soils under agro-climatic conditions of Pakistan where Zn deficiencies have been widely reported (Rashid, 1996). The present study was conducted to characterize Zn adsorption in some soil series varying in clay and $CaCO_3$ contents.

MATERIALS AND METHODS

Soil samples from 10 sites varying in pH, $CaCO_3$ and texture were collected. The soils were air dried, ground and passed through a 2-mm sieve to collect samples having size < 2 mm.

For the adsorption study 2.5g soil was shaken with 25 ml 0.01M $CaCl_2$ containing Zn concentrations of 0, 5, 10, 15, 20, 25, 70, and 120 mg L^{-1}, for 24 hours at 25^0 C. This process was proceeded for each soil. After shaking, soil solution was filtered through Whatman No.42 filter paper. After filtration Zn concentration was determined by atomic absorption spectrophotometer (Perkin Elmer A Analyst 100 U.S.A). Adsorption isotherms were constructed following the methods described by Rowell (1994). Zn adsorption capacity was determined by subtracting the equilibrium Zn concentration in solution from the added Zn.

Freundlich Model

The modified Freundlich model used to describe the soils in this work is as follows:

$$X = aC^b$$

X = Amount of Zn adsorbed per unit weight of soil (mg kg^{-1})
C = Equilibrium Zn concentration in soil solution (mg L^{-1})
a and b are constants which represent the intercept and slope of the sorption isotherms respectively.

Langmuir Model

$$C/(x/m) = 1/kb+C/b$$

Where,
x/m = Amount of Zn adsorbed per unit weight of soil (mg kg^{-1})
C = Equilibrium Zn concentration in soil solution (mg L^{-1})
k = It is a constant related to bonding energy of Zn to the soil.
b = It is the maximum adsorption capacity of soil.

RESULTS AND DISCUSSION

Soil samples used in this study were collected from ten different sites and their physico chemical characteristics are given in Table 1. $CaCO_3$ % age ranged from 4.46 in Eminabad to 10.6 in the Kotli soil series. pHs of all the soil series was in alkaline range and electrical conductivity (ECe) of saturated extract was less than 4 dS m^{-1}. The clay content ranged from 8 to 32%. Available Zn was less than 0.6 mg L^{-1} in all the soil series indicating their status as deficient from crop availability point of view (Sharma and Lal, 1993) and thus required Zn application in order to avoid probable yield losses while organic matter content was low i.e. < 1%.

Zn adsorption behavior

The adsorption of Zn increased when Zn concentrations increased in the contact solution in all the soils. Similar results were also reported by Narwal (1995) and Wada (1978). Maximum adsorption of Zn of 1089.6 mg kg^{-1} was seen on Kotli soil series and the minimum of 1036.8 mg kg^{-1} was observed in Shahdra soil series at the highest level of added Zn.
The maximum adsorption of Zn in the Kotli soil series might be due to highest contents of $CaCO_3$ (10.6 %), maximum amount of clay (32 %) and relatively high pH (8.2). Soil carbonates are important sites for the absorption of added Zn (Udo *et al.*, 1970). The higher pH increased the adsorption of Zn as a result of complexation of Zn by OH ions and a higher net negative charge (Shuman, 1986). Also, the clays have high sorption sites that allow the non exchangeable (specific) sorption of Zn (Randal and Bruce, 1991). Majority of the soil series i.e. Sultanpur, Shahpur, Pindorian, Shahdra, Bhalekai, Pucca, Eminabad and Wazirabad had higher pH values (Table 1) but Zn adsorption in these soils were less, because all the soil series were coarse textured with a lower $CaCO_3$ and clay contents, which helped to explain its lower adsorption capacity (Shukla and Mittal , 1979).

Freundlich and Langmuir adsorption isotherms of soils

The adsorption isotherms were examined according to the linear form of the Freundlich equation (Log Zn C vs. Log x / m) which gave a linear fit (Table 2 & Fig. 2). Values of the exponent (b) in Freundlich equations were found more than 1 in case of all the ten soils with maximum value 1.6754 noted in the Kotli soil series while minimum value 1.4042 was seen in the equation

Table 1. Physical and chemical characteristics of the selected soils series

Sr. No.	Soil series	EC_e (dS m^{-1})	pHs	$CaCO_3$	Sand	Silt	Clay	O.M	DTPA Extractable Zn (mg kg^{-1})	Textural class
				%						
1	Kotli	2.38	8.2	10.6	40	28	32	0.58	0.56	Clay loam
2	Sultanpur	1.94	8.4	5.80	57	25	18	0.52	0.52	Sandy clay loam
3	Shahpur	2.35	7.8	4.58	62	22	16	0.69	0.42	Sandy loam
4	Pindorian	2.31	8.1	4.60	43	37	20	0.62	0.56	Loam
5	Bhalwal	2.40	8.3	9.80	45	27	28	0.74	0.51	Clay loam
6	Shahdra	2.10	8.0	6.53	72	20	8	0.55	0.33	Loamy sand
7	Bhalekai	3.30	8.2	5.83	54	29	17	0.47	0.46	Sandy loam
8	Pacca	2.9	7.8	4.50	52	27	21	0.39	0.39	Sandy clay loam
9	Eminabad	3.10	7.9	4.46	45	33	22	0.60	0.44	Loam
10	Wazirabad	2.40	8.2	6.70	60	22	18	0.45	0.42	Sandy loam

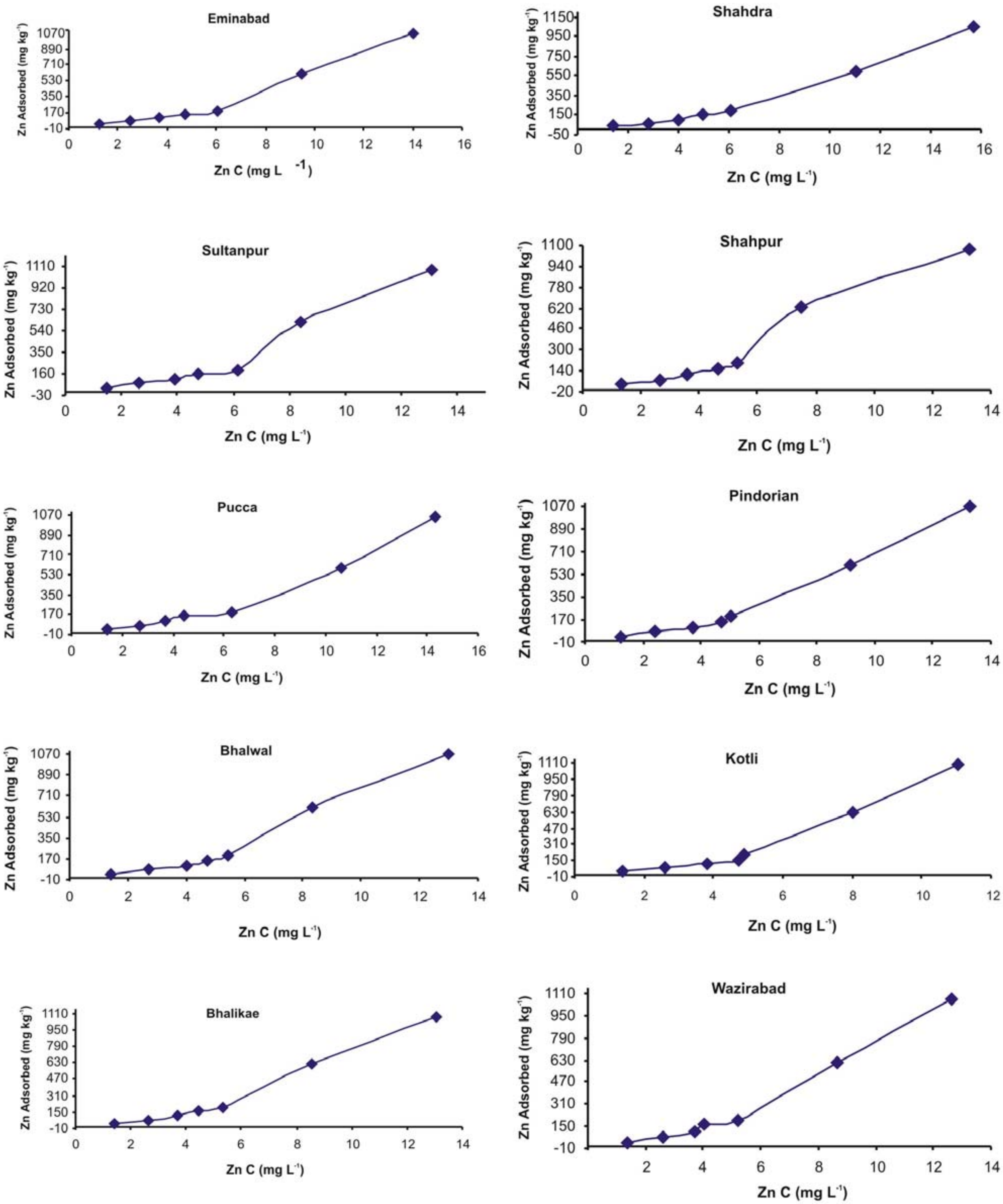

Fig. 1. Adsorption isotherms of Zn on some selected soil series of Punjab

Table 2. Comparisons of adsorption equations of ten selected soils along with their R^2 values

Sr. No.	Soil series	Equations	R^2
1	Shahdra	Freundlich Y=1.4042x +1.2523 Langmuir Y=-0.0018 x +0.0424	0.98** 0.95**
2	Sultanpur	Freundlich Y=1.5833x +1.189 Langmuir Y=-0.0027 x +0.0442	0.95** 0.87*
3	Shahpur	Freundlich Y=1.5294 x +1.2611 Langmuir Y=-0.0023 x +0.0397	0.97** 0.90**
4	Pindorian	Freundlich Y=1.4583 x +1.3156 Langmuir Y=-0.002 x +0.0377	0.97** 0.91**
5	Bhalwal	Freundlich Y=1.5850 x +1.2029 Langmuir Y=-0.0027 x +0.0432	0.96** 0.88*
6	Kotli	Freundlich Y=1.6754 x +1.1917 Langmuir Y=-0.0032x +0.0434	0.96** 0.92**
7	Bhalekai	Freundlich Y=1.5946 x+1.2128 Langmuir Y=-0.0025 x +0.0415	0.98** 0.91**
8	Pacca	Freundlich Y=1.4547 x +1.2528 Langmuir Y=-0.002 x +0.0416	0.98** 0.91**
9	Eminabad	Freundlich Y=1.4114x +1.315 Langmuir Y=-0.0019 x +0.0387	0.96** 0.88*
10	Wazirabad	Freundlich Y=1.5646 x +1.2569 Langmuir Y=-0.0024 x +0.0393	0.98** 0.91**

** Significant P=0.05
* Significant P=0.01

of Shahdra soil series. The Freundlich equation is an empirical equation and corresponds to a model of adsorption in which the affinity term decreases exponentially as the amount of adsorption increases. Gregory *et al.* (2005) stated that the advantage of the Freundlich isotherm is that it assumes unlimited sorption sites which correlated better with a heterogeneous soil medium having different chemical/physical properties.

These results are similar to those of Shuman (1977), who also related the adsorption capacity of soils to different physical and chemical properties of soils, including texture, clay contents, and pH. As for as the R^2 values in Freundlich equations were concerned these were highly significant (at $P < 0.05$) in all the ten equations, suggesting that the data were well fitted to the Freundlich adsorption isotherm equations. These results were comparable to the work reported by Hannan *et al.* (2007) with respect to the adsorption isotherms.

The Langmuir equation was first used to describe P adsorption by Olsen and Watanabe (1957) and has since been widely used (Ryden *et al.*, 1977b; Ghosh and Biswas, 1987). The adsorption data were plotted also according to the linear form of the Langmuir adsorption isotherm i.e. Zn C vs. Zn C/(x/m) (Table 2 & Fig. 3), R^2 values in Langmuirian equations were

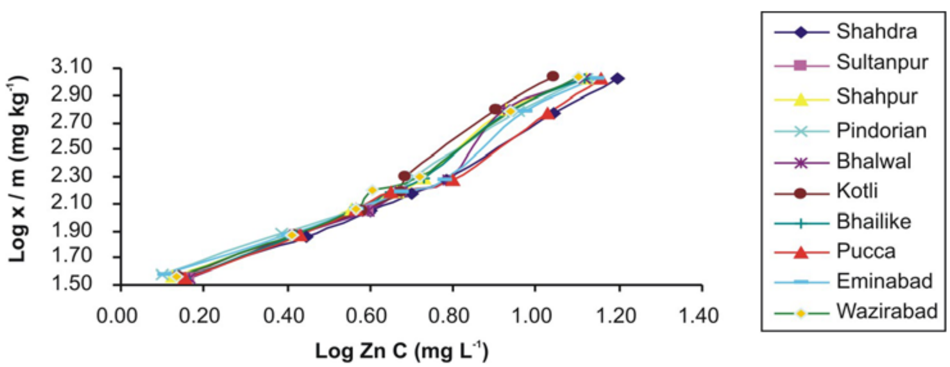

Fig. 2. Freundlich adsorption isotherms of the ten selected soil series

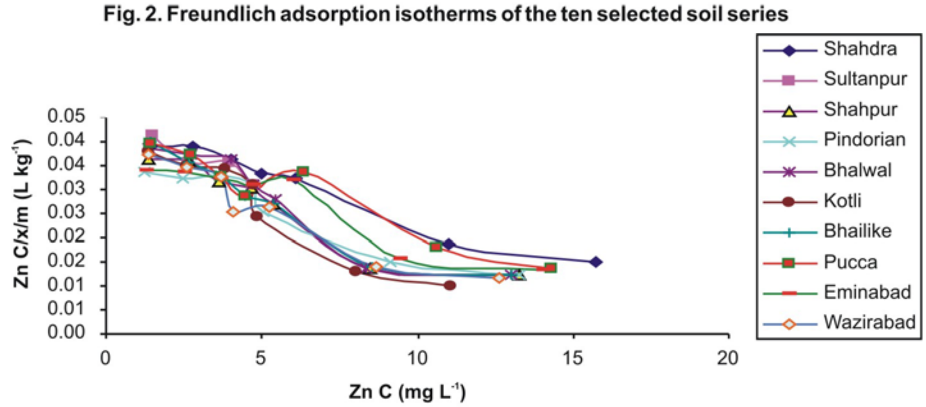

Fig. 3. Langmuir adsorption isotherms of the ten selected soil series

significant in case of all the soils. These results were in close agreement with those previously obtained by Udo *et al.*, (1970) and Shuman (1975).

CONCLUSIONS

- Adsorption of Zn increased with the increasing level of applied Zn.
- The data were best fitted in both linearized Freundlich and Langmuir models.

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