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THE EFFECT OF ORGANIC MATTER TYPES ON THE BEHAVIOR OF ZINC IN SEDIMENTARY SOILS OF DIFFERENT TEXTURES

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***Abstract**. This research paper has discussed the zinc (Zn) adsorption-desorption processes in calcareous alluvial soils with different textures that were amended with various organic materials. Two soils (sandy loam, T1; clay loam, T2) gathered in Al-Musayyib District, Babil Governorate, Iraq, were described in the terms of chosen physical and chemical characteristics. In a laboratory equilibrium experiment, 2 g of soil were mixed with 20 mL of $ZnSO_4$ solution (5, 10, 25, 50, 100 and 150 mg L^{-1}) with the amendment of cattle, sheep or poultry manure. The Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were used to determine adsorption and subsequent desorption by the use of 0.01 N $CaCl_2$. Langmuir gave the most consistent fit to the adsorption data, which had an R^2 value of 0.88 to 0.98, versus 0.86 to 0.96 with both Freundlich and D-R. Langmuir maximum adsorption capacity (Xmax) was between 29.22 to 256.41 mg kg^{-1}, meanwhile the value of D-R adsorption energy was between 8.74 to 11.81 kJ mol^{-1} and this shows that ion exchange was predominant. Overall, heavy-textured soil exhibited higher retention and low desorption of Zn compared to the light-textured soil. Sheep manure enhanced adsorption capacity in several cases, whereas poultry manure tended to reduce Zn retention, particularly in the light-textured soil. The results demonstrate that soil texture and organic amendment type jointly control Zn behavior and that the Langmuir model is the most suitable for describing Zn adsorption under the conditions of this study.*

***Keywords**; Adsorption; Calcareous alluvial soils; Desorption; Organic amendments; Zinc.*

1. INTRODUCTION

Zinc (Zn) is an essential micronutrient for plant nutrition. In alluvial soils, zinc occurs in several forms, including zinc dissolved in the soil solution, exchangeable and adsorbed zinc on the surfaces of colloids and iron and manganese oxides, and zinc associated with organic matter [1].

Organic matter markedly affects zinc behavior in soils because it contains reactive functional groups capable of binding Zn, and its effect may proceed in two directions depending on the nature of organic matter and soil conditions. On the one hand, some decomposition products and organic acids can form soluble complexes with zinc, enhancing its mobility in the soil solution; on the other hand, humic substances may increase zinc adsorption and retention within organo–mineral complexes, thereby decreasing its soluble fraction. This effect also varies with organic matter source (cattle, sheep, and poultry manures) [2].

Soil texture is also a key factor controlling zinc behavior; clayey soils have higher specific surface area and cation exchange capacity, which increases zinc adsorption compared with sandy soils and may reduce its availability to plants [3]. On the contrary, zinc transport in sands soils is not as steady and thus there is a higher chance of the soil being leached and wasted out of root zone [4]. Since the idea of thermodynamics holds significant importance in explaining the presence of zinc and its changes in soils, the research sought to:

1- Study zinc behavior in alluvial soils of different textures (light and heavy).

2- Evaluate the effect of organic matter type on zinc behavior.

3- Determine the best equation to describe zinc behavior.

2. MATERIALS AND METHODS

2.1. *Sampling site*

Two soil samples differing in texture were selected: a light-textured soil (T1) and a heavy-textured soil (T2), collected from agricultural areas in Babil Governorate, Al-Musayyib District. Representative samples were transported to the laboratory for preparation; they were air-dried, crushed, and passed through a 2-mm sieve, stored in plastic containers, and submitted for the required analyses and laboratory experiments.

2-2. Determination of selected chemical and physical properties of the study soils:

The following methods were used to determine selected chemical and physical properties of the study soils, as shown in Table (1).

2.3.1. *Particle-size distribution*

Particle-size fractions were determined using the pipette method as described by [5].

2.3.2. Electrical conductivity (EC) and pH

Electrical conductivity (EC) and pH were measured in a 1:1 soil:water extract according to the method described by [6].

2.3.3 Soil organic matter (SOM)

Soil organic matter was determined using the wet digestion method according to Walkley and Black as cited in [7].

2-3-4. Soluble zinc:

Soluble zinc was determined in a 1:1 soil extract with distilled water as described in [8] using an atomic absorption spectrophotometer (AAS).

2.3.5. Available zinc:

Available zinc was determined by extraction with DTPA and TEA and then measured using an atomic absorption spectrophotometer according to the method described by [9].

2-3-6. Total zinc:

Total zinc was determined by digesting the soil sample with a mixture of hydrochloric acid and perchloric acid [10].

Table 1- Some chemical and physical properties of the study soils

Samples / Properties **Samples / Properties**		**T1**	**T2**	**Unit**
EC1:1		2.95	3.35	dS m^{-1}
pH		7.60	7.64	-
SOM		7.9	9.8	
Soluble Zn		0.21	0.44	mg kg^{-1}
Available Zn		0.89	1.42	
Total Zn		37.32	47.54	
CEC		19.86	25.24	cmolc kg^{-1} soil
Soil separates	Sand	650	280	g kg^{-1} soil
	Silt	250	340	g kg^{-1} soil
	Clay	100	380	g kg^{-1} soil
Texture		Sandy loam	Clay loam	

2-4. Organic amendments and adsorption-desorption experiment

The laboratory study followed a factorial arrangement consisting of two soil textures × three organic amendments (cattle, sheep, and poultry manure) × six added Zn concentrations. Each treatment was prepared in three replicates, and each amendment was applied at a rate equivalent to 10 t ha^{-1} on a 2-g soil basis. The organic materials were mixed thoroughly with the soils, and no pre-incubation period was used before equilibration with the Zn solution.

For the adsorption step, 2 g of air-dried soil were placed in 50-mL plastic centrifuge tubes, and 20 mL of $ZnSO_4$ solution containing 5, 10, 25, 50, 100, or 150 mg L^{-1} Zn were added. The tubes were shaken for 5 h at 25 °C and left for 24 h to attain equilibrium. Suspensions were then centrifuged for 15 min, filtered, and the Zn concentration in the equilibrium solution was determined by atomic absorption spectrophotometry [11].

The amount of adsorbed Zn was calculated from the difference between the initial and equilibrium concentrations using Equation (1) [12]:

$$q_e = ((C_i - C_e) \times V) / W \quad (1)$$

where qe is the adsorbed Zn (mg kg^{-1}), Ci is the initial Zn concentration (mg L^{-1}), Ce is the equilibrium Zn concentration (mg L^{-1}), V is the solution volume (L), and W is the soil mass (kg).

For desorption, 20 mL of 0.01 N $CaCl_2$ were added to the soil residue after adsorption. The tubes were shaken for 5 h at 25 °C, centrifuged, and analyzed for Zn in the desorption extract.

2.5.Isotherm modeling and statistical analysis

Adsorption and desorption data were evaluated using the linearized Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) equations. For the Langmuir model, Ce/qe was plotted against Ce to estimate the maximum adsorption capacity (Xmax) and the bonding constant (K), and the maximum buffering capacity (MBC) was calculated as Xmax × K. For the Freundlich model, log qe was plotted against log Ce to estimate the constants a and n. For the D-R model, ln qe was plotted against ε^2 according to Equations (2) and (3) [12]:

$$\ln qe = \ln qm - K\varepsilon^2 \quad (2)$$

$$E = 1 / \sqrt{(2K)} \quad (3)$$

where qm is the theoretical adsorption capacity, K is the D-R constant, ε is the Polanyi potential, and E is the mean adsorption energy. The coefficient of determination (R2) was used to compare model performance. Symbols of significance used in the tables (the star and the two stars) were not deleted to show that regression significance was at P 0.05 level and P 0.01 level respectively. Student t-test consisting of P 0.05 was used to evaluate differences between means where appropriate.

3.Results and Discussion

3.1. Selected properties of the study soils

These two soils were distinctively different (Table 1) in the context of their texture and related chemical properties. T1 was sandy loam as compared to T2, clay loam. The heavy-textured soil was also richer in the SOM, soluble Zn, available Zn, total Zn as well as CEC in comparison with the light-textured soil. These variations imply that T2 presented a bigger reactive surface and more adsorption sites and as will be anticipated these would favour Zn retention.

3.2. Application of Langmuir equation in the description of zinc adsorption and desorption.

Zn adsorption was well characterized by the Langmuir model in each treatment with an R2 of 88 to 98 (Table 2). The Xmax estimates were between 256.41 and 29.22mg kg^{-1}. The highest value was obtained in the heavy-textured soil amended with sheep manure, whereas the lowest value was recorded in the light-textured soil amended with poultry manure. In general, the higher adsorption capacity of the heavy soil is consistent with its greater clay content and CEC, which increase the number of active sorption sites and enhance Zn retention in calcareous media [13].

The Langmuir bonding constant (K) ranged from 0.27 to 2.66 L mg^{-1}, and MBC ranged from 30.33 to 415.62 L kg^{-1}. The maximum MBC occurred in the heavy-textured soil amended with cattle manure, indicating a strong capacity to buffer Zn concentration in solution. Stable decomposition products from farmyard manures can enhance organo-mineral associations and strengthen Zn retention, whereas more soluble organic constituents may keep a greater portion of Zn in solution [14].

For desorption, Table (4) shows that Xmax ranged from 25.51 to 222.22 mg kg^{-1}, with the highest desorption in the light-textured soil with sheep residues and the lowest in the heavy-textured soil with poultry residues. The K constant for desorption ranged from 0.20 to 2.22 L mg^{-1}; the highest value occurred in the light-textured soil treated with cattle manure and the lowest in the heavy-textured soil treated with cattle manure, while MBC ranged from 20.33 to 277.78 L kg^{-1}. The values of the coefficient of determination (R2) were quite good (0.72 -0.99) meaning that the Langmuir equation is sufficient to describe the behavior. This superiority of light soils in desorption is explained by the reduced number of high-energy adsorption sites, as well as reduced clay and CEC, which retains more zinc in easily exchangeable, weakly bound forms, easily replaced by $CaCl_2$ solution. Reduced desorption in heavy soils can be connected with a greater fixation of zinc on clay and carbonate surfaces or its conversion to more fixed forms (specific adsorption / surface precipitation) and makes it less displaceable [15].

Table (2) Langmuir equation constants for zinc adsorption in the study soils

Parameters / Soil treatments	Linear equation	Xmax (mg kg^{-1})	K (L mg^{-1})	MBC (L kg^{-1})	R2 %
Heavy texture + cattle manure	Y=0.0024x+0.0064	156.25	2.66	415.62	96**
Heavy texture + sheep manure	Y = 0.0081x + 0.0039	256.41	0.48	123.07	97**

Heavy texture + poultry manure	Y = 0.0111x + 0.0073	136.98	0.65	89.03	98**
Light texture + cattle manure	Y = 0.0325x + 0.0089	112.35	0.27	30.33	88**
Light texture + sheep manure	Y = 0.0223x + 0.0213	46.94	0.95	44.59	90**
Light texture + poultry manure	Y = 0.0189x + 0.0345	29.22	1.81	52.88	91**

* $P \leq 0.05$; ** $P \leq 0.01$.

Table (3) Langmuir equation constants for zinc desorption in the study soils

Parameters / Soil treatments	**Linear equation**	**Xmax (mg kg^{-1})**	**K (Lmg^{-1})**	**MBC (L kg^{-1})**	**R2 %**
Heavy texture + cattle manure	Y = 0.0492x + 0.01	100.00	0. 20	20.33	78**
Heavy texture + sheep manure	Y = 0.0413x + 0.0246	40.65	0.596	24.21	72*
Heavy texture + poultry manure	Y = 0.0248x + 0.0392	25.51	1.581	40.32	87**
Light texture + cattle manure	Y = 0.0036x + 0.008	125.00	2.222	277.78	91**
Light texture + sheep manure	Y = 0.0153x + 0.0045	222.22	0.294	65.36	98**
Light texture + poultry manure	Y = 0.0161x + 0.0082	121.95	0.509	62.11	99**

* $P \leq 0.05$; ** $P \leq 0.01$.

3.3. Use of the Freundlich equation to describe zinc adsorption

The data on adsorption could also be explained by the Freundlich equation with R2 between 86 and 96 percent (Table 4). The adsorption-capacity constant (a) was between 18.09 and 81.97 mg kg^{-1} and the adsorption-capacity constant was mostly higher in the heavy-textured soil as compared to the light-textured soil. This pattern confirms the fact that Zn had more locations that could retain it in the heterogeneous surface of the finer-textured soil [16]. Moreover, more stable organic amendments (particularly sheep residues) facilitate the growth of organo-mineral complexes/coatings and improve Zn fixation in calcareous soils when Ca_2 is present [17], and poultry residues can facilitate soluble forms that retain Zn in solution and decrease the adsorption abilities [18]. The n values ranged from 1.00 to 1.78; the highest value occurred in the heavy-textured soil treated with cattle manure due to enhanced formation of more stable humic substances that bind to clay and provide stronger adsorption sites [19]. In contrast, n decreased in the heavy-textured soil treated with poultry manure because of blocking of active sites and surface coverage by DOM, along with formation of soluble metal–DOM complexes that reduce Zn affinity to the solid phase.

Table (4) Freundlich equation constants for zinc adsorption in the study soils

Parameters / Soil treatments	**Linear equation**	**a (mg kg^{-1})**	**n**	**R %**
Heavy texture + cattle manure	Y = 0.5646x + 1.9066	80.64	1.78	96**

Heavy texture + sheep manure	Y = 0.8614x + 1.9137	81.97	1.16	96**
Heavy texture + poultry manure	Y = 1x + 1.8947	78.46	1.00	94**
Light texture + cattle manure	Y = 0.9132x + 1.3897	24.53	1.09	89**
Light texture + sheep manure	Y = 0.7154x + 1.3279	21.27	1.40	86**
Light texture + poultry manure	Y = 0.6835x + 1.2576	18.09	1.47	87**

* $P \leq 0.05$; ** $P \leq 0.01$.

3.4. Use of the D–R equation to describe zinc adsorption

Table (5) shows that the D–R equation constants indicate that the maximum adsorption capacity of zinc (qm) ranged between 724.48 and 10855.29 mg kg^{-1}. The highest value occurred in the heavy-textured soil treated with poultry manure, and the lowest in the light-textured soil treated with poultry manure. The higher qm in the heavy soil is attributed to the abundance of micropores in clay; with rapid decomposition of poultry manure, amorphous organic materials form and increase surface heterogeneity and interparticle porosity, which raises the capacity estimated by the D–R model.

K values ranged from 0.003587 to 0.006550, with the highest in the heavy soil + poultry manure and the lowest in the heavy soil + cattle manure. Since K is inversely related to adsorption energy, its higher value under poultry manure indicates lower-energy and faster adsorption (physical adsorption/ion exchange) due to the abundance of negative sites resulting from ... The adsorption energy (E) ranged from 8.74 to 11.81 kJ mol^{-1}; the highest value occurred in the heavy soil + cattle manure as a result of formation of more stable humic substances that bind strongly to clay minerals, whereas the lower value under poultry manure is associated with surface coating by dissolved organic matter and blocking of high-energy sites. The fact that E values fall within 8–16 indicates that the dominant mechanism is ion exchange [20].

Table (5) D–R equation constants for zinc adsorption in the study soils

Parameters / Soil treatments	Linear equation	Qm (mg kg^{-1})	K (kJ mol^{-1})	E (kJ mol^{-1})	R %
Heavy texture + cattle residues	Y = -0.0036x + 7.1196	1236	0.0036	11.81	96**
Heavy texture + sheep residues	Y = -0.0056x + 8.6153	5515	0.0056	9.46	96**
Heavy texture + poultry residues	Y = -0.0066x + 9.2924	10855	0.0066	8.74	93**
Light texture + cattle residues	Y = -0.0064x + 8.0999	3294	0.0064	8.83	88**
Light texture + sheep residues	Y = -0.005x + 6.9132	1005	0.005	9.98	84**

Light texture + poultry residues	Y = -0.0048x + 6.5855	724	0.0048	10.21	84**

*Significance level 0.05 **Significance level 0.01

3.5. Selection of the best equation to describe zinc adsorption

When selecting the best equation to describe zinc adsorption, researchers often rely on statistical criteria (such as R^2), while also considering the consistency of the equation constants with soil chemical behavior and their ability to provide clear interpretive indicators (such as maximum adsorption capacity and bonding energy), and ensuring that they do not contradict model assumptions when applied to soil–solution systems. Consequently, preference cannot be made based on R2 alone, but rather, based on the statistical fit, reasonable constants and interpretability as one package.

Using the R2 values of the adsorption constants in the laboratory experiment, Table (6) above shows that the Langmuir equation was the best fit, with a range of 0.88 to 0.98 (mean 0.94), then the Freundlich equation was best fit (0.86 to 0.97; mean 0.92), and the Dubinin-Radushkevich (D-R) equation (0.85 to 0.97; mean 0.91). Accordingly, the equations can be ranked in describing zinc adsorption (overall statistical fit) as: Langmuir > Freundlich > Dubinin–Radushkevich, which is broadly consistent with findings reported for calcareous soils.

The superiority of Langmuir in calcareous soils is logical because zinc adsorption often tends to show saturation at higher concentrations due to a limited number of high-activity sites on clay and carbonate surfaces. The Langmuir equation represents this behavior clearly because it provides the maximum adsorption capacity and a constant related to bonding energy, facilitating comparison between treatments near saturation. In contrast, although Freundlich did not exceed Langmuir in R^2, it provides a better description of heterogeneity and adsorption intensity through the n parameter , The D–R equation is interpretively complementary because it focuses on adsorption energy (E) to determine the nature of zinc adsorption; E values ranged from 8.74 to 11.81 kJ mol^{-1}, which falls within 8–16 kJ mol^{-1} and is often interpreted as chemical ion-exchange, i.e., substitution of Zn^{2+} from the equilibrium solution for other cations held on negatively charged surfaces of clay and organic matter[20].

Table (6) Coefficient of determination (R^2) for the equations used to describe zinc adsorption

Soil treatments	Langmuir (R^2, %)	Freundlich (R^2, %)	D–R (R^2, %)
Heavy texture + cattle residues	96	96	96
Heavy texture + sheep residues	97	96	96

Heavy texture + poultry residues	98	94	93
Light texture + cattle residues	88	89	88
Light texture + sheep residues	90	86	84
Light texture + poultry residues	91	87	84

4. Conclusion

Zinc behavior in the studied alluvial soils was governed jointly by soil texture and organic amendment type. The heavy-textured soil generally retained more Zn and released less Zn during desorption than the light-textured soil, reflecting the effect of higher clay content and CEC. Among the tested models, Langmuir provided the best overall description of Zn adsorption, while D-R energy values (8.74-11.81 kJ mol^{-1}) indicated that ion exchange was the dominant mechanism. In various treatments, sheep manure increased adsorption capacity but poultry manure was likely to decrease Zn retention, especially in the light-textured soil. These results imply that the management of Zn in the calcareous alluvial soils must consider the texture as well as the source of amendment. Since this was done in controlled laboratory conditions future studies are advised to confirm the results in field conditions and give details of the amendment application in future clearly to enhance reproducibility.

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