Zinc Sorption in Calcareous Soils as Influenced by Biochar and Humic Acid: A Langmuir and Freundlich Isotherm Study

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Abstract

The study was conducted to evaluate the sorption behavior of zinc in three calcareous soils with different CaCO3 contents for three different samples amended separately with biochar and humic acid. Modeling of the adsorption properties was quantified by Langmuir and Freundlich models. Surface soil samples from Penjwen (low-Calcareous), Kani-Panka (medium-Calcareous), and Tasluja (High-Calcareous) soils were collected. Different doses of Biochar (0, 1 and 2%) and humic acid (0, 1 and 2%) were applied alone. The sorption of Zn on the material was measured using the batch equilibrium method and the experimental results were best fitted to the Langmuir and Freundlich models successfully described zinc sorption to estimate the values of Q max, KL, RL, MBC, KF, n and R^2. to the value of R2 is greater in freunlich Model than Langmuir Model, the Freundlich the highest average zinc sorption percentage was recorded in Soil (S1) treated with 1% biochar (54.22%), indicating a clear improvement in the soil's ability to retain zinc. In contrast, the lowest average sorption percentage (26.86%) was observed in Soil S3 treated with 2% humic acid, reflecting a reduction in sorption efficiency under this treatment. Soil (S2) exhibited intermediate values, with the highest average sorption percentage reaching 43.16% under 1% biochar. Overall, biochar treatments were more effective in increasing zinc sorption than humic acid treatments, particularly at the 1% application rate, whereas increasing the amendment rate to 2% did not consistently improve sorption efficiency. This indicates that the response depends on both the type of amendment and the calcium carbonate content of the soil.

Keywords: Zinc Sorption, Biochar, Humic acid, Calcareous soils, Langmuir, Freundlich isotherm.

Introduction:

Zinc (Zn) is a micronutrient essential for a variety of physiological and biochemical processes that take place in plants, such as enzyme activation, chlorophyll biosynthesis, protein synthesis, carbohydrate metabolism, and hormone regulation. Zinc deficiency is one of the most common micronutrient deficiencies in agricultural soils, especially in calcareous soils in arid and semi-arid regions. The high calcium carbonate ($CaCO_3$) content and alkaline pH of these soils significantly decrease Zn availability since dissolved Zn^{+2} is strongly sorbed on soil particles[1].

Calcium carbonate content, clay minerals, soil organic matter, cation exchange capacity (CEC), and pH are some of the soil properties that influence the sorption of zinc. These factors control the number and affinity of adsorption sites, and thus the fate, mobility and plant availability of applied zinc fertilizers. The knowledge of the sorption behavior of zinc is essential for better

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management of zinc micronutrients and efficiency of fertilizer utilization in calcareous soils[2].

Recently, there has been a lot of interest in the use of organic amendments in a sustainable way to enhance soil fertility and help manage soil nutrient dynamics. Biochar has a unique porous structure, a big specific surface area and many oxygen functional groups that can enhance the soil cation exchange capacity and offer more sorption sites for metal ions. Similarly, humic acid has a large number of carboxyl and phenolic functional groups, which can surface complex with Zn^{+2} and in turn affect its retention in soil depending on soil properties and rate of application[3].

Equilibrium isotherm models are often used to assess the adsorption behavior of Zn. Two of these equations, the Langmuir and Freundlich equations, are predominantly used and are quantitative in nature, giving information on adsorption capacity and adsorption intensity. Parameters calculated from these models, such as Qmax, KL, RL, MBC, KF, n and R^2 can be used to compare zinc sorption capacity among different soils and determine the effect of amendments. The experimental sorption data for the three soils studied under various biochar and humic acid treatments were used to report the adsorption constant[4].

While many studies have focused on the behavior of zinc in agricultural soils, there is limited knowledge about the effects of biochar and humic acid on zinc sorption, in calcareous soils with varying calcium carbonate levels, under environmental conditions of the Kurdistan Region of Iraq. Thus, this study was intended to test the sorption of zinc in three calcareous soils amended in isolation with biochar and humic acid, and with varying carbonate contents. Langmuir and Freundlich models were used to analyze the sorption data, in order to identify the characteristics of the sorption and to find the best amendment to improve the zinc retention in calcareous soils. While several studies have examined the sorption of Zn in agricultural soils, little information is available on comparative effects of biochar and humic acid on the sorption of Zn in calcareous soils with varying CC concentration. Furthermore, only a few studies have assessed these amendments individually with both Langmuir and Freundlich isotherm models under environmental conditions of the Kurdistan Region of Iraq[5].

Furthermore, the effect of $CaCO_3$[3] on the adsorption behavior of zinc and the effectiveness of organic amendments to increase the retention of zinc is not well understood. Hence, this study aims to address these knowledge gaps by comparing the capacity of three calcareous soils, each amended with a zinc sorbent (biochar or humic acid), to better understand the sorption behavior of zinc in calcareous soils, which is relevant for the better management of zinc fertilizer in calcareous soils.

Materials and Methods

Soil Sampling and Characterization The soil samples were collected from three surface soil samples (0-30 cm) from the agricultural fields of Penjwen (S1), Kani-Panka (S2) and Tasluja (S3), Sulaymaniyah Province, Kurdistan Region, Iraq (table 1). The soils were of low, medium and high calcium carbonate (CaCO3) content, respectively. Soil samples were collected and air-dried, lightly crushed, and passed through a 2 mm sieve before being kept for laboratory analyses and adsorption experiments. Selected soils were characterized for some selected physical and chemical properties According to[6].

Experimental Design

A laboratory zinc adsorption experiment was conducted using a completely randomized factorial design. Three calcareous soils

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differing in calcium carbonate content were used: Penjwen (S1, low CaCO3), Kani-Panka (S2, medium CaCO3), and Tasluja (S3, high CaCO3). Two organic amendments, biochar and humic acid, were evaluated separately. Each amendment was applied at three rates: 0%, 1%, and 2% (w/w). The treatments were independently applied to each of the three soil samples, and each treatment was replicated three times.

Following amendment application, zinc sorption was evaluated using the batch equilibrium technique with zinc sulfate (ZnSO4) solutions at different initial zinc concentrations. After equilibration, the suspensions were shaken under controlled laboratory conditions, centrifuged, and filtered, and the equilibrium zinc concentration was determined using Atomic Absorption Spectrophotometry (AAS).

Table (1) GPS coordinates of soil sample study sites

Samples	Plase	GPS	% $CaCO_3$
S_1	Penjwen	35˚40'9.50988"N 45˚11'19.572"E	1.5
S_2	Kani panka	35˚23'27.6"N 45˚44'33.76212"E	23
S_3	Tasluga	35˚39'10.98612"N 45˚57'39.77388"E	52

Zinc Sorption Experiment

The batch equilibrium technique was used to determine zinc sorption in the three studied soils. Zinc sulfate ($ZnSO_4$) solutions with different initial Zn concentrations were added to the soil samples. The soil–solution suspensions were equilibrated and shaken under controlled laboratory conditions. After equilibration, the suspensions were centrifuged and filtered, and the equilibrium Zn concentration in the filtrate was determined using Atomic Absorption Spectrophotometry (AAS).

The amount of zinc adsorbed by the soil was calculated using the following equation:

$Zn^{+2} = ((Ci-Cf)/W)\times V$ ……..(1)

Where:
qe = amount of adsorbed Zn (mg kg^{-1}).
C0 = initial Zn concentration (mg L^{-1})
Ce = equilibrium Zn concentration (mg L^{-1})
V = volume of the solution (L)
W = weight of the soil (kg)
These variables and units correspond to those reported in the experimental methodology of the file. Polyphenol Freundlich and Langmuir equations[7] were applied to fit the data from isotherm studies.

qe = Kf Ce 1/n ……(2)
qe= (KL qm Ce)/(1+ KL Ce)…….(3)
Where:
qe = is the amount of adsorbed metal concentration at equilibrium(mg kg^{-1})
Ce = is the concentration of the metal in solution at equilibrium (mg L^{-1}).
qm = is the maximum adsorption of metal on soil (mg Kg^{-1}), KL (L Kg^{-1}), KF (L Kg^{-1})..(5)
1/n are constants.
For every stage of the experiment, the distribution of each metal between sorbent and solution following equilibration was expressed in terms of the distribution coefficient (Kd) [8].

The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor (RL) that can be defined by the following relationship[9]

RL= 1/1+KL Ci …..(6)
Where:
Ci = is the initial concentration (mg/L).
Kl= is the Langmuir equilibrium constant (L/mg).
The value of the separation parameter RL provides important information about the

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nature of adsorption. The value of RL indicated the type of Langmuir isotherm to be irreversible (R=0), favorable (0<R,<1), linear (R=1), or unfavorable (R>1). It can be explained apparently that when kL > 0, the sorption system is favorable[10].

Statistical Analysis

The experimental data were subjected to analysis of variance (ANOVA) to determine the significance of differences among treatments. Treatment means were compared using Duncan's Multiple Range Test (DMRT) at the 5% probability level ($P \leq 0.05$). In addition, Regression analysis was performed to assess how well the experimental zinc sorption data fitted the Langmuir and Freundlich adsorption isotherm models.

Results and Discussion

Effect of Biochar on Zinc Sorption

Table (3) shows that biochar application led to a significant impact on zinc sorption in all the soils studied, as shown by the adsorption data. The magnitude of the response was dependent on soil properties, especially on calcium carbonate content. The Langmuir maximum adsorption capacity (Qmax) of the soil increased from 3.8 mg kg-1 for the control treatment to 4.2 and 4.4 mg kg-1 after 1 and 2% biochar application, respectively, in the low calcareous soil (S1). Similarly, the Langmuir adsorption constant (KL) was not significantly different between treatments, and the calculated RL values were all below 1, suggesting good adsorption of zinc under all experimental conditions. This indicates an increase in the number of effective adsorption sites and the soil's ability to retain zinc ions. This is due to an increase in the specific surface area of biochar, an increase in functional groups (COOH - OH), the formation of complexes between zinc and organic matter, and an increase in (CEC)[11].

Effect of Humic Acid on Zinc Sorption

Table (3) shows that Zinc sorption was also affected by humic acid, but the effect varied in different soils. The application of 1 and 2 % humic acid resulted in an increase of Qmax from 3.8 to 4.4 and 4.5 mg kg^{-1} respectively in Penjwen soil (S1). This increase suggests that humic acid contained other functional groups which could bind Zn^{2+} ions by surface complexation[4].

However, the Qmax of the high calcareous soil (S3) decreased gradually with 1% humic acid application and again with 2% humic acid application, both of which were 4.4 and 4.1 mg kg-1, respectively, compared to the control. This decrease could be a competition between soluble organic compounds and soil adsorption surfaces in highly calcareous soils[5].

These observations were also confirmed by the Freundlich parameters, as the KF and n values, showed that it has a favorable adsorption behavior in all treatments, and the two types of adsorption mechanisms, namely homogeneous and heterogeneous, were responsible for zinc retention in the studied soils[12].

Comparison of Langmuir and Freundlich Isotherm Models

Table (3) shows the Langmuir and Freundlich isotherm models were able to describe the adsorption data acquired in this study well. The coefficient of determination (R^2) values, however, showed that each model was suitable for each soil type and amendment treatment. Adsorptive sorption in the studied soils could be relatively well described by the Langmuir model indicating the existence of energetically similar finite adsorption sites for the sorption of zinc. The

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high Qmax values after application of biochar and humic acid indicates that the amendments were indeed effective in increasing the adsorption capacity of calcareous soils, further supporting the results obtained.

The Freundlich model also gave good agreement with the experimental data. Calculated KF values showed difference in adsorption affinity of zinc among the three soils and the adsorption intensity parameter (n) showed that the adsorption was favorable for all the treatments. The combination of good fits with acceptable Langmuir and Freundlich equations implies that the soils used for this study contained both homogenous and heterogenous surface reactions during zinc adsorption.

Comparisons of the three soils indicated that adsorption behavior was correlated well with calcium carbonate content. Under the control treatment, high-calcareous soil (S3) had the highest adsorption capacity, while biochar application resulted in the highest adsorption capacity for low and medium-calcareous soils (S1 and S2). Humic acid, on the other hand, yielded inconsistent results as affected by soil properties and application level. The results obtained show that the inherent physicochemical characteristics of soil play an important role on the efficiency of zinc retention in soil with the use of organic amendments.

The results of this study give useful information for predicting the behaviour of zinc in calcareous soils and for choosing suitable soil amendments to increase the efficiency of zinc fertilizers. The observed differences among soils emphasize the importance of considering soil properties when developing micronutrient management strategies[4][5][12][13].

(RL) coefficient in choosing the adsorption preference

(RL) is defined as a constant value that predicts the adsorption preference for the maximum regulatory capacity of ionic elements. This constant was derived from the Langmuir equation to predict the nature of adsorption, whether the adsorption regime is favored or not. Adsorption can be favored when it is as follows ($0<RL<1$), not favored when ($RL>1$), irreversible ($RL = 0$), and linear ($RL = 1$) (Chen et al. 2008). The (RL) values of the studied soils varied between (0.0100) and (0.00122), as shown in Table (10). The decrease in RL values and their approach to zero confirms that zinc adsorption has become very strong, which is a known characteristic in calcareous soils rich in calcium carbonate. It indicates a high affinity of soil surfaces for zinc adsorption and an increase in the strength of its association with adsorption sites, which is consistent with what was mentioned by[1][4]

Conclusions

The present study has shown that the sorption of zinc was different in three calcareous soils due to differences in the content of calcium carbonate and soil properties. The use of biochar in general led to an increase in the sorption of zinc and an increase in maximum sorption capacity, especially in the low and medium calcareous soils. The other variable affected by humic acid was zinc sorption, which was affected by both the rate of application and the soil type.

The Langmuir and Freundlich isotherm models were found to be suitable for the adsorption of zinc in all the soils. The adsorption parameters (Qmax, KL, RL, MBC, KL, n, and R^2) suggested good zinc adsorption and showed both models were appropriate for the evaluation of zinc retention in calcareous soils.

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Table 2: Some soil chemical and physical properties

Soile propertes	**Units of measurement**	**S1**	**S2**	**S3**
pH		8.36	7.86	7.69
EC	$ds.m^{-1}$	0.63	0.62	0.98
$CaCO_3$	gm ,kg^{-1}	1.5	23	52
OM		18.00	29.80	38.70
Avalable Zinc	(ppm) gm ,kg^{-1}	0.84	1.12	1.58
Dessolved Zinc		0.90	0.68	0.32
Exchangeable Zinc		1.98	1.84	0.62
Total Zinc		42.65	33.78	28.98
Na^{+1}	Mmol.L^{-1}	0.23	0.33	0.42
K^{+1}		0.15	0.08	0.11
Ca^{+2}		1.02	1.14	1.20
Mg^{+2}		1.76	2.32	1.06
Cl^{-1}		1.39	0.88	1.20
HCO_3^{-1}		1.32	2.98	1.25
SO_4^{-2}		10.11	0.86	16.30
CEC	Cmol(+).kg	22.40	36.50	33.97

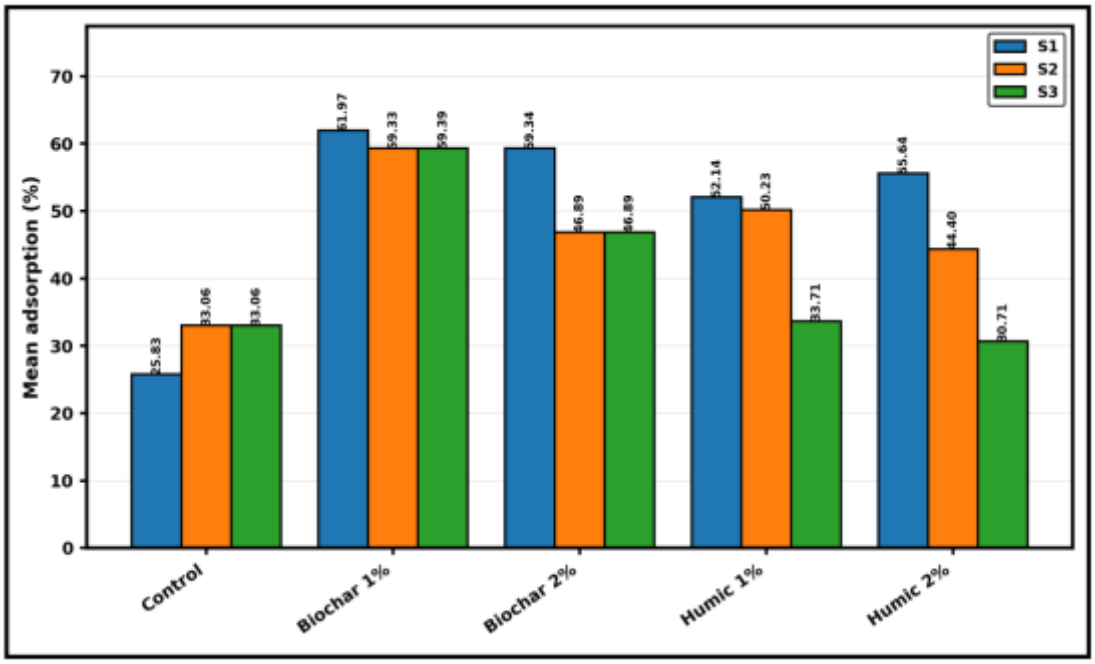
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Table (3) : Langmuir and Freundlich Isotherm constants

Sand	gm kg^{-1}	278.10	148.60
silt		370.50	279.50
clay		351.41	571.90
texture		Clay loam	Clay

Samples	Treatment	Langumuir isotherm constants					Freundlich isotherm constants		
		R_L	MBC	R^2	K_L l mg^{-1}	Q_{max} mg kg^{-1}	R^2	K_F l kg^{-1}	n
Penjwen low $CaCO_3$ S_1	control	0.0122	0.0503	0.841	0.01217	3.8	0.9267	1.0193	0.872
	1% Biochar	0.0109	0.0456	0.9161	0.01087	4.2	0.9259	0.7534	0.8552
	2%Biochar	0.0104	0.0452	0.9076	0.01039	4.4	0.9439	0.7871	0.8838
	Control	0.0122	0.0462	0.841	0.01217	3.8	0.9267	1.0193	0.872
	1%Humic	0.0105	0.0460	0.9278	0.01046	4.4	0.939	0.771	0.8395
Kani panka meadeam $CaCO_3$ S_2	2%Humic	0.0102	0.0459	0.9368	0.01021	4.5	0.949	0.7873	0.8227
	control	0.0108	0.0454	0.9136	0.01082	4.2	0.9372	1.0049	0.9788
	1% Biochar	0.0100	0.0460	0.0921	0.01000	4.6	0.9487	0.8286	0.8432
	2%Biochar	0.0100	0.0460	0.9255	0.01000	4.6	0.9737	0.8252	0.791
	Control	0.0100	0.0454	0.9136	0.01217	4.2	0.9136	1.0049	0.9788
Tasluja High $CaCO_3$ S_3	1%Humic	0.0100	0.0459	0.982	0.00998	4.6	0.968	0.8045	0.7895
	2%Humic	0.0102	0.0456	0.9257	0.01015	4.5	0.978	0.8423	0.7818
	control	0.0100	0.0460	0.9133	0.01001	4.6	0.9471	0.9384	1.0191
	1% Biochar	0.0100	0.0460	0.8908	0.01002	4.6	0.9819	0.875	0.8411
	2%Biochar	0.0111	0.0459	0.8677	0.01114	4.1	0.9873	0.9365	0.7999

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Fiffer (1): Avrage Zinc Sorption across different Soils & treatment

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