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RESEARCH PAPER

Comparison between Different Models for the Zn Adsorption in Some Calcareous Soils of Erbil Governate

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A B S T R A C T:

This study was investigated to evaluate Zn adsorption using some adsorption isotherms in calcareous soils in Erbil governorate. Soil samples were taken from twelve different agricultural sites Duplicate 1 gm of soil samples were adjusted at 298° K with 50 ml of 0.01 M CaCl2.7H2O solution containing a series of Zn concentrations (0, 2, 4, 8, 16, 32, and 64) mg kg-1 using ZnSO4.7H2O. In each soil sample the amount of Zn adsorbed was calculated by using Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Harken-Juren isotherms. The results relieved that the Langmuir model was best fitted to the Zn adsorption in the studies soils, as it had the higher R2 and lowest S.E which were 0.923 and 0.002 at 298 ˚K respectively. While the lowest value of R2 (0.749 at 298 °K) was recorded by Harken-Juren equation. Based on the results, the effectiveness of the models in description of Zn sorption were arranged as follow: Langmuir > Freundlich > Dubinin-Radushkevich > Temkin > Harken-Juren. The lowest binding energy and maximum adsorption was recorded by Langmuir model which was regarded as the best model.

Keywords: Zinc, Adsorption models, Calcareous soil, Binding energy, Maximum adsorption.
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1. INTRODUCTION :

In the earth's crust, zinc (Zn) 24th most well-known trace element and it's considered an essential trace element. Zinc can be observed in various concentrations in soil, the common zinc background level in most soils around the world is between 10 to 100 mg Zn in kg of soil (Alloway, 2013). By definition, zinc is one of the trace element groups and is considered an essential heavy metal that has a density of 7.134 g cm^{-3}, zinc is important for human health along with healthy plant metabolism and growth (Noulas et al., 2018).

Adsorption of zinc is a process that controls the availability of the zinc in soil solution, zinc ions are physically or chemically bonded or adsorbed to the solid surface of soil particles known as an adsorbent.

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However, even in solutions at higher pH values with non-sulfide, an observable quantity of zinc could remain dissolved while it contains common anions, moreover, redox potential doesn't affect its solubility (Jones et al., 1972). Also (Al-Niaimi et al., 2017) observed that the temperature can affect the adsorption of micronutrients ion as the adsorption rise along with increasing temperatures which may be explained by an increase in ion mobility.

Kurdistan is well known for calcareous soil enrichment and increasing $CaCO_3$ concentrations causes a decrease in zinc availability (Mam-Rasul, 2019). Calcareous soils encourage mineral precipitation as smithsonite ($ZnCO_3$) (Sheikh-Abdullah, 2019). The distribution equilibrium of zinc between each soil fraction is highly influenced by soil chemical properties like pH, cation exchange capacity (CEC), and dissolved organic carbon (DOC) (Khoshgoftarmanesh et al., 2018). (Alloway, 2009) ; (de Santiago-Martín et al., 2014).

Zinc is a necessary element for plants which is required in a small quantity and as Erbil soil is calcareous soil and have alkali pH which reduces the availability of Zn in agricultural soil. It's important to investigate the amount of Zn adsorbed in those soils. The aim of this research was to determine the phenomena of Zn adsorption through the adsorption isotherms in some calcareous soils and identify the best fitting isotherm models.

2. MATERIALS AND METHODS

2.1.Soil Sampling:

Soil samples were taken from the soil surface (0-30) cm depth at 12 locations in Erbil Governorate in Kurdistan as shown in table 1.

Table 1. Location of samples

No.	Location of samples	GPS reading	
1	Haji Omaran	36.668799 N	45.037678 E
2	Zinwe	36.688168 N	45.016458 E
3	Khalan	36.692403 N	44.987657 E
4	Kawrgosk	36.348541 N	43.803001 E
5	Tandura	35.927212 N	43.930942 E
6	Dolabakra	35.939121 N	44.06852 E
7	Ainkawa	36.265774 N	43.995282 E
8	Gajnikan	36.344693 N	43.998605 E
9	Qurshaklo	35.927212 N	43.930942 E
10	Barzan	36.935945 N	44.035458 E
11	Shanadar	36.810442 N	44.235001 E
12	Mergasor	36.864096 N	44.261824 E

2.2 Laboratory analysis: Soil Physico-Chemical Analysis

The physical and chemical analysis were done for each soil sample, as shown in table 2, the physical analysis included determination of the soil bulk density (g cm^{-3}) which was measured according to (Klute et al., 1986) procedure. Particle size distribution (g kg^{-1}) was done by using hydrometer method as described by (Klute, 1986). The chemical analysis included: The electrical conductivity of the soil solution was measured using the EC-meter model 2052 WRH (Laboratory, 1954). Total Calcium Carbonates (T-$CaCO_3$) which was determined by using phenolphthalein indicator as described by (Richards, 1954). Active calcium carbonate (A-$CaCO_3$) was determined according to (Loeppert and Suarez, 1996). Cation exchange capacity was determined according to (Polemio and Rhoades, 1977). Soil pH was calculated using HANNA pH-meter, model EDGE procedure of (Boyd and Tucker, 1992). sodium and potassium was determined according to (Hesse, 1971). Calcium carbonate, carbonate and bicarbonate and SO_4^{-2} was determined according to (Jackson, 1958). The available phosphorus was extracted by Olsen's method as described by (Estefan, 2013).

2.3 Batch equilibrium of Zn adsorption

Available Zn was extracted by using (0.005 M DTPA+ 0.01 M $CaCl_2$ + 0.1 M TEA) method, and then extractable Zn was measured by using atomic adsorption spectrophotometer. The adsorption process was studied by equilibrating a duplicate, 1 gm of each soil samples was hold in plastic bottles and equilibrated with 50 ml of 0.01 M $CaCl_2.7H_2O$ solution containing a series of Zn concentrations (0, 2, 4, 8, 16, 32, and 64) mg kg^{-1} of $ZnSO_4.7H_2O$. The suspensions were shacked for 10 minutes at 340 RPM and kept at (298° K) temperatures for 24 hours, for each soil sample, same procedure was followed. After 24 hours the soil suspensions were filtered through Whatman filter paper No.42 and two drops of toluene were added to each suspension to inhibit the microbial activity. And then Zn in each solution was determined by using atomic adsorption spectrophotometer.

2.4 Adsorption isotherm

Adsorption isotherm have been used to gain information on the nature and intensity of the interaction between both soil constituents and added soluble Zn. The models [Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Harken-Juren] were used to evaluate Zn adsorption.

3 RESULTS

3.1. Physical and Chemical Properties of the Studied Soils

The physical and chemical properties of 12 agricultural soils samples were shown in table 2, the studied soils varied in texture classes ranging from (clay to silty loam). Maximum amount of clay content was found in Shanadar (41.115) and minimum was found in Gajnikan (8.615). Maximum amount of sand was found in

Table 2. Some selected chemical and physical properties of the studied soils

NO	Location	CEC Cmol.Kg^{-1}	pH	$CaCO_3$ %	Active $CaCO_3$ %	Active & total $CaCO_3$ ratio	EC $dS.m^{-1}$	P mg kg^{-1}	K^+ mg kg^{-1}	Ca^{2+} mg kg^{-1}	Na^+ mg kg^{-1}	Cl^- mg kg^{-1}	HCO_3^- mg kg^{-1}	SO_4^{2-} mg kg^{-1}	PSD g kg^{-1}			Textures	Bulk density g cm^{-3}	Mg^{2+} mg kg^{-1}
															Clay	Sand	Silt			
1	Haji- Omran	8.01	7.99	14.63	3.5	0.239	0.323	4.21	3.56	72	18.57	56.60	219.60	598.38	108.65	479.85	411.5	L	1.19	52.80
2	Zinwe	31.73	7.39	3.16	2.10	0.665	0.293	5.8	58.77	80	16.71	56.80	244.00	1048.19	245.15	468.35	286.5	L	0.98	76.80
3	Khalan	37.51	7.03	2.77	1.30	0.469	0.387	6.4	44.52	72	16.71	99.40	268.40	1165.49	320.15	413.85	266	C L	0.84	115.20
4	Kawrgosk	12.64	7.37	22.54	14.05	0.623	0.607	4.22	26.71	336	59.42	113.60	244.00	2134.52	120.15	463.85	416	L	1.21	67.20
5	Tandura	24.56	7.62	22.93	10.80	0.471	0.391	4.32	44.52	72	33.43	92.30	195.20	1215.52	361.15	93.35	545.5	SCL	1.02	110.40
6	Dolabakra	21.45	7.58	24.91	14.30	0.574	0.363	4.6	17.81	104	35.28	113.60	146.40	797.12	261.15	222.85	516	SiL	1.07	52.80
7	Ainkawa	23.00	7.77	22.14	11.95	0.540	0.353	4.81	16.03	128	29.71	92.30	195.20	674.77	311.15	172.85	516	SiCL	1.25	19.20
8	Gajnikan	14.32	7.39	21.35	12.05	0.564	0.814	5.56	32.06	208	33.43	92.30	170.80	1565.15	86.15	97.85	816	Si	0.94	76.80
9	Qurshaklo	23.27	7.43	18.58	13.10	0.705	0.629	4.79	60.55	192	55.71	127.80	170.80	1707.61	311.15	297.85	391	CL	1.02	96.00
10	Barzan	20.54	7.68	13.44	6.55	0.487	0.408	5.85	7.12	72	14.86	99.40	195.20	724.71	186.15	322.85	491	L	1.03	72.00
11	shanadar	29.22	7.44	1.58	0.65	0.411	0.605	4.72	8.90	64	22.28	120.70	146.40	702.73	411.15	306.85	282	C	0.96	76.80
12	Margasor	24.35	7.57	2.37	1.70	0.717	0.589	4.66	17.81	96	22.28	134.90	170.80	762.43	311.15	331.85	357	CL	0.96	67.20

Haji-Omaran (47.985) while Tandura had the lowest amount of sand (9.335). Highest amount of silt was found in Gajnikan (81.6) and lowest was in Khalan (26.6). The results showed that Ankawa has the highest bulk density (1.25) and Khalan has lowest bulk density (0.84).

Soil pH values were ranged between (7.03 - 7.99) which indicates that all soils are slightly to moderately alkaline. EC value was ranged between (0.293 – 0.814) dS m^{-1}, the results indicated that soil samples were non saline soil. Maximum amount of (EC) was found in Gajnikan (0.814 $dS.m^{-1}$) and minimum was found in Zinwe (0.293 $dS.m^{-1}$). Total Calcium carbonate was ranged between (1.58 - 24.91 %) the lowest values was found in Shanadar location and the highest value was found Dolabakra in soil. This indicates that all soils were calcareous soil. Active Calcium carbonate was ranged between (0.65 - 14.30 %). The lowest value was found in Shanadar location and the highest value was found in Dolabakra soil. Highest value of (CEC and available Phosphorus) were found in Khalan (37.51 Cmol kg^{-1}, 6.4 mg kg^{-1}) respectively, and minimum was in Haji-Omaran (8.01 Cmol kg^{-1}, 4.21 mg kg^{-1}) respectively. Highest amount of (Potassium) was found in Qurshaklo (60.55 mg kg^{-1}) and lowest in Haji-Omaran (3.56 mg kg^{-1}). (Ca, Na, SO_4) were highest in Kawrgosk (336, 59.42, 2134.52 mg kg^{-1}) while lowest (Ca) was in Shanadar (64 mg kg^{-1}), lowest (Na) was in Barzan (14.86 mg kg^{-1}) and lowest amount of (SO_4) was found in Haji Omaran (598.38 mg kg^{-1}). Mergasor represented the highest amount of (Cl) which was (134.90 mg kg^{-1}) while Haji-Omaran represented the minimum amount of it (56.60 mg kg^{-1}). Highest amount of (HCO_3) was found in Khalan (268.40 mg kg^{-1}) and minimum amount in Dolabakra and Shanadar (146.40 mg kg^{-1}). Highest (Mg) was in Khalan (115.20 mg kg^{-1}) while lowest was in Ankawa (19.20 mg kg^{-1}).

3.2. Zinc Adsorption in the Studied Soils

Maximum adsorption rate and the adsorption binding energy are the most basic technique to describe adsorption characterization of Zn. To be useful in evaluating experimental results, the adsorption equation should not only provide a reasonable fitting to the sorption isotherm data, but it should also provide equation parameters with physiochemical significant values (Holford, 1982). The data in figure 1 indicated how the fitting straight line between 1/(x/m) and 1/C was used to derive the Langmuir constants for Zn adsorption. One of the advantages of the Langmuir equation was its ability to calculate the adsorption maximum and binding energy from the regression line of equation. Table 3 shows that the values of (K_L) which is the constant related to bonding energy of Zn to the soil, were ranged between (84 – 4) at 298˚K in the studied soils, the maximum value was found in Gajnikan, whereas the minimum value was found in Khalan and Haji-Oamaran. While the values of (q_{max}) which is the measuring of soil adsorption capacity were ranged between (2000 – 476) at 298˚K in the studied soils, the maximum value was found in Barzan, and the minimum value was found in Gajnikan.

Freundlich adsorption isotherm was drawn by plotting a straight line between log x/m, and log C at temperature 298˚K in the studied soils, as shown in figure 2. Table 3 shows that the values of (K_F) which is the Freundlich constant related to sorption capacity were ranged between (1107 – 617) at 298˚K in the studied soils, the maximum value was found in Haji-Omaran, whereas the minimum value was found in Khalan. In Freundlich equation, (n) values represent the soil's ability to hold cations and the stability of forming complexes between cations and soil constituents (Buchter et al., 1989). The results shown in Table 3 indicate that the range of (n) values for Zn in the studied soils were ranged between (2.532 – 1.980) at 298˚ K, the maximum value was found in Gajnikan, whereas the minimum value was found in Khalan.

Temkin adsorption isotherm was drawn by plotting a straight line between qe (adsorbed amount of Zn) and ln Co (equilibrium concentration) at temperature 298˚ K in the studied soils, as shown in figure 3. Also as shown in Table 3 the values of maximum binding energy (K_T) which is the binding of equilibrium constant conforming to the maximum binding energy in were ranged between (122 – 16.962) at 298˚ K in the studied soils, the maximum value was found in Mergasor, whereas the minimum value was found in Khalan. But the values of the heat of adsorption (constant B) were ranged between (450 – 278) at 298˚ K in the studied soils, the maximum value was found in Haji-Omaran, while the minimum value was found in Tandura.

Dubinin-Radushkevich adsorption isotherm was drawn by plotting a straight line between ln qe and ε^2 (Polanyi sorption potential) at temperature 298 ° K in the studied soils, as shown in figure 4. Table 3 shows the Dubinin-Radushkevich equation constants, the highest values of (K_D) were ranged between (-0.015) and (-0.038) at 298 ° K in the studied soils. The maximum values were found in both Tandura and Gajnikan, and the minimum value was found in Haji-Omaran. The values of (qm) which is the maximum adsorption capacity (mg g^{-1}) were ranged between (1957 – 873) at 298 ° K in the studied soils. The highest value was found in Haji-Omaran, while the lowest value was found in Zinwe. This may be due to the higher pH value in Haji-Omaran soil comparing to other locations.

Harken-Juren adsorption isotherm was drawn by plotting a straight line between $1/q^2$ and log Ce,as shown in figure 5. Table 3 shows the Harken-Juren equation costants, the values of (A_H) were ranged between (0.054 – 0.033) at 298° K in the studied soils. The maximum value was found in Haji-Omaran, and the minimum value was found in Khalan. The values of (B_H) were ranged between (0.611 – 0.290) at 298° K in the studied soils. The maximum value was found in Haji-Omaran, while the minimum value was found in Mergasor.

3.3 A comparison Between Different Equations Used for the Interpretation of Zn adsorption Data

The figures (1, 2, 3, 4, and 5) were drawn according to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harken-juren equations. The fitting of these models is estimated by coefficient of determination value (R^2) of their regression lines, and the standard error (S.E).

The results in figure (5) and table (4) shows that the Harken-Juren equation does not correspond well with the Zn sorption data as determined by the R^2 with a mean value of 0.749, as well as the same results in figure (3) and table (4) shows that the Temkin equation does not fit well with the Zn sorption data as estimated by the R^2 with a mean value of 0.967 at 298 ° K temperature, in comparison to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations as shown in table (4). The Dubinin-Radushkevich equation fits more to the Zn adsorption than the Temkin and Harken-Juren equations as shown in figure (4) and table (4) as determined by the R^2 with a mean value of 0.836 at 298° K temperature.

As shown in figure (2) and table (4) the Freundlich Equation fits better to the Zn adsorption than the Temkin and Dubinin-Radushkevich equations.

The Langmuir equation has a good coincide with the Zn sorption data in comparison to the other equations depending on the R^2 and standard error. The results in figure (1) and table (4) indicated that the mean values of the R^2 and standard error (SE) were 0.923 and 0.002 at 298° K temperature. Based on the results the effectiveness of these equations in description of Zn sorption is arranged as follows:

Langmuir>Freundlich>Dubinin-Radushkevich>Temkin> Harken-Juren

4. DISCUSSION

4.1 Soil physicochemical properties

The highest CEC value in Khalan may be due to the high amount of clay content which causes increase in surface area and thus provide more exchangeable sites in soil as reported by (Ramos et al., 2018). While the lowest value of CEC Haji-Omaran may be attributed to low amount of clay content as well as high value of bulk density since increase in bulk density causes decrease in total pore space in coarse textured soils compared to finer textured soils (NRCS, 2008).

4.2 Zinc Adsorption in the Studied Soils

Applied Langmuir equation, the result in Langmuir equation shows that Khalan had the lowest K_L value among other locations, this may be attributed to the site had the lowest pH value which increased the mobility of Zn (Alloway, 2013). While according to the results of the Freundlich equation, Haji-Omaran had a highest capacity for Zn adsorption than the other locations due to highest (K_F) value and lowest (n) value. This could be caused by the high pH values in Haji-Omaran soil, high value of pH in soil solution causes increase in the adsorption process of Zn (Mattias et al., 2010).The maximum pH value indicates a low amount of H^+ in the soil solution, and the competitive process between H^+ and cations on the binding site will reduce, resulting in cation adsorption in the solution (Abat et al., 2012).

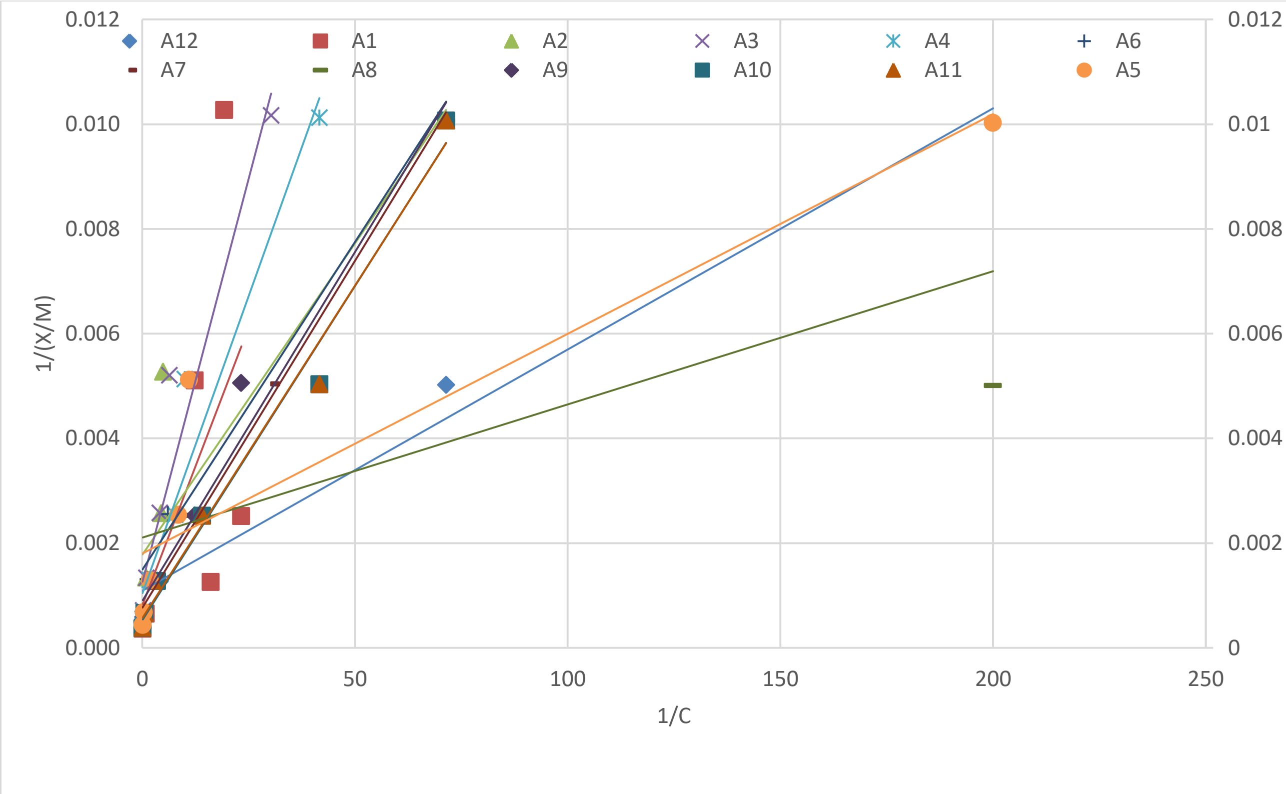

Figure1. Linear form of Zn adsorption in the studied soils according to Langmuir equation at 298 °K

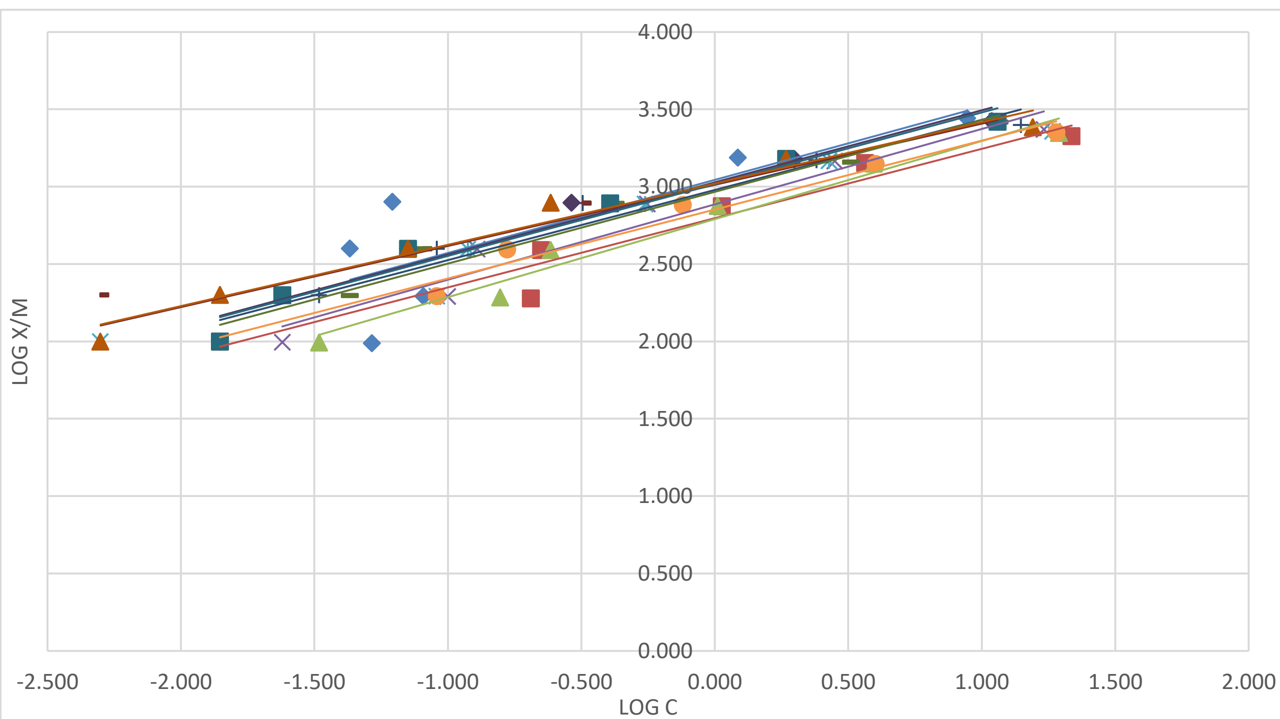

Figure 2. Linear form of Zn adsorption in the studied soils according to Freundlich equation at 298 °K

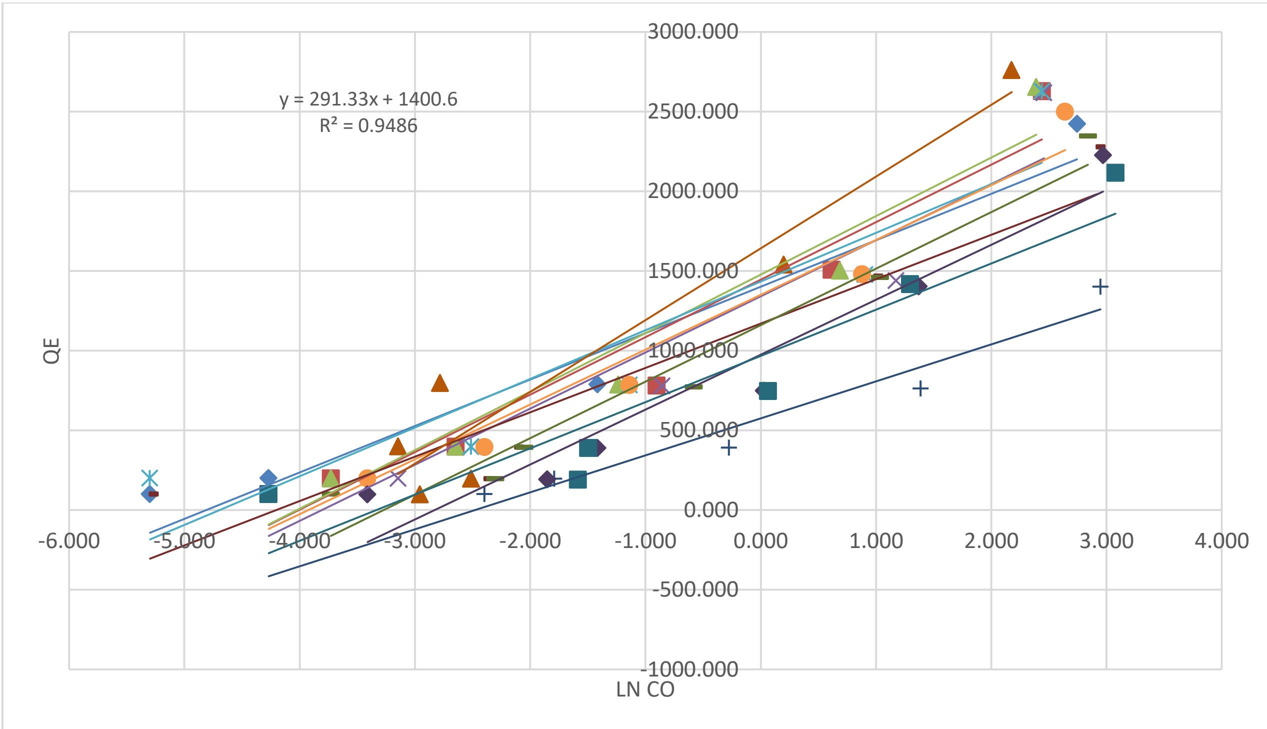

Figure 3. Linear form of Zn adsorption in the studied soils according to Temkin equation at 298 °K

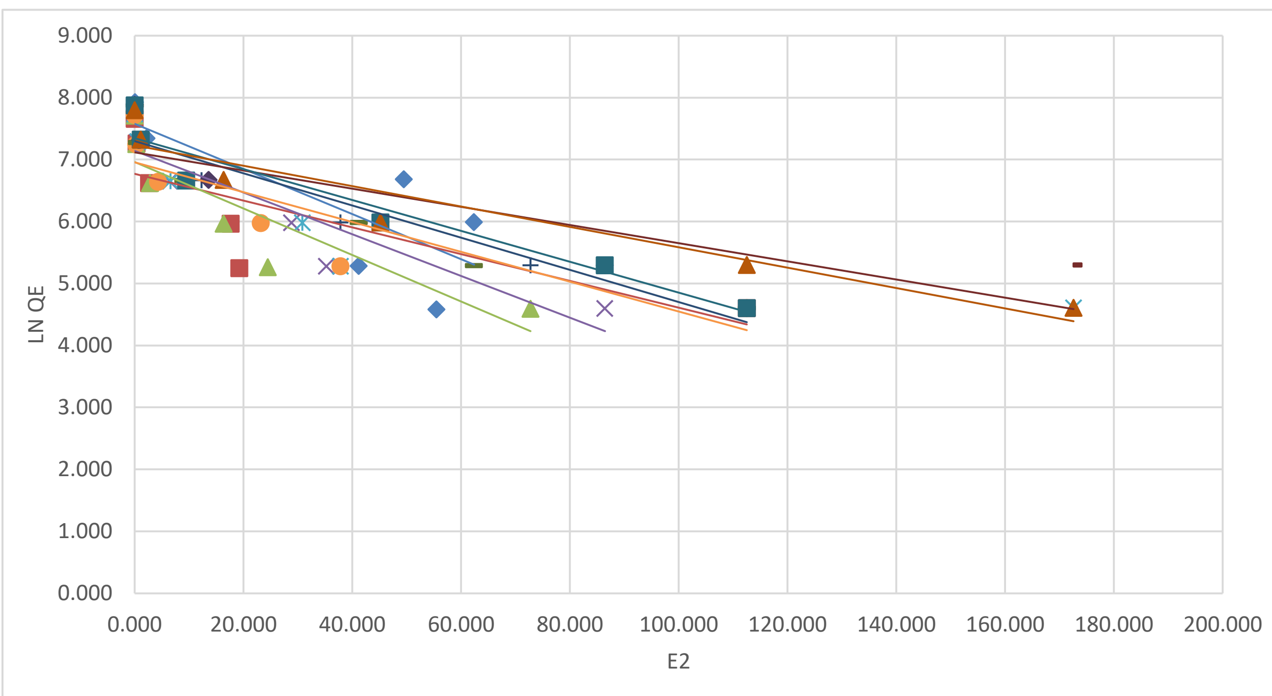

Figure 4. Linear form of Zn adsorption in the studied soils according to Dubinin-Radushkevich equation at 298 °K

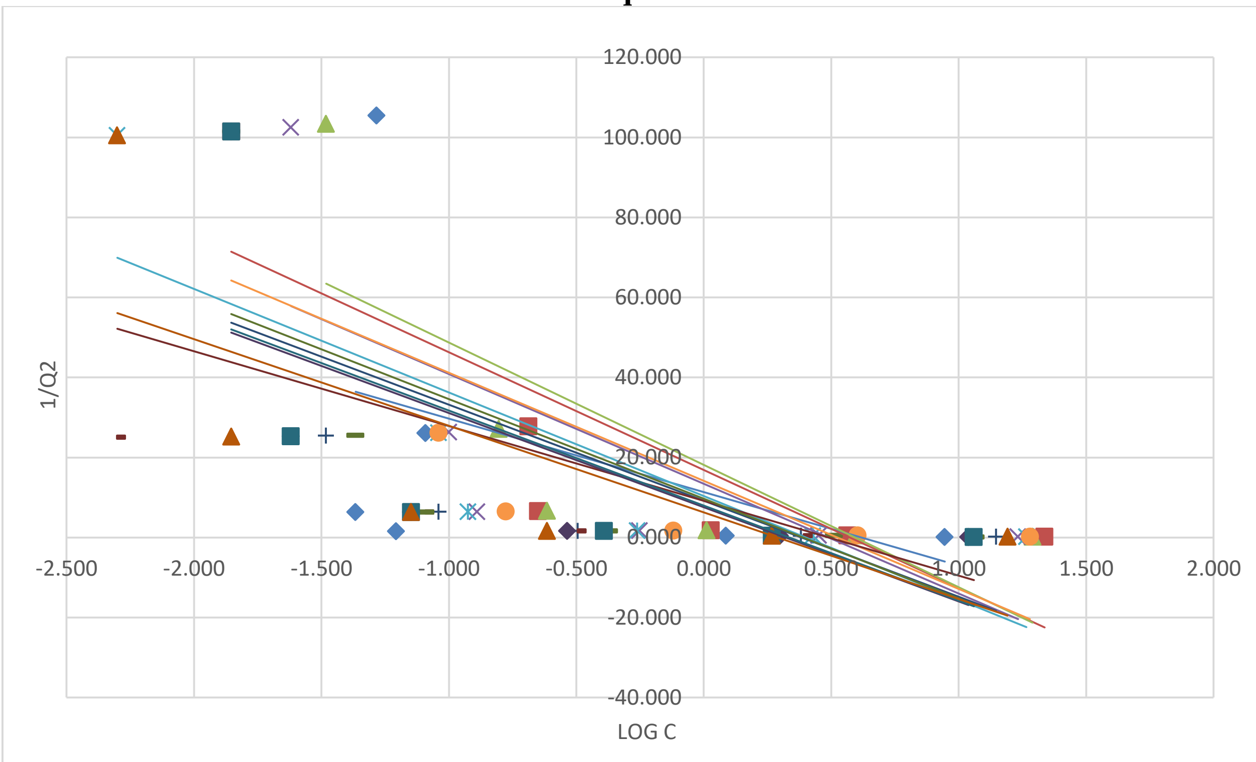

Figure 5. Linear form of Zn adsorption in the studied soils according to Harken-Juren equation at 298 °K

Table 3. Parameters of Zn adsorption for Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Harken-Juren at tempreture 298 ̊K

Locations	Langmuir		Freundlich		Temkin		Dubinin-Radushkevich		Harken-Jura	
	K_L	q_{max}	K_F	n	K_T	B	K	qm	A_H	B_H
Haji-Omaran	4	1250	1107	2.114	38.283	450	-0.036	1957	0.054	0.611
Zinwe	18	556	627	2.232	27.994	290	-0.022	873	0.034	0.573
Khalan	4	833	617	1.980	16.962	344	-0.038	1054	0.033	0.599
Kawrgosk	5	1000	769	2.053	26.417	354	-0.034	1261	0.036	0.483
Tandura	43	556	811	2.451	66.820	278	-0.015	966	0.038	0.394
Dolabakra	15	667	711	2.242	34.295	303	-0.024	1049	0.037	0.524
Ainkawa	8	1250	951	2.203	50.754	344	-0.026	1479	0.042	0.387
Gajnikan	84	476	1028	2.532	109	305	-0.015	1228	0.053	0.485
Qurshaklo	9	1111	925	2.160	45.015	352	-0.026	1431	0.040	0.389
Barzan	5	2000	1067	2.146	55.980	367	-0.025	1610	0.042	0.317
Shanadar	6	1667	1038	2.155	54.982	361	-0.025	1548	0.042	0.333
Margasor	24	909	1047	2.525	122	291	-0.016	1382	0.046	0.290
Mean=	**19**	**1022**	**891.5**	**2.233**	**54.106**	**337**	**-0.025**	**1320**	**0.041**	**0.449**

Table 4. Coefficient of determination (R^2) and standart error (S.E) for Langmuir,Freundlich, Temkin, Dubinin-Radushkevich, Harken-Juren at tempreture 298° K

Locations	Langmuir		Freundlich		Temkin		Dubinin-Radushkevich		Harken-Jura	
	R^2	S.E	R^2	S.E	R^2	S.E	R^2	S.E	R^2	S.E
Haji-Omaran	0.894	0.002	0.731	0.224	0.925	183.817	0.620	0.515	0.563	16.902
Zinwe	0.828	0.002	0.945	0.209	0.985	323.514	0.666	0.481	0.774	16.243
Khalan	0.925	0.002	0.968	0.211	0.982	337.593	0.813	0.486	0.778	16.554
Kawrgosk	0.941	0.002	0.945	0.214	0.989	356.333	0.875	0.493	0.751	16.410
Tandura	0.827	0.002	0.955	0.212	0.983	347.330	0.713	0.489	0.746	16.096
Dolabakra	0.895	0.002	0.977	0.210	0.977	339.773	0.813	-0.010	0.702	0.015
Ainkawa	0.995	0.002	0.959	0.217	0.990	378.311	0.968	0.499	0.717	16.244
Gajnikan	0.851	0.002	0.990	0.219	0.899	396.090	0.722	0.504	0.864	0.022
Qurshaklo	0.977	0.002	0.968	0.218	0.975	393.038	0.953	0.502	0.810	16.244
Barzan	0.985	0.002	0.982	0.220	0.978	401.142	0.980	0.506	0.747	16.246
Shanadar	0.984	0.002	0.964	0.219	0.954	397.637	0.970	0.505	0.788	16.245
Margasor	0.974	0.002	0.970	0.216	0.969	368.91	0.942	0.496	0.753	16.097
Mean=	**0.923**	**0.002**	**0.946**	**0.216**	**0.967**	**351.958**	**0.836**	**0.455**	**0.749**	**12.776**

4.3 Comparison Between Different Equations Used for the Interpretation of Zn adsorption Data

Generally, the Langmuir equation have a good coincide with the Zn sorption data in comparison to the Freundlich, Dubinin-Radushkevich, Temkin and Harken-Juren equations. These results are agreement similar with earlier report by which showed that the Langmuir equation fits the Zn adsorption data better that the other equations when added $ZnSO_4.7H_2O$ to 12 soils from different parts of Erbil governorate.

5. CONCLUSION

The Langmuir equation has a good coincide with Zn Adsorption data due to its highest R^2 (confident of determination) and lowest standard error values compared to the other models. In comparison between the studied soils, Barzan soil had a high capability of Zn adsorption due to its high value of (q_{max}) and low value of (K_L). On the other hand, Freundlich equation best fitted the Zn Adsorption data as determined by its high value of R^2 and low value of standard error. In comparison between the studied soils, Haji-Omaran had a high capability of Zn adsorption due to its high value of (K_F) and low value of (n).

Based on the results the effectiveness of these equations in description of Zn sorption is arranged as follows:

Langmuir>Freundlich>Dubinin-Radushkevich>Temkin> Harken-Juren

The main physicochemical properties which affected the Zn adsorption was the pH. Our results showed that increase in pH caused increase in the adsorption of Zn.

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