Mono and competitive adsorption of Zn, Cu and Mn in different calcareous soils

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ABSTRACT

Soil carbonate is considered an effective adsorbent to trace element retention. Many researchers have studied the preferential adsorption of those heavy metals on calcareous soils. In 2021- 2022, an experiment was conducted in agriculture college laboratories to assess the mono and competitive of three trace elements (Cu, Zn, Mn) on three calcareous soils that differ in their $CaCO_3$ content. Calcareous representative soil samples were collected from different Nineveh governorate and north Iraq locations. The adsorption experiment was carried out using the batch method by equilibrating 2.5 gm soil with 25 ml of a solution containing concentrations of (1.5, 10, 20, 30, 40, 50, 60 and 70 mg. L^{-1}) of all traced elements in the same concentrations. Sorption isotherms were characterized using linear Langmuir and Freundlich equations. Results showed huge differences in sorptions capacities and other studied parameters. All studied soils showed a high maximum adsorption capacity Q_{max} and strength binding for Cu than Zn and Mn. On the basis of Q_{max} and distribution coefficient values (Σkd) for each studied soil and element, the selectivity sequence was as follows Cu>Zn >Mn. Gibbs free energy (-ΔG) values were decreased as the sorption capacity decreased too. In mono and ternary adsorption system, Langmuir isotherms were of H-type whereas Freundlich isotherms were of C-type. The soil properties such as $CaCO_3$, pH, Clay, C.E.C, and O.M were significantly related to trace elements adsorption.

Keywords: Qmax, Σkd, Adsorption capacity, Adsorption tendency, Co-existence.

Adsorção mono e competitiva de Zn, Cu e Mn em diferentes solos calcários

RESUMO

O carbonato do solo é considerado um adsorvente eficaz para retenção de oligoelementos. Muitos pesquisadores estudaram a adsorção preferencial desses metais pesados em solos calcários. Em 2021-2022, foi realizada um experimento em laboratório na faculdade de agricultura para avaliar a mono e a competitividade de três oligoelementos (Cu, Zn, Mn) em três solos calcários que diferem no seu teor de carbonato de cálcio ($CaCO_3$). Amostras representativas de solo calcário foram coletadas de diferentes províncias de Nínive e locais do norte do Iraque. O experimento de adsorção foi realizado pelo método descontínuo, equilibrando 2,5 g de solo com 25 ml de uma solução contendo concentrações de (1,5, 10, 20, 30, 40, 50, 60 e 70 mg. L^{-1}) de todos os oligoelementos nas mesmas concentrações. As isotermas de sorção foram caracterizadas usando equações lineares de Langmuir e Freundlich. Os resultados mostraram enormes diferenças nas capacidades de sorção e outros parâmetros estudados. Todos os solos estudados apresentaram maior capacidade máxima de adsorção Qmax e força de ligação para Cu do que para Zn e Mn. Com base nos valores de Qmax e coeficiente de distribuição (Σkd) para cada solo e elemento estudado, a sequência de seletividade foi Cu>Zn>Mn. Os valores de energia livre de Gibbs diminuíram à medida que a capacidade de sorção também diminuiu. Nos sistemas de adsorção mono e ternário, as isotermas de Langmuir eram do tipo H, enquanto as isotermas de Freundlich eram do tipo C. As propriedades do solo como $CaCO_3$, pH, Argila, C.E.C e O.M foram significativamente relacionadas à adsorção de oligoelementos.

Palavras-chave: Qmax, Σkd, Capacidade de adsorção, Tendência de adsorção, Coexistência.

1. Introduction

Calcareous soils are widely spread in arid and semi-arid regions, including Iraq, and form about (15-35%) of the total Iraqi area (Fadhal and Ismaeal, 2023; Noori and Ismaeal, 2023). Calcium carbonate in calcareous soils dominantly controlled soil chemical characteristics such as high pH value, cation exchange capacity, and soluble calcium (Mesquita et al., 2000; Noori and Ismaeal, 2023; Fadhal and Ismaeal, 2023). Increasing pH value expose trace element to several reactions on carbonate active surfaces like adsorption retention, precipitation, and complexation and leads to reducing those elements' bioavailability in soil solution (Osman et al., 1980; Al-Jumaily et al., 2022; Qadir and Al-Obaidi, 2024).

Zinc, Copper, and Manganese are important nutrient elements for plant growth and at the same time have more affinity to adsorb and interact with amorphous oxide, organic acid's functional groups, and on carbonate surfaces leading to deficiency symptoms on plant tissues (Dandanmozd and Hosseinpur, 2010; Obaid et al., 2023). The Knowledge of the kinetics of adsorption-desorption reactions is essential to understanding the interaction of the elements with soil properties and their fate in the soil profile (Yang et al., 2021; Al-Janabi et al., 2023).

Adsorption-desorption studies can be well documented by computing different adsorption isotherms (Rahman et al., 2021). The Langmuir and Freundlich equations and calculation of distribution coefficient (Kd) are useful tools for comparing the adsorption capacity of different soils or materials for any metal when measured under the same conditions (Iyengar and Raja, 1983). Industrial and municipal wastes are contributed directly with major polluted sources which usually generate a solution of multi-components (Gomes et al., 2001).

In this situation several heavy metals cations will compete with each other on soil components consequently, competitive adsorption or mobilization by the soil becomes of major importance in determining heavy metals' fate in soil (Brümmer et al., 1986). Competitive adsorption of heavy metals is key to predicting the mobility or retention of any metal in polluted Soil using the Kd parameter (Zhang and Zheng, 2007). Many researchers have found that the co-existence of heavy metals reduces their adsorption tendency on the solid phase (Serrano et al., 2005; Li et al., 2013; Gui et al., 2006).

Soil carbonate is an effective material for heavy metal retention because it has a higher negative surface charge with a wide surface area and functional carbonate groups, which have high affinity to adsorb heavy metals with different mechanisms. Several studies have been conducted on the preferential adsorption of heavy metals in calcareous soils (Jalali and Moharrami, 2007). The objective of this study is to evaluate the effect of carbonate levels in calcareous soils on the adsorption sequence of three heavy metals Cu, Mn, and Zn.

2. Material and Methods

Three samples of representative surface soil were collected at depth (0-20 cm) from different locations in Mosul, Nineveh Governorate, Iraq (Table 1, Figure 1) for the years 2021-2022. Samples were dried, crushed, and passed through a 2 mm sieve, then the chemical and physical analyses were conducted. Soils belong to Haplocalcids, Vertic Haplo Calcids (Soil Survey Staff., 1999). Chemical and physical characteristics were determined according to methods of soil analysis (Page et al.,1982; Al-Qattan and Al-Khafagi, 2023).

Organic matter was determined by dichromate oxidation and the cation exchange capacity was obtained by treating the soil with neutral 1N NH4OAC and 1N NH4OANa. Electrical Conductivity (EC) and soil (pH) was measured using 1:2.5 soil-to-water suspension. Soil textures were determined according to Bouyoucos (1962). The absorption experiment was carried out in a plastic stoppered tube with a 50 ml volume. The sorption isotherms were obtained for each soil sample by equilibrating 2.5 g soil with 25 ml of a solution containing concentrations of (1.5, 10, 20, 30, 40, 50,60, and 70 mg L^{-1}) of all trace elements in the same concentrations.

The solutions were prepared by using sulfate salts $CuSO_4 . 5 H_2O$, and $ZnSO_4 . H_2O$, and $MnSO_4 . H_2O$ of these metals in a background of 0.01 M of $CaCl_2$. Soil suspensions were shaken for 2 hours and allowed to dynamically equilibrate for 24 hours at room temperature (25°C). The trace element concentration in the equilibration solution was measured by a GBC 933plus atomic absorption device. Sorbed metal by soil was calculated with the following equation 1 (Dandanmozd and Hosseinpur, 2010).

Table 1. The coordinates of the soil sampling locations in the study areas using GPS.

Locations of soils		E (Longitude)	N (Latitude)
1. North	Shiraykhan	43°24′35.01″E	36°42′33.35″N
2. East	Alqasr	43°13′44.91″E	36°13′39.95″N
3. West	Hamidat	43°26′55.11″E	36°12′59.16″N

$$M =((Ci\text{-}Cf)/W)\times V \qquad (1)$$

Where:

M = is the concentration of adsorbed metal (mg kg^{-1}).

Ci = is the initial concentration of metal in equilibrated solution (mg L^{-1}).

V = is the solution volume ml.

W = is the weight of the soil (gm).

Cf= is the final concentration of metal in equilibrium solution after filtration (mg L^{-1}).
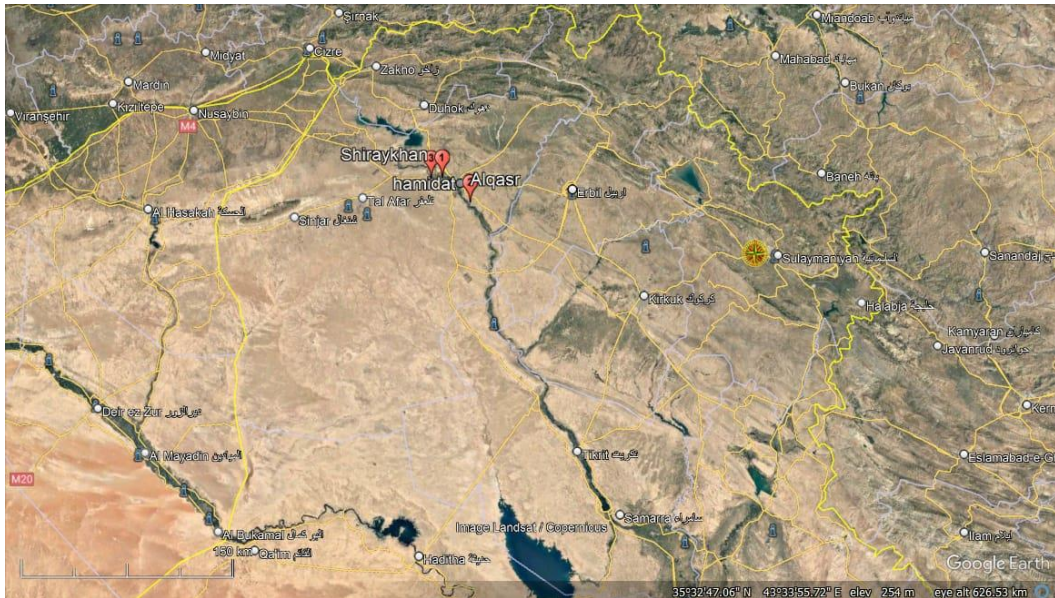
Figure 1. Soil sampling locations in Mosul, Iraq

Polyphenol Freundlich and Langmuir equations (Giles et al., 1974) were applied to fit the data from isotherm studies.

$$qe = Kf\ Ce\ 1/n \qquad (2)$$

$$qe = (K_L\ qm\ Ce)/(1+K_L\ Ce) \qquad (3)$$

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 ($L\ Kg^{-1}$).

$1/n$ 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) (Sprynskyy et al., 2011):

$$Kd = qe/Ce \qquad (4)$$

Gibbs' differential molar free energy for the specific adsorption was calculated using the following equation (Sprynskyy et al., 2011):

$$dG0 = -RT\ lnKd \qquad (5)$$

Where:

$dG0$ = is the thermodynamic adsorption potential (the Gibbs' differential molar free energy of adsorption, kJ/mol).

R = is the universal gas constant (8.314 J/mol K)

qm = is the maximum adsorption of metal on soil ($mg\ Kg^{-1}$), KL ($L\ Kg^{-1}$), KF ($L\ Kg^{-1}$)

T = is the adsorption absolute temperature (298 K).

Joint distribution coefficients (KdΣsp) were also calculated for each soil to establish the preference order of adsorption of the metals by the soil (Jalali and Moradi, 2013).

$$KdΣsp = ΣCMj,\ adsorption\ /\ ΣCMj,\ solution \qquad (6)$$

Where:

Cj = adsorption, Cj, solution are the concentrations of metal j in the soil ($mg\ kg^{-1}$) and in the solution ($mg\ l^{-1}$).

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 (Anirudhan and Radhakrishnan, 2008).

$$RL = 1/1+KL\ Ci \qquad (7)$$

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 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 (Chen et al., 2008). After collecting the data, the analysis was done with spss program for the t-test, and the data were divided into two groups. The test was done with probability levels of 0.01 and 0.05 to know if had significance or not (Johnson and Bhattacharyya, 2019).

3. Results and Discussion

Some physiochemical properties of selected soils are shown in Table 2. Calcareous soils were neutral, slightly alkaline, and low in organic matter and Ec values ranged from 0.73 – 1.23 ds m^{-1}. The calcium carbonate equivalent was 230.9, 306.2, 379.8 gm kg^{-1} for low, moderate, and high CaCO3 contents, respectively. C.E.C ranged from 20 -25 Cmolec Kg^{-1} and clay content varied from 135 - 492 gm kg^{-1}.

Table 2. Soil physicochemical properties of the studied soil (Mosul, Iraq)

PSD mg kg^{-1}				pH	EC$_e$ dS m^{-1} at 25°C	CEC cmol$_c$ kg^{-1}	O.M.	CaCO$_3$
Clay	Silt	Sand	Texture				mg kg^{-1}	
492	130	378	Clay	7.57	1.23	25	13.3	379.8
300	383	317	Clay loam	7.42	0.87	22	11.4	306.2
135	406	459	loam	7.31	0.73	20	10.5	230.9

Figure 2 shows Langmuir curves and Figure 3 shows Freundlich curves for a single Cu, Zn, and Mn adsorption system on calcareous soils with different CaCO3 content. A high R2 (0.80 - 0.97) or determination coefficient indicates that both equations adequately described heavy metals adsorption but the Langmuir equation was closer to experimental results than Freundlich by higher R2. All curves for both equations are somewhat vertical and indicated a positive relationship between initial concentrations and adsorbed metals on the soil solid phase.

Sorption is a term used to describe metals removed from solution by selling absorbent in different mechanisms like retention, occlusion reaction, and complexation (Serrano et al., 2005). Heavy metals adsorption is influenced by soil properties like pH, C.E.C, Organic matter, content, CaCO$_3$, Clay minerals, and heavy metals properties and concentrations (Srivastava et al., 2005) Langmuir and Freundlich parameter data are shown in Table 3.

Maximum adsorption capacity values of single adsorption (Q$_{max}$) for Zn, Cu, and Mn were (114.94, 628.93 and 126.58 µg.gm^{-1}) respectively. The differences in Qmax values between adsorbed metals are attributed to soil and metal properties. Mesquatta et al., (2000) mentioned that at the same pH value, more Cu than Zn was adsorbed due to differences in hydrolysis constant values for Cu and Zn compounds (Spark et al., 1995). Besides Cu and Zn could be adsorbed and precipitate as M(OH$^+$) (elements hydroxides) on carbonate surfaces. Mn Q$_{max}$ value was more than the results obtained in the present study, which could be attributed to the capacity of calcareous soils for Mn retention and Mn hydrolyzed species Mn(OH$^+$) which has a high affinity on carbonate surfaces (Karimian and Ahangar, 1998).

As calcium carbonate in studying soils increased, Qmax values for adsorbed metals were increased as well, except Cu in moderate CaCO$_3$ content. While in soils with high CaCO$_3$, Cu Q$_{max}$ (628.93 mg kg^{-1}) increased compared to that in moderate CaCO$_3$ content (175.44 mg kg^{-1}). Adsorption capacity for Zn (114.94 mg kg^{-1}) and Mn (and 126.58 mg kg^{-1}) decreased compared to that in the moderate CaCO$_3$ content, 156.25 and 138.89 mg kg^{-1}, respectively. This may be due to Ca^{+2} activity in soil solution which shifts absorbent zero-point charge (PHz) to the left and reduces soil metal selectivity coefficient due to the metal hydrated ion species and their ability to compete for Ca^{+2} adsorption on specific and non-specific sites (Baghenejad et al., 2016) .

Maximum buffering capacity (MBC) values of studied soils for Cu, Zn, and Mn ranged between (10.67, 12.59, 14.93 L gm^{-1}). The differences in the (MBC) quantity values among studied elements are pretend to the different values of Qmax and bonding energy for the studied elements because (MBC) in Langmiur equation obtained by the equation (Boning energy* Maximum adsorption),this parameter indicates the soil capacity resistance to the change in soil solution concentration (AL-jumaily et al., 2022). This parameter can be related to soil properties such as C.E.C , pH , clay mineral and metal concentration.

The parameter (RL) used to predict adsorption favorite in the batch adsorption process (Equation 7). This parameter is derived from the Lungmiar equation to predict the adsorption nature and whether the sorption system is favorable or unfavorable. Favorable (0 < RL <1), unfavorable (RL), irreversible (RL = 0), and liner (RL = 1) (Chen et al., 2008). The values of RL for Cu, Zn and Mn range between (0.437-0.895) for the studied calcareous soils with different CaCO3 content indicating that all metal adsorption is favorable.

The adsorption reaction of studied metals Cu, Zn, and Mn in a single sorption system with different calcareous soils is spontaneous and exothermic as values of (-dG°) are negative. From table (3) it is clear that adsorption (-dG°) for studying metals is between (-4.86 to -7.30 KJ.mole^{-1}). Adsorption standard free energy is related to the energy of adsorption bonding. So, the values of the free energy increased as Kd values increased. The range of (-dG°) values indicated that the type of adsorption is physical because physical adsorption is characterized by free energy values up to 40 KJ mole^{-1} (Sprynskyy et al., 2011).

The most important parameter in the Freundlich equation is the (K$_F$) distribution coefficient, which is defined as, adsorped metal quantity on the absorbent solid phase to the metal concentration in the liquid phase at equilibrium. This parameter may be considered as an affinity or strength bond of metal on a solid phase and can be used to predict the adsorption or the mobility of heavy metals (Morera et al., 2001).
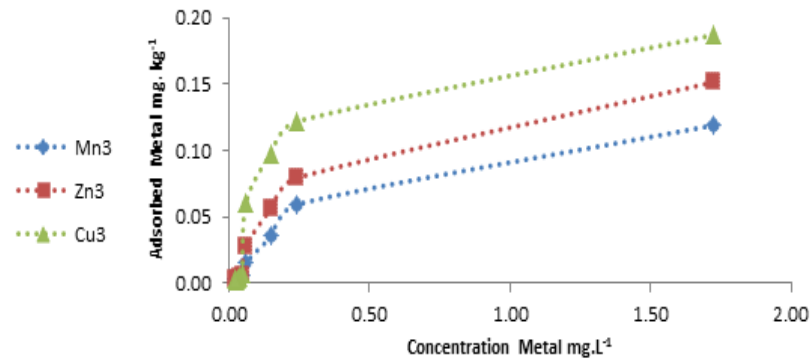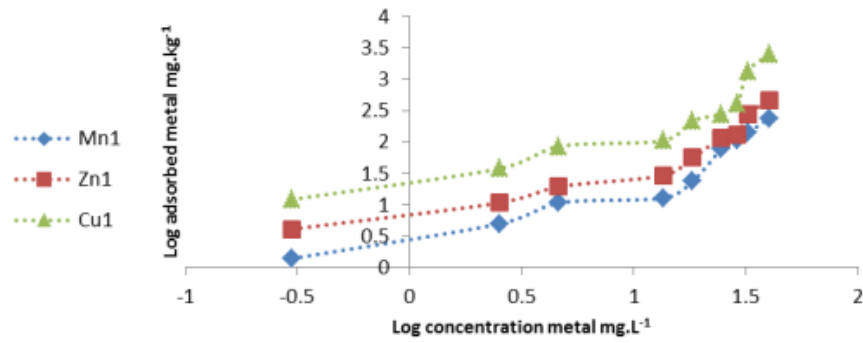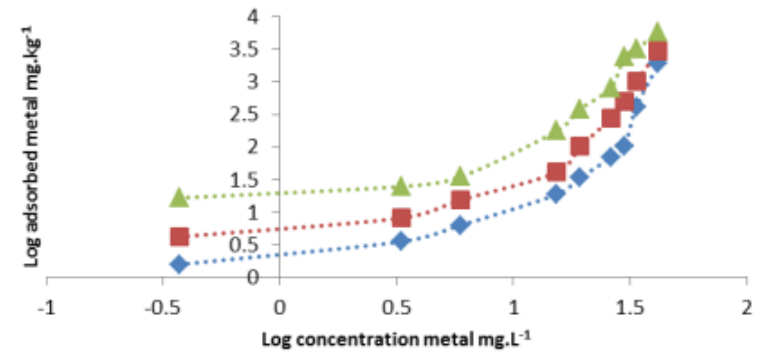
Soil2
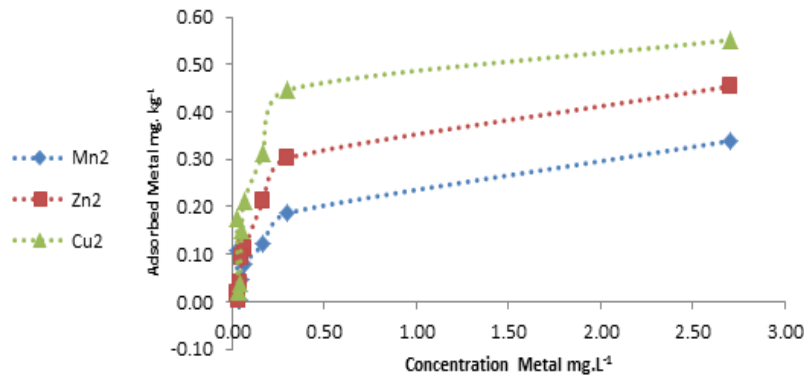
Soil1
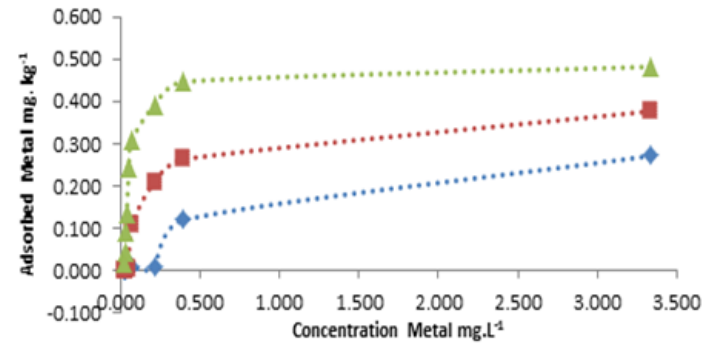
Soil3

Figure 2. Mono Sorption Isotherms Langmuir equation for Cu, Zn, and Mn (Mosul, Iraq)
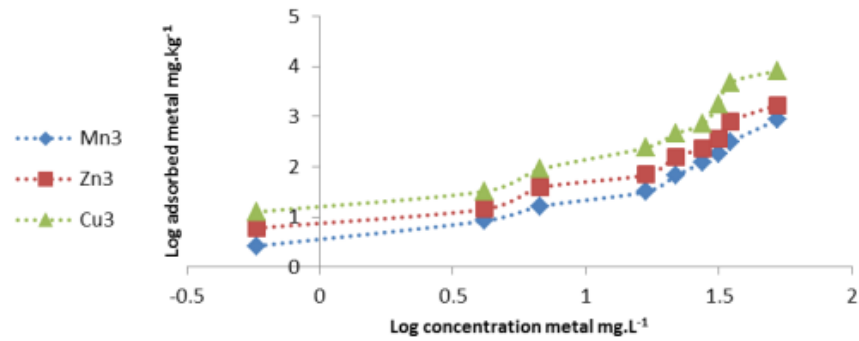
Figure 3. Mono Sorption Isotherms Freundlich equation for Cu, Zn, and Mn (Mosul, Iraq)

Table 3. Parameters of Langmuir, Freundlich, and linear isotherms for the sorption of mono elements of the studied soil (Mosul, Iraq)

Soil No.	Metal	Langmuir parameters						Freundlich parameters			Linear	
		Q_{max} mg kg^{-1}	K_L l mg^{-1}	R^2	MBC	R_L	Gibbs' free energy (kJ/mol)	n	K_F l kg^{-1}	R^2	Kd l kg^{-1}	R^2
1	Cu	628.93	0.0170	0.9793	10.67	0.895	-7.30	0.803	20.71	0.8428	19.04	0.689
	Zn	114.94	0.1096	0.9636	12.59	0.474	-6.94	0.798	23.99	0.8520	16.48	0.680
	Mn	126.58	0.1179	0.9387	14.93	0.470	-6.52	0.759	29.59	0.8393	13.95	0.730
2	Cu	175.44	0.1140	0.9342	20.00	0.473	-6.58	0.901	11.96	0.8511	14.27	0.643
	Zn	156.25	0.1506	0.9142	23.53	0.465	-6.01	0.871	14.24	0.8057	11.34	0.900
	Mn	138.89	0.2581	0.9014	35.84	0.443	-5.77	0.826	19.56	0.8303	10.28	0.945
3	Cu	185.19	0.0925	0.9457	17.12	0.478	-5.46	0.971	4.85	0.8551	9.06	0.970
	Zn	147.06	0.1447	0.9242	21.28	0.466	-5.24	0.954	7.58	0.8443	8.32	0.961
	Mn	123.46	0.2862	0.9130	35.34	0.437	-4.86	0.920	9.09	0.8351	7.12	0.979

Note. Q_{max}= Maximum adsorption capacity , K_L= Langmuir equilibrium constant , MBC= Maximum buffering capacity, K_F= Distribution Coefficient, Kd= Determination Coefficient.

The values of (K_F) for studying metals in different calcareous soils for a single adsorption system ranged from 4.85 - 29.59 L.gm^{-1} (Table 3). The highest (K_F) values for Cu, Zn, and Mn, were obtained in the highest CaCO$_3$, soil, while (K_F) values in other soils for the same metals were decreased as CaCO$_3$, decreased too. Besides the effect of soil factors on metals retention and mobility, such as the nature of clay minerals, organic matter, and pH, many researchers have reported that soil carbonates controlled the adsorption of heavy metals in calcareous soils (Compton and Pritchard, 1990; Maftoun et al., 2002; Elzinga and Reeder, 2002).

The Freundlich equation's slope indicates the adsorption tensity and the reciprocal of this parameter may be used as an adsorption favorite indicator (AL-Degs et al., 2006). A slight slope (n<1) indicates a favorable sorption process over the range of study concentrations, while a steep slope (n>1) indicates the favorite at high concentrations (Frimmel and Huber, 1996). For all studied metals in calcareous soils, (n) values are less than (1), which indicates favorable sorption at the range of experimental concentrations (Alghamdi and Alasmary, 2022).

Figure 4 shows the competitive adsorption of study metals. The interaction of metals in soil solution affects the sorption-absorption phenomenon of each other, leading them to be either fixed or mobile. Table 4 shows Langmuir isotherms study calcareous soils for Cu, Zn, and Mn in a triple ion solution system. Isotherms of these adsorption curves (Table 4) correspond soil affinity to the adsorbate metals at low concentrations which decrease at higher

concentrations of added metals due to the saturation of available sorption sites, (Shaheen et al., 2017; Sipos, 2021). Heavy metals adsorption data in soil systems are very important to know the fate of any element in soil solution and to understand the process of soil-heavy metals interaction to establish useful models which can be applied to risk evaluation (Vega et al., 2006; Yang et al., 2021).

Table 4 shows the values of Lungmiur parameters in the triple ion system for Cu, Zn, and Mn in different calcareous soils. The Qmax values in triple competitive adsorption ranged between (27.7-212.77 mg kg^{-1}) with the sequence order Mn < Zn < Cu for studying soils with different carbon content. The higher adsorption selectivity for copper over zinc with the soil adsorbing complex was reported by Flogeac et al., (2007), he mentioned that because the electric negativity of cu is more than Zn. The values of Qmax for Cu, Zn, and Mn in a triple competitive system are less than Qmax values in a mono adsorption system. Because heavy metal adsorption is depressed by metal competition (Mesquita, 1996). Morera et al., (2001), found that the co-existence of heavy metals reduces their adsorption tendency in the solid phase.

The values of (R_L) parameter in the Langmuir equation are very close and range between (0.495-0.437). These values indicated that the competition of studied metals has the same adsorption favorite in calcareous soils where R_L values ranged between (0< R_L<1) according to Chen et al., (2008). Adsorption-free energy of study metals in calcareous soils has been calculated using (Equ 5).

Soil1

Soil2

Soil3
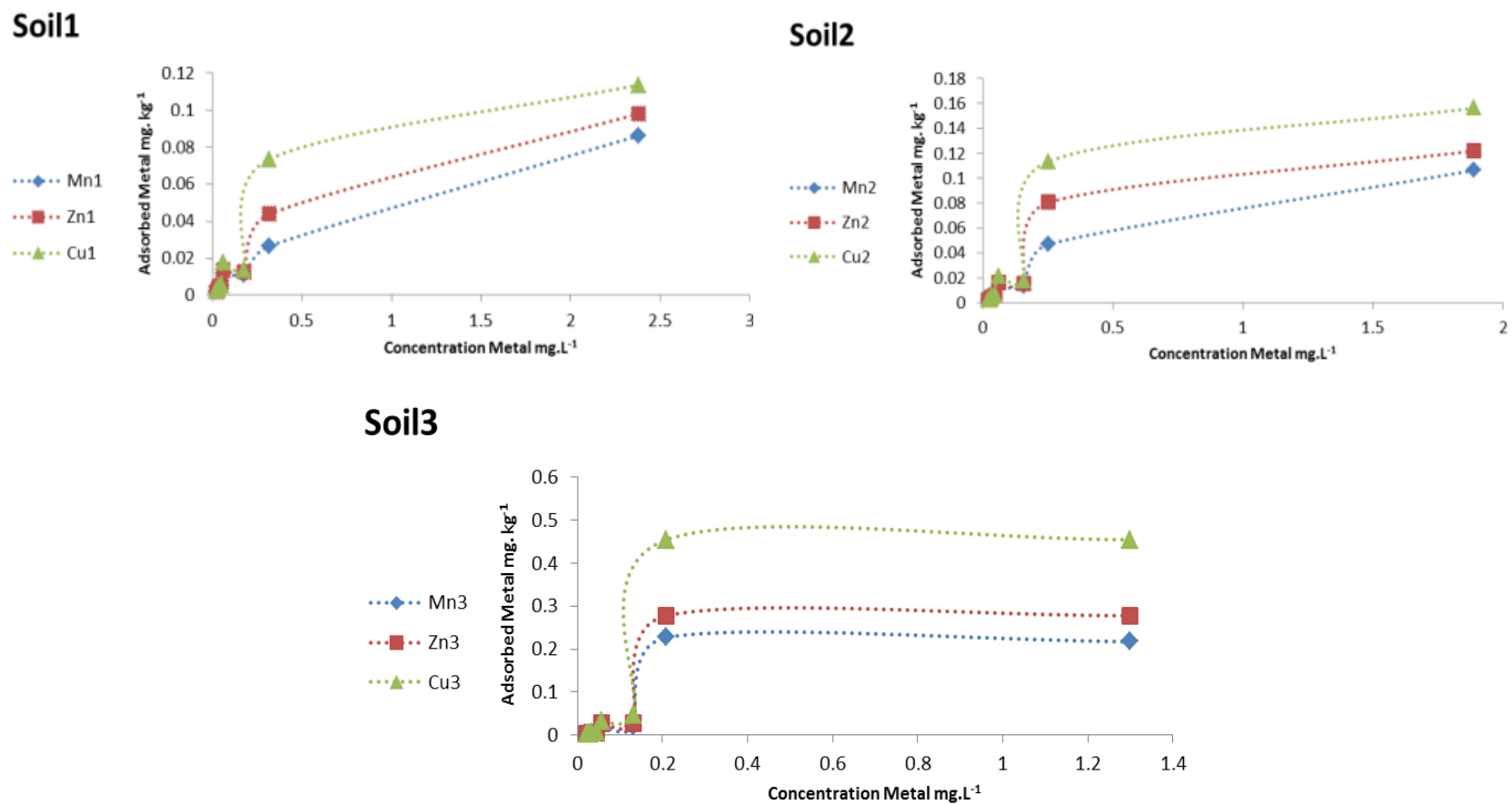
Figure 4. Competitive Sorption Isotherms Langmuir equation for Cu, Zn, and Mn(Mosul, Iraq).

Table 4. Parameters of Langmuir, Freundlich, and linear isotherms for the sorption of ternary elements of the studied soil (Mosul, Iraq) elements of the studied soil (Mosul, Iraq)

Soil No.	Metal	Langmuir parameters						Freundlich parameters		Linear parameters	
		Q_{max} mg kg^{-1}	K_L l mg^{-1}	R^2	MBC	R_L	Gibbs' free energy (kJ/mol)	n	K_F l kg^{-1}	R^2	Kd l kg^{-1}	R^2
1	Cu	212.77	0.0770	0.9696	16.39	0.482	6.37-	0.957	2.015	0.8622	13.09	0.726
	Zn	151.52	0.1429	0.9235	21.65	0.467	-5.90	0.889	1.956	0.8835	10.81	0.888
	Mn	100.00	0.2874	0.9087	28.74	0.437	-5.47	0.813	1.715	0.8493	9.10	0.898
2	Cu	163.13	0.0933	0.9164	15.22	0.495	-5.73	0.977	1.876	0.8631	10.09	0.912
	Zn	147.06	0.1331	0.9212	19.57	0.487	-5.31	0.936	1.836	0.8557	8.54	0.898
	Mn	125.79	0.2049	0.9432	25.77	0.474	-4.86	0.908	1.773	0.8703	7.11	0.853
3	Cu	46.73	0.1704	0.9250	7.96	0.480	-4.80	0.949	1.453	0.8231	6.95	0.665
	Zn	39.68	0.2355	0.9412	9.35	0.474	-4.39	0.934	1.406	0.8413	5.89	0.764
	Mn	27.70	0.3878	0.9537	10.74	0.463	-3.99	0.927	1.315	0.8521	5.00	0.871

Note. Q_{max}= Maximum adsorption capacity, K_L= Langmuir equilibrium constant , MBC= Maximum buffering capacity, K_F= Distribution Coefficient, Kd= Determination Coefficient.

As shown in Table (4) Gibbs free energy, of studying metal ranges between (-3.99 to -6.37 KJ.mole) and increased as Kd values increased within the physical adsorption limit. The values of the adsorption energy differ from one to another depending on metal affinity and soil $CaCO_3$ content in the following order Mn <Zn < Cu. The exothermic characteristics of the sorption process for Zn and Cu in a competitive system have been reported by Sprynskyy et al., (2011). The soil binding energy coefficient varied as $CaCO_3$ content varied between study soils and ranged from 0.077 - 0.3878 L gm^{-1}, and all studied soils showed a higher adsorption affinity for Cu than other metals.

Binding strength obtained from sorption isotherms should be considered only qualitatively because they are related to the change of free energy for different adsorption species. (Van Riemsdijk et al.,1986). According to Serrano et al., (2005), the high values of binding energy are related to specific metal adsorption on high-energy surfaces with low dissociation constants while the lower values of bending energy are related to metal sorption on low-energy surfaces with high dissociation constants. (Adhikari and Singh, 2003).

K_{Lb} in the Lungmiur equation represents maximum buffering capacity (MBC) according to the assumption, at low concentrations x/c = K_{Lb}, since x/c is the ratio of adsorbed metal to the metal concentration in equilibrium solution, it is termed the distribution coefficient and is designated by (Kd). (Iyengar and Raja, 1983; AL-jumaily et al., 2022). MBC values for the

Langmuir equation in the triple competitive system for Zn, Cu, and Mn in studying calcareous soils ranged between (7.96-28.74 L gm^{-1}). The variations in MBC values are related to the variation in Qmax and binding energy values. Mn has a higher MBC value due to the multiple ion species in natural soil pH, competing as monovalent cations or nucleated as $MnCO_3$ species on $CaCO_3$ surfaces (McBride, 1979).
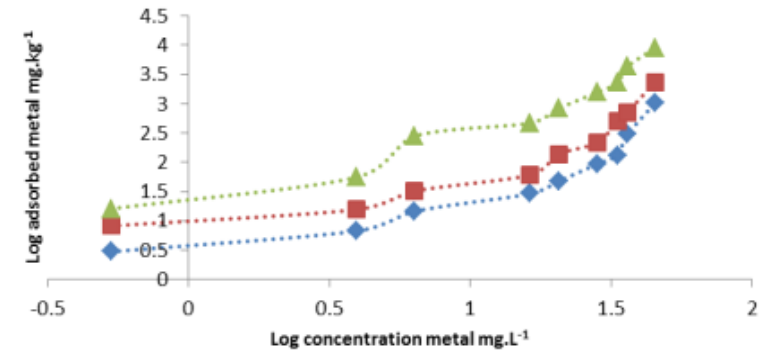
Freundlich adsorption isotherms for Cu, Zn, and Mn in a triple competitive system by selecting calcareous soils are shown in figure (5). Sorption isotherms for these metals illustrate differences in shape and amount adsorbed due to variations in soil properties. Metal sorption isotherms were fitted to C-type sub-group f isotherms according to Giles classification which indicates the adsorption of hydrated molecules. Frundlich parameter K_F or distribution coefficient values for Cu, Zn, and Mn in selected soils ranged between (1.315-2.015 L gm^{-1}) (Table 4).

K_F values for Cu were higher than Zn and Mn indicating that Cu was the most retained cation while Mn was the lowest K_F value indicating that in the competition this element is easily exchanged and substituted by Cu and Zn. The higher affinity of selected soils for Cu adsorption is probably due to a high number of active sites on $CaCO_3$ surfaces with high specificity for Cu (Jalali and Moradi, 2013). The slope or (n) value in Freundlich isotherm represents adsorption tensity or adsorption favorite. (n) values for Zn, Cu, and Mn ranged between (0.813-0.977).
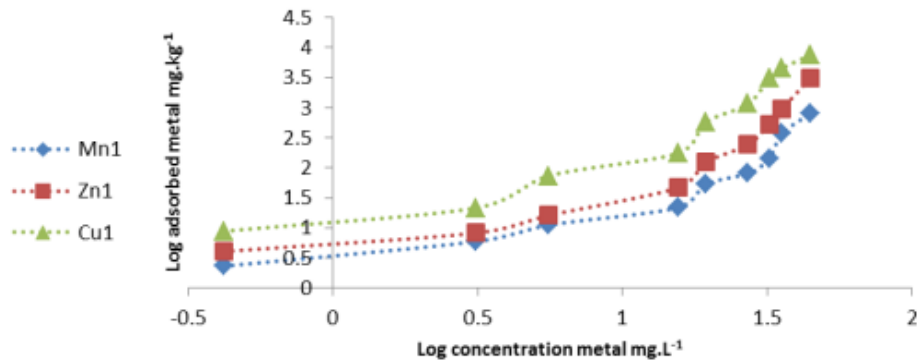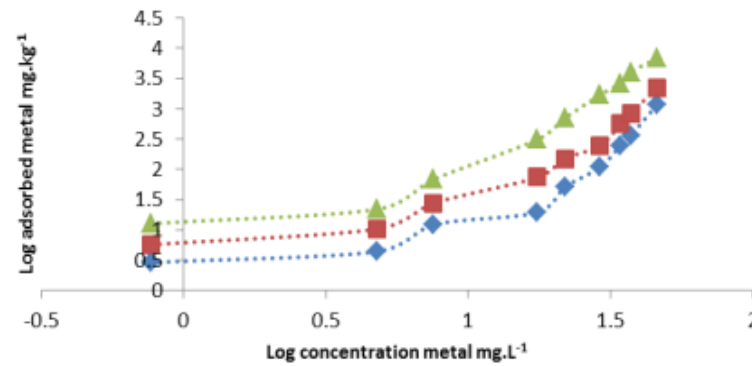
Figure 5. Competitive Sorption Isotherms Freundlich equation for Cu, Zn, and Mn (Mosul, Iraq).

Table 5. The simple linear correlation coefficient between Qmax, ΣKd, and some soil properties (Mosul, Iraq).

Metal		pH	EC	CEC	OM	CaCO$_3$	Clay
Q$_{max}$	Cu	0.950**	0.888**	0.942**	0.908**	0.976**	0.963**
	Zn	0.838**	0.740*	0.823**	0.770*	0.886**	0.862**
	Mn	0.646*	0.516*	0.626*	0.554*	0.716*	0.680*
Kd	Cu	0.995**	0.966**	0.992**	0.977**	1.000**	0.998**
	Zn	0.991**	0.957**	0.989**	0.969**	0.999**	0.996**
	Mn	0.994**	0.965**	0.991**	0.976**	1.000**	0.998**

*Significant at the 0.05 probability level. ** Significant at the 0.01 probability level**.**

That indicates the favorite of study metals adsorption at high concentrations according to Frimmel and Huber (1996). K$_d$ isotherms parameters obtained from the relationship between adsorbed metal and metal concentration in equilibrium solution. The determination coefficient K$_d$ values of studying metals ranged between (0.66-0.89) and K$_d$ values of studying metals ranged between (5-13 L gm^{-1}). The order of adsorption metals according to K$_d$ values was Cu> Zn> Mn on selected calcareous soils. Mckenzie (1980) reported that the higher affinity of soils for Cu adsorption may be due to the existence of a greater number of active sites with high specificity for Cu.

Depending on the results obtained for Q$_{max}$, K$_d$, and K$_F$ in this study for both mono and triple adsorption system, the selected sequence found was Cu>Zn> Mn. This sequence may follow the order of the electronegativity of these metal cations which is Cu, 1.9 Zn 1.6 Mn 1.5 (Shaheen et al., 2013; Yatim et al., 2018) mentioned that electronegativity is a very important factor in determining metal cations chemisorb with the highest preference. Table (5) shows the simple linear correlation coefficient between Q$_{max}$, ΣK$_d$, and some soil properties.

Soil properties influenced the maximum adsorption of Cu, Zn, and Mn due to the high significance of simple linear correlation except for Mn. Mn had a weak significance related to Ec and O.M (r = 0.51 and 0.55 - p<0.05). The highest correlations were between Q$_{max}$ of Zn, Cu, Mn, and CaCO$_3$, which teaches the high affinity of these metal ions to carbonate surfaces. Generally, the linear correlation coefficient between Q$_{max}$ and soil properties may suggest the adsorption of hydrolyzed ion species formation according to the high correlation between max and pH. Also, there was a highly significant correlation between ΣK$_d$ and soil properties at p <0.05. For a competitive adsorption system, the most strongly soil properties related to Cu, Zn, and Mn adsorption were CaCO$_3$, Clay, C.E.C, and pH.

4. Conclusions

Calcareous soils have a high affinity towards trace element ions adsorption. Detailed research of mono and competitive sorption processes between three trace elements (Cu, Mn, and Zn) was performed on three calcareous soils with different CaCO$_3$ content using sorption isotherms. Trace elements sorption was described satisfactorily by the Langmuir and Freundlich isotherms. In the mono and competitive adsorption system, Langmuir sorption isotherms were of H-type whereas Freundlich isotherms were of C-type. As determined by Qmax and distribution Coefficient ΣKd, Cu was sorbed in greater amounts with high binding strength compared to Zn and Mn.

Generally, the selectivity sequence for studied metals was Cu>Zn> Mn in all studying soils because of the specificity adsorption of Cu by Clay, CaCO3, and Organic matter. Trace element adsorption capacity in studying soils depends significantly on the soil properties. The values of Gibbs free energy, decreased as the maximum adsorption capacity decreased too, and correspond to the physical adsorption and indicate exothermic sorption process. The correlation analysis for mono and competitive adsorption showed a high correlation between studying metals adsorption and soil properties. The most strongly related to Cu, Zn, and Mn adsorption were Clay, CaCO3, C.E.C, and pH.

Authors' Contribution

Hudhaifa Maan Al-Hamandi: analysis and interpretation of data and he is the corresponding author, guided the research; Mijbil Mohammad Aljumaily: writing a manuscript, analysis and interpretation of data. Mohammed. Ali. Al-Obaidi: acquisition of data, author of the idea, guided the research.

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