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Research Article

Copper Adsorption Behavior in Selected Calcareous Torrifluvents Soil

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Abstract | Copper adsorption by five calcareous Torrifluvents soil was evaluated by equilibrating 2 g of each soil sample with concentrations of Cu that covered a range from 0 to 200 ug ml^{-1}. The effect of copper (Cu) carriers was also examined using two carriers including sulphate and diethylenetriaminepentaacetic acid (DTPA). Results show that all soil types have a high affinity for Cu adsorption with sulphate, especially soil with high clay and organic matter content, whilst a weak affinity was noticed for Cu with DTPA. Adsorption isotherms of L and C types were noticed with copper sulphate, whereas S type was noticed with DTPA. Four physicochemical equations were used to describe Cu adsorption in the studied soils including Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. Depending on the highest value of the determination coefficient (r^2), the highest value of (t) and the lowest standard error ($S.E_e$), the Temkin model, compared to the other used models is considered the best one describing copper adsorption at both copper carriers.

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Introduction

Copper is an essential micronutrient for plant growth, although it is needed in small quantities (Mortvedt, 2000; Yang *et al*., 2013). It is a redox-active transition element with roles in photosynthesis, respiration, C and N metabolism, and protection against oxidative stress. Like iron (Fe), it forms highly stable complexes and participates in electron transfer reactions. It is involved in the formation of many plant enzymes, including diamine oxidase, superoxide dismutase, cytochrome c oxidase, polyphenol oxidase, and ascorbate oxidase (Marchners, 2012). The symptoms of copper deficiency vary by crop, but one consistent sign is the yellowing of young leaves, resulting from the importance of copper in enzymes found in chloroplasts. In crops, such as corn and small grains, young leaves turn yellow and fail to grow properly. As the condition progresses, the young leaves lose their color and become pale, while older leaves die off. Advanced stages of copper deficiency are marked by necrotic areas on the tips and edges of leaves, which is similar to the damage caused by a lack of potassium (Havlin *et al*., 2016). Adsorption is one of the interactions that occur between element ions and soil colloidal surfaces by different electrical forces, restricting the movement of these ions depending on their concentration and the properties of these surfaces (Sposito, 2008). It is one of the important processes in determining the biological abundance of nutrients in the soil, as it controls the concentrations of these elements (Vlček and Pohanka, 2018). Copper adsorption is one of the essential processes that determine its availability to plants and its presence in the soil, as it restricts its movement and prevents its absorption (Goldberg, 2005). The equations used to describe adsorption are beneficial techniques that enable us to identify the strength of the binding of element ions to the soil, the amount of adsorption, describe the nature of the adsorption process and the adsorption capacity. All of these equations are experimental, and their constants have no theoretical basis related to properties of the soil. These equations were proposed as a basis for describing the adsorption of gases on solid surfaces and then modified to describe the adsorption of ions on solids. The isotherm used to describe and appraise the most significant properties of an adsorbent, for example, adsorbent proclivity, adsorption limit, adsorption component, and quantitative circulation of adsorbate on the adsorbent and mass arrangement (Yang *et al*., 2013). Due to the extremely low organic matter, alkaline pH, and high carbonate minerals content of Iraqi soils, most of the economic crops grown there suffer from a deficiency of this element. Therefore, adding copper fertilizers to the soil or spraying plants with copper-containing solutions is necessary to correct the concentration in the plant.

Due to the scarcity of information available on the behavior of copper fertilizers in Iraqi soils in general and in the soils of Diyala Governorate in particular, our work aimed to study the effect of the type of carrier and the concentration of the addition on copper adsorption in some calcareous sedimentary soils of Diyala Governorate.

Materials and Methods

Five samples were collected from the surface layer (0–30 cm) of calcareous soils in Diyala Governorate, Iraq, as shown in Table 1. The first one (S_1) is classified as Vertic Torrifluvent. The rest are Typic Torrivluvents. Before use, the soil samples were air dried and crushed to pass through a 2-mm sieve. Particle size analysis was carried out using the hydrometer method according to (Al-Tamimi and Namir, 2017).

Table 1: *Location and coordinates of soil samples used in the study.*

Soil No.	Location	Coordinates
S_1	Mouradia	33°39'10.5"N, 44°36'25.2"E
S_2	Al-Huwaider	33°45'50.6"N, 44°37'18.9"E
S_3	Jadida Al-Shatt	33°37'29.2"N, 44°25'33.3"E
S_4	Buhriz	33°42'51.2"N, 44°38'28.1"E
S_5	Al-Azeem	34°11'47.8"N, 44°33'02.9"E

Organic matter, electrical conductivity, pH, calcium carbonate, active calcium carbonate, and DTPA-extracted copper were determined according to (Al-Tamimi, 2025). Table 2 reports particle size distribution and some chemical characteristics of the studied soils. The adsorption isotherm of Cu was determined after equilibrating 2 g of soil in 60 ml plastic tube with 40 ml of Cu solution in 0.01 M NaCl solution. Added copper concentration was 0, 10, 20, 40, 80, 120, 160 or 200 µg mL^{-1} as CuSO4 or Cu-DTPA. Tubes were stoppered and placed in an end-over-end shaker. They were shaken for 2 hrs., then kept overnight for equilibrium. Soil's suspension was immediately filtered through Whatman filter paper No. 42, and then copper was determined using an atomic adsorption spectrophotometer. The amount of metal sorbed was calculated by subtracting the amount of metal remaining in the equilibrium solution from

Table 2: *Some physical and chemical characteristics of the study soils.*

Soil No.	ECdS m^{-1}	pH	Cu-DTPAmg Kg^{-1}	O.M	$CaCO_3$	Clay	Silt	Sand	Texture
				g Kg^{-1}					
S_1	1.88	7.39	2.11	6.50	248	557	153	290	Clay
S_2	1.52	7.21	7.77	16.50	246	274	153	573	Sandy Clay Loam
S_3	2.26	7.73	3.14	7.40	247	374	153	473	Sandy Clay
S_4	2.49	7.50	1.48	4.50	248	135	279	586	Sandy Loam
S_5	3.44	7.82	0.72	3.90	248	141	277	582	Sandy Loam

the initially added. Four physicochemical equations were used to characterize copper sorption these are; Langmuir ($C_e/Q_e = 1/K_l\,b + C_e/b$), Freundlich ($\ln Q_e = \ln K_f + b \ln C_e$), Temkin ($Q_e = b \ln K_t + b \ln C_e$) and Dubinin-Radushkevich ($\ln Q_e = \ln b - K_d\, \varepsilon^2$) equations, where C_e = concentration of copper ion in equilibrium solution, Q_e = quantity of sorbed copper ion; K_l, K_f, K_t, K_d constant (k_l constant releated to binding strength according to Langmuir equation) and b constant (b = maximum sorption according to Langmuir equation). Statistical parameters were used to choose the most suitable equation that characterizes copper sorption.

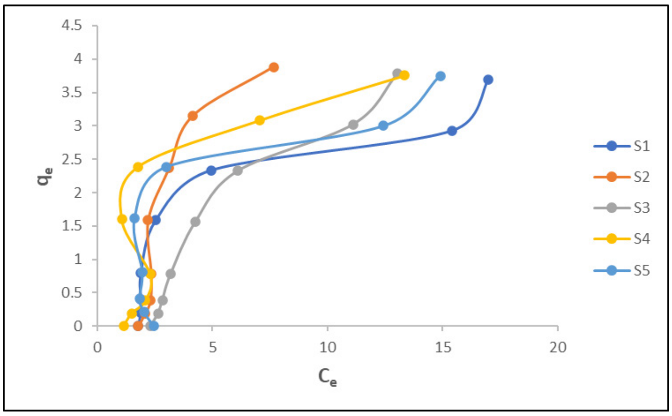

Figure 1: *Adsorption curves of copper added as $CuSO_4$*

Results and Discussion

Table 3 show the concentration of added copper and the remaining concentration in the soil solution after the dynamic equilibrium process for the study soils, which were added in the form of $CuSO_4$. All soils showed a good adsorption capacity at all concentrations, especially the concentrations of 160 and 200 µg mL^{-1}. As for Table 4, it shows the concentration of added copper and the remaining concentration in the soil solution after the dynamic equilibrium process for the study soils, which were added in the form of Cu-DTPA. All soils showed a high adsorption capacity at all concentrations of Cu addition. Figure 1 shows the adsorption curves of copper added in the form of CuSO4 for the five study soils. These curves slightly differed in their shapes. The adsorption curve appeared like an L shape for soil 2, and like C shape for the other soils. This difference is related to the difference in the soil's content of clay and organic matter, specifically soil S_2, which is characterized by a relatively high content of organic matter compared to the other soils. It contains twice as much organic matter as soils 1 and 3, and four times more than soils 4 and 5. Despite the fact that it contains half the amount of clay found in soil 1. This is perhaps due to the ability of organic matter to adsorb copper and form complexes with it (Bakour, 2016).

Table 3: *Concentration of added copper and remaining copper in the equilibrium solution as $CuSO_4$*

equilibrium concentration µg ml^{-1}					Initial concentration µg ml^{-1}
S_5	S_4	S_3	S_2	S_1	
2.46	1.14	2.30	1.77	1.78	0
2.04	1.49	2.64	2.07	1.87	10
1.83	2.09	2.83	2.30	1.89	20
1.95	2.31	3.19	2.33	1.89	40
1.62	1.07	4.26	2.20	2.53	80
3.01	1.77	6.10	3.12	4.96	120
12.44	7.04	11.12	4.15	15.42	160
14.90	13.35	13.04	7.67	17.00	200

Table 4: *Concentration of added copper and remaining copper in the equilibrium solution as Cu-DTPA.*

equilibrium concentration µg ml^{-1}					Initial concentration µg ml^{-1}
S_5	S_4	S_3	S_2	S_1	
2.54	1.14	2.30	1.77	1.78	0
3.80	2.91	2.34	2.95	2.99	10
5.57	5.60	4.92	5.68	5.65	20
10.25	9.96	9.58	9.74	9.81	40
11.71	11.29	10.81	11.09	11.02	80
16.26	15.72	15.54	15.47	15.26	120
21.22	21.44	20.29	21.04	20.25	160
27.58	26.15	24.86	26.96	25.21	200

These complexes contribute to retained copper and preventing its loss from the soil through leaching and preventing its adsorption by plant roots (Zhou and Wong, 2003). Copper bound to organic matter constitutes about 59% of the total copper in the soil (Rutkowska *et al.*, 2013). Figure 2 shows the adsorption curves of copper added in the form of Cu-DTPA for the five soils. The curves appeared in the form of the letter S, which indicates a weak ability of the soil to adsorb increasing amounts of copper. We recognize that there are no differences in the behavior of the five soils in Cu adsorption. This is due to the presence of the chelating compound DTPA conjugated with copper. It forms strong complexes with it, restricting its movement in the soil, and eliminate the effect of the rest components of soil, such as clay and organic matter.

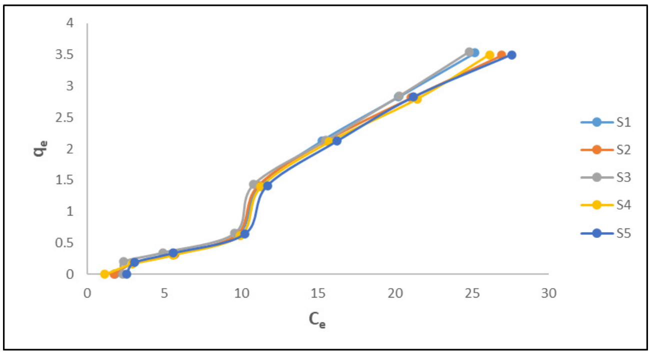

Figure 2: *Adsorption curves of copper added as Cu-DTPA*

The analysis of the adsorption equations provides us with useful and important information about the adsorbed amount of the element and the strength of its association with the adsorption sites. To describe the copper adsorption reactions in the studied soils, four equations were used. These are the Freundlich equation, the Langmuir equation, the Temkin equation, and the Dobbin equation. To determine the best equation, the values of the coefficient of determination, the estimated standard error, and t values were adopted using the highest value of the coefficient of determination r^2 and t, and the lowest value of the estimated standard error. The results obtained in Tables 3 and Table 4 show that the Temkin equation was the best in describing the relationship between the copper concentration in the equilibrium solution and the adsorbed amount, as it gave the highest value of the correlation coefficient at 0.82, and the lowest value of the standard error at 0.62 and the t valu was 7.73 with $CuSO_4$. The equations used can be arranged according to their ability to describe the adsorption of copper added as $CuSO_4$ in the following order, based on the highest value of the correlation coefficient and t value, and the lowest value of the standard error: Temkin's equation > Dobbin's equation > Freundlich equation > Langmuir equation. In the case of Cu-DTPA, the correlation coefficient value was 0.82, the standard error value was 0.54, and the t value was 5.27.

The equations used can be arranged according to their ability to describe the adsorption of copper when added as chelated copper in the following order, based on the highest value of the correlation coefficient and t value, and the lowest value of the standard error: Temkin's equation > Freundlich equation > Dobbin's equation > Langmuir equation. These results differ from those of some copper adsorption studies in other regions. The Freundlich equation was the best at describing copper adsorption in some calcareous soils from Sulaymaniyah Governorate (Karim, 2020), while the Langmuir equation was superior in describing copper adsorption in some sedimentary soils from Basra Governorate (Yassin and Fakher, 2016).

Table 5: *Statistical parameters of adsorption equations with $CuSO_4$.*

Soil No.	Langmuir equation			Freundlich equation			Temkin equation			Dubinin equation		
	r^2	t	$S.E_e$	r^2	t	$S.E_e$	r^2	t	$S.E_e$	r^2	t	$S.E_e$
S1	0.04	0.18	2.61	0.64	3.28	0.63	0.90	7.41	0.43	0.65	-3.34	0.58
S2	0.06	0.95	4.05	0.51	2.61	0.83	0.86	6.18	0.59	0.64	-3.27	0.68
S3	0.06	-1.21	4.75	0.70	4.69	0.51	0.98	17.99	0.62	0.64	-3.29	0.67
S4	0.01	-0.07	2.54	0.33	1.65	0.93	0.64	3.26	0.78	0.64	-3.26	0.68
S5	0.01	0.07	2.63	0.50	2.23	0.76	0.71	3.79	0.67	0.64	-3.30	0.65
Mean	0.04	-0.02	3.32	0.60	2.89	0.73	0.82	7.73	0.62	0.64	-3.29	0.04

Table 6: *Statistical parameters of adsorption equations with Cu-DTPA*

Soil No.	Langmuir equation			Freundlich equation			Temkin equation			Dubinin equation		
	r^2	t	$S.E_e$	r^2	t	$S.E_e$	r^2	t	$S.E_e$	r^2	t	$S.E_e$
S1	0.06	-3.49	6.80	0.53	11.51	1.80	0.81	5.06	0.55	0.50	-3.03	1.45
S2	0.05	-3.01	6.02	0.54	11.15	0.62	0.83	5.32	0.54	0.53	-3.04	2.33
S3	0.02	-2.50	3.81	0.67	10.31	0.46	0.84	5.59	0.46	0.43	-2.94	1.63
S4	0.05	-3.36	6.63	0.43	11.56	0.74	0.76	4.33	0.55	0.24	-3.07	1.67
S5	0.05	-3.13	5.71	0.64	11.73	0.49	0.86	6.05	0.63	0.58	-2.99	0.87
Mean	0.05	-3.10	5.79	0.56	11.25	0.82	0.82	5.27	0.54	0.46	-3.01	1.59

Conclusions

Results showed that the amount of copper adsorbed by the five soils increased with the increasing level of applied copper. Copper adsorption in the studied soils was highly correlated with clay and organic matters. The effects of clay and organic matters were highly inhibited by using DTPA as a carrier. Therefore, studies should be intensified on the use of chelating compounds to reduce the loss of trace elements from the soil.

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Novelty Statement

This study updates the current knowledge on copper adsorption and provides new insights into its mechanisms, with the novelty lying in the superior performance of the Temkin equation in describing copper adsorption, contrary to previous studies where other equations were found to be more effective.

Author's Contributions

Sarah Muayad Bahjat: Formal analysis, Iinvestigation, Resources, Funding acquisition, wrote the manuscript.
Raad Abdel-Kareem Al-Tamimi: Conceptualization, Methodology, Supervision.

Generative AI or AI assisted technology statement
The authors declare that no generative AI and AI assisted technology was used in the creation of this manuscript.

Conflicts of Interest
The authors declare that they have no conflict of interest.

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