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Organic materials and their effect on the adsorption and release of zinc in gypsum soils.

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ABSTRACT

A zinc adsorption experiment was carried out on three soils with different gypsum contents, to which sheep were added to increase zinc adsorption. Poultry, estimated at (12,026) kg. mg^{-1} zinc, the lowest amount of zinc adsorbed on average was recorded in the third soil G3 (189 g.kg-1 gypsum) with mefoles from whole cow ears (8.99) kg.mg -1. A decrease in release values is observed at low levels of zinc addition. The reason may be due to the high content of organic matter in the soil, as organic complexes form with zinc ions, making it challenging to release, or due to the binding of zinc to specialized sites for adsorption, as the force of its displacement was insufficient, which led to the soil holding it. In addition to precipitation on the surfaces of metals and oxides, especially with the pH value (7.76-7.10), which encourages the precipitation of most minor elements, including zinc.

***Keywords*:** organic manure, zinc, gypsum soils, organic poultry, adsorption.

INTRODUCTION

Gypsum soils vary in different types of soils over a wide range in arid and semi-arid areas. Gypsum soils are widespread in confined areas. Their rainfall ranges between (150-400) mm/year, which depends on irrigated agriculture and are accompanied by many events of multiple contributions, which are often related to the dissolution of gypsum. It has a negative impact on the soil and other reliable effects on the soil, especially those related to its distinctive plant and physical characteristics, its level of fertility, as well as the shallowness of the soil. The susceptibility of gypsum soils to food processing is a limiting factor for agricultural production because gypsum is a significant source of calcium at the expense of other ions. Due to the low moisture content, the soil rate in dry areas is low. Therefore, there are characteristics of these soils that are acquired from the original material, as their effect on washing the expected dissolved salts and colloids from the surface horizons to the subsurface horizons is limited [1].

Organic matter plays an important role in improving the physical and chemical properties of the soil. Given the low percentage of organic matter in the soil of dry climates, increasing the soil's organic matter content is extremely important as it increases the fertility of agricultural soil. Organic matter added to the soil, whether it is plant residues or animal waste, plays an important role in determining the physical and chemical properties of soil, as these materials directly affect improving soil structure and increasing the stability of soil aggregates. It also increases the soil's ability to retain water and is a storehouse of nutrients necessary for plant nutrition and preserving the soil surface from erosion and erosion. There is a growing interest in using organic waste to improve the soil's physical and chemical characteristics and fertility and increase its productivity by increasing the percentage of organic matter in the soil.

Zinc is an important micronutrient for plants, as it plays an important role because of its effect on various metabolic processes, such as the effectiveness of enzymes, the synthesis of proteins, carbohydrates, nucleic acids, and fat metabolism [2]. The percentage of soils that suffer from zinc deficiency is estimated at about 10-30% of the world's total soils, and 83% of Iraqi soils suffer from a deficiency of this element for reasons related to its chemical behavior in the soil and its exposure to adsorption, sedimentation, and stabilization [3]. Zinc is present in the soil in many forms, including in the form of free ions in the soil solution, or in the form of complexes, or fixed within the mineral structure of carbonate minerals, silicate clays, or oxides in the soil, or it may be non-extractable or adsorbed on the solid surfaces of soil particles.

Materials and Methods

Thermodynamic adsorption of zinc:

The zinc (Zn^{+2}) adsorption experiment was carried out by taking (1) liter of zinc chloride solution in the form of ($ZnCl_2$) with a concentration of 1000 $mg.L^{-1}$, by dissolving 2.085 grams of zinc chloride in a volume of distilled water with shaking to ensure complete dissolution and completion of the volume to 1000 ml with distilled water, then make the following dilutions using the dilution law, which are (0, 10, 20, 30) mg. L^{-1} zinc in the form ($ZnCl^2$), and complete the volume of 40 ml of distilled water for each dilution, as each of these concentrations is added to 2 grams For all soil parameters, the equilibrium suspensions were shaken for two hours on a shaker. Then they were left for 24 hours to reach a state of dynamic equilibrium at a constant temperature (298 degrees Kelvin). After achieving thermodynamic equilibrium, the suspension was filtered, the filtrate was collected, and the concentration of dissolved copper was estimated. In the equilibrium solution, using an atomic absorption spectroscopy device. (AAS) (Atomic Absorption Spectrophotometry) [4]

$$\mathbf{Zu^{+2}\text{-}ad} = \frac{(\mathbf{zin-zfin})}{\mathbf{w}} \times \mathbf{v}$$

Reverse adsorption (release) of copper at dynamic equilibrium:

The remaining soil treatments were used in the adsorption experiment to study the release of zinc and reveal the ability of the soil to retain zinc. (40) ml of calcium chloride ($CaCl_2$) extraction solution at a concentration of (1.0) was added to the soil in tubes, and shaken for two and a half hours on a Shaker device.) and at a constant temperature (298 K), then left for 24 hours to ensure dynamic equilibrium, then the solution was separated using centrifugation, after which the zinc was determined [4].

Table 1. Some chemical and physical properties of the soil under study.

Texture	Sand	Silt	Clay	$CaSO_4.2H_2O$	O.M	C.E.C	E.c	PH	Soil
	gm.kg^{-1}					C.mole.kg^{-1}	ds.m^{-1}		
SCL	185	462	353	62	9.87	13.50	2.20	7.76	First
SCL	228	444	328	128	8.4	11.80	2.41	7.46	Second
Clay Loam	153	544	303	189	7.12	9.95	2.37	7.10	Third

Table 2. Some chemical characteristics of the organic waste used in the study.

C/P	C/N	% C	% K	% P	%N	EC 5:1	PH 5:1	Adjective Fertilizer
79.12	17.99	45.89	1.98	0.58	2.55	8.05	7.40	Sheep waste
47.68	10.59	41.96	2.76	0.88	3.96	6.98	7.03	Poultry waste
76.69	17.44	40.65	1.62	0.53	2.33	9.22	7.76	Cow waste

Results and Discussion

Adsorption is defined as the process of attraction of ions with different electrostatic and ionic forces on the layer between the surface of the solid phase and the liquid phase [5]. To study zinc adsorption, an equilibrium process was carried out between the ions that have the property of adsorption and the solution and the surface of the solid phase on which adsorption occurs. This is done by shaking a known concentration of zncl2 solution under a constant temperature (298 k) for a certain period of time where equilibrium occurs [6].

A zinc adsorption experiment was conducted on three soils with different gypsum content to which different organic wastes were added. After incubation for 8 weeks after adding a ZnCl2 solution, the results from Table (3) showed an increase in the adsorbed amount of zinc with an increase in the initial concentration of zinc added to the soil, as the highest adsorbed amount of zinc was recorded as an average in The second soil has a content of (128 gm.kg^{-1} gypsum) with organic poultry manure, which is estimated at (12.026) kg. mg^{-1} zinc. The lowest amount of zinc adsorbed on average was recorded in the third soil G_3 (189 gm.kg^{-1} gypsum) with organic cow waste, as it reached (8.99) kg. Mg^{-1}, when zinc ions are added to the soil, these ions are subject to bonding forces ranging from weak attractive forces to strong chemical bonds by the ions of the soil solution on the one hand and by the negative charges present on the colloidal surfaces on the other hand, and these bonding forces depend on Many factors, including: concentration, ion size, ionic activity, valence, substitution capacity, ion exchange constants, type and density of negative charges on colloidal surfaces [7] . so we note that at low concentrations, zinc ions will tend to adsorb on Sites with high charges on the adsorption surfaces until all specific and nonspecific sites are saturated.

Table (3) indicates in general that there is a decrease in the amounts of adsorbed zinc whenever we tend to increase the amounts of gypsum in the soil. This is due to the increase in the amounts of calcium ions competing for the adsorption sites, so that the zinc ions associated with a lower binding energy remain, and also that the gypsum particles do not carry electrical charges on their surfaces. Negative, which is a source of calcium ions and sulfates [8]. Thus, increasing the competition of calcium ions for zinc ions to occupy the active sites, and perhaps the gypsum coated the effective adsorption surfaces for the clay minerals. Thus the gypsum affects the adsorption of zinc ions. As for the reason for the superiority of the second soil G_2 (128 g. kg^{-1} gypsum) in the adsorption process over the first G1 It has a content of (62 g.kg^{-1}) of gypsum, although it contains a higher percentage of gypsum. The reason may be due to the high content of calcium carbonate in the second soil, which is considered one of the basic components for zinc adsorption into the soil.

Release of adsorbed zinc:

The process of liberation (desorption) can be defined as replacing certain ions with specific adsorption capacity with another ion in an adsorbed state, i.e., the release of the adsorbed ion. Several factors affect the release of heavy elements added to the soil, including the characteristics of the soil and the type and level of the heavy element, the additive, temperature, and reaction time.

We conclude from Table (4) regarding the difference in the amount of zinc released from the amount of zinc adsorbed in $mg.kg^{-1}$ soil unit, that the difference in the amount of zinc adsorbed on the surfaces of the soil under study was clear due to the physical and chemical characteristics such as the content of those soils of organic matter and the quality of the resulting organic acids. These factors affect the amount of zinc adsorbed and the values of the binding energy, and the difference in the amount of zinc adsorbed and the difference in the values of the binding energy resulting from the difference in adsorption sites into specialized and non-specialized sites causes a difference in the amount of released zinc. The high binding energy leads to a decrease in the zinc released into the soil solution. In contrast, the low binding energy leads to an increase in the released zinc and the ease of its removal and movement into the soil solution.

In addition to the effect of the amount of zinc adsorbed, the amount of liberated zinc increases with the increase in the amount of zinc adsorbed, thus increasing the readiness of this element in the soil solution and making it available for absorption by the plant roots [9] [10]

It is also noted that the release values differ depending on the levels of zinc addition and the type of organic waste. It is noted that at low levels of addition of zinc (10) $mg\ kg^{-1}$, its release values ranged (1.21, 0.87), but it is noted that there is an increase in the release values of adsorbed zinc at levels The high addition is (30.20) mg.L-1, as the values for all types of soil range between (1.03-3.02) mg.L-1. A decrease in release values is observed at low levels of zinc addition, and the reason may be due to the high soil content. Of the organic matter, as it forms organic complexes with zinc ions, making it difficult to liberate it, or because the zinc is bound to specialized sites for adsorption, as its displacement force was insufficient, which led to the soil holding it, as well as its deposition on the surfaces of minerals and oxides, especially with the pH value (7.76-7.10). Which encourages the precipitation of most of the minor elements, including zinc [11], as it is precipitated in the form of zinc sulphate ($ZnSO_4$) due to the high percentage of gypsum. These factors combined gave the zinc adsorbed in these soils a high binding energy, especially at low levels of addition.

As for the increase in the release values of adsorbed zinc at high levels of zinc addition (20.30) $mg.l^{-1}$, the reason may be due to the high amount of zinc adsorbed in those soils or adsorption on non-specialized sites, which weakened the binding energy as it facilitated the process of returning zinc. To the soil solution when extracted with calcium chloride solution, these factors combined gave the zinc adsorbed in those soils a low binding energy, especially at high levels of addition.

Table No. (3) Adsorbed quantities of zinc in soils with different gypsum content with various organic wastes

Adsorption rate	Initial concentration of zinc						Type of organic waste	Gypsum content
	30		20		10			
	Adsorbed	Balanced	Adsorbed	Balanced	Adsorbed	Balanced		
11.753	16.6	13.4	12.51	7.49	3.85	6.15	Poultry	
11.553	16.36	13.64	12. 30	7.7	4	6	Sheep	G1/62
11.356	16.12	13.88	12.1	7.9	4.15	5.85	Cows	
12.026	17	13	12.73	7.27	3.65	6.35	Poultry	
11.8	16.77	13.23	12.46	7.54	3.82	6.18	Sheep	G2/128
11.536	16.35	13.65	12.24	7.76	3.98	6.02	Cows	
10.253	14.71	15.29	10.63	9.37	4.58	5.42	Poultry	
10.163	13.7	16.3	9,90	10.1	4.88	5.12	Sheep	G3/189
8.99	13.03	16.97	9.04	10.96	5.1	4.9	Cows	

Table (4) : Released amounts of zinc in soils with different gypsum content and different organic residues

Initial concentration of zinc

Release rate	30		20		10		Type of organic waste	Gypsum content
	Desorption	Adsorbed	Desorption	Adsorbed	Desorption	Adsorbed		
2.63	4.26	16.6	2.18	12.51	1.46	6.15	Poultry	
2.32	3.84	16.36	1.92	12. 30	1.21	6	Sheep	G1/62
1.7	2.8	16.12	1.24	12.1	1.07	5.85	Cows	
2.85	4.53	17	2.31	12.73	1.72	6.35	Poultry	
2.6	4.12	16.77	2.18	12.46	1.51	6.18	Sheep	G2/128
1.89	3.02	16.35	1.44	12.24	1.21	6.02	Cows	
2.21	3.6	14.71	1.83	10.63	1.22	5.42	Poultry	
1.97	3.16	13.7	1.72	9,90	1.05	5.12	Sheep	G3/189
1.36	2.2	13.03	1.03	9.04	0.87	4.9	Cows	

Conclusions

A decrease in the amounts of adsorbed zinc occurs whenever we tend to increase the amounts of gypsum in the soil. This is due to the increased calcium ions competing for the adsorption sites, so the zinc ions remain bound with a lower binding energy. Also, the gypsum particles do not carry negative electrical charges on their surfaces, which are a source of calcium and sulfate ions. Thus, increasing the competition of calcium ions for zinc ions to occupy the active sites, and perhaps the gypsum coated the effective adsorption surfaces of the clay minerals. Thus, the gypsum affects the adsorption of zinc ions. As for the increase in the release values of adsorbed zinc at high levels of zinc addition (20.30) mg.l^{-1}, the reason may be due to the high amount of zinc adsorbed in those soils or adsorption on non-specialized sites, which weakened the binding energy as it facilitated the process of returning zinc. To the soil solution when extracted with calcium chloride solution, these factors combined gave the zinc adsorbed in those soils a low binding energy, especially high levels of addition**.**

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المواد العضوية وتأثيرها على امتزاز وتحرر الزنك في الترب الجبسية.

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لخلاصة

تم اجراء تجربة امتزاز الزنك على ثلاث ترب ذات محتوى جبسي مختلف أضيف إليها مخلفات عضوية اظهرات النتائج زيادة الكمية الممتزة للزنك بزيادة التركيز الاولي للزنك المضاف للترب اذ سجلت اعلى كمية ممتزة للزنك كمعدل في التربة الثانية ذات محتوى (128 غم.كغم-1جبس) مع المخلف العضوي دواجن والتي تقدر (12.026) كغم. ملغم-1 زنك اما اقل كمية ممتزة للزنك كمعدل سجلت في التربة الثالثة *G3*(189 غم.كغم-1جبس) مع المخلف العضوي ابقار اذ بلغت (8.99) كغم. ملغم-1 .يلاحظ انخفاض في قيم التحرر عند مستويات الإضافة المنخفضة من الزنك وقد يعود السبب إلى ارتفاع محتوى التربة من المادة العضوية اذ تكون معقدات عضوية مع أيونات الزنك فيصعب تحرره او بسبب ارتباط الزنك بالمواقع المتخصصة للإمتزاز اذ قوة الازاحة له كانت غير كافية مما ادى إلى مسك التربة له فضلا عن الترسيب على سطوح المعادن والاكاسيد ولا سيما مع قيمة الاس الهيدروجيني*PH* (7.10-7.76) والذي يشجع على ترسيب أغلب العناصر الصغرى ومنها الزنك.

الكلمات المفتاحية : المخلفات العضوية ،زنك ،التربة الجبسية ، مخلفات الدواجن ، الادمصاص.