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The Effect of biochar on the copper regulatory capacity in some Salah El-Din soils

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ABSTRACT

Capacity and intensity curves were applied to study the condition of copper element in three soils with different gypsum content (hydrated calcium sulfate) symbolized by (G1) gypsum percentage 10%, (G2) gypsum percentage 20%, and (G3) gypsum percentage 35%. Three types of biochar prepared from plant residues were added to them: rice plant residue biochar (R), wheat plant residue charcoal (W), and corn plant residue charcoal (Z). Plant biochar was added at a rate of 1%. The samples were incubated for 100 days, then the capacity and intensity experiment was conducted in a thermally identical medium (Ca-Cu) using the Beckett method, the aim of which was to establish some thermodynamic parameters. After drawing the capacity and intensity curves, the regulatory capacity potential was calculated, as its values varied between (18315-41765) $(\text{Cmolc.Kg}^{-1}/\text{mol.L}^{-1})^{1/2}$. The highest values were in low-gypsum soil, adding corn residue biochar (G1z,) and the lowest values were in soil High gypsum added wheat residue biochar (G3W) As for the type of biochar, corn residue biochar outperformed the other types. As for the values of mobile copper, the ratios ranged between (-0.101-- -0.451) Cmolc.Kg^{-1}. The highest values were in high gypsum soil added wheat residue charcoal (G3W) and the lowest values were in medium gypsum soil added corn residue biochar (G2Z). The free energy of substitution was all positively charged and its values ranged between (34.557-27.358) K.Joule. The highest values were in low gypsum soil added wheat residue biochar (G1W) and the lowest values were in medium gypsum soil added corn residue biochar (G2Z). The values of the Capon coefficient ranged between (2789-1648) $(\text{L.mol}^{-1})^{0.5}$, the highest values were in low gypsum soil added corn residue biochar (G1z,), and the lowest values were in High gypsum soil, addition of wheat residue biochar (G3W). The research results indicated, according to the capacity and intensity law, a strong correlation between the amount of ions in the liquid and solid phases of the soil for the nine soils. The values of the determination coefficient ranged between (0.78-0.99). The values of the relative activity of copper were low, ranging between (16.042-8.780) 10^{6-} (L.mol-1) $^{0.5}$. The values of the regulatory capacity increased in all soils, with a clear decrease in their values with the increase in the percentage of gypsum. The values of mobile copper decreased in all soils due to the addition of biochar. The free energy values were positive for all soils, indicating the absence of spontaneity in the nature of the reaction. The coefficient of Gabon was high for all soils, which means a strong correlation and low copper release. Therefore, these soils need to be fertilized with copper. biochar can also be added to soils contaminated with trace elements, especially copper, to reduce the effect of copper, its movement, and its availability in the soil contaminated with it. The type of biochar, corn plant residues, was superior to Other species in most of the studied traits.

KEYWORDS: Gypsum soil, biochar, capacity and intensity, regulatory capacity, modified Gabon coefficient.

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1. INTRODUCTION

Gypsum soils (soils containing hydrated calcium sulfate) constitute a large part of the soils of Salah al-Din Governorate, used in the production of vegetable, fruit and grain crops, and a large part of them are pastures for livestock. Gypsum ratios vary from one horizon to another, and in general, the gypsum ratio increases with increasing depth. Gypsum contains important nutrients (calcium and sulfur), but many problems begin to appear when gypsum ratios exceed 20%, some of which are physical, some chemical, some fertile and some mineral, such as the problem of weak or non-existent construction, and in some horizons, gypsum solubility and what gypsum dissolution causes in the soil body, high pH values and low availability of minor and major elements (1). These soils also contain percentages of calcium carbonate, the percentages of which vary from one horizon to another. Studies have mentioned the existence of an inverse relationship between the distribution of gypsum and lime in them (2,3,4). Among the negative effects of calcium carbonate and calcium sulfate is that they cause a decrease in the availability of major and minor elements, including copper, through sedimentation processes. (5) Adsorption and copper are nutrients that plants need in their life cycle in limited quantities, but their loss from the soil causes a disruption in vital functions. In gypsum soils, the availability of copper decreases as a result of the process of adsorbing or precipitating as sulphates, carbonates or hydroxides (6). The amount of dissolved copper does not exceed (0.25 mg/kg), ready (0.85 mg/kg) and total (25 mg/kg) in the surface layer and decreases to less than that in the subsurface layers (7). Copper is present in the soil solution or adsorbed on its surface or fixed within the crystalline structure of primary and secondary soil minerals, as it is fixed within the bodies of living organisms (8). Many elements called microelements have a direct and indirect effect targeting the ecosystem, human health and other organisms when the permissible limits are exceeded (9,10). Gypsum soils are characterized by high pH values and are classified as alkaline or basic, thus providing the conditions for holding and retaining copper. For the elements in the form of adsorption or precipitation and reduces readiness more when accompanied by the availability of organic matter in its various forms, including charcoal (11,12), plant waste is a by-product of the agricultural production process and includes plant roots, leaves, stems, floral parts and fruits. In most cases, they are left in the field or burned to become one of the sources of environmental pollution and a source of carbon dioxide gas and a nutrient for the global warming process. These materials can be treated and thermally matured in isolation from the air and converted into biochar that can be a remedy for these soils and improve their chemical and physical properties. It is called biochar, which is a solid organic material that has undergone a thermal decomposition process in the presence of a limited amount of oxygen and under the influence of high temperatures. This product can be used to improve the properties of gypsum soils due to its high carbon content. It can also contribute to reducing the side effects of carbon gases and contribute, albeit slightly, to reducing the problem of global warming and climate change (13). Temperature plays a decisive role in the quality of biochar. At 400°C or more, the quality of coal begins to decline due to the decline in the percentage of carbon, which is the main component of coal (14). Coal is an important storehouse of major and minor nutrients such as phosphorus, potassium, iron, copper, and others that plants need to complete their growth and production requirements. Biochar is used to improve soil by improving its organic content and thus improving the physical, fertility, and chemical properties of the soil (15,16,17). (18) indicated that adding biochar to soil increased its ability to retain nutrients and reduced the loss of these elements through leaching. Biochar contains charged functional groups, such as carboxyl and phenol, which interact with cations in the soil (such as calcium, potassium, and magnesium), which increases the soil's ability to exchange cations. The researcher (19) pointed out the prominent role played by biochar in cleaning soil contaminated with minor elements. Biochar absorbs these minerals by binding to active sites on its surface, which reduces their movement in the soil and limits their availability to plants and groundwater (20). In order to give a clear picture of the process of copper ion exchange in gypsum soils and to reach some scientific facts used in the process of ion exchange, we go towards using the thermodynamic method and capacity and intensity relationships in order to describe the state of copper between the liquid and solid phases of the soil. A study of the values of the regulatory capacity of the copper ion potential under any conditions shows the soil's ability to preserve the element against any depletion process from the liquid and solid phases of the soil (21). Many studies have indicated the existence of a state of opposition and competition between calcium and copper when they are present in the same solution (22,23,24). Given the absence of a study showing the effect of gypsum and types of biochar on the availability of the copper element, our study aims to determine the values of the regulatory capacity for copper adsorption under conditions of overlapping gypsum ratios and types of biochar, as well as to know the spontaneity of the reaction or not by adopting thermodynamic criteria.

2. MATERIALS AND METHODS

2.1. Three soil samples with different gypsum content were selected, the first soil with low gypsum content of 10% symbolized by (G1), a second soil sample with medium gypsum content of 20% symbolized by (G2), and a third soil with high gypsum content of 35% (G3) from the agricultural fields of the College of Agriculture, Tikrit University, with 5 kg for each soil prepared in the laboratory. Three types of charcoal were selected, the first biochar from rice husks, the second biochar from wheat biochar, and the third biochar from corn charcoal. They were prepared according to what was mentioned in (25). biochar was added at a rate of 1%. The final number of samples was nine. The samples were incubated for 100 days with a humidification and stirring period, after which they became ready. Samples symbolized (G1R, G1W, G1z, G2R, G2w, G2Z, G3R, G3W, G3Z). This was followed by estimating some of the chemical and physical properties of the soil (26). Then the three copper images were measured. (27) Cation exchange capacity (28).

2-2- Thermodynamic adsorption of copper in gypsum soils.

Transparent plastic containers with a volume of 100 ml with a tight stopper were used to study this adsorption. The containers were prepared with the number of concentrations of copper prepared from copper sulfate CuSO4 added as follows (2.5, 5, 10, 25, 50, 100, 250 $mg.L^{-1}$) added to 2 g of soil. The volume was completed to 40 ml with CaCl2 M solution (0.01). After that, the plastic containers were shaken with a shaker for 120 minutes and left to equilibrate for 48 hours. Then, the suspension in the containers was separated to obtain the equilibrium solution in which copper, calcium, magnesium, and EC were measured. The amount of copper adsorbed on the surface of the solid phase was calculated as cu-quantity The adsorbed and liberated copper ions were calculated using the equation below (22).

$$Cu^{+2}\text{ ad} = \frac{(Ci-Cf)}{W} \times V \text{ -------}1$$

Cu^{+2} ad= adsorbed copper ions ($mg\ kg^{-1}$)

Ci = initial concentration of added copper ions ($mg\ L^{-1}$)

Cf= the concentration of copper ions in the equilibrium solution ($mg.l^{-1}$)

W=weight of the soil sample

V = volume of solution added.

The copper intensity of the equilibrium solution, cu-intensity, which is referred to as the relative effectiveness of copper in the equilibrium solution, was calculated according to the ratio law, as mentioned by (33), and the calculations were made according to the following equation:

$$AR_{cu} = \frac{acu}{a\ Ca + a\ Mg} \text{--------}2$$

ARcu: Relative effectiveness of copper

The mathematical relationship is drawn between the amount of copper adsorbed (Δcu±) which represents the copper in the solid soil phase (Q) quantity on the y-axis and the intensity of copper in the liquid soil phase (I) intensity on the x-axis which is (ARcu) and through this relationship and depending on it the following constants for iron can be found:

1- Mobile iron: Labile – cu which is calculated from the extension of the linear relationship towards the y-axis Δcu-.

2- Copper effectiveness ratios at equilibrium: AR cu which is the point of intersection of Q/I with the x-axis

3- Regulatory capacity of iron potential: PBCcu. It is calculated mathematically from the result of dividing the mobile copper / copper effectiveness ratios at equilibrium.

4- Copper preference factor: KGcu. The preference coefficient for Gabon KG- is calculated according to (34) by dividing the regulatory capacitance of the copper voltage divided by the soil CEC

KG- = CEC / PBC_{cu} --------3

5- The free energy of substitution: ΔG It can be calculated from the equation proposed by (35).

–ΔG = 2.303 RT log ARcu ……….(4)

3. RESULTS AND DISCUSSION

3-1- Properties of study soil and biochar

The physical and chemical properties of the selected soils shown in Table (1) show the roughness of the texture and the low clay content and the texture of the soil is (loam) for the three soils. It is also noted that the percentage of clay separation decreases with the increase of gypsum. The organic soil content is low and was 1% and the decrease increases with the increase of gypsum and with the decrease in the values of clay separation and organic matter. The values of cation exchange capacity are low (15, 12.5 and 11), $Cmol\ kg^{-1}$. The percentages of lime and gypsum are high and an inverse relationship is noted in their distribution, which is that lime increases in the first soil and then decreases with the increase of gypsum

Table (1): Some characteristics of soils.

Analysis	Unit	Soil gypsum content 15%	Soil gypsum content 25%	Soil gypsum content 35%
Sand	$gm\ kg^{-1}$	420	450	480
Silt	$gm\ kg^{-1}$	410	400	400
Clay	$gm\ kg^{-1}$	170	150	120
Texture		Loam	Loam	Loam
O.M	$gm\ kg^{-1}$	10	7	5
CEC	$Cmol\ kg^{-1}$	15	12.5	11

EC	**dS m^{-1}**	**2.5**	**2.2**	**2.14**
pH		**7.85**	**7.55**	**7.45**
CaSO4.2H2O	**gm kg^{-1}**	**150**	**250**	**35**
CaCO3	**gm kg^{-1}**	**200**	**185**	**125**
Molten Cu	**mg kg^{-1}**	**0.014**	**0.012**	**0.010**
Available Cu	**mg kg^{-1}**	**0.019**	**0.017**	**0.016**
Total Cu	**mg kg^{-1}**	**1.735**	**1.357**	**1.311**

This is consistent with what was obtained in (2). The results also show that there is a difference between the three types of biochar, as the biochar produced from corn residues recorded the highest values in organic content, electrical conductivity and total copper concentration, with the coal produced from rice residues leading in the cation exchange capacity characteristic. The results are shown in Table (2). As for coal analyses, electrical conductivity and pH were measured according to (29), nitrogen according to (30), organic carbon according to (31), and cation exchange capacity (32)

Table 2: Some characteristics of biochar

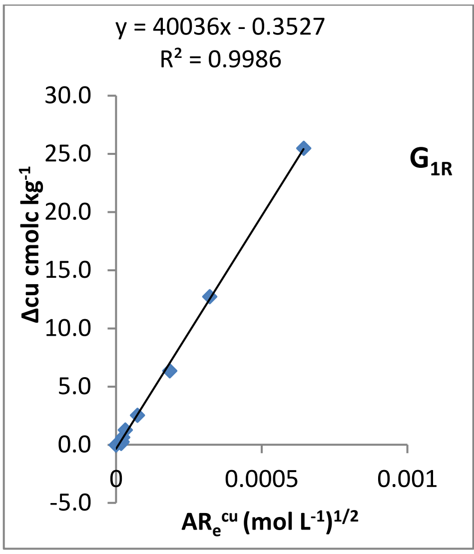
Analysis	Unit	Rice charcoal	Wheat residue charcoal	Corn residue charcoal
Total cu	mg kg^{-1}	0.035	0.018	0.165
N	%	2.5	2.7	2.8
C	%	44	34	35
Ph		7.88	7.58	7.60
O.M	%	61	55	66
EC	dS m^{-1}	4.26	4.32	4.45
CEC	Cmol kg^{-1}	27.87	24.32	22.43

3.2. Capacity and intensity relationships.

Through our study of the capacity and intensity relationship of the copper element, we obtain a perception that reflects the amount of copper stored in the soil, through which we can predict the behavior of this element and the dynamics of its adsorption and release, which is directly linked to the regulatory capacity, as it is the controller of the availability of elements in the soil (36). Therefore, the readiness of copper is expressed by relationships called capacity and intensity curves (33) and the time during which the relationship is drawn for the nine study soils. Figures 1-9 show the relationship as linear behavior. The slope of the linear relationship indicates the regulatory capacity of the copper ion potential and the breaker indicates the mobile copper ions (37). **Table (3)** shows the equation of the straight line, the values of mobile copper, and the coefficient of determination for the capacity and intensity curves.

Table 3: Equation of a straight line and the coefficient of determination

Gypsum ratio	**Type of coal**	**soil symbol**	**Equation**	**cu-Labile Cmol$_c$.Kg^{-1}**	**R^2**
Gypsum %15 ratio	Rice charcoal	G_{1R}	y = 40036 x – 0.3527	-0.357	0.99
	Wheat residue charcoal	G_{1W}	y = 34620 x – 0.3004	- 0.300	0.99
	Corn residue charcoal	G_{1Z}	y = 41765 x – 0.3011	- 0.301	0.97
Gypsum %25 ratio	Rice charcoal	G_{2R}	y = 27290 x – 0.378	- 0.378	0.94
	Wheat residue charcoal	G_{2W}	y = 28727 x – 0.4363	- 0.436	0.93
	Corn residue charcoal	G_{2Z}	y = 28157 x – 0.4517	- 0.451	0.96
Gypsum %35 ratio	Rice charcoal	G_{3R}	y = 20617 x – 0.1722	- 0.172	0.87
	Wheat residue charcoal	G_{3W}	y = 18315 x – 0.1012	- 0.101	0.78
	Corn residue charcoal	G_{3Z}	y = 22126 x – 0.1761	- 0.176	0.98


y = 40036x - 0.3527
R² = 0.9986
G1R
Δcu cmolc kg-1
ARecu (mol L-1)1/2
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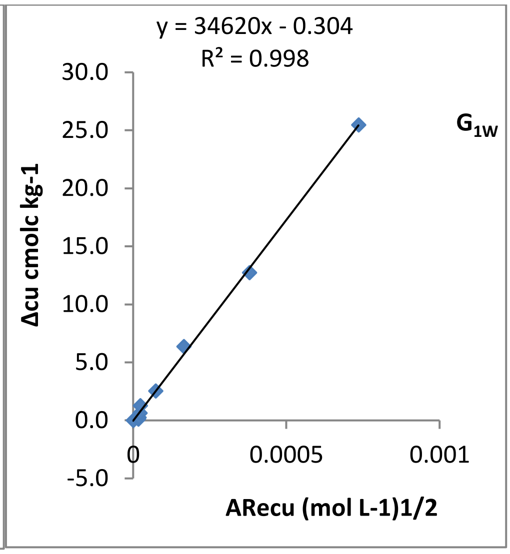
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001


y = 34620x - 0.304
R² = 0.998
G1W
Δcu cmolc kg-1
ARecu (mol L-1)1/2
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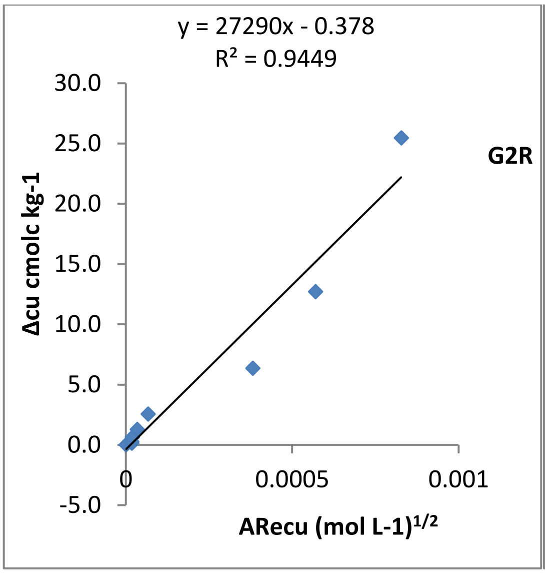
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001


y = 27290x - 0.378
R² = 0.9449
G2R
Δcu cmolc kg-1
ARecu (mol L-1)1/2
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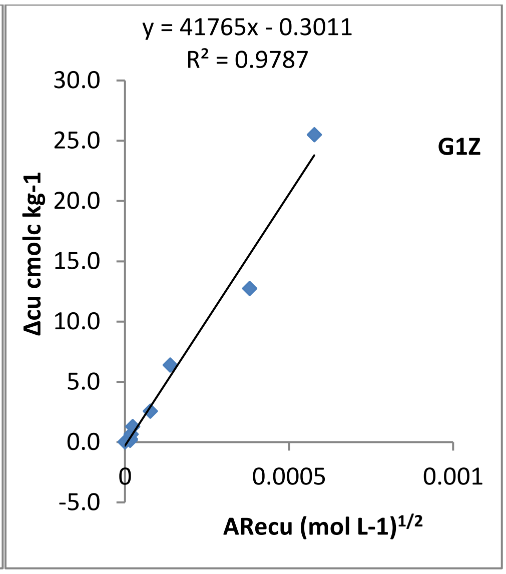
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001


y = 41765x - 0.3011
R² = 0.9787
G1Z
Δcu cmolc kg-1
ARecu (mol L-1)1/2
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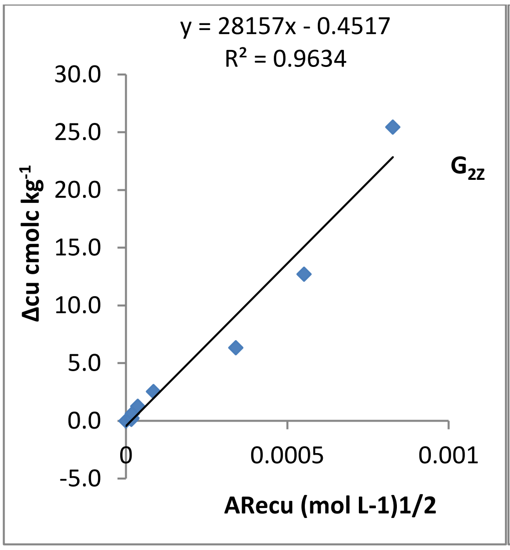
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001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R² = 0.9634
G2Z
Δcu cmolc kg-1
ARecu (mol L-1)1/2
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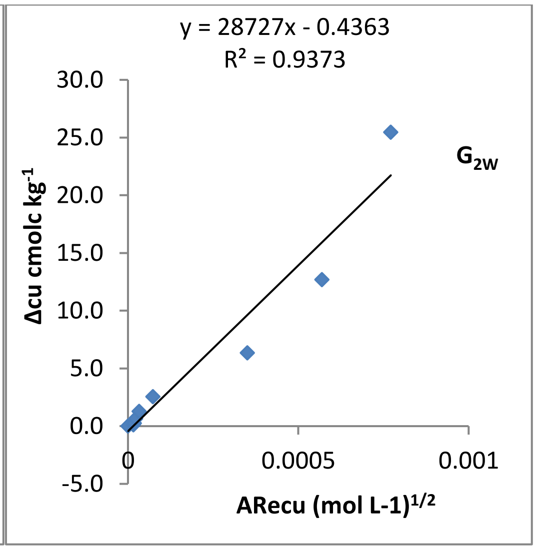
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001


y = 28727x - 0.4363
R² = 0.9373
G2W
Δcu cmolc kg-1
ARecu (mol L-1)1/2
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
0
0.0005
0.001

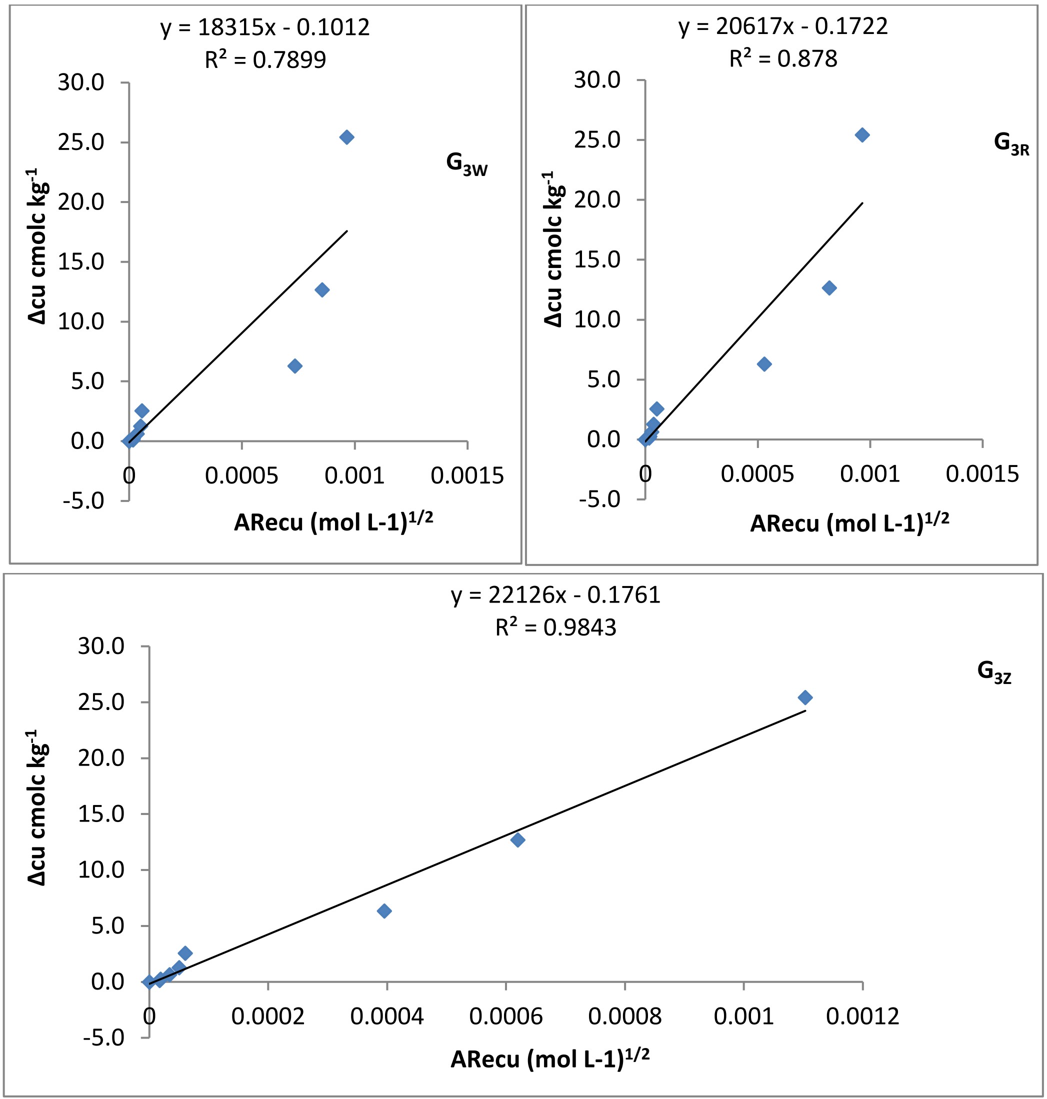


Figure 1: shows Capacity and intensity shapes (GR1-G3z) for copper in the selected soils with different biochar

3-3- movable copper or unstable space : Table (3) shows the values of copper in the unstable space calculated from the curve of the relationship between capacity and intensity when reaching the equilibrium state and tends to negative values with the Y-axis, representing the intersection of the curve drawn between the intensity of copper and its capacity according to (38). These values highlight a very important concept which is (Bio-available) and also clarify another concept which is (Phyto-available) for trace elements in general and copper in particular. The values of mobile copper ranged between (-0.101,-0.45 $Cmolc.Kg^{-1}$) with the highest values in soil with high gypsum content and wheat residue coal addition, and the lowest values in soil with medium gypsum content and wheat residue biochar addition. As for the variation of copper values for the three soils due to the difference in the type of coal added, it was as follows: For the first soil with low gypsum content and its interaction with the three types of coal, its values ranged between (-0.30,-0.30,-0.35 $Cmolc.Kg^{-1}$ with a capacity rate of (-0.316) $Cmolc.Kg^{-1}$. As for the soil with medium gypsum content and its interaction with the three types of coal, its values ranged between (-0.38,-0.44,-0.45) $Cmolc.Kg^{-1}$ with a capacity rate of (-0.423) $Cmolc.Kg^{-1}$. As for the soil with high gypsum content, its values were (-0.17,-0.10,-0.18). $Cmolc.Kg^{-1}$ and at a capacity rate of (0.15-) $Cmolc.Kg^{-1}$ all values were generally negatively charged, the highest rates were in soils with high gypsum content in addition to the low value of mobile copper in all three soil treatments. The difference in the values of mobile copper for the nine soils of the study results from the difference in the values of the regulatory capacity potential of the copper ion, which may be due to its relationship to the physical and chemical properties represented by the difference in their content of separated clay, organic matter, and calcium carbonate. (39) also indicated that organic matter can form insoluble or slightly soluble organic compounds, that humate binds in large quantities with copper and zinc in neutral and basic media, as these three factors work to increase the retention of elements, especially copper, and reduce the values of mobile copper, so the soil with a high gypsum content was the highest soil in terms of the rate of mobile copper due to its low content of clay or organic matter as well as calcium carbonate, so the binding force is less than in other soils, and this supports the results of the capacitance effort from the decrease in its value with the increase in the soil content of gypsum, and this is consistent with the results (41,40). The reason may also be related to the number of active sites and the occurrence of the adsorption process on them, which are characterized by a higher binding force for copper, which reduces the value of mobile copper because the high sulfate content in them works to cover or encapsulate the active sites and tends to cause multi-layer adsorption or adsorption on inactive sites, which facilitates its separation into the soil solution, and the low results of the values of mobile copper are consistent with what was mentioned by (42) the increase in the values of mobile copper after sixty days of its addition. For soil, (43) indicated that the values of the mobile element indicate a high release of the element into the liquid phase, and that soils with higher adsorption give a higher release. As for the values of the determination coefficient, they ranged between (78-99)%,at an average of 96

3-4- **Copper ion voltage regulation capacity** : Table (4) indicates the values of the regulatory capacity of the copper element potential, as these values represent the slope of the straight line of the relationship between the intensity of copper ions in the soil solution and the capacity, which is an important function that shows the ability of the study soil to hold the copper element against any process of loss or depletion of soil copper from both its liquid and solid phases and supply the soil solution in case of deficiency, with the inability to measure the release of copper from the non-exchanged phase to the exchanged phase, but it is possible for us to measure the soil's ability to maintain the change, which gives a good function for the release process (34,33). These values ranged between (18315-41765) $(\text{Cmolc.Kg}^{-1}/\text{mol.L}^{-1})^{1/2}$, and from it, it is noted that their values are high for all soils, which reflects the ability of these soils to retain nutrients, especially copper, but there are high values and others that are lower, as it is noted that there is a slight variation within a single soil and a vast variation between the three soils. The variation in the values of this characteristic for a single soil shows the superiority of adding corn residue biochar to the rest of the types of coal, followed by rice residue coal, then wheat residue coal for the three soils. Which may be due to the high exchange capacity of corn and rice biochar over wheat biochar, as for the decrease in the regulatory capacity effort with the increase in the soil gypsum content to reach more than 50% of its initial value with the doubling of the gypsum percentage at the expense of other soil components of clay and organic matter, the reason for this may be attributed to the possibility of gypsum encapsulating the clay particles as well as the decrease in its clay content, as soils with a high gypsum content are found in the subsurface horizons, which causes a decrease in their organic matter content and the decrease in both factors, clay and organic matter, contributes in turn to the decrease in the values of the cation exchange capacity. This decrease indicates the ease of copper release from these soils compared to other soils with high values. The reason for this may also be due to the low retention and adsorption of copper ions by gypsum, in addition to the high solubility of copper by reducing the pH of the soil solution. This clearly explains the low ability of gypsum soils to supply elements in the long term. The variation in the regulatory capacity potential of copper potential in soils with different gypsum content may also be due to the difference in the proportions of fine separators in clay and fine silt soils, which causes a variation in the difference in the charge density on the adsorption surfaces, or the reason may be attributed to the difference in the number of active sites designated for adsorption and the difference in their ability to hold copper and trace elements (44,45). The high values of this characteristic may also be due to the high content of calcium carbonate in the soil, which increases its adsorption capacity, or it may be attributed to the high affinity between copper and the organic matter and between copper and carbonates on the other hand, and this is consistent with what was obtained (46,47), where he mentioned that the adsorption of minor elements on calcium carbonates and considering it a storehouse for copper and minor elements is slow to prepare. These soils are characterized by a high capacity for preparation in the long term and the possibility of compensating for the depleted element (48).

Table (4) Constants calculated from intensity and capacity curves and calculated Capon coefficient

	PBC_{cu}	**$(10^{-3}) \times AR^0_{cu}$**	**$-\Delta G_{cu}$**	**K_G^-**
	$(\text{Cmol}_c.\text{Kg}^{-1}/\text{mol.L}^{-1})^{1/2}$	$\text{mol.L}^{-1/2}$	K.Joule	$\text{L.mol}^{-1})^{0.5}($
G_{1R}	40036	8.809×10^{-6}	28.843	2669
G_{1W}	34620	8.677×10^{-6}	34.557	2304
G_{1Z}	41765	7.209×10^{-6}	29.340	2784
G_{2R}	27290	13.851×10^{-6}	27.721	2183
G_{2W}	28727	15.878×10^{-6}	27.493	2298
G_{2Z}	28157	16.042×10^{-6}	27.358	2252
G_{3R}	20617	8.538×10^{-6}	28.920	1833
G_{3W}	18315	5.580×10^{-6}	29.974	1648
G_{3Z}	22126	7.958×10^{-6}	29.094	2011

3-5- Copper effectiveness (AR0): To identify the sites where copper ions are adsorpted on the surface of the solid phase of gypsum soils, the relative activity values of copper ions are adopted in order to detect those sites. Table (4) shows that the relative activity values indicate the intensity of copper ions in the liquid phase of the soil in a state of equilibrium when there is no loss or gain of ions in the soil. The relative activity values of copper ions varied between (8.780-16.042) 10^{-6} $(\text{L.mol}^{-1})^{0.5}$, the lowest values were in the low gypsum soil with the addition of biochar to wheat residues and the highest values were in the medium gypsum content soil with the addition of biochar to corn residues. The relative activity values are low for the nine treatments, but the variation among those samples may be due to the presence of water in the composition of gypsum soils, which increases the solubility of calcium. The high abundance of calcium ions in the gypsum soil solution will reduce the effectiveness of copper ions or trace elements in the same solution based on the law of proportions that pushes towards increasing the regulatory capacity of gypsum soils, and this is consistent with what we obtained from the results of the capacity values. The organizational in Table (3) or the reason may be due to the occurrence of adsorption on the edge sites of the building (Edge Site) or the occurrence of adsorption on (Planner Positions) (49), the reason may be due to the fact that the adsorption process was not limited to solid surfaces but was accompanied by the occurrence of copper fixation processes between the layers of minerals or between the layers of biochar, and this is consistent with what was obtained (47), the decrease in the values of the relative effectiveness of copper in the low-gypsum soil may be due to the high content of clay separator.

3-6- free energy substitution

The most important thermodynamic functions to reach knowledge of the spontaneity of the reaction or not, and through them we can see the state of copper present in the liquid phase of the soil and on the exchange complex, which is the result of expressing the heat capacity and randomness of the reaction and is also used to link the changes that occur to the energy of the adsorption reactions (50). The results shown in Table (4) indicated the non-spontaneity of the reaction for all nine study soils because all their values carry a positive charge. It is also noted that there is a discrepancy between the values of the free energy between the three types of soils and between the interactions of gypsum soils with the types of coal, as their values ranged between (34.557-27.358) K.Joule, and at an average of (29.256) K.Joule. The highest values were in the soils with low gypsum content, adding biochar, wheat plant residues, and the lowest values were in the soil with medium gypsum content. According to what was mentioned (51), the high values of the free energy for a certain soil indicate a decrease in its readiness for that element and it needs to be fertilized with that element. Accordingly, all soils The nine need to be fertilized with copper due to the high free energy values of the nine soils. It is noted from the values that the variation between the values of the same soil is almost negligible in the two soils (G3, G2) except for the first soil (G1) where the difference between the biochar additions is more obvious and in the first and third soils the superiority is for the addition of biochar to the wheat plant residues. This means that the process of replacing copper with calcium does not occur automatically and it needs an activation energy sufficient to overcome the strength of the binding energy of the surface absorbing the copper element to ensure the replacement process from the adsorption site (52). The reason may be attributed to the high content of the first soil with a low gypsum content of organic matter and due to the high affinity between copper and organic matter or it may be due to the adsorption of copper on calcium carbonate or as a result of the precipitation process in the form of copper carbonate (40,53). (39) It was indicated that organic matter can be insoluble or low-soluble organic compounds. It was mentioned that humate is associated in large quantities with copper and zinc in neutral and basic media.

3-7- Gapon Factor: Referring to the capacity and intensity curves, we can calculate the modified Gapon coefficient by dividing the potential of the regulatory capacitance of the copper ion by the cation exchange capacity of the study soils (34.54). The values of the Gapon coefficient in Table (4) show a decrease in the values of this factor with the increase in the soil gypsum content. The soil with low gypsum content and the addition of corn waste biochar recorded the highest values, which were (2784)($L.mol^{-1})^{0.5}$, while the lowest values were in the soil with high gypsum content and the addition of wheat waste biochar (1648) $(L.mol-1)^{0.5}$. It is also noted that there is a variation in the same soil resulting from the difference in the type of biochar. Here we note that the highest values for the three soils were associated with the biochar of corn residues, which may be attributed to the high exchange capacity of the values of the biochar of corn residues. The decrease in the values of the Gapon coefficient with the increase in the soil content of gypsum may be attributed to the difference in the adsorption surfaces as a result of the difference in the proportions of the three separators, in addition to the existence of a variation in the values of calcium carbonate and sulfate and the organic soil content, which causes a variation in the values of the binding energy, which in turn affects the adsorption behavior (55,56). It may also be attributed to the decrease in the soil content of the clay separator and organic matter with the increase in gypsum, which works to increase the adsorbed amount in addition to increasing the binding energy as a result of the high affinity between copper and organic materials. The reason may also be attributed to the increased content of this soil of calcium carbonate higher than other soils, as well as the high proportions of clay separators in it, and both factors push towards increasing the amount absorbed or precipitated by carbonates and sulfates, all of which push towards increasing the binding energy. This is consistent with what was obtained by (12,40) in their study on copper adsorption in gypsum and calcareous soils, and it is also consistent with our results for this research in the values of the regulatory capacitance potential, which increased with the decrease in the values of sulfates in the soil and decreased with the increase in the soil content of sulfate and calcium carbonate. The reason for this may be due to the increase in the values of the adsorption capacity on specialized and non-specialized sites on the surfaces of the internal adsorption sites between the layers and the external ones on the clay mineral sites (45,56). The reason for this may also be due to the association of copper with organic matter and types of biochar, as it works to hold it with great force or works to chelate that element (58) .

4- CONCLUSIONS

The nine study soils resulting from the interaction of the three soils and the three types of Biochar have a high ability to preserve copper from loss and depletion due to the high values of their regulatory capacity, and this capacity decreases with the increase in the soil content of hydrated calcium sulfate. The biochar of corn plant residues was characterized by the highest values of the regulatory capacity of the copper ion potential and the free energy of substitution, depending on the positive values of the free energy of substitution, all soils need to be fertilized with copper.

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