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THE EFFECT OF ADDING SOME ORGANIC AND MINERAL SUBSTANCES TO CALCAREOUS SOIL ON ADSORPTION AND DESORPTION OF COPPER AND ITS REMOVAL EFFICIENCY FROM SOIL

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Abstract

A laboratory experiment was conducted to study the effect of some organic materials (active charcoal, Corn citrus, Palm trunks) and mineral (Bentonite and Phosphate rock) on adsorption and release of Copper in soil. Calcareous soils with silty clay loam (SiCL) were selected and the above treatment materials were added with one level (10% by weight), taking 5 g of the mixed soil. Copper was added in concentrations 0, 2.5, 5, 10, 20, 30, 40 mg L^{-1} containing Calcium chloride at a concentration of 0.01 M, completed the volume to 50 ml and the forms were shaken for 24 hours and left for another 24 hours for chemical equilibrium at a temperature of 298 ± 2 K using batch technique and determinate the dissolved Copper of the equilibrium solution and adsorbed Copper. To calculate the released amount of Copper of soil, soil samples for the adsorption study were treated (after filtration were removed) with Calcium chloride solution 0.01 M, and complete volume to 50 ml, shake for 24 hours, and the amount of Copper dissolved in equilibrium solution was estimated and then estimated the amount of release Copper. The results showed that the active charcoal was superior in giving the highest adsorbent amount of Copper and then Corn citrus, Palm trunks, Bentonite and phosphate rock amounted to 38.46, 30.30, 16.66, 15.78, 8.84 mgCu kg^{-1} The values of binding energy varied according to the treatment materials. The highest values were in Phosphate rock, then Palm trunks, Bentonite, active charcoal and Corn citrus at 0.246, 0.162, 0.121, 0.116, 0.106ml g^{-1} respectively. As for the values of copper release, it was in the same order of materials used in adsorption, where the values were 11.49, 9.61, 8.19, 5.61, 5.43 mg Cu kg^{-1} respectively. Treatment of Phosphate rock exceeded the binding energy values, then Corn citrus, Bentonite ,Palm trunks and active charcoal, with values of 3.61, 3.59, 1.58, 0.53, 0.34ml g^{-1}, respectively. The results also showed the efficiency of the treatment materials used to remove Copper from the soil contaminated by the order next: Active charcoal>Corn citrus>Palm trunks>Bentonite> Phosphate Rock.

Keywords: Processing materials, adsorption and desorption of Copper, removal efficiency.

Introduction

Copper is one of the basic micronutrients of the plant and its quantities are low in soil. Soil content of total Copper ranges from 25 to 75 mg kg^{-1} (Kabata - Pendias, 2011). There are many forms of Copper In the soil that are dissolved in soil solution and exchanged on the surfaces of clay minerals and organic matter and trapped in crystalline metal sheets (Al - Naimi, 1999). Calcareous soils are poor in their available Copper content because they contain carbonate minerals that precipitate Copper in the form of Copper carbonate ($CuCO_3$). This process is one of the most important processes that effect on the amount of active Copper for soil solution in calcareous soils (Ponizovsky *et al.*, 2007). Copper is introduced to agricultural soils by adding fungicides, fertilizers, waste residues of panting factories, and mining operations (Li *et al.*, 2007). Adsorption is a process of physiochemical reaction to bind the ions to the outer and inner surfaces of soil particles and thus reduce their availability to plant (Robbin *et al.*, 1999). There are three types of adsorption are physical ,chemical and exchangeable (Sawyer and McCarty, 1978), physical adsorption is a non-specific adsorption with weak gravitational forces (Van der waals forces) between molecules that are free to move over adsorbed surface may be in the form of layers and is inverse, but the chemical adsorption is due to strong bonding forces and be in the form of a molecular layer on adsorption materials surface and the adsorbents are not free movement and it rare inversely (Chen *et al.*, 2001). In most soils, the biological availability of the Copper is dominated by adsorption and desorption processes. Singh *et al.* (1994) indicated that the process of adsorption and desorption of Copper from exchange complex and crystal structure to soil solution and inverse are the process responsible for the movement and distribution of Copper in the soil and its availability for plants. Isotherm models are like the Langmuir equation used to describe the interaction between adsorbed ions and the adsorption surface, it is a simplified expression of adsorption of one layer of adsorbent on a surface containing a specified number of adsorption sites of equal energy and no adsorption movement on the surface of the adsorbed materials (Kamari and WanNagh, 2009). Heavy metals (elements with an atomic weight between 62.5-200.6 g and a specific weight greater than 5 (Srivastava and Majumder, 2008) are among the most important environmental pollutants affecting health and the environment as a result of their accumulation in the bodies of living organisms, many of which are toxic such as Copper, Nickel and Cadmium (Fu and Wang, 2011), it is become necessary to reduce contaminants in the soil using some techniques such as separation membranes, electrochemical deposition, ion exchange and adsorption (KCMPT, 2007). Adsorption is one of the important chemical methods used to treat contamination of soil and water by the use of a substance that has the ability to adsorb some heavy metals such as Copper (Sharma and Sharma, 1986), has been used recently many organic and minerals materials such as active charcoal, Bentonite and Phosphate rock to reduce the concentrations of harmful heavy metals in soil, Kermit *et al.* (2006) have pointed out the significant role of active heavy metals are porous and possess large numbers of surface pores that are susceptible to adsorption, and on the outer surfaces there is an increase in negative charges that contribute effectively to adsorption of positive ions such as Copper (Ghayad, 2012).

Shawky *et al.* (2002) explained the significant role of organic matter such as Palm trunks and Corn citrus in the adsorption process as a result of the increase of the positive ion exchange capacity in soil when added. Gabriel (2011) explained that phosphate rock is one of the mineral substances used in the treatment of soils contaminated with heavy metals by adsorption, chelation and the formation of complexes. Mohajeri *et al.* (2018) show that Bentonite is an absorbent and stabilizer of heavy metals in the soil even when it is at high concentrations because it has a high ion exchange capacity. The aim of this research is to study the effect of some organic and mineral materials on the adsorption and desorption of Copper in the treated soil and determine its efficiency in removing Copper.

Materials and Methods

A calcareous soil with silty clay loam mixture (SiCL) was selected from the surface layer (0-30 cm) of one of the fields of the old site of the College of Agricultural Engineering Sciences in Abu Ghraib, air dried, milled and nickled with a 2 mm diameter sieve and carried out the physical and chemical analyzes according to the methods in Page *et al.* (1982) and Bashour and Al-Saiegh (2007) as shown in table 1. Some organic materials (active charcoal, Corn citrus and Palm trunks) and mineral (Bentonite and Phosphate rock) were added as treated materials by 10% by weight (table 2 shows some chemical properties). 5 gm of soil with the added material was taken and put in the centrifuge tubes and complete the volume to 50 ml with a series of copper solutions in concentrations of 0, 2.5, 5,10, 20, 30, 40 mg L^{-1} containing Calcium Chloride at a concentration of 0.01 M to reduce changes in ionic strength in three replicates. The tubes were shaken for 24 hours and then left for another 24 hours for chemical equilibrium at a temperature of 298 ± 2 K and then separated the filtrate from the precipitate using a centrifuge. The concentration of Copper in the equilibrium solution were determinate by atomic absorption spectrophotometer and the adsorption amount was calculated from the following equation: (Anwer *et al.*, 2016).

$$Q = V (Co – Ce)/ W$$

Since:

Q: adsorbed element quantity ($mg^{-1}kg$)
V: volume of adsorbent solution (ml)
Co: Initial concentration of solution (mgL^{-1})
Ce: Concentration of solution after equilibrium (mg^{L-1})
W: adsorbent weight (gm)

To study the desorption of copper, Soil samples were treated with calcium chloride solution at 0.01 M and completed volume to 50 ml , shaken for 24 hours and the filtrates were separated using centrifuge then determinate Copper concentration by atomic absorption spectrophotometer. The adsorption and desorption processes of copper described using the single-surface Langmuir equation (for their superiority over the other equations surface Langmuir equation (for their superiority over the other equations in the description of these processes (Janabi, 2016 and Yassin and Fakhir, 2016)) are described in the following linear form:

$$C/X = 1 / k\ Xm + C / Xm$$

Since:

X: amount of adsorbed copper ($mgkg^{-1}$)

C: copper concentration in equilibrium solution (mgL^{-1})

Xm: maximum adsorption capacity (mg^{-1})

K: bonding energy coefficient of copper on the soil surface (L^{-1} mg)

Table 1 : Some chemical and physical characteristics of the study soil.

Adjective	Unit	Value
Soil reaction pH 1: 1	----------	7.48
Electrical Conductivity EC 1: 1	dS m^{-1}	1.86
Cations Exchange Capacity (CEC)	C.mole+Kg^{-1}	22.59
Organic Matters	gKg^{-1}	7.16
Carbonate Minerals	gKg^{-1}	230.24
Dissolved ions	mmole.L^{-1}	
Calcium	mmole.L^{-1}	4.10
Magnesium	mmole.L^{-1}	3.47
Sodium	mmole.L^{-1}	1.12
Potassium	mmole.L^{-1}	0.59
Carbonates	mmole.L^{-1}	Nil
Sulphate	mmole.L^{-1}	1.22
Bicarbonate	mmole.L^{-1}	0.91
Chloride	mmole.L^{-1}	12.46
Sand	gKg^{-1}	142.00
Silt	gKg^{-1}	556.80
Clay	gKg^{-1}	301.20
Texture		Silty Clay Loam (CEC)

The values of Xm and k are calculated by plotting the relationship between C/X values and C values and obtaining a straight line with a slope of 1/Xm and its intersection with the y-axis representing 1/k Xm through which the value of k is calculated. Desorption Index (DI) is calculated of the slope of the straight line of the adsorption and desorption equations of the Langmuir equation according to the following criteria.

Table 2: Some chemical characteristics of processing materials.

Adjective	Unit	Processing materials				
		Active charcoal	Corn citrus	Palm trunks	Bentonite	Phosphate rock
pH	------	7.41	7.36	7.42	7.11	7.46
EC	dSm^{-1}	3.39	3.43	5.34	3.78	5.88
Organic carbon(O.C)	gKg^{-1}	394.61	315.21	322.70	-------	--------
(Organic Matter O.M)	gKg^{-1}	680.30	543.42	556.33	---------	--------
C/N Ratio	--------	96.24	50.51	88.89	--------	-------
Cations Exchange Capacity (CEC)	$C.mole+Kg^{-1}$	86.52	64.17	61.55	58.89	48.95
Total Nitrogen	$mgKg^{-1}$	4.10	6.24	3.63	0.59	1.93
Total Phosphours	$mgKg^{-1}$	3.11	4.18	1.92	0.28	108.14
Total Potassium	$mgKg^{-1}$	3.48	4.67	3.39	3.88	0.81

Results and Discussion

Effect of adding processing materials on adsorbed Copper

Figures 1-5 shows the adsorbed amount of Copper in the soil treated with different processing materials (Active charcoal, Corn citrus, Palm trunks, Bentonite and Phosphate rock) at different concentrations of Copper, as the increase in adsorbed amount with increased concentrations of Copper was evident. The effect varied with different treatment additives and their characteristics. The single-surface Langmuir equation was used to describe the adsorption process in soil samples treated with different processing materials for its superiority to other equations in the description of the process of adsorption and the possibility of calculating the two important criteria of which are the maximum adsorption (Xm) and binding energy (k). The results shows can be used this equation to describe the adsorption through the high values of the regression factor (R2) which ranged from 0.825 - 0.933 (table 3). The additives processing materials affected on the values of maximum adsorption capacity, the adsorbed quantities varied according to the materials and their characteristics.

Table 3 : The values of maximum adsorption capacity, bonding energy, and determination coefficient of the Langmuir equation used to describe Copper adsorption in soils treated with different processing materials.

No.	Processing materials	Maximum (Xm) adsorption ($mgkg^{-1}$)	Binding Energy(k) (Lmg^{-1})	Equation	Regression Coefficient (R^2)
1	Active charcoal	38.46	0.166	Y=0.026x + 0.224	0.895
2	Corn citrus	30.30	0.106	Y=0.033 x +0.309	0.881
3	Palm trunks	6.66	0.162	Y= 0.060x + 0.371	0.825
4	Bentonite	15.38	0.121	Y=0.065 x + 0.534	0.855
5	Phosphate rock	8.84	0.246	Y=0.113x + 0.459	0.933

DI = 1 represents the complete release of adsorbed Copper.
DI <1 represents a positive hysteresis and a fraction of Copper is strongly associated with the adsorbent.
DI = no release of adsorbed Copper.

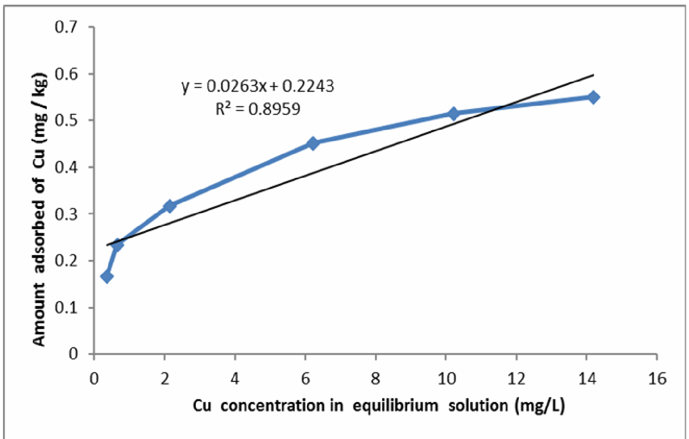

Fig. 1: The Langmuir isotherm of Cu adsorption in soil treated with active charcoal.

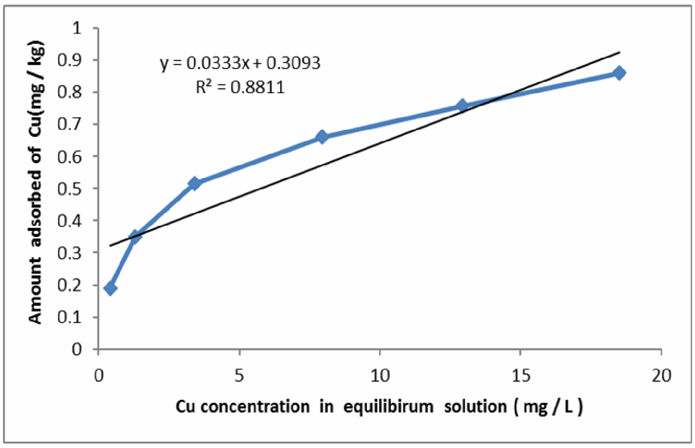

Fig. 2 : The Langmuir isotherm of Cu adsorption in soil treated with Corn citrus.

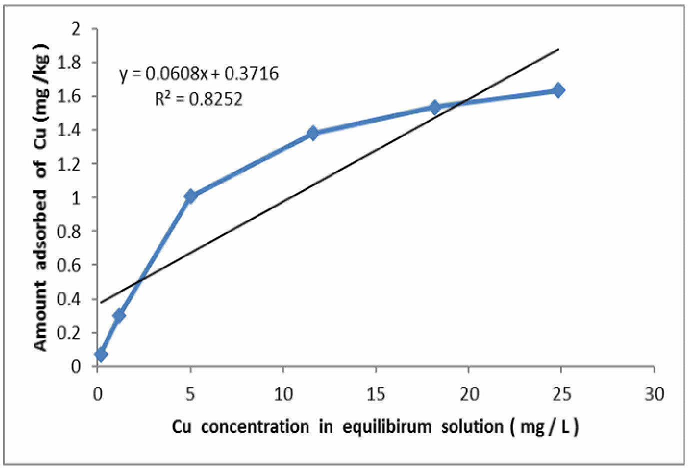

Fig. 3 : The Langmuir isotherm of Cu adsorption in soil treated with palm trunks.

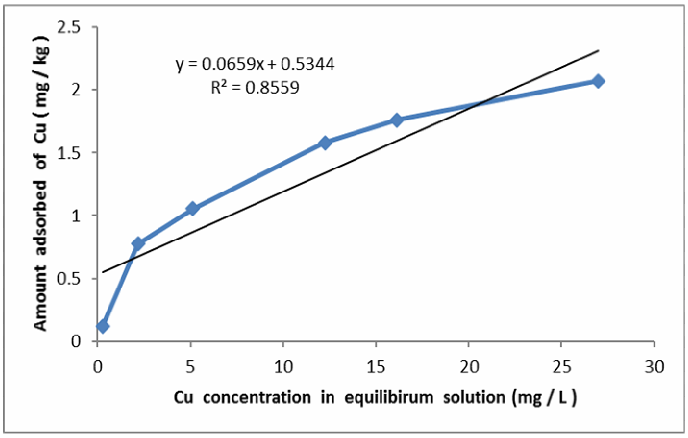

Fig. 4 : The Langmuir isotherm of Cu adsorption in soil treated with Bentonite.

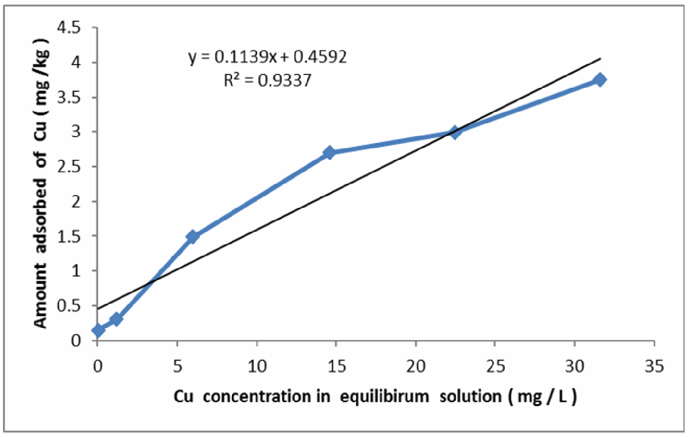

Fig. 5 : The Langmuir isotherm of Cu adsorption in soil treated with phosphate rock.

The highest amount of active charcoal treatment was 38.46 mg Cu kg^{-1}, then treated with Corn citrus, Palm trunks, Bentonite and finally Phosphate rock was 30.30, 16.66, 15.38, 8.84 mg Cu kg^{-1}. The superiority of soil treated with active charcoal in giving it the largest adsorbent amount is due to the fact that active charcoal is a substance that possesses a huge number of surface and internal pores that increase the area exposed to adsorption relative to the actual effective volume of the material (Aslam *et al*., 2005), as this is consistent with what was referred to Mohammed *et al.* (2018) showed that large active charcoal was able to adsorb heavy meatls ions for having the greatest value for ΔG◦ (change in free energy). The treatment of second-grade corn citrus and palm trunks, which are organic materials that have the ability to bind with heavy metal ions such as Copper to form different complexes, this consistent with Yobouet *et al.* (2010) and al-Balkhi (2010), they showed that the heavy metals, like Copper Associated with organic matter by chelating and in varying proportions. Senesi (1992) shows that organic materials contain fulvic and humic acid, which have active groups oxygen-containing such as carboxylic, phenolic, and amino groups, which play a prominent role in the binding of element ions by Salicylate and Phthalic sites, or the most stable compound containing carboxylic groups. The treatment of Bentonite came in fourth place in maximum adsorption capacity of Copper, may be due to the fact that the Bentonite stabilizer and good adsorption of heavy metal ions in the soil because it has a high cations exchange capacity, but less than those in active coal and organic matter (Mohajeri *et al*., 2018). The treatment of phosphate rock has finally come in the value of the maximum adsorption capacity of Copper because it is one of the sedimentary rocks used in the treatment of contaminated soils as a mineral material through the process of adsorption and chelation to form complexes with ions of heavy metals in the soil (Brown *et al*., 2005). The binding energy recorded the highest value in the treatment of phosphate rock amounted to 0.246 liters mg^{-1} and then treated palm trunks, Bentonite and active coal and finally corn citrus was 0.162, 0.121, 0.116, 0.106 L kg^{-1} in turn.

The superiority of phosphate rock treatment may be attributed to the high affinity between copper and phosphate rock, The treatment of palm trunks comes as one of the organic materials that contain in their composition on humic acids that have the ability to catch and bind heavy metal ions By forming chelates with different chemical properties, they are less powerful than phosphate rock (Tamimi, 1997).

Effect of treatment materials on release of Copper in soil

Figures 6-10 show the amount of Copper released in the soil treated with different processing materials. The Langmuir equation proved successful in describing the process of Copper liberation through high values of the regression coefficient (R^2), which ranged from 0.938 - 0.998. Table 4 indicates that there is a variation in the quantities released according to the additives. The active charcoal treatment outperformed the largest release amount of 11.49 mg Cu^{-1} kg followed by corn citrus, palm trunks, Bentonite and phosphate rocks, the values were 9.61, 8.19, 5.61, 5.43 mg Cu kg^{-1}, respectively.

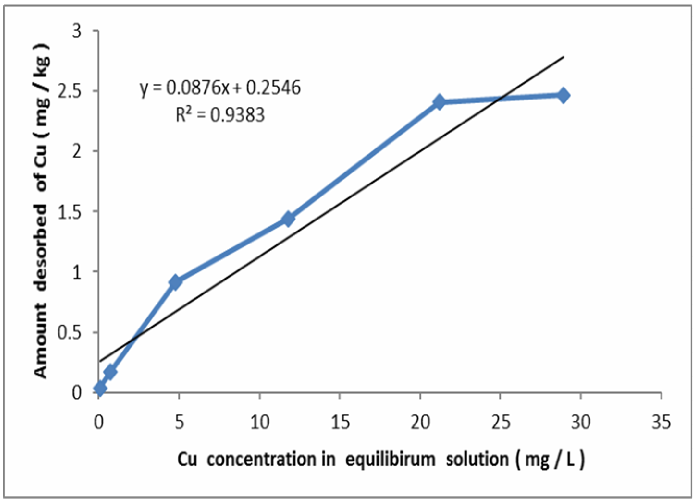

Fig. 6 : The Langmuir isotherm of Cu desorption in soil treated with active charcoal.

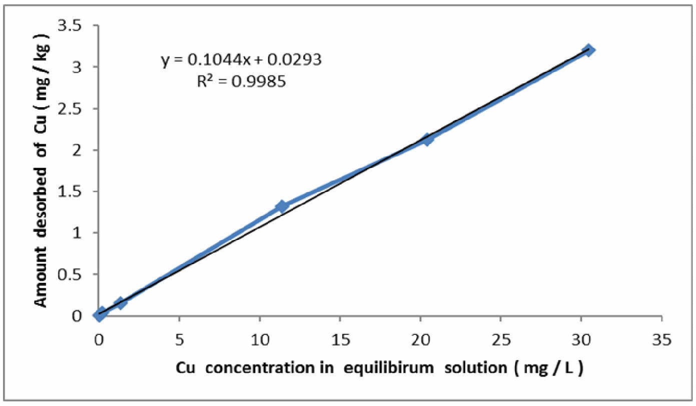

Fig. 7 : The Langmuir isotherm of Cu adsorption in soil treated with Corn citrus.

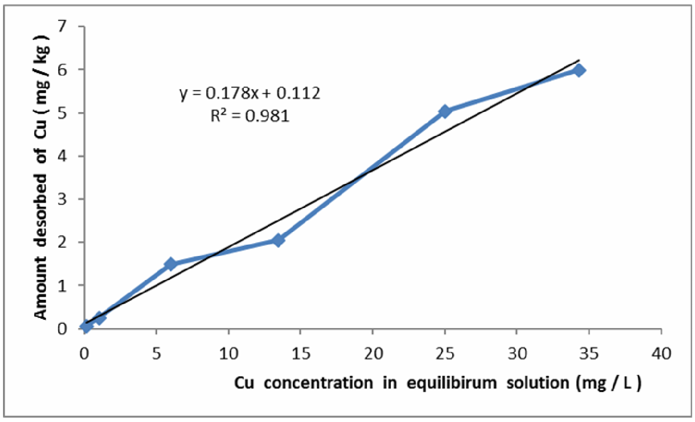

Fig. 9 : The Langmuir isotherm of Cu desorption in soil treated with Bentonite.

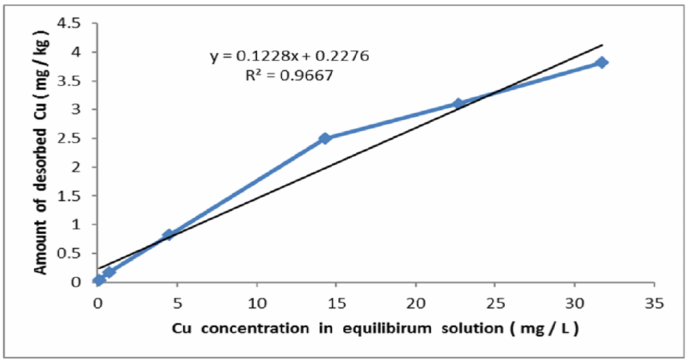

Fig. 8 : The Langmuir isotherm of Cu desorption in soil treated with palm trunks.

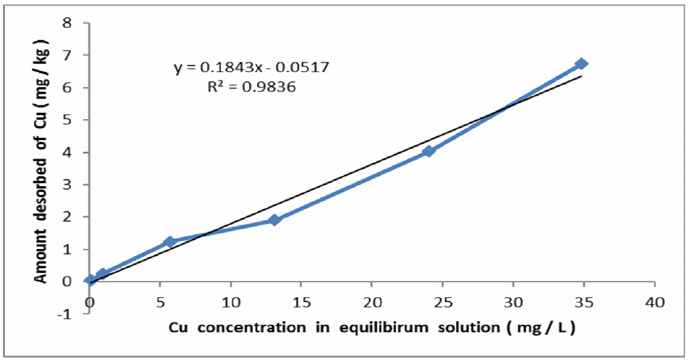

Fig. 10. The Langmuir isotherm of Cu desorption in soil treated with phosphate rock.

Table 4 : Maximum liberated amount, binding energy and determination coefficient of Langmuir equation used to describe Copper release in soils treated with different treatment materials.

No.	Processing materials	Maximum (Xm) desorption ($mgkg^{-1}$)	Binding Energy(k) (Lmg^{-1})	Equation	Regression Coefficient (R^2)
1	Active charcoal	11.49	0.342	Y=0.087x + 0.254	0.938
2	Corn citrus	9.61	3.597	Y=0.104x + 0.029	0.998
3	Palm trunks	8.19	0.537	Y=0.122x + 0.227	0.966
4	Bentonite	5.61	1.589	Y=0.178x + 0.112	0.981
5	Phosphate rock	5.43	3.610	Y=0.184x + 0.051	0.983

The superiority of the active charcoal treatment may be due to the large capacity of coal in adsorption, so that the amount stored is greater and twice the binding capacity between them (table 3), therefore, the amount released more, while organic materials (such as corn citrus and palm trunks) have less adsorption capacity (Table 2). Mineral materials (Bentonite and phosphate rock) come last because the adsorbed amount of Copper on their outer surfaces is lower and thus less susceptible to copper release.

Results of table 3 shows a variation in binding energy values, the highest values in the treatment of phosphate rock was 3.61 Lg^{-1} and then corn citrus, Bentonite, palm trunks and finally the active coal treatment was 3.59, 1.58, 0.53, 0.34 Lg^{-1} respectively. The superiority of the phosphate rock treatment in giving the greatest value of binding energy may be due to its great ability to chelate heavy metals ions in the soil and formation of fixed complexes, this is consistent with Browm *et al.* (2005). The large capacity of phosphate rock in the removal of ions of heavy metals such as Copper and a maximum adsorption capacity of 114 mmol kg^{-1} phosphate rock, this is consistent with Al-Zawy (2004) and Ani (2001) showed that the reason of phosphate rock ability to adsorb heavy metal ions such as Copper is the high affinity of phosphate rock to bond with these ions.

Desorption Index (DI)

The desorption index refers to the ratio of the adsorbed quantity to the released quantity and expresses the soil susceptibility to adsorption and desorption, If there is a significant restriction of pollutants in the soil, there is no release process and therefore there is no problem with soil pollution. When release process occurs, pollutants become free to cause pollution and hysteresis occurs through which the adsorbed ion is not completely released and thus no congruence between adsorption and desorption curves (Businelli *et al.*, 2004).

It is noted from the results of table 5 that the values of the desorption index of the soil to which the different treatment materials were added exceeded 1 and thus represent the complete release of Copper, Therefore, these high values (1.62 - 3.34) reveal the presence of pollution in the soil with Copper element.

Table 5 : The desorption index for soil treated with different processing materials.

No.	Processing materials	Maximum desorption (Xm) ($mgkg^{-1}$)	Maximum adsorption (Xm)) ($mgkg^{-1}$)	Desorption index
1	Active charcoal	11.49	38.46	3.34
2	Corn citrus	9.61	30.30	3.15
3	Palm trunks	8.19	16.66	3.02
4	Bentonite	5.61	15.38	2.74
5	Phosphate rock	5.43	8.84	1.62

Efficiency of treatment materials in removing Copper from soil

The results of table 2 show that the processing materials differ in their ability to adsorb Copper ions and remove them from the contaminated soil due to differences in the properties of these materials. Maximum adsorption capacity represents the susceptibility of materials to adsorption as much as possible copper ions in the soil by forming complexes or precipitated materials and restriction (Heike, 2004) any removal of soil solution, thus, it is considered a measure of the ability of the adsorbent material to remove elemental ions from the soil solution or equilibrium solution.

The results indicate that the active charcoal has highest adsorption amount of Copper amounted to 38.46 mg Cu kg^{-1} and then corn citrus, Palm trunks, Bentonite and finally phosphate rock with values of 30.30, 16.66, 15.38, 8.84 mg Cu kg^{-1}. The superiority of the active charcoal is due to its many internal pores and cavities, which increase the surface area and its large Copper adsorption capacity. This is consistent with what Ghyad (2003) and Lucas and Cocero (2003), they explained that the reason for this is due to the increase of negative charges on the active surfaces of active charcoal, which makes it a very strong adsorbent material, as agreed with Muhammad *et al.* (2018) have shown that the value of ΔG° for active charcoal (which is evidence of the automatic adsorption process) is large and thus increases its adsorption capacity. From the above we conclude the possibility of using additives in the removal of Copper as a chemical treatment of water and soil contaminated by it.

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