Iraqi Journal of Agricultural Sciences –2019:50(2):638-645 Al-Hassoon & et al.

COPPER ADSORPTION IN TWO DIFFERENT SOIL TEXTURE

S. N.H. Al-Hassoon A.S. J. Z. Al-Hayani M. A.J. Al-Obaidi
Lecturer Lecturer Prof.
Dept. of Soil Sciences &Water Dept. of Environment Technology Dept. of Soil sciences &Water Resources.
College of Agric. En. Sc. College of Environment Science & Resources . College of Agric.
University of Baghdad Technology. University of Mosul . &Frosty .University of Mosul
enga.samira58@gmail.com Sattarjubair@yahoo.com maalolobaidi.@yahoo.com

ABSTRACT

This research was conducted to study the physico-chemical behavior of copper in predominance soil orders (Entisols) Jadriya and Najaf of Iraq . Two different locations were chosen according to the variation in their soil orders and physical and chemical properties. Cu adsorption phenomenon were carried out to study copper adsorption using two different soil textures of the surface layer 0-0.3 m with clay loam for the Jadriya site, University of Baghdad and the second (sandy loam) to the site of Najaf by using batch equilibrium at (298 ^{o} Kelvin) . Langmuir equation was used to describe the copper adsorption processes in the studied soils. Diffusion Coefficient, the Maximum Buffering Capacity, the Equilibrium Buffering Capacity and the Supplying Parameter in soil .The main results could be summarized as follows, the adsorption equation Langmuir obtained the highest values of the R^2 in the description of copper isotherm adsorption in both soil , the Diffusion Coefficient value ranged widely from 8316-14476 ml gm^{-1} with, copper maximum adsorption 5000 -10000 mmol kg^{-1}, bonding energy values were 0.13-1.43 L mmol^{-1}, Maximum Buffering Capacity was ranged between 667 to 14286 L kg^{-1}, the copper Equilibrium Buffering Capacity 656 to 11960 L kg^{-1}, Cu-Supplying Parameter in two soils were ranging from 0.67 to 1.36 Thermodynamic parameters of copper adsorption, the diffusion coefficient (R_L), 0.07 to 0.06, and Gibss free energy are negative values and are consistent with diffusion coefficient values that are less than (1) 0.018 to 0.203 (Kj mol. kelvin^{-1}), for the two soil textures respectively , which means that the reaction of the adsorbed copper is spontaneous reaction.

Key words : langmuir, supplying parameter, maximum buffering capacity

مجلة العلوم الزراعية العراقية -2019 :50(2):638-645 الحسون وآخرون

إمتزاز النحاس في تربتين مختلفتي النسجة

سميرة ناصر حسون الحسون عبدالستار جبير زين الحياني محمد علي جمال العبيدي
مدرس مدرس استاذ
علوم التربة والموارد المائية تقانات البيئة علوم التربة والموارد المائية
كلية علوم الهندسة الزراعية كلية علوم البيئة وتقاناتها كلية الزراعة والغابات
جامعة بغداد جامعة الموصل جامعة الموصل

المستخلص

تم اجراء هذا البحث لدراسة السلوك الفيزيوكيميائي للنحاس في تربتي الجادرية والنجف في العراق إذ تم اختيار موقعين مختلفين وفقا للاختلاف في رتب التربة والخواص الفيزيائية والكيميائية لدراسة إمتزاز النحاس باستخدام تربتبن مختلفين في النسجة من الطبقة السطحية 0-0.3 م ، الاولى ذات نسجة مزيجة طينية لموقع الجادرية. جامعة بغداد والثانية مزيجة رملية لموقع النجف باستخدام إتزان الدفعة في (298^{o} كلفن) . استعملت معادلة لانكماير لوصف إمتزاز النحاس في تربتي الدراسة ، ومعامل الانتشار أو التوزيع والسعة التنظيمية العظمى لجهد الايون في التربة والسعة التنظيمية عند الاتزان في التربة ومعامل التجهيز الغذائي في التربة . بينت النتائج ان معادلة لانكماير أظهرت أعلى قيم لمعامل التحديد في وصف إمتزاز النحاس في كلا التربتين ، وتراوحت قيم معامل التوزيع 8316 – 14476 مل غم$^{-1}$ ، وتراوح الإمتزاز الاعظم للنحاس 5000– 10000 مليمول كغم$^{-1}$ وطاقة الربط 0.13-1.43لتر مليمول$^{-1}$ ، والسعة التنظيمية العظمى 667 – 14286 لتر كغم$^{-1}$ ، والسعة التنظيمية عند الاتزان 656 – 11960 لتر كغم$^{-1}$ ، ومعامل التجهيز الغذائي في التربتين 0.67 – 1.36 . بلغ معامل الديناميكا الحرارية لإمتزاز النحاس 0.07– 0.06 ، وكانت الطاقة الحرة للـ Gibssقيم سالبة وتتفق مع قيم معامل الانتشار التي تكون أقل من 1 ، Kj mol. kelvin^{-1} 0.018 – 0.203 لكلا التربتين ، على التوالي مما يعني أن إمتزاز انحاس هو تفاعل تلقائي .

الكلمات المفتاحية : لانكماير ، معامل التجهيز الغذائي ، السعة التنظيمية العظمى

***Received:23/7/2018, Accepted:31/10/2018**

INTRODUCTION

Copper is a necessary nutrient for plant growth. In recent years, attention has been focused on copper poisoning more than copper deficiency due to environmental. Maftoun *et al.* (22) explained the importance of studying the thermal adsorption of copper in terms of environment or agriculture. The copper is present at equilibrium state between the liquid and solid phases of soil . Al-Tamimi (6) confirmed that the high values of copper distribution are associated with the high adsorption potential of the sites as they have high bonding capacity. The adsorption becomes non-qualitative at high concentrations as the adsorption sites become busy and lead to a decrease in the value of the copper distribution coefficient. The difference in the tendency of copper to bind to the soil components is due to the hydrolysis constant of P_{Kh}, electrolysis, acidity, precipitation and solubility (K_{sp}) of the sediments. Liu Chen *et al.* (21) found that adsorption is an effective and economical means of removing pollutants, especially from wastewater. The adsorption of positive ions on the soil surfaces determines the relative distribution of the adsorbed ion and its retention on both the reciprocal and non-reciprocal phases (specific and non-specific adsorption). The removal of the copper by the soil surfaces can be attributed to different mechanisms such as ion exchange and adsorption. The ion penetrates the crystalline clay network through the gaps on the surface and the channels leading to the grid, replacing heavy ions with the existing ions that are often sodium or calcium (29). The adsorption occurs due to the bonding of the metal ions with the active and available adsorption sites on the different soil surfaces. Such as spatial interference, especially when the ionic metal is large and the active sites on the surface are close together (28). The amount of adsorption depends on the concentration of the added element and the degree of reaction of the solution. In this area, adsorption is the result of two processes. The first is the cation exchange process in its usual conventional concept. This mechanism is related to the positive reciprocal capacitance and the negative electrical charge of the soil resulting from the corresponding and practical substitution The other is the formation of different internal and external surface complexes, which are independent of the fixed charge of soil and are closely related to their variable charge obtained from amphitheater ionization in some of their surface sites and this adsorption has an effect On the physico-chemical properties of the soil and the electrolyte point where the net charge is zero after this phase. Soil reactions occur as they are deposited from the dissolved ionic species in the solution or occur on the surface of the solid phase after adsorption which is the beginning of a complete precipitation over time. Similar to the adsorption process, they are identical in terms of stored energy, so that the separation between them is concentrated on the spatial extension of each, so adsorption is a two-dimensional phenomenon , whereas sedimentation is a three-dimensional phenomenon (20,33) noticed the values of the maximum regulatory capacity (MBC) of the ion energy in the soil is an important criterion in the description of soil pollution by copper and the high values show that the ionic type adsorbed element has a low link card causing heavy movement and migration (Heavy Metals Migration) To the depth of the soil, which makes these soils with self-purification and high regulation capacity to confront pollution The values of thermodynamic functions are very important in explaining the occurrence of the process of adsorption in terms of determining the direction, operation and nature of the forces controlling them, The regularity of molecules in the adsorption system that occurs as a result of interference . This study aims at studying the adsorption behavior of the copper element and its adsorption capacity in two different soil textures at different levels of copper, according to Langmuir equation . The high density of the clay makes the quantity used smaller and the surface area compared to the carbonate minerals. Therefore, increasing the clay content and its type, as well as increasing the content of both carbonate and organic matter as additional surfaces increase the efficiency of adsorption, which may provide alternative material for use in the removal and purification of waste water from these metals (12,25) . Due to the difference in the amount of adsorption between soils, the soil content of clay, surface area, calcium carbonate, organic matter and the exchange capacity of positive ions (12,18) . Ibrahim *et al.* (16) noticed the role of physical and chemical properties in the adsorption process, that the difference between soils may be due to the role of minerals in the process of adsorption as the soil metals adsorption of copper from the soil solution after it gets hydrolysis and because of this process will be the sum of a number of ionic dissolved species as shown in the following equation:

$$\mathbf{Cu^{2+}\ \underset{\longrightarrow}{H_2O}\ Cu\,(H_2O)_n^{2}\ OH^{-} \rightleftharpoons CuOH(H_2O)^{+}_{(n-1)}}$$

equation to describe the adsorption mechanism.

MATERIALS AND METHODS

Two soil samples were selected, the first was clay loam represented the Jadriya site. University of Baghdad, and the second was sandy loam represented the site of Najaf, Iraq. Soil samples from surface horizon (0-0.3 m) were collected air dried, crushed and sieved through 2 mm sieve prior to soil analysis. Physicochemical properties were determined using standard method in (Carter and Gregorich, 9) . The cation exchange capacity (CEC) of soil was estimated according to the method proposed by Papanicolaou (24), as shows in Table 1

Table 1. Some chemical and physical properties of two different soil texture

Texture	g Kg^{-1}						Cmol+ g CEC	dSm^{-1} EC	PH
	Clay	silt	Sand	$CaCO_3$	gypsum	OM			
Clay loam	349	408	243	154	1.20	11.35	14.50	1.3	7.7
Sandy loam	40	296	667	188	2.32	11.60	14.13	3.2	7.6

Cu- adsorption

Cu-sorption by soil samples were done by placed 2 g of soil in a 50 ml centrifugal tube . Six levels of copper (60, 80, 100, 120, 140 and 180 mg L^{-1}) were added using copper nitrate [$Cu\ (NO_3)_2.3H_2O$) , in a typical 0.03 ml solution of calcium nitrate $Ca(NO_3)_2\ .4H_2O$ as an electrolyte solution to reduce changes in ionic strength by 10: 1 (volume of solution added 20 ml) with three replicates. Soil suspensions were shaken for 6 hours and equilibrated for 24 hr at 298 K^o ±1. Concentration of Cu in the clear extract solution was determined using Atomic Absorption Spectrophotometer . Concentration of Cu sorped by soils was calculated from the difference between the initial and final concentration of Cu in the equilibrium solution (8)

$$\mathbf{Cu}_{\mathbf{adsorbent}} = \frac{\mathbf{C_{intial} - C_{final}}}{\mathbf{w}} \times \mathbf{V} \quad ---(\mathbf{1})$$

Whereas : $Cu_{adsorbent}$ = concentration of the adsorbed Cu (µg g^{-1}).

C_{in} = ion concentration of Cu before equilibrium (µg ml^{-1})

C_{fin} = concentration of Cu ion after equilibrium (µg ml^{-1})

V = volume of added solution (ml)

w = weight of soil (g).

Cu adsorption – data were described by using Langmuir equation :

$$\frac{\mathbf{C}}{\mathbf{X/m}} = \frac{\mathbf{1}}{\mathbf{KS_m}} + \frac{\mathbf{1}}{\mathbf{S_m}} \qquad ------(\mathbf{2})$$

Whereas X/m = The amount of Cu adsorbed (µg g^{-1})

C = The equilibrium Cu concentration (µg ml^{-1})

S = The amount of Cu adsorbed (µg g^{-1})

K = bonding energy

The constants of Langmuir equation after the relationship between the C/X values and the C values were calculated to obtain a straight line . Thus, the line slope represents 1/b , and the intersection with the Interceptor axis represents a value of 1/ Kb

Distribution Coefficient (K_d) = S / C ----- (3)

Maximum Buffering Capacity (MBC) = K_1Xm -------- (4)

=Equilibrium Buffering Capacity (EBC)

$K_1\ Xm_1 / (1+\ K_1\ C_1)^2$ ---------- (5)

Supplying parameter SP=$((C^*q) / (K_1)^{0.5}))^{0.5}$ -- (6)

Gibbs free energy - ΔG = 2.303 RT ln K --- (7)

Diffusion coefficient $R_L = 1/(1+K_1\ )\ C_o$ -- (8)

Where: X/m, q=The amount of Cu adsorbed (µg g^{-1})

C = The equilibrium Cu concentration (µg ml^{-1})

S = The amount of Cu adsorbed (µg g^{-1})

Xm = the maximum adsorption value

K_1 = bonding energy

T = absolute temperature, R = constant gases

RESULTS AND DISCUSSION

Maximum adsorption

The values of the bonding energy obtained and the maximum adsorption capacity are a real guide to the nature of the real interaction between the added ion and the adsorption surface and this is consistent with what was reached (Al Janabi and Al Rubi , 2 ; Mehmadani, 23) . The maximum quantities adsorpted of copper (II) on the studied soils indicating higher values of maximum adsorption capacity (5000-10000) and at average of 7,500 mmol^{-1} kg^{-1} (7) , demonstrated that in clay minerals ,an atom of lower position valence replaces one of higher valance, resulting in deficit of positive charge , or Cu-isotherm curves. Some adsorption isotherm may be interpreted as a combination of chemical and physical adsorption curves. This may be attributed to many adsorption sites at the surface of soil when the solution concentration is low ,and the adsorption rate is high ,since the adsorption amount is not saturated .Non-specific adsorption and physical adsorption was the main process in this stage .And then the adsorption sites were gradually occupied by Cu^{2+} ,so the increase rate of adsorption amount became slow then the adsorption-isotherm curve tended to be gentle and finally reached adsorption equilibrium. This process may due to specific adsorption and chemical adsorption (18) . For proper evolution of the environmental threat posed by Copper on its availability it is necessary evaluated the copper individual sorption characteristics-Langmuir equation were fitted to sorption data to predict the behavior of copper sorption by the soils. The Langmuir equation irrespective of copper added ,gave a better fitness (R^2) , these found actions were agree with (Hosseinpur and Dandanmmozd,15)

Cu- bonding energy

The affinity of Cu bonding varied with soil types and metal concentration . The values of the bonding energy is a real guide to the nature of the real interaction between the added ion and the adsorption surface and this is consistent with what was reached (Al Janabi and Al Rubi,2; Mehmadani, 23), also could be used to partially explain the widespread Cu^{2+} deficiency in plants grown Calcareous soils. Table 2 shows these values for the copper reaction ranged from 0.13-1.43 L mmol^{-1} to the sites of Jadriya and Najaf, respectively, at average of 0.78 L mmol^{-1}, this can be explained as one of the following: ionic deposition in the form of carbonate and the replacement of the added ion type replacing calcium in carbonate and ion adsorption on the carbonate surface. The ability of carbonate minerals to adsorption of ionic species to copper is due to the presence of electrical charge on the surfaces of carbon metal resulting from the refraction of the calcite metal surfaces and the relatively small positive ion ions that are carried into the crystal while the large negative charge carbonate ions rush outward causing a negative charge surface of crystalline or minute calcium carbonate.

Diffusion coefficient

Table 2 shows the values of the copper diffusion coefficient (K_d) at 8316 – 14476 ml gm^{-1} with an average of 11396 ml gm^{-1} , due to the variation of the soil components used, reflecting the soil 's ability to retain the element and is related to the movement of the element in the soil solution. The high values of the copper diffusion coefficient show the role of mineral and organic colloids in the soils, which may cause adsorption and precipitation of these elements on the surface of colloids (17,27) . Covelo *et al.* (11) found that correlated with which component of soil, which is inversely proportional to the initial concentration of the element. These results are consistent with findings of (Soares, 30 ; Al-Sabah, 5 ; Alloway,4) . The high amount of the clay makes the quantity used smaller and increase of surface area, compared to the carbonate minerals. Therefore, increasing the clay content and the type of clay minerals, as well as increasing the content of both carbonate and organic matter as additional surfaces increase the efficiency of adsorption, which may provide alternative material for use in the removal and purification of waste water from these metals (12, 25). Due to the difference in the amount of adsorption between soils, the soil content of clay, surface area, calcium carbonate, organic matter and the exchange capacity of positive ions (13,18)

. Ibrahim *et al*. (16) noticed the role of physical and chemical properties of the soil in the adsorption process, that the difference between soils may be due to the role of clay minerals in the process of adsorption as the soil minerals adsorped copper from the soil solution after it gets hydrolysis and because of this process will be the sum of a number of ionic dissolved species .

Mathematical description of copper adsorption

The mathematical description of the adsorption of copper the soil of the study sites in Figs. 1 and 2 was shown in the linear mathematical formula of the single-surface Langmuir formula, which proved efficient in the mathematical description of adsorption reactions in soils through the high values of the R^2 (0.97- 0.99) . It is noted from the previous two forms that the nature of the path was of type H-Type, where the copper is characterized by rapid reaction with the soil solution towards the solid soil phase and then adsorption and the possibility of deposition in high concentrations, especially if we take into account that these soils calcareous degree of interaction is agree with (Ahmed ,1), noting the increase in the amount of adsorption linearly in the following few additions, and with the increase of the primary added concentration, a reflection occurs in the inflection point. We conclude from this clearly that there are two types of adsorption surfaces for these soils, clay is the first surface while carbonate minerals are the second surface of the adsorption process (10,17).

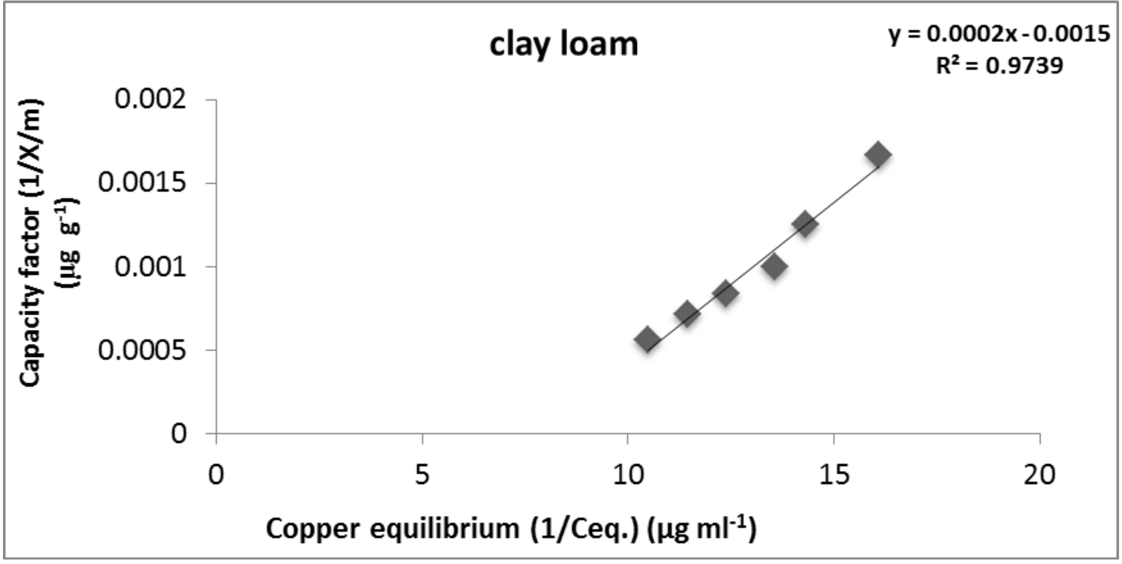

Figure 1. The graphic relationship between the adsorbed copper as a function of its concentration in the equilibrium solution of the Jadiriya site

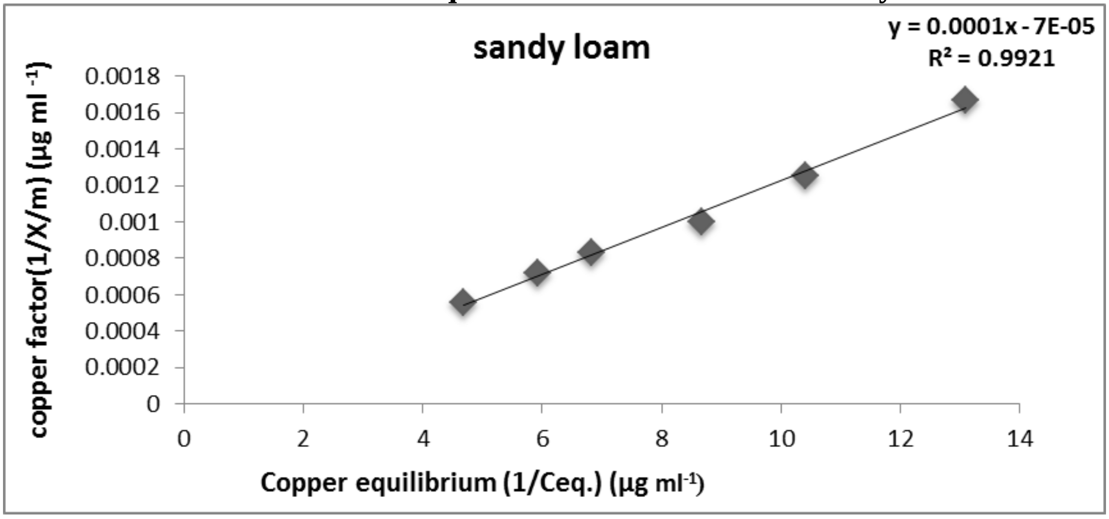

Figure 2. The graphic relationship between adsorbed copper as a function of its concentration in the equilibrium solution of Najaf site

The shape of adsorption isotherm can be used to diagnose the adsorption mechanism and the nature of adsorption. It is assumed that adsorption from solution in continuous function of the concentration of the solution.(14) , Molecular interaction of solution components with the adsorbent and with each other in the surface and bulk solutions affect the shape of the adsorption from solution. Figures of copper adsorption isotherm are shown in Figs1 and 2 . The shape of Cu-adsorption curve on soil according to the Giles classification The isotherm of mentioned system obeyed Langmuir equation leading to the assumption of high adsorption affinity between the copper II and clay surface in addition to the formation of one adsorption layer of copper II on the soil surface. According to Giles interpretation for the adsorption isotherm shape the copper II could be oriented parallel to the surface of clay. In other meaning ,an excess of negative charge. This excess of negative layer charge is externally compensated by the adsorption on the layer surfaces of actions ,which are too large to be accommodator in the interior of crystal. In aqueous solution ,the compensating cations on the layer surfaces may easily be exchanged by other cations available in solution. The behavior of clay in solution can be predicted by Gouy-chapman's theory according to the concept of diffuse double layer (34).This fact means that ,the clay particles in aqueous solution are charged

Maximum buffering capacity (MBC) :

The results in Table 2 shows the Maximum Buffering Capacity (MBC) of copper, values were ranging from 667 to 14286 L kg^{-1}, with an average of 5857 L kg^{-1}. The difference between the two soil textures is due to the different nature of adsorption, and the difference between the adsorption values and the bonding energy in the high energy sites is due to the difference in the ion's readiness at the different locations of the adsorption curve. The increase in the amount of ions and the decrease of ion bonding energy in such soils clearly means the adsorption surfaces to the soil solution cause increased propagation rates of this ions and increase its availability for absorption by the plant (19) .

Table 2. The maximum buffering capacity (L kg^{-1}) and the maximum buffering capacity at equilibrium (L kg^{-1}) and Supplying parameter for the soils under study

Texture	(K) L mmol^{-1}	(X_m) mmol^{-1} kg^{-1}	(MBC) L kg^{-1}	(EBC) L kg^{-1}	R_L	G Kj mol. Kelvin^{-1}	SP
Clay loam	0.13	5000	667	660	0.07	-0.018	0.67
Sandy loam	1.43	10000	14288	11960	0.06	-0.203	1.36
Average	0.78	7500	5857	5405	0.06	-0.110	1.11

The Equilibrium Buffering Capacity (EBC)

The results in Table 2 shows the values of the copper Equilibrium Buffering Capacity (EBC). were ranged from 656 to 11960 L kg^{-1}, with a mean average of 5405 L kg^{-1} . The difference in the EBC values of the two textures is due to the different nature of adsorption of copper. The increase in the amount of ion adsorbed and the low bonding energy of the ion in such soils means that it is easily released from the adsorption surfaces to the soil solution, thus increasing the propagation rates of this ion, which increases its absorption.

Cu-Supplying parameter (SP) in soil

The results in Table 2 shows the values of the copper processing coefficient, ranging from 0.67 to 1.36, with a mean of 1.11 . The difference in the values of the Cu-Supplying Parameter (SP) in soil is due to the different nature of copper adsorption. The difference in the value of adsorption and binding energy in high energy locations is due to the difference in ion readiness at the different locations of the adsorption curve. The increase in the amount of ion adsorbent (q) and the decrease in the bonding energy of ion (k) in such soils means that it is easy to be released from the adsorption Soil, surfaces causing increased propagation rates of this ions and more abundances to be absorbed by the plant (3)

Thermodynamic parameters of copper adsorption

Table 2 shows the values of the Diffusion coefficient (R_L), with values 0.07 and 0.06 for

Jadiriya and Najaf respectively, with an average of 0.06, which means that copper is easily released from the adsorption surfaces to the soil solution, increasing the propagation rates of this ions and increasing its abundance in the liquid phase of the plant , (32) , and the free energy substitutions (-0.018) - (-0.203) Kj mol Kelvin^{-1} for the two soil textures respectively, with an average of (-0.110) which means that the reaction of the adsorbed copper is spontanious reaction . All free energy values are negative values and are consistent with diffusion coeff

REFERENCES

1. Ahmad, K.; I.A. Bhatti; M. Muneer; M. Iqbal and Z. Iqbal .2012. Removal of heavy metals (Zn, Cr, Pb, Cd, Cu and Fe) in aqueous media by calcium carbonate as an adsorbent . International Journal of Chemical and Biochemical Sciences (ISSN 2226-9614) 2 : 48-53
2. Al Janabi. F. K. and M. A. Al-Robiaee 2016. Kinetic of copper adsorption in calcareous soil. The Iraqi Journal of Agricultural Sciences. 47(2): 621-626
3. Al-Hadede, A. A. A. 2009. Phosphorus adsorption in calcareous soil of different characteristics.Journal of Tikrit University For Agriculture Sciences .9 (2) : 434 – 441
4. Alloway, B. J. 2013. Heavy Metals in Soils. Third Edition ,Blackie Academic and Professional. London, Springer Science +Business Media Dordrecht. pp:51-95
5. Al-Sabah, B. J. J..2007. Studying the Physico - Chemical Behavior of Mineral Elements Contaminating the Shatt al - Arab Water and Sediments. Ph.D. Dissertation, Faculty of Agriculture, University of Basra .pp :144-159
6. Al-Tamimi, H. J. 2004 . A kinetic model for copper sorption processes of the calcite surface. II . Distribution coefficient for solid solution . Basrah J. of Sci. 22 (1):23 .
7. Bradl,H.B.2004.Adsorption of heavy metal ions on soil constituents;J.Colloid Interface Sci.,277:1-18
8. Businelli, D. F.; L. Massaccesi and A. Onofri . 2009. Evaluation of Pb and Ni mobility to groundwater in calcareous urban soils of Ancona, Italy. Water, Air, and Soil Pollution 201:185-193.
9. Carter M. R and E. G. Gregorich .2008. Soil Sampling and Methods of Analysis 2nd. ed. CRC Press is an Imprint of Taylor & Francis Group, an Inform Business. pp. :1-198
10. Chen, A.H; Liu SC, C.Y.Chen 2008. Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. Journal of Hazardous Materials. 154: 184-191.
11. Covelo,E.F.; F.A.Vega and M.L. Andrade . 2007. Simultaneous sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn in acid soils II: soil ranking and influence of soil characteristics. J. Hazard. Mater., 147 : 862-870
12. Das,B.; N.K. Mondal ; p. Bhaumik; K. C. Roy and C,R. ,Das. 2013.Removal of copper from aqueous Solution using alluvial soil of Indian origin : Equilibrium Kinetic and Thermodynamic Study J. Mater,. Environ Sci . 4(4): 392-408
13. Ghomri, F. ; A. Lahsini ; A. Laajeb and A. Addaou 2013.The removal of heavy metals ions (Copper, Zinc, Nickel and Cobalt) by nature bentonite. Morocco. Larhyss Journal, ISSN 1112-3680, n° 12, Janvier 2013, pp. : 37-54
14. Goldberg S. 2002.Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Science Socity of America Journal,66:413-421.
15. Hossenpour.A.R. and F.Dandammoed .2010. Sorption characteristic of copper in some calcareous soil of western Iran-Journal of American Science ;6(11):103-108
16. Ibrahim, H.; A. El-Kady; N. Ammar; L. Meesuk; P. Wathanakul and M. Abdel-Wahhab . 2011.Application of isotherm and kinetic models for the removal of lead Ions from aqueous solutions.. J. Environ. Eng., 139(3):349.
17. Jalali, M. and S. Moharami .2007. Competitive adsorption of trace elements in calcareous soils of Western Iran. Geoderma, 140: 156-163.
18. Jiang, W.; T. Tao and Z. Liao.2011. Removal of heavy metal from contaminated soil with chelating agents. Open J. Soil Sci., 1, :70–76
19. Krishnamurti, G.S.R. and R. Naidu . 2008. Chemical speciation and bioavailability of

trace metals. in: violante, A. ; P.M. Huang and G.M. Gadd (eds). Biophysico-Chemical processes of heavy metals and metalloids in soil environments wiley inter science, New York, pp.: 419-466

20. Li, J.-S.; P.Wang and L. Liu 2013. Environmental prediction model for dynamic release of Lead in contaminated soil under washing Remediation . EJGE. 18:55-70

21. Liu,C.hen, S. -C. and C.-Y. Chen. 2008. Comparative adsorption of Cu (II), Zn (II) and Pb (II) ions in aqueous solution on the cross linked Chitosan with epichlorohydrin, Journal of Hazardous materials. 2008;154:184 – 191

22. Maftoun, M. N. Kariman and F. Moshiri. 2002. Sorption characteristics of copper(II) in selected calcareous soils of Iranin relation to soil properties common. Soil Sci. Plant Analysis 33: 2279-2289.

23. Mehmedani L, A.M .2016.Adsorption bhavior of copper in some calcareous soils from Duhok Governorate. Science Journal of university of Zkho,4 (2):159-310

24. Papanicolaou E. P..1976. Determination of cation exchange capacity of calcareous soils and their percent base saturation. Soil. Sci. 121: 65-71

25. Pare, S.; I. Persson; B. Guel; D. Lundberg; L. Zerbo; S. Kam and K. Traoré .2012. Heavy metal removal from aqueous solutions by sorption using natural clays from Burkina Faso. Afr. J. Biotechno., 11: 10395–10406.

26. Peter S.H. .2010. Trace Elements in Soils. ,A John Wiley and Sons ,Ltd., Publication UK. pp. :441-445

27. Sastreet, J.; G. Rauret and M. Vidal .2006. Effect of the cationic composition of sorption solution on the quantification of sorption-desorption parameters of heavy metals in soils. Environ. Pollut., 140: 322-339

28. Selim, H. M. 2013.Transport and retention of heavy metal in soils: competitive sorption. Advances in Agronomy. 119: 275-30

29. Selim, H.M. and H. Zhang . 2013.Modeling approaches of competitive sorption and transport of trace metals and metalloids in soils. J. Environ. Qual. 42 : 640-653.

30. Soares, M.R. 2006.Distribution Coefficient (K_d) of Heavy Metals in Brazilian Soils. 18th World Congress of Soil Science July 9-15, 2006 Philadelphia, Pennsylvania, USA.pp :139-141

31. Unda bestid,T.S.; Nir.G.Rytaw-C; C Seban; E. Monila and C.Magueda .2002. Modeling adsorption-desorption of Cu on edge and planer sites of montimorillonite-Environ. Soil.Sci., Technol .36 (12):2677-2683

32. Vega,F.A.; E.F. Covelo; J.J.Vazques and L. Abdrade .2007. Influence of mineral and organic components on copper, lead and zinc sorption by acid soils. J. Environ. Sci. Health. Part A-Toxic/Hazard. Subst. Environ. Eng. 42:2167–2173

33. Violante, A. ; V. Cozzolino; L. Perelomov; A.G. Caporale and M. Pigna .2010. Mobility and bioavailability of heavy metals and metalloids in Soil environments. J. Soil. Sci. Plant Nutr. 10 (3): 268-292.