



## EFFECTS OF PARTIAL ACIDULATED PHOSPHATE ROCK AND COMPOST ON ADSORPTION AND DESORPTION CAPACITIES OF COPPER IN CALCAREOUS SOIL

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### ABSTRACT

In this present laboratory study, partial acidulated phosphate rock (40% PAPR) and compost have been used to study their effects on adsorption and desorption capacities of copper in calcareous Iraqi soil. The results showed increases capacity of soil to adsorb copper with increasing concentrations of the added copper in presence of PAPR and compost. Adsorption curves showed two phases, first phase was rapprochement values of copper adsorption of the copper added solutions 2.5, 5.0 and 10 mg Cu L<sup>-1</sup>, and second phase was different values of copper adsorption at concentrations 25, 50 and 100 mg Cu L<sup>-1</sup>. The percentage of copper adsorption capacity took the following ranking in the used treatments (soil+compost) > (soil) > (soil+compost+40%PAPR). Desorption study of the adsorbed copper showed decrease desorption capacity values with increase of the adsorbed copper amounts in compost and 40% PAPR treatments. The attained adsorbed copper was 82.23% at 2.5 mg Cu L<sup>-1</sup> solution and 52.23% at 10 mg Cu L<sup>-1</sup> solution. The desorption capacity of copper values were highest in (soil) treatment followed by (soil+compost) treatment and lowest in (soil+compost+40%PAPR) treatment.

**KEYWORDS:** Adsorption isotherm curve, PAPR, Compost, Adsorption and desorption capacities.

### INTRODUCTION

Copper is an important micronutrient and trace amounts are essential for crop growth. However, high concentrations of copper will produce toxic effects. Copper involves with many metabolic processes in plants and activates of many enzymes and has positive effects in growth and yield of many crops (Alloway, 1995). For most agricultural soils, bioavailability of Cu<sup>2+</sup> is controlled by adsorption process (Xie, 1996). There are two types of minerals that are involved in the adsorption – desorption of Cu<sup>2+</sup>: permanent charge and variable charge. Permanent Charge minerals such as montmorillonite carry a negative charge as a result of ion substitution during the formation of minerals (Bertsch and Seaman, 1999). In spite of having the most soils acceptable of total copper, the available amount of copper is considered as a limiting and important factor and presence of high organic matter or high level of phosphorus may either decrease or increase its availability in soil (Kabata-Pendias, 2001). Organic matter binds copper more tightly than other micronutrients and this reduces availability to crops and then sufficient copper is released to support normal crop growth after decomposing of organic matter (Schulte and Kelling, 1999). The adsorption is considered one of the important processes in soil that may effect on fate and movement of the nutrients such as P, K, S, Cu, Zn, Mn and Bo (Hunter, 1980), while the adsorption capacity is the relation between the amount of the adsorbed matter by the solid part of soil and its quantity in soil solution at equilibrium. Adsorption mechanisms of copper on soil oxides, clay minerals and organic matter were studied by many

workers such as Yu et al (2002); Xiong (2005); Shariff and Esmail (2012); Das et al (2013); Alganabi and Al-Rubaye (2016). The desorption capacity is the amount of the released nutrient to soil solution compared with its adsorbed amount. The physical and chemical properties of soil, soil minerals and organic matter are considered as important factors affecting copper desorption (Singh et al, 1994; Yu et al, 2002; Yuan et al, 2007; Abat, 2010; Shariff and Esmail, 2012). The overall objectives of this study are to quantify soil copper adsorption – desorption behavior and study effects of adding compost and 40% PAPR on adsorption and desorption of copper.

### MATERIALS AND METHODS

#### Soil and treatments

Soil samples were collected from college of agriculture field, Abu-ghraib, Baghdad, Iraq. Composite soil sample was air dried, ground, and passed through a 60-mesh sieve to use. Some of the soil chemical and physical properties are given in Table 1. Three kinds of treatments were chosen in this study, they were Soil, (Soil+Compost) and (soil +Compost +40%PAPR, partial acidulated phosphate rock), the weights of soil, compost and 40%PAPR were 5g, 10g compost kg<sup>-1</sup>soil and 20g PAPR kg<sup>-1</sup>soil respectively. Some of the chemical properties of the used compost are shown in Table 2. The phosphate rock (PR) was brought from Akashat region, Al-Ramade governance, Iraq and some of its chemical properties are shown in Table 3. Enough amount of this PR was treated with concentrated H<sub>2</sub>SO<sub>4</sub> at rate to produce 40%PAPR by using the method that was suggested by Yagodin (1984).

Capacities of copper in calcareous soil

**TABLE 1.** Some properties of the soil

pH	1:1	7.40
EC e	dS.m <sup>-1</sup>	4.13
Organic matter	%	1.36
Olsen available P	mgPKg <sup>-1</sup>	13.75
Avail. N	mgKg <sup>-1</sup>	166.5
Avail. K	mgKg <sup>-1</sup>	485
CEC	Cmolc.kg <sup>-1</sup>	20.20
Carbonate minerals	%	16.9
Field capacity	%	30
Soil texture		SiCL

**TABLE 2.** Some of chemical properties of Ekashat phosphate rock

pH	1:1	7.5
ECe	dSm-1	3.0
K1+	mgKg-1	728
SO42-	%	0.246
Ca2+	%	29.25
P	%	10.22
Mg2+	mgKg-1	280
Na1+	mgKg-1	310

**TABLE 3.** Some of chemical properties of Compost

pH	1:1	7.82
ECe	dSm <sup>-1</sup>	5.92
P	%	1.31
N	%	2.5
K	%	1.40
Organic C	%	48.5
C/N ratio		19.4

**Adsorption capacity of copper ion**

The materials of the last three treatments were placed into 100 ml polypropylene centrifuge tubes, and 50 ml of solution containing 0,2,5,10,25,50 and 100 mg Cu L<sup>-1</sup> (equal to 0,25,50,100,250,500 and 1000 mg C kg<sup>-1</sup>soil)(as Cu(NO<sub>3</sub>)<sub>2</sub>) was added to each tube. The suspensions were shaken at 200 rpm for 2h at 25 centigrade and then equilibrated in a dark incubator for an additional 22h .At the end of designated time ,the suspensions were centrifuged at 2500 rpm for 10 min and filtered through 0.45-um filter paper .Ten milliliters of the filtrate were transferred into a 10 ml polypropylene centrifuge tube for measuring Cu<sup>2+</sup> concentration using atomic absorption spectrometry .Total amount of the adsorbed Cu<sup>2+</sup> (q) was calculated by the difference between the total applied Cu<sup>2+</sup> in the equilibrium solution(Yu. et al,2002).

**Desorption capacity of adsorbed copper ion**

The residue Cu-enriched soil separated from the supernatant solution by centrifugation ,from the above adsorption experiment ,was treated with 50ml-0.005M DTPA to each tube and the suspensions were shaken at 200 rpm for 2h at 25centigrade and equilibrated for an additional 10h . The equilibrated suspensions were then centrifuged at 2500 rpm for 10 min and then filtered .Ten milliliters of the filtrate were pipetted into a 10 ml polypropylene centrifuge tube for measuring Cu<sup>2+</sup> concentration using atomic absorption spectrometry (Yu. et al, 2002).

**RESULTS**

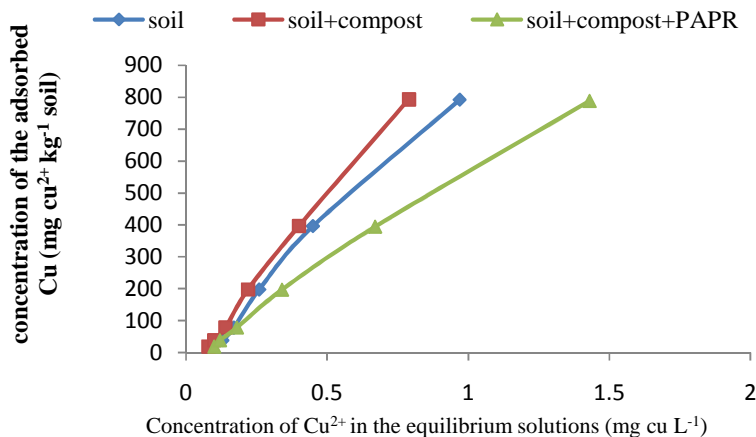
**Adsorption capacity of copper ion**

Table 4-shows that adsorption of Cu<sup>2+</sup> increased with increase of Cu concentration in the equilibrium solution in soil, (soil+compost) and (soil+compost+40%PAPR) treatments. Adding compost gave the highest values of the adsorbed Cu<sup>2+</sup> compared with the other treatments. The adsorbed copper concentrations the composed added treatment were 19.36 and 793.68 mg.Cu kg-1 soil for Cu<sup>2+</sup> solutions 25 and 1000 mg Cu.kg-1soil respectively. This result reflects the role of organic matter to bind strongly copper ions (Alganabi and alrubaye,2016) . Slopes of the isotherms curves (Fig. 1) reflected high adsorption capacity in soil,( soil+compost) and (soil+compost+40%PAPR) treatments ,possibly because Cu<sup>2+</sup> involves multiple adsorption sites (McBride,1995 and Alcacio et al,2001) and the high capability for calcareous (carbonate minerals) to adsorbed and precipitate Cu<sup>2+</sup> as CuCO<sub>3</sub>(Kabata-Pendias,2011). Using compost gave the highest slope of the adsorption isotherms, It is possibly due to high C.E.C of soil and organic matter colloids and the high affinity of organic matter to adsorbed copper (Kabata-Pendias,2011).Adding 40%PAPR gave the lowest slopes of adsorption isotherms. This may be due to the high competition between P and Cu on adsorption sites of the organic and clay colloids (Alneame,1999 and Kabata-Pendias ,2011). The used soil adsorbed more than 79% of the copper in the 1000 mg Cu kg<sup>-1</sup>soil concentration ,suggesting that the soil might not reach its maximum adsorption capacity even at the

designed highest Cu<sup>2+</sup> loading .Similar findings were also like Alganabi and Al-Rubaye (2016).

**TABLE 4.** Characteristics of Cu<sup>2+</sup> adsorption

Cu <sup>2+</sup> added (mg kg <sup>-1</sup> soil)	Adsorbed Cu <sup>2+</sup> (mg Cu kg <sup>-1</sup> soil)		
	soil	Soil+ compost	Soil+ compost+ 40% PAPR
25	19.28	19.36	19.20
50	38.96	39.20	39.04
100	78.64	78.88	78.56
250	179.92	198.24	197.28
500	396.40	396.80	394.64
1000	792.24	793.68	788.56



**FIGURE 1:** Adsorption isotherms of Cu<sup>2+</sup>

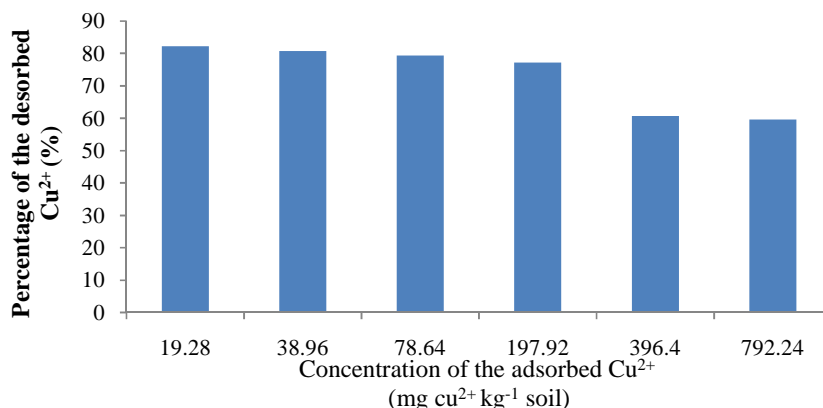
**Desorption capacity of the adsorbed copper ion**

Most of the adsorbed Cu<sup>2+</sup> in the soil ,(soil+compost) and (soil+compost+40%PAPR) treatments was readily desorbed by 0.005M-DTPA.It can be noticed that the percentage of the desorbed copper from the soil treatment ranged from 59.59% for the adsorbed value 792.23 mg Cu kg<sup>-1</sup>soil to 82.23% for the adsorbed value 19.28 mg Cu Kg<sup>-1</sup>

<sup>1</sup>soil ,This means that from 17.77% to 40.41% of the total adsorbed Cu<sup>2+</sup> was recovered by DTPA (Table 5 and Fig. 2).The proportion of the desorbed Cu<sup>2+</sup> decreased with increase the concentration of adsorbed Cu<sup>2+</sup> and these may reflect high tightly bonded between copper and soil collides (McLaren and Grawford,1973).

**TABLE 5.** Characteristics of Cu<sup>2+</sup> desorption

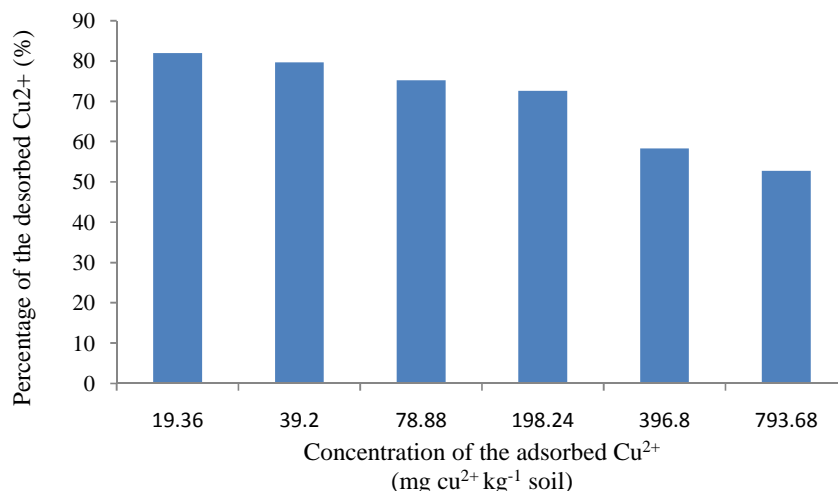
Cu <sup>2+</sup> added (mg kg <sup>-1</sup> soil)	Cu <sup>2+</sup> Desorption %		
	soil	Soil+compost	Soil+compost+40%PAPR
25	82.23	81.93	81.70
50	80.77	79.67	78.59
100	79.43	75.17	75.94
250	77.13	72.59	65.18
500	60.72	58.31	66.44
1000	59.59	52.78	52.56



**FIGURE 2.** The relation between percentage of the desorbed Cu<sup>2+</sup> with concentration of the adsorbed Cu<sup>2+</sup> in (soil) treatment.

Mixing the compost with soil gave a range of desorption rate of copper from 81.93% for the adsorbed value 19.36 mg Cu kg<sup>-1</sup>soil to 52.78% for the adsorbed value 793.68 mg Cu Kg<sup>-1</sup>soil (Table 5 and Fig. 3 ).This may be probably

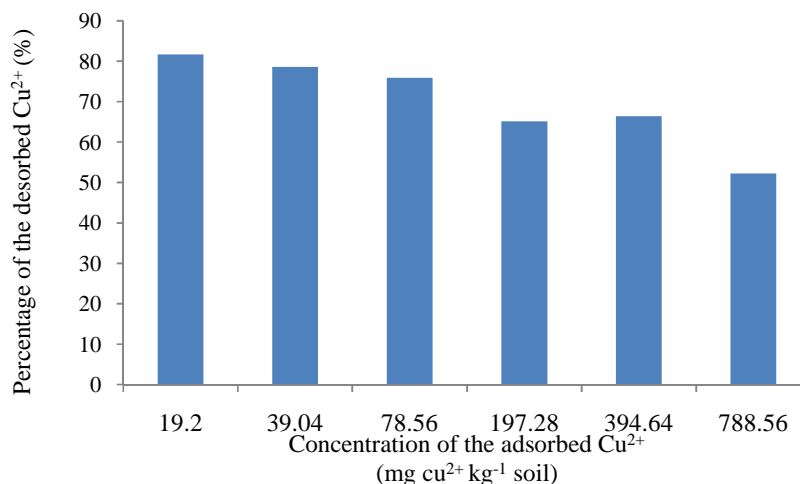
due to the fact that organic matter is the affected factor in fixation of the micronutrients such as Cu<sup>2+</sup> by increasing the adsorbed amount of copper (Robert,1983).



**FIGURE 3.** The relation between percentages of the desorbed Cu<sup>2+</sup> with concentration of the adsorbed Cu<sup>2+</sup> in (soil+compost) treatment

The percentages of the desorbed copper when compost and PAPR were mixed with the soil are shown in Table 5 and Fig 4. The desorbed copper percentages were 81.70 ,78.59 ,75.49 ,65.18 ,66.44 and 52.32% for the adsorbed copper values 19.2 ,78.56 ,197.28 ,394.64 and 788.56 mg Cu Kg<sup>-1</sup>soil respectively. This treatment resulted less values of the desorbed copper compared with (soil) and

(soil+compost) treatments and this may be probably to increase the surface area of soil organic and mineral colloids and clay minerals and PAPR and then, the adsorbed copper amounts increased while their desorption amounts decreased (Liu et al,2011;Alrubaye et al,2016 and Aljanabi and Al- Rubaye,2016).



**FIGURE 3.** The relation between percentage of the desorbed Cu<sup>2+</sup> with concentration of the adsorbed Cu<sup>2+</sup> in (soil+compost+40%PAPR) treatment

**REFERENCES**

Abat, M. (2010) Retention, release, and plant availability of copper and zinc in three tropical peat soil of Sarawak. MSc thesis, University of Adelaide, Malaysia.

Alcacio,T.E., Hesterberg, D., Chou,W.Q., Martin, J.D., Beauchemin, S. and Sayers, O.E. (2001) Molecular scale characteristics of Cu(II) bonding in goethite-hamate complexes. *Geochim. cosmochim.Acta* 65,1355-1366.

Alloway, B.J. (1995) *Soil processes and the behavior of metals*. Blackie academic and professional, London.

Alneame, S.N. (1999) *Fertilizers and soil fertility*. University of Mosul press.2<sup>nd</sup> ed. Iraq.

Aljanabi, F.K. and Al-Rubaye, M.A. (2016) Kinetics of copper adsorption in calcareous soil. *The Iraqi Journal of Agricultural sciences (TIJAS)* 47,621-626.

- Al-Rubaye, M.A., Nasir, K M. and Munaf, D.F. (2016) Kinetics of dissolution of phosphate rock, partial acidulated phosphate rock and tri superphosphate in calcareous soil. RJPBCS, 7,886-890.
- Bertsch, P. & Seaman, J. C. (1999) Characterization of complex mineral assemblages, Proc. Natl. Acad. Sci. 96, 3350-3357.
- Das, B., Mondal, N.K., Bhaumik, R., Roy, P., Pal, K.C. and Das, C.R. (2013) Removal of copper from aqueous solution using alluvial soil of Indian origin. J. Mater. Environ. Sci. 4,392-408.
- Hunter, A.V. (1980) Laboratory and green house techniques for nutrient survey studies to determine the soil amendments required for optimum plant growth. Orange city, Florida (USA), Agro. Services International, Inc.
- Kbata-Pendias, A. (2011) Trace elements in soils and plants. CRC press. Taylor and Francis group.
- Liu, M., Deng, Y., Zhan, H. and Zang, V.(2001) Adsorption and desorption of copper (II) from solution on new spherical cellulose adsorbent, Journal of Applied Polymer Science 84,478-485.
- McBride, M.B. (1995) Toxic metal accumulation from agricultural use of sludge. J. Environ. Qual. 24,5-15.
- McLaren, R.G. and Grawford, D.V.(1973) Studies on soil copper . 1: Fractionation of copper . Soil Sci. 24,172-181.
- Robert, D.H. (1983) Effect of soil pH on adsorption of lead, copper, zinc and nickel. Soil Sci. Soc. Am. J.47, 47-51.
- Shulte, E.E. and Kelling, K.A. (1999) Soil and applied copper, understanding plant nutrient, University of Wisconsin.
- Singh, R.R., Prasad, B. and Choudhary, S.N. (1994) Desorption of copper in calcareous soils. Journal of Indian Society Soil Science, 42,555-558.
- Shariff, R.M. and Esmail, L.S. (2012) Adsorption-desorption for some heavy metals in presence of surfactant on six agricultural soils. IJ RRAS. 12:3.
- Yagodin, A.B. (1984) Agricultural chemistry. Mir publisher. Moscow, P-375.
- Yu, S.Z., He, L., Huang, C.Y., Chen, G.C. and Calvert, D.V. (2002) Adsorption – desorption behavior of copper at contaminated levels in red soils from china. J. Environ. Qual. 31, 1129-1136.
- Yuan, S., Xi Z., Jiang, Y., Wan, J., Wu, C., Zheng H. and Lu, X.(2007) Desorption of copper and cadmium from soils enhanced by organic acids. Doi, 10, 1016.
- Xie, Z. (1996) Chemical balance of soil copper, Adv. Environ. Sci. 4, 1-23.
- Xiong, X. (2005) Effects of clay amendment on adsorption and desorption of copper in water repellent soils, AJSR 43,397-402.