

# Effects of Organic Ligands and pH on Copper Extractability from Soils of Arid Region

E.A.Elkhatib, M.E.Saleh, A.M.Mahdy and N.H.Barakat <sup>1</sup>

## ABSTRACT

Low molecular weight dissolved organics can play an important role in controlling metal solubility. The effect of organic ligands citrate, malate, and succinate on the extractability of Cu was investigated in a range of Cu-treated soils varying widely in soil characteristics. The soils used are referred to as clay, calcareous and sandy soils. Experimental parameters were adjusted to investigate the effect of pH and organic ligands on Cu extractability. To account for the ligand effect on Cu desorption, the three amended soils were extracted with solutions buffered at constant pH. The ability of ligand ions to extract Cu at initial pH solution followed the general order: citrate > malate > succinate. The observed trends in extractable Cu are related to Cu-ligand stability constants.

The effect of pH on ligand extractable Cu was investigated by extracting Cu with solutions at pH values between 5.0 and 8.0. The pH of ligand solution strongly affected extractable Cu. Increasing pH has resulted in marked decrease in the amounts of ligand extractable Cu, which suggests that the greater Cu-bonding affinity shifts from ligand to soil as pH increases. For all ligands, Extractable Cu was least in clay soil while the sandy soil exhibited the highest release; copper extractability from calcareous soil was intermediate.

## INTRODUCTION

Copper provides a vital nutritional component for plants, animals and humans. A copper deficiency causes retardation of plant growth and may cause many adverse effects on blood vessels, bone, central nervous system, kidney, liver and enzymes in animals and human. High concentrations of copper in irrigated soils and ground water can also be a problem. Copper may pose a threat to agricultural production and may impact the health of humans and animals (Owen, 1981; Zamuda and Sunda, 1982).

Many contaminants have been reported as sources of heavy metals pollution in soil and ground water, e.g., exhaust, waste water and solid wastes from industrial production, fertilizers and pesticides. Agricultural practices constitute significant non-point sources of metals. The main sources of this type of pollution are impurities in fertilizers, pesticides, refuse derived compost, wood preservatives and corrosion of metal objects like metal roofs and fences (Alloway, 1995).

The mobility of heavy metals depends on their chemical speciation, which in turn is related to the chemical properties of soil. For example, in some types of soil the presence of carbonates effectively immobilizes Cu by providing an adsorbing surface or by buffering the pH (Dudley et al., 1991). Soil parameters, such as pH, organic carbon content, iron and manganese oxide content and total metal content affect the distribution of copper among different soil fractions (Fic and Schrcter, 1989).

Evidence suggests that metal complexation with inorganic and/or organic ligands in soil can have dramatic influence on mobility and bioavailability of metals to soil organisms and plants (Chaney, 1988). The extent of metal-ion retention by clay has been shown to vary with the adsorption isotherm parameters, solute concentration of competing cations, bonding constant) and with other factors such as pH and type of clay mineral, e.g., type of ligand (Egozy, 1980; Inskeep and Baham, 1983; Puls and Bohn, 1988). Copper movement is often associated with the movement of organics and inorganic constituents of soil (Reed, 1993). Although copper movement has been observed in soils, the effects of organic ligands on copper release from soils are not well understood. In this study, therefore, we have investigated the effect of pH and organic ligands on the extractability of Cu in a range of Cu-treated soils varying widely in chemical characteristics.

## MATERIALS AND METHODS

### Soils:

Samples of three surface soils (0-30cm) which differed in location, origins, texture and calcium carbonate content were used. One was a clay alluvial soil (Torrifluvents), the second was a calcareous soil (Calciorthids) and the third was a sandy loam desert soil (Quartzipasmment). Hereafter, the soils will be referred to as clay, calcareous and sandy soils respectively.

The soils were air-dried, passed through a 2 mm sieve and stored in plastic bags before use. The pH values of the soils were measured in a 1 : 2 soil-water, conductivity (EC) was measured and soluble cations and anions were determined in the soil paste extracts. The organic matter content was determined by the method of Walkly and Black (Nelson and Sommers, 1982) and

<sup>1</sup> Department of Soil and Water Sciences, College of Agriculture, El-Shatby, Alexandria University, Egypt. Received Feb. 15, 2006, Accepted March. 15, 2006.

the cation exchange capacity by the method of Thomas (1982). Particle size analysis was determined by the hydrometer method (Black, 1965). Selected chemical and physical properties of the three soils studied are shown in Table 1.

#### Organic acids:

Organic acids that occur naturally in soils and differ in number of functional groups were selected for the study. The selected organic acids are citric, malic and succinic.

Table 2 lists some of the characteristics of the organic acids.

#### Adsorption isotherms:

Subsamples of the soils were treated with 150 ug/g Cu as  $\text{CuSO}_4$ . After adding Cu, the soils were incubated at field capacity for 6 wks, during which the soils were subjected to four wet-dry cycles. After 6 weeks the soils were air dried, crushed to pass through a 2mm sieve and stored in polyethylene bag for chemical analysis.

Adsorption isotherms were obtained by batch studies. Soil samples (1g) were mechanically shaken for 24 h at 25°C in separate polypropylene tubes with 30 ml of 0.01 M  $\text{CuSO}_4$  aqueous solution containing Cu as  $\text{CuSO}_4$  ranging in concentration from 5 to 150 mg  $\text{L}^{-1}$ .

At the end of the shaking period, the samples were centrifuged and filtered. The concentrations of Cu in the supernatant were determined using atomic absorption spectrophotometry (AAS). The amount of Cu adsorbed was estimated from the difference between the amount added and the amount remaining in the solution.

#### Extraction of Cu:

Duplicate 1g samples of air dried soil were placed in polypropylene centrifuge bottles and 50 ml of appropriate organic acid solution (3mM) were added. The samples were shaken in an end-over-end shaker for 12 hrs and centrifuged and filtered. Copper was determined in soil extracts using atomic absorption spectrometry (AAS).

#### Effect of pH on Ligand-Extractable Cu:

The effects of pH on ligand extractable Cu were investigated by extracting Cu with solution at pH values between 5.0 and 8.0. Duplicate 1g samples of air dried soils were placed in centrifuge bottles and 50 ml of appropriate organic acid solution (3mM) and the pH was adjusted by using either organic acid or dilute NaOH at pH values (5.0,5.5,6.0,6.5,7.0,7.5,8.0) for the three soils. Following equilibration, Cu was extracted as mentioned earlier.

The samples were centrifuged for 30 minutes equilibration, filtered, and pH was measured. Copper in

the extract was determined using atomic absorption spectrometry (AAS)

## RESULTS AND DISCUSSION

#### Sorption of Cu on the Studied Soils:

Figure (1) shows the adsorption isotherm of Cu by clay, calcareous and sandy soils. A large concentration range was utilized for these isotherms, including relatively high Cu concentrations. These high concentrations are of interest since they may exist in Cu-polluted sites and are viewed to represent a disparate mode of contamination and transition into the food chain (Davies, 1980).

For describing sorption of Cu in the soils studied, it is convenient to refer to the isotherm classification proposed by Giles et al., (1960), who distinguished four main types of isotherms corresponding to different solute adsorbent interactions. This classification has been used lately to describe heavy metals adsorption on soils (Harter 1983). The four isotherms are named L, H, C, and S.

The clay soil had the highest affinity for Cu; the sandy soil exhibited the least affinity. Copper sorption on calcareous soil was intermediate between that observed for sandy and clay soils. A decreasing slope as equilibrium concentrations increased characterized the sorption isotherms for calcareous and sandy soils. Such sorption behaviour is consistent with L-type isotherm and is explained by the high affinity of the adsorbent for the adsorbate at low concentrations, which then decreases. When affinity increases, the shape of isotherms becomes the H-type, as in the case of sorption isotherm for the clay soil (Figure 1). For both L and H isotherms, the distribution coefficient decreases as the adsorbed amount increases. These isotherms are consistent with heterogeneous surfaces having a range of adsorption sites from high to low energy (Sparks 1995).

The quantity of Cu sorbed by the soils followed the trend clay > calcareous > sandy (Figure 1). It is noted from Table (1) that the clay soil shows the highest values for organic matter, clay content, and cation exchange capacity. This observation is supported by a report of Anderson et al. (2002) that total heavy metal concentration correlated with the effective cation-exchange capacity, clay content and organic matter content

#### Effect of pH and Organic Ligands on Cu Extractability:

Concentration of extractable Cu varied as a function of both soil and organic ligand (Figure 2). For all ligands, the least Cu was extracted from the clay soil and

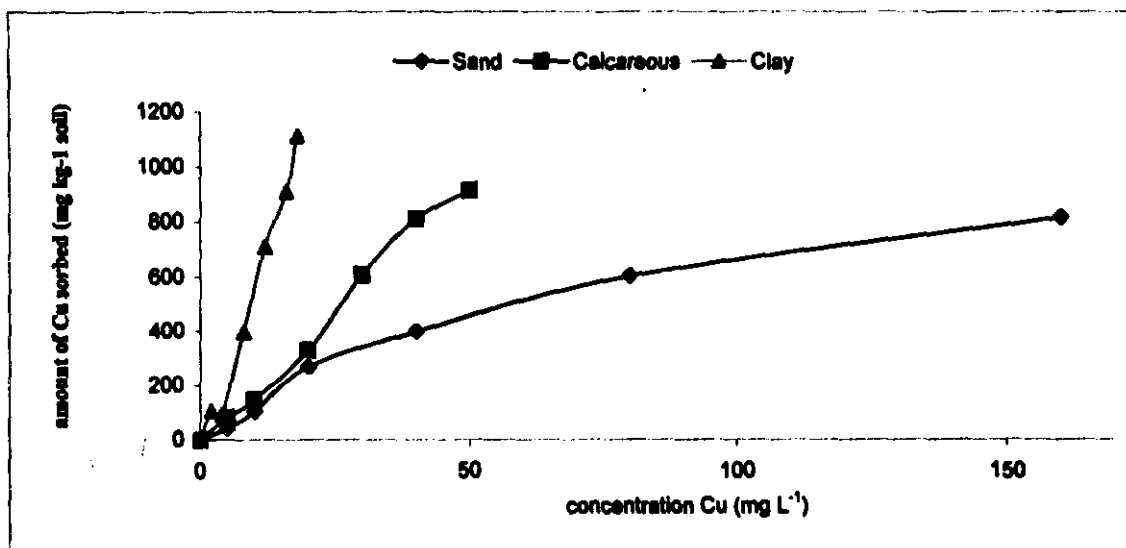
**Table 1. Selected Chemical and Physical Characteristics of the three Soils**

Type of soil	pH	E.C dS.m <sup>-1</sup>	Clay %	Silt %	Sand %	Total Carbonate %	Organic matter %	CEC Cmol (p <sup>+</sup> ) kg <sup>-1</sup>
Clay	8.4	0.75	44.6	14	41.9	3	1.4	33
Calcareous	7.9	4.54	26.8	6.4	44.9	26	0.21	18
Sandy	8	1.12	19.4	1.3	79.3	19	0.79	11

**Table 2. Relevant Properties of low-molecular- weight used in the study**

Organic acids	Chemical formula	Molecular weight	Ligand Form	pk <sub>a</sub> <sup>+</sup>
Malic	HO <sub>2</sub> CCH <sub>2</sub> CH(OH)CO <sub>2</sub> H	134.09 g	H <sub>2</sub> L	3.46,5.1
Succinic	HOOCCH <sub>2</sub> CH <sub>2</sub> COOH	118.09 g	H <sub>2</sub> L	4.16,5.61
Citric	C(OH)(COOH)(CH <sub>2</sub> COOH) <sub>2</sub>	192.13 g	H <sub>3</sub> L	3.13,4.78, 6.43

pk<sub>a</sub><sup>+</sup> values were adopted from Serjeant and Dempsey (1979)

**Fig.1. Copper sorption isotherms for the three soils studied**

the largest amount was extracted from the sandy soil. These differences in extractable Cu are not consistent with the Cu sorption capacities of the soils, (Figure 1). Consequently, the greatest Cu was extracted from the coarse textured soil and least from the high-Cu-affinity soil. Cavallaro and McBride (1984) suggested that oxide component of the soil clay was more significant than the organic component in Cu sorption and fixation.

The amount of Cu extracted is a function of both soils and solution characteristics. Therefore, the most

important factor controlling Cu desorption in the absence of organic-metal complex is soil characteristics.

In the presence of organic ligands, both the affinity of soils for Cu and the nature of organic ligand control the extent of desorption. Among the organic ligands studied, the citrate ion extracted the largest amount of Cu and succinate ion extracted the least (Figure 2).

The ligand species at any given pH is controlled by the reaction:



Where

$$[H_{x-1} A^-] = [H_x A] K_a / [H^+]$$

and where  $H_x A$  is undissociated anionic ligand and  $H_{x-1} A^-$  is the dissociated anionic ligand. At any given pH, the form of the ligand will vary with the  $pK_a$  of the appropriate organic acid ( Naidu and Harter1998). Furthermore, ligand ion release is controlled by factors such as LE Chatelier's principles which stated that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change." So processes that remove either the ligand ions on the protons from the reaction cite will also enhance the dissociation processes. Such processes may include adsorption of ligand ions by soils or formation of metal-ligand bonds.

To account for the ligand effect on Cu desorption, the three amended soils were extracted with solutions buffered at constant pH (Figure 2). The ability of ligand ions to extract Cu at pH 3.1 to 3.3 followed the general order:

citrate > malate > succinate.

The stability of Cu-ligand complexes varies considerably with the nature of ligand ions (Table 2). Among the ligands studied, succinate is the least stable of the organics and the amount of Cu released by succinate was the smallest among the organic ligands. The greater stability of the citrate and malate-complexes led to greater efficacy of citric and malic acids in desorbing Cu from soils than succinic acid. Besides, succinic acid with a smaller acid dissociation constant ( $pK_a$  value = 4.16) provided fewer anions for complexing with Cu than the other two acids ( $pK_a$  3.13, 3.46).

To study the effect of pH on Cu extraction in the presence of organic ligands, the soils were extracted with solutions at different pH values ranging from 5 to 8.0. The effect of organic ligands at varying pH is shown in figure 3. The pH of ligand solution strongly affected extractable Cu. Increasing pH has resulted in marked decrease in the amounts of ligand extractable Cu (figure3), which suggests that the greater Cu-bonding affinity shifts from ligand to soil as pH increases. Temminghoff et al.(1997) reported that soil pH changed the affinity of soils for heavy metals which may be caused by pH-dependent proton competition and surface charge densities on soil colloids. The smaller amounts of Cu extracted at higher pH suggested that increasing soil pH leads to a marked increase in the net surface negative charge density and this in return coupled with greater Cu sorption( Brown et al.,1997).

Despite the differences in solution pH, the largest amount of Cu was still extracted by citrate and the least

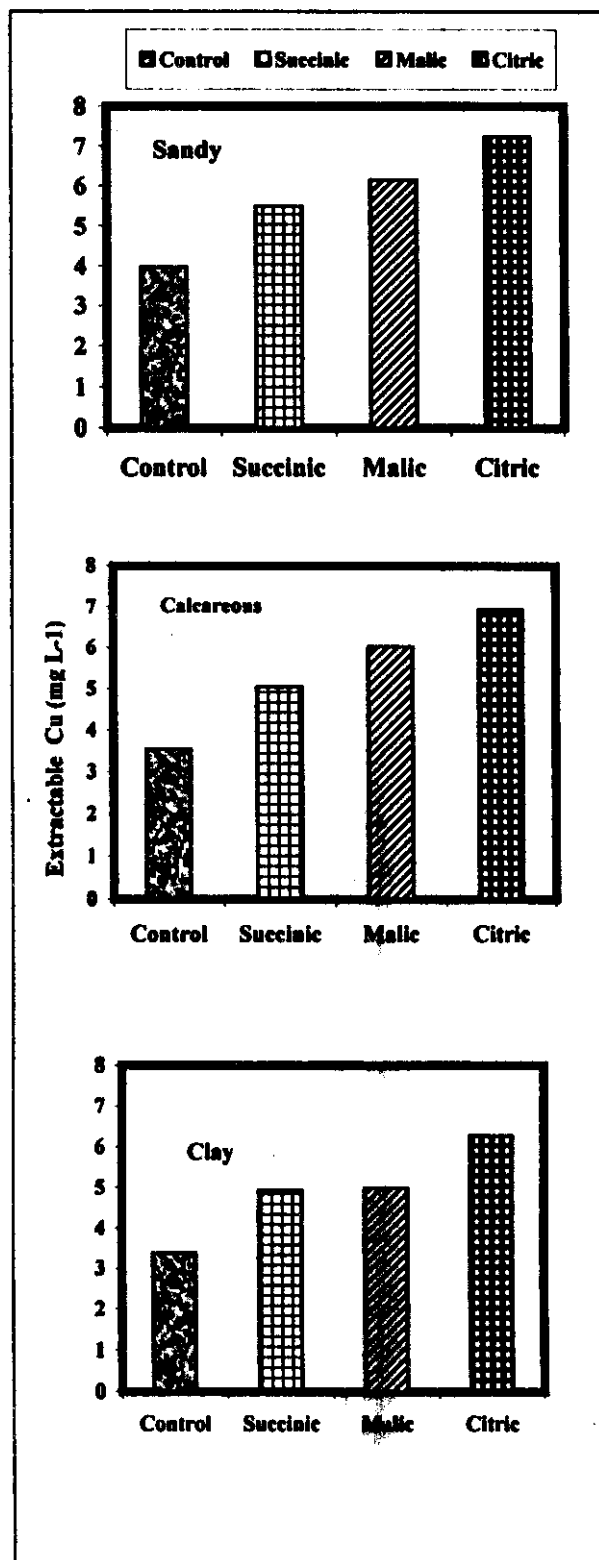


Figure2. Copper extraction from sandy, calcareous and clay soils by various organic ligands at constant pH .

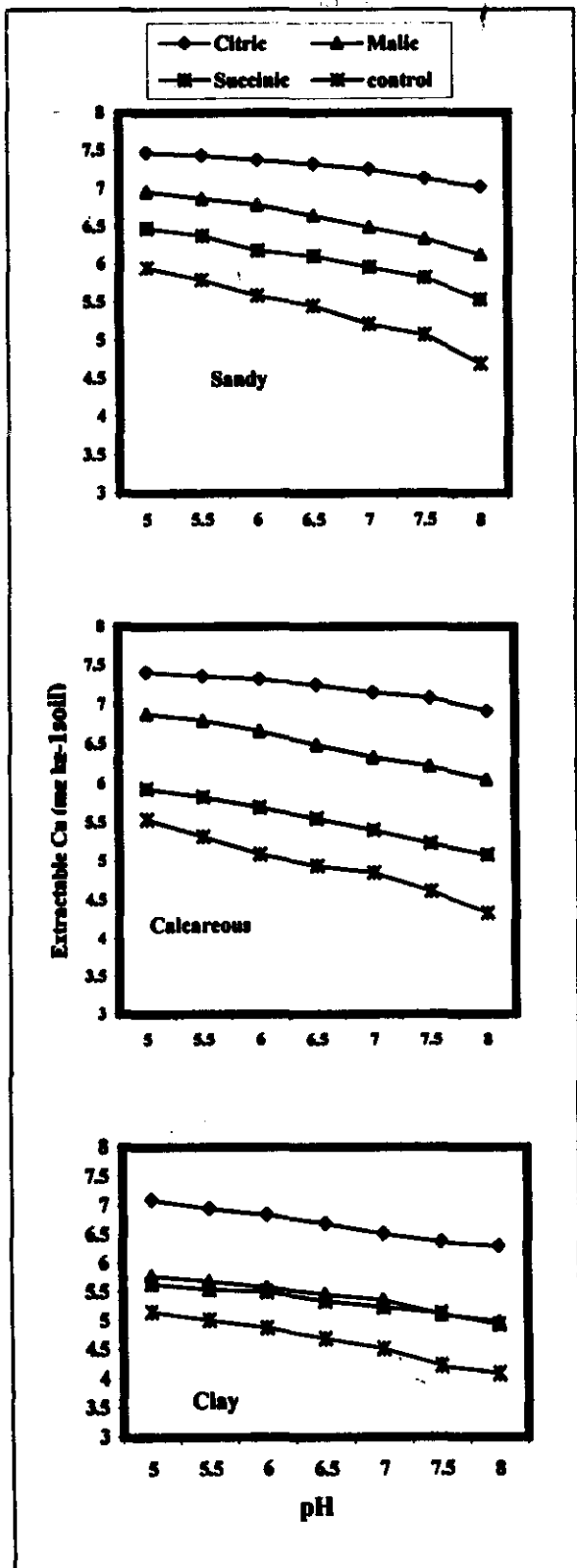


Figure 3. Effect of pH and organic ligands on the amount of extractable Cu

by succinate indicating that the observed trends in extractable Cu are related to Cu-ligand stability constant.

Extractability of Cu was least in clay soil while the sandy soil exhibited the highest release, copper extractability from calcareous soil was intermediate (Figure 3). The quantity of Cu extracted from soils followed the trend

Sandy > Calcareous > Clay

The low Cu desorption associated with the clay soil suggests that Cu sorbed by clay soil can not be desorbed readily back into solution. It further suggests that most Cu ions are specifically chemically sorbed by both organic matter and layer silicate clays. Soil organic matter contains many important functional groups, such as -COOH and -OH groups. These active components can readily bind metal ions and form complexes that are difficult to be extracted. Lower organic matter content of soil also favored desorption of metals from soils. The higher soil CEC generally coexisted with higher content of clay and organic matter, and showed strong ability on the sequestration of metals (Stewart et al., 2003) and vice versa.

The clay soil under study showed the highest values for organic matter, clay content and cation exchange capacity whereas sandy soils showed the lowest values of these properties (Table 1). Similar observations have been reported in trace metal desorption studies for soils (Barrow, 1986; Hogg et al., 1993).

Desma et al. (1993) examined the cumulative amounts of native soil Cu desorbed from four of the experimental soils during 10 successive 2-h desorption periods. And the results showed that the amounts and patterns of desorption differed between the soils. The cumulative amount of native Cu desorbed ranged from 0.087 mg Cu kg<sup>-1</sup> for the Waikari soil up to 0.171 mg Cu kg<sup>-1</sup> for the Temuka soil, and they found that the amount of Cu that can desorb readily from soil depends not only on the total amount of labile Cu in the soil but also on soil pH, temperature, and, in the case of added Cu, on the length of time since addition of the Cu to the soil.

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## الملخص العربي

### تأثير المعقدات العضوية والـ pH على سلوك تحرر النحاس في أراضي المناطق الجافة

السيد الخطيب وماهر صالح واحمد مهدي وناديه بركات

منحني الأدمصاص في الأراضي الرملية والجيرية من النوع L بينما في الأراضي الطينية كان يتبع النوع H (H-type) ولقد عزى ارتفاع قدرة الأراضي الطينية على إدمصاص عنصر النحاس إلى ارتفاع محتواها من المادة العضوية ونسبة الطين.

٢- قدرة المعقدات العضوية على استخلاص عنصر النحاس من الأراضي تحت الدراسة كانت كمايلي:

الستريك < الماليك < السكسينيك

وقد عزى ذلك إلى معامل الثبات لهذه المعقدات

٣- تأثر استخلاص عنصر النحاس من الأراضي بدرجة حموضة المستخلص فزيادة pH المستخلصات أدى إلى انخفاض كمية النحاس المستخلص من الأراضي وذلك بالنسبة لجميع المستخلصات المستخدمة في هذه الدراسة وقد أرجع ذلك إلى ارتفاع مقدرة الأرض على مسك العناصر عند زيادة درجة الـ pH.

٤- أن أفضل كمية مستخلصة من عنصر النحاس كانت من الأرض الطينية وأعلى كمية مستخلصة كانت من الأرض الرملية وذلك عند استخدام الأحماض العضوية. وتبين أيضاً من الدراسة أنه في غياب المعقدات العضوية يكون العامل المتحكم في عملية تحرر العنصر من الأرض هو صفات الأرض ولكن في وجود المعقدات العضوية مع العنصر يكون العامل المتحكم هو قدرة الأرض وكذلك خصائص المعقدات العضوية.

أجريت هذه الدراسة بهدف التعرف على سلوك تحرر النحاس في بعض الأراضي المصرية ودراسة تأثير درجة الـ pH بعض المعقدات العضوية على تحرر النحاس من هذه الأراضي.

ولإنجاز هذه الأهداف أخذت عينات سطحية من ثلاثة أراضي (طينية ورملية وجيرية) مختلفة النشأة والقوام والمحتوى من كربونات الكالسيوم وعوملت بـ ١٥٠ جزء في المليون نحاس في صورة كبريتات نحاس وتم تعريضها لدورات ابتلال وتجفيف لمدة ٦ أسابيع عند السعة الحقلية. تم إجراء تجربة أدمصاص على الأراضي الثلاث وذلك باستخدام تراكيز تتراوح من ٥ إلى ١٥٠ جزء في المليون نحاس على درجه حرارة ثابتة وتم حساب كمية النحاس المدمصة عن طريق الفرق بين الكمية المضافة والكمية المتبقية في المحلول. وفي تجربة معمليه تم استخلاص النحاس من الأراضي الملونة بالنحاس وذلك باستخدام ثلاثة أحماض عضوية (الستريك والماليك والسكسينيك). وتم قياس النحاس في المستخلص بواسطة جهاز الامتصاص الذري. بالإضافة إلى ما سبق تم دراسة تأثير الـ pH على النحاس المستخلص بواسطة الأحماض العضوية وذلك باستخلاص النحاس بواسطة الأحماض العضوية (ستريك-ماليك-سكسينيك) عند قيم pH تتراوح من ٥ إلى ٨ وقياس النحاس في المستخلص بواسطة جهاز الامتصاص الذري

ولقد أتضح من نتائج الدراسة مايلي:

١- أن قدرة الأرض الطينية على ادمصاص عنصر النحاس كانت أعلى من قدرة الأرض الجيرية وتليها الأرض الرملية. وكان شكل