Journal of Kerbala University , Vol. 7 No.4 Scientific . 2009

Studying of Citric acid Efficiency in Removal of lead and copper with neutralization of Soil's Bicarbonate

دراسة كفاءة حامض ألستريك في إزالة الرصاص والنحاس و معادلة بيكاربونات التربة

علاء حسن الفرطوسي جنان نعمه محمد
قسم وقاية النبات – كلية الزراعة قسم الكيمياء الصيدلانية – كلية الصيدلة
جامعة البصرة – البصرة – العراق
*E-mail:ahalfartoosy@gmail.com

Summary

The Efficiency removal of lead and copper and neutralization of Calculus contain of soil by organic acid (Citric acid) as a chelating were carried out by using of UV-Spectrophotometry technique. The result demonstrated the complexation formulating between the Citric acid and heavy metals. The high efficiency of Citric acid played an important role in removal of lead and copper with neutralization of soil's bicarbonate , in addition to these removal were increased by increasing the Citric acid. The Enhancing of Citric acid in phytoextraction lead and copper caused slowly growing of plant , reducing of Electrical conductivity ,pH and increase soil's porosity.

Key word: Citric acid , Bicarbonate , Copper and Lead , soil

الخلاصة:

أجريت دراسة كفاءة إزالة الكاتيونات الموجبة الرصاص والنحاس ومعادلة المحتوى القاعدي للتربة القاعدية باستخدام حامض ألستريك.إذ استخدم الحامض كعامل ساحب للعناصر عن طريق امتصاصها بالنباتات وقدرت الكاتيونات باستخدام تقنية الأشعة فوق البنفسجية .بينت النتائج كفاءة التركيز العالي للحامض في معادلة التربة القاعدية فضلا عن إن تلك الإزالة ازدادت بزيادة تراكيز الحامض ، كما إن الاستخلاص بالنبات للعناصر الثقيلة سبب بطء نموه النباتات ، خفض قيمة التوصيل الكهربائي و درجة تفاعل التربة وزيادة مساميتها.

1. Introduction

Large area of agricultural soils are contaminated by heavy metals and salinity that mainly originate from industrial activities , mining , smelting of ferrous are metals, exhaust gas and fuel energy production[1].

Most heavy metals are toxic for plants , especially lead has been shown to be toxic effect on variety metabolic process essential to, plant growth and development including photosynthesis transpiration , DNA synthesis and metabolite activity [2].

Studies undertaken during the last decades have shown the organic complexation is important for number of trace element metal.

An important fraction (30-99.9%) of metals including ,copper ,ion ,nickel and zinc are complexed by natural and anthropogenic organic Ligand this organic complexation is thought to decrease activity and scavenging by suspended particulate matter the metal – organic Ligand complexes are strong with reported conditional stability constant Log KMeL M+2 : Metal ,L: Ligand , Co(II) 15.6 – 16.1 , Cu(II) 10-13, Fe(III) 18.8-21.2 ,Ni(II) >17 ,Zn(II)10 [3].

Chemically chelate is a compound from complexion of cations with organic compounds resulting in airing structure.

Citric acid which was used in carry study is one of the organic acids commonly used as chelating agents and neutralization [4],Citric acid form square planer complex with heavy metals through binding to citrate anions with cations. phytoremediation is a novel clean up technology for removal of contaminate from polluted water and soils ,in phytoremediation the plant uptake capability and the availability of the pollutant in the medium are important [5] so , adding of chelating agent [6] enhancing phytoremediation by increasing the bioavailability of heavy metals.

The aim of the present study was to evaluate the citric acid efficiency in removal the soil containments with heavy metals lead and copper in addition to soil´s bicarbonate neutralization.

2-Materials and Methods

2-1.Chemicals

All commercial materials were received from Pharmacy college / Basrah University including: ,Sulfuric acid , Phenophaline ,Methyl orange ,lead acetate , copper chloride ,Citric acid and Distilled water.

2-2. Apparatuses

Buret ,Pipet , conical flask ,Funnel , filter paper, Volumetric phials and UV visible.

2-3. Assay of Lead and Copper in Soils Samples

2-3-1. Preparation of Solution

Various standard solution from lead acetate and copper chloride were prepared with concentration 2,5,10,15,20,25 ppm for each element.

2-3-2.Procedure

Add 15 g of dry soil dust to 100 ml Distilled water then the filtration was measured by UV-Visible [٧].

2-4.Efficincy of CA in Removal of lead and copper from soil suspension

various series concentration of CA (2 , 3 , 6 , 10 and 15)% were added for soil samples. After 30,60 and 120 minutes addition , the concentration of lead and copper were assayed.

2-5. Studying of Soil properties after CA addition

Physiochemical properties of soil were studied at water laboratory ,department of soil sciences and water , Agriculture college, Basrah University.

Samples were prepared to measure some Physiochemical properties, by pass the samples after drying through sieve, soil samples assayed practical size distribution according to described procedure by [8] also the [9] was depended in Bulk density by Core while [10] procedure was followed in cations an inions assayed.

2-6. Bioassay of CA effectiveness in plant Growth

The experiment was carried out by using the six pots , they were filled with 100 g soil. These pots cultured with the Garden Cress Lepidium sativum seeds by 10 seed per pot in weeds laboratory / Agriculture college / Basrah University. Two treatments were used , First was sprayed with water and second was sprayed with citric acid . After 30 days from the culture ,the growth of Garden Cress Lepidium sativum was compared between them as a Morphology.

2-7. Efficiency Studying of Citric acid in Removal of Bicarbonate

a. 10 ml of soil suspension was put in conical flask , three drops from Phenophaline was added ,if the color became pink it means there is carbonate .
b. The sample was titrated with 0.01 M sulfuric acid To the disappear of pink color, The volume recorded as (y).
c. Some drops of methyl orange were added to the sample ,then titrated with sulfuric acid to the color change from yellow to orange. The volume recorded as (Z).

Meq HCO_3 /L = (Z – 2 y) × NH_2SO_4 /ml in liqut × 1000 [11].

2-8. Statistical analysis

The results of paragraph no. 2-3 was analyzed using linear simple correlation for pearson in properly level o.o1% using one-way analysis of variance (ANOVA) to test for significance, by application of computer program SPSS.

3. Results and Discussion

3-1. Calibration Curve of Lead and copper

Fig 1 and 2 showed the calibration curves which is depended in this study and its obtained by Ultra Violate Technique. Its represented the relationship between the Absorption and Concentrations which carried out at the λ Max 320 nm for Lead and 350 nm for copper.

A linear correlation was observed between the concentration and the absorbance according to the statistic analysis . The correlation coefficient valued r = + 0.99 in case of lead and + 0.99 in case of copper respectively . This provided an indicator which linked the variables.

3-2. Efficiency of CA in Removal of lead and copper from soil suspension

The fig 3 showed the efficiency of CA in reducing the heavy metals (pb and cu) from the soil suspension. It observed that the CA concentrations 2,3,6,10 % reduce the concentrations of pb and Cu from 2.5 , 0.8 to 2.4 ,1.9 ,1.4 , 1.15 and to 0.49 , 0.40 , 0.34, 0.18 ppm for both Lead and Copper respectively , also the results illustrated that the high concentration of CA 15% caused large reducing in lead and copper 0.1 and 0.009 ppm respectively.

Complete removal of lead and copper were observed sequence with increasing the CA concentration, this belonging to that the organic acid (citric acid) was effective in removing heavy metals from the soil , mainly owing to the better solublization of the metals at low pH conditions in the soil solution provided by citric acid [12].

Also the citric acid is a tricarboxylate is using as chelating agent , act complexion with cations such as lead and copper (pic 1). In addition to [13 , 14] reported that the addition of citric acid and its salts selectively increase uranium mobility in soil and subsequently also plant uptake. The authors suggest that the strong mobilization of uranium by citric acid is due to the formation of citrate–uranyl complexes rather than to the decreased pH.

3-3. Efficiency of Citric acid in Removal of bicarbonate from Soil suspension

An estimation study of bicarbonate was studied in order to determine the efficiency of several citric acid concentrations in removal of bicarbonate from soil suspension(Table 1).

The citric acid concentrations 2, 3, 5, 10, % lowered bicarbonate content to 0.0018, 0.0006, 0.00045, 0.00006 meq /L. respectfully compared with its content before treatment was 0.0026 meq / L.

The citric acid played an importance role in reduced the bicarbonate level because of neutralizing the solution by the additive the H2SO4 , leading to low of soil´s pH 5.6 – 6.0 [15].

The [16] showed that the citric acid is an electrolyte component have the ability to maintain an acidic pH for the soil with low buffering capacity in addition to it's a polyprotic acid there for it has a buffering capability and can neutralized in coming base component.

Table 1 : Efficiency of Citric acid in neutralized the bicarbonate of soil suspension

Citric acid Concentrations (%)	Volume of H2SO4 (ml)	Meq /L of Bicarbonate
2	1.8	0.0018
3	0.6	o.ooo6
5	0.45	0.00045
10	0.06	0.00006

3-4. Effect of Citric acid in Growth Response of Plant

When citric acid was applied to treated soil with Seeds ,the growth was observed to be slowly compared with an irrigated by CA (picture 2).This because CA enhanced the uptake of toxic matter by plants result reducing in their growth and biomass .

Heavy metals uptake from plants controlled by three main factors :

pH of soil : its found through studied that heavy metals uptake is depended upon pH soil increase as decreasing the later. Since low pH in hence the solubility of heavy metals then increasing its uptake [١7 ،18].

Sorption : CA has sorption characteristic to remove copper and lead ions from aqueous solution[19,20].

Citric acid is used as chelating agent for extraction of heavy metals ions from contaminated soil (formation complexation between Citric acid and ions). [21,22,23,24].

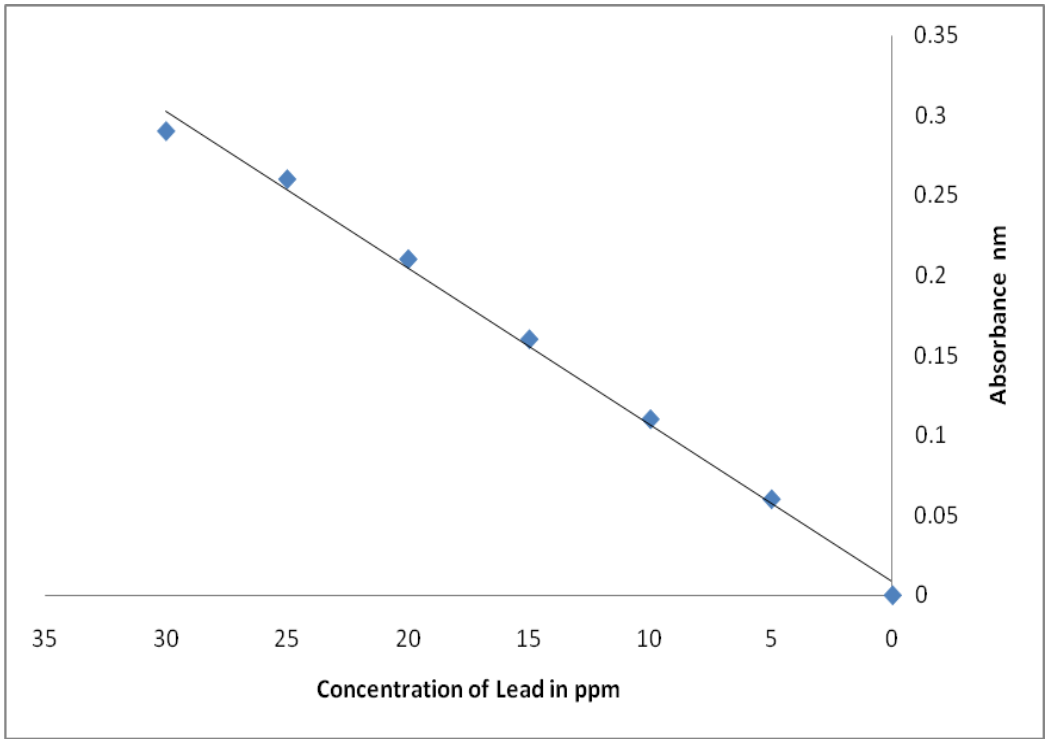


Fig (1): Calibration curve of Lead

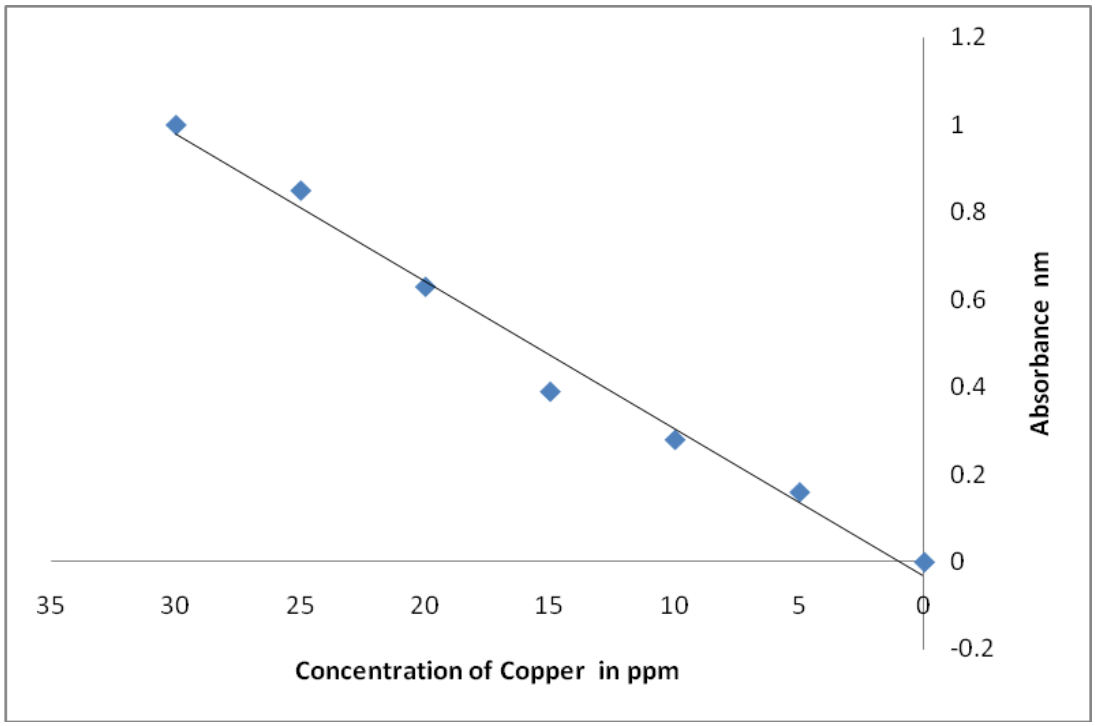
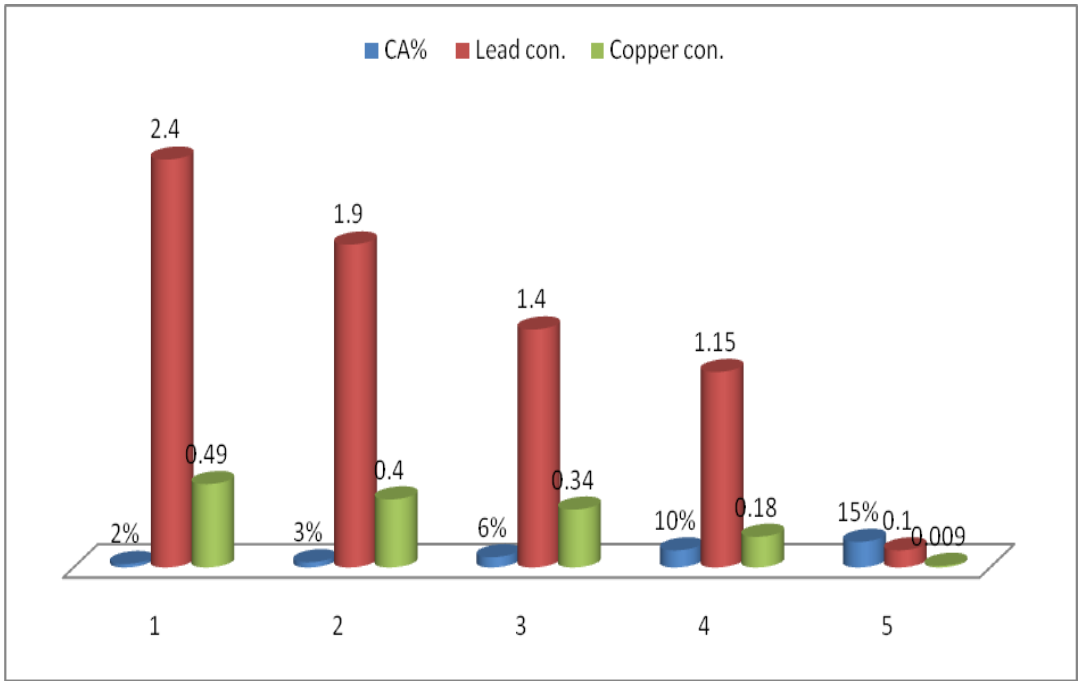


Fig (2): Calibration curve of Copper



Fig(3) showed the percentage removal of lead and copper by using citric acid

Picture (1): show the complex between citric acid with lead

Pic (2):The effect of CA on plant growth *Lepidium sativum*
a:plant irrigated with CA
b:plant irrigated with water

3-5. Effect of Citric acid addition on Soil Properties

Through the studying of physiochemical properties of soil (Silt Clay Loam) at the laboratory, it's found the CA had high efficiency enhanced these characteristics .

Table (2) illustrated :

1. Increasing porosity from 20% to 33% for soil treated with water only and to 28% for soil treated CA.
2. Decreasing in pH and EC ,the pH decreased from 7.14 to 7.11 and 7.10 for both soil treated with water and CA respectively.
   These results indicated to important role of CA in an enhanced of soil characteristics by removal of salinity lead to good aerotation.

Table (٢): Soil properties were used in this study

Treatment	MS	PW	PV	Pb g/Cm^3	PS g/Cm^3	Porosity%	pH	E.C dm/cm	Texture %		
									Clay	Silt	Sand
Soil before used	130.91	40.15	52.1	1.3	1.62	20	7.14	3.9	35.94	51.2	12.8
Soil used without CA	42.67	31.28	34.4	1.1	1.64	33	7.11	2. 3	35.94	51.2	12.8
Soil used with CA	43.71	28.58	34.2	1.2	1.65	28	7.10	2.0	35.94	51.2	12.8

4- References

1. **Brümmer, G., J. Gerth and U. Herms.(1986).** Heavy metal species, mobility and availability in soils. Z. Pflanzenernaehr. Bodenkd. 149:382–398.
2. **Molinari R. , T. Poerio and P. Argurio.(2005).**Polymer assisted Ultrafiltration Copper-Citric chelate removal from wash solutions of contaminated Soil. J. Applied Electrochemistry. Vol. 35(4):375-380.
3. **Ndung'u k.,R.P. Franks,K.W.Bruland ,A.R. Flegal.(2003)**.Organic complexiation and total dissolved trace metal analysis in estuarine waters: comparision of solvent – extraction graphite furnace atomic absorption spectrometric and chelating resin flow injection inductively coupled plasma-mass spectrometric analysis.Analytica Chimica Acta 481:127-138.
4. **Johansson A.(2002). CONVERSATIONS ON CHELATION AND MINERAL NUTRITION.** from internet. Page 1-4.
5. **Lopez M.,J.R.Peralta-videa,T.Benitez and J.L.Gardea-Torresdey.(2005)**.Enhancement of lead uptake by alfalfa (Medicago sativa using EDTA and a plant growth promoter.Chemosphere vol 61(4):595-598.
6. **Hornburg, V., and G. Brümmer. (1993).** Heavy metals in soils: 1. Experiments on heavy metal mobility. (In German, with English abstract.) Z. Pflanzenernaehr. Bodenkd. 156:467–477.
7. **Al-Omran L.S.Z.(1990).**Analytical study for lead pollution in Basrah . M.Sc Thesis college of Education –Basrah University.78pp.
8. **Day,O.R. 1965**.Particle fraction and particle size analysis In Methods of soil analysis. Monograph 9-Am.Soc.Agran-Madison

9. **Black;G.B. and Canstantin;G.K.1965**.Influence of particle size distribution in soil compaction. Hilgadia. P507-509.
10. **Page, J.B.1982.**Advantage of the pressure pycnometers for measuring the pore space in soils. Soil Sci.Soc.Am.proc.12.p81-84.
11. **Taj aldeen M.M. and E.B.Yaqub.(1988). Principles of Soil**.printed of Basrah university-Agriculture college-University of Basrah.53pp.(In Arabic).
12. **Gray, C.W., R.G. McLaren, A.H.C. Roberts, and L.M. Condron.(1999).** Solubility, sorption and desorption of native added cadmium in relation to properties of soils in New Zealand. Eur. J. Soil Sci. 50:127–137.
13. **Ebbs, S.E., W.A. Norvell, and L.V. Kochian. (1998).** The effect of acidification and chelating agents on the solublisation of uranium from contaminated soil. J. Environ. Qual. 27:1486–1494.
14. **Huang, J.W., M.J. Blaylock, Y. Kapulnik, and B.D. Ensley. (1998).** Phytoremediation of uranium-contaminated soils: Role of organic acids in triggering uranium hyperaccumulation in plants. Environ. Sci. Technol. 32:2004–2008.
15. **Wadleigh C. H. and J. W. Brown.(1952).** The Chemical Status of Bean Plants Afflicted with Bicarbonate-Induced Chlorosis Botanical Gazette, Vol. 113, No. 4. pp. 373-392.
16. **Lee H. S. , k. lee, S. kim and s. ko.(2003).**Effect of soil Buffering Capacity and Citric acid in Electrolyte on Electrokinetic Remediation of Mine Tailing Soils .J. Ind.Eng.Chem.,Vol9(4):360-365.
17. **Molinari R. , T. Poerio and P. Argurio.(2005).**Polymer assisted Ultrafiltration Copper-Citric chelate removal from wash solutions of contaminated Soil. J. Applied Electrochemistry. Vol. 35(4):375-380.
18. **Seelig B. D.(2000).** Salinity and Sodicity in North Dakota Soils. North Dakota State University Agriculture and University Extension:p: 1-4.
19. **Lei M. , B. Liao , p. Qin, S. Khan .(2008)** .Fraction Distributions of Lead ,Cadmium ,Copper and Zink in Metal contaminated soil before and after extraction with Disodium Ethylendiamintetraacetic Acid. Communication s in soil science and plant analysis .vol 39(13-14): 1963 – 1978.
20. **Low K.S. , C.K. Lee and S.M. Mak .(2004).** Sorption of copper and Lead by Citric acid modified wood. Wood Science and Technology .vol 38(8):629 – 640.
21. **Dong D. , X. Zhao, X. Hua , J. Liu and M. Gao.(2008).** Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China. Journal of Hazardous Materials Vol. 162, (2-30) : 1261-1268.
22. **Joseph L. Uveges, L. Andrea Corbett and K. M. Tarun.(2002).** Effects of lead contamination on the growth of Lythrum salicaria (purple loosestrife). Elsevier Science Ltd. Volume 120, Issue 2, Pages 319-323.
23. **Khodadoust A.P., K.P. Reddy and K. Maturi.(2005).** Effect of Different extraction agent on matter and organic contaminate removal from a field soil. J. of Hazardous Materials.B117 :15-24.
24. **Li-ying J. and Y. Xiao-e.(2004).** Chelators effect on soil Cu extractability and uptake by Elsholtzia splendens. J Zhejiang Univ SCI 5(4):450-456.