STUDIES ON THE REMOVAL OF SOME HEAVY METALS FROM CONTAMINATED SOIL

Yasser M. Abd El-Megeed[1*], I.R. Mohamed[2],

N.A. Atia[2] and M.S. Abd El-Ghany[1]

1. Nuclear Materials Authority, P.O. Box 530 Maadi, Egypt.
2. Soil Sci. Dept., Fac of Agric., Zagazig University.

ABSTRACT

The purpose of this investigation was to assess retention of Cu and Ni from soil pre-contaminated with them as well as their removal using different solutions. Materials used for retention (immobilization) were bitumen, potassium humate, Taflla (Shall) and calcium carbonate. Cetric and oxalic organic weak acids were used for removal of metals from soil by washing. The soil samples were collected from the surface layer (0 – 30 cm) in field of Inchass area, Sharkia governorate, Egypt (a sandy loam).Soils were pre-contaminated with 500 µg Cu or Ni /g as copper sulfate or nickel chloride.

Experiment (1) involved application of bitumen, potassium humate, Taflla (Shall) and calcium carbonate as immobilization agents, which were added to the pre-contaminated soils in amounts of 0.5, 1.0 or 2.0% then incubated for 28 days. Bitumen was the most effective immobilizing agents for both copper and nickel followed by potassium humate then Taflla and finally $CaCO_3$. The effectiveness was increased by increasing the percent of addition from 0.5 to 2%.

Experiment (2) involved the application of the citric and oxalic weak organic acids in amounts of 0.5 - 3.0% to evaluate the leaching efficiency for the two studied elements, where tested soil samples packed in Perspex columns. Oxalic acid was more effective than citric acid in case of copper leaching away from the contaminated soil while in case of nickel, the citric acid was more effective than the oxalic acid.

Keywords: Removal, heavy metals, immobilizing agent, oxalic and citric acid.

* Corresponding author: Yasser M. Abd El-Megeed ,　Tel.: +0188142099
E-mail address: Yaso 7446@Yhoo.Com

INTRODUCTION

Pollution of soils with heavy metals may be present naturally or as a result of the common human activities through combustion of coal and oil, application of fertilizers, pesticides, sewage sludge, dredged sediment disposal and emissions from metal processing operations and other industrial wastes. Soils contamination with heavy metals, especially Cu and Ni poses a long-term risk to ground water quality and ecosystem health (Gad and Zaghloul 2007). With increase the demand of using sewage effluents in irrigation, there is a great awareness in heavy metal accumulation in edible crops, this need to treatment of such waters or contaminated soil to the permissible limits.

Copper is among the more mobile of heavy metals in soils or depositional material. It exhibits a great ability of chemically interaction with mineral and organic components of the soil. Nickel is a serious pollutant and readily available to plants, so it may be highly phytotoxic (Martinez *et al.*, 2003).

The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal release from contamination sources, cation exchange, specific adsorption into surface of minerals and soil organic matter and precipitation of secondary minerals, (Manceau *et al.,* 2000; Mcbride *et al.,* 1997; Mcbride, 1999 and Morin *et al.,* 1999). The relative importance of these processes depends on soil pH and its composition. In general, cation exchange reactions and complexation with organic matter are most important in acidic soils, while specific adsorption and precipitation are more important at near neutral to alkaline pH values, (Eid, 2004).

The present work aims to assess the ability of some organic and inorganic agents retention of Cu and Ni from soil pre-contaminated with them as well as to evaluate the ability of different organic acids for removal these heavy metals from pre-polluted soils with them.

MATERIALS AND METHODS

Soils

Soils used in the experiments were collected from the surface layers (0 – 30 cm) of a field in

Inchass area, Sharkia governorate, Egypt. The soil was a sandy loam where it was taken from field under arable cultivated and irrigated by sewage water for about 80 years.

Some physical and chemical characteristics of this soil are shown in Table 1.

Methods Used for Analysis

Meachanical analysis was determined according to the international pipette method. (Piper, 1950).

Chemical analysis was carried out according to Jackson (1967).

The total Cu or Ni were measured using UV- VIS Spectrophotometer model SP – 8001 according to Marczenko (1976).

Soil Remediation Techniques

Remediation techniques studies involved either immobilization of the two heavy metals (copper and nickel) in contaminated soil samples using different immobilizing agents or washing with two different organic acids. The soil samples were pre-contaminated with 500 µg Cu /g as copper sulfate or 500 µg Ni / g as nickel chloride, however, the total

contamination were reached to 513 and 511 for Cu and Ni µg/g respectively.

Immobilizing Agents

Four commercial materials were tested in this study as immobilization agents, they are:

Two organic materials namely; Bitumen and potassium humate (products of Chemicals for Modern Buildings Co. and Xiamen Spring Sunshine Co. respectively).

Two inorganic materials namely; Taflla (Shale) (a product from Egyptian Gulf Co. for Chemicals) and $CaCO_3$ analytical reagent.

Immobilization Technique

Soils were artificially contaminated with Cu or Ni to the level of 500 µg/g soil then the pre-contaminated soil samples were subjected to the followings:

The dry pre-contaminated soil samples (20 g portions) were firstly treated by any of the four immobilizing agents (bitumen, K-humate, Taflla or $CaCO_3$) at a rate of 0.5, 1.0 or 2.0% in a 100 ml glass bottle and mixed thoroughly.

The treated soil samples were mixed with 20 ml of deionizer water then dried in an incubator

Table 1. Some physical and chemical characteristics of soil from Inchass area

Characteristic	Value
Particle size distribution, %	
Sand	73.4
Silt	12.5
Clay	14.1
*Texture class	S.L
OM, %	1.61
$CaCO_3$, %	2.55
**PH	8.20
***E.C, dS/m	0.62
***Soluble ions, mmole/l	
Ca^{++}	0.06
Mg^{++}	0.16
Na^+	0.04
K^+	0.12
CO_3^{--}	--
HCO_3^-	0.01
Cl^-	0.03
SO_4^{--}	0.22
Total content, µg/g	
Cu	13
Ni	11

* S.L: Sandy loam   ** Soil-water suspension (1: 2.5)
*** Soil water extracts (1:5).

at 40 °C (Shaker occasionally) for 3.5 days.

The soil samples were subjected to wetting (with 10 ml deionizer water) then drying through eight cycles for 28 days.

At the end of incubation period, the soil samples were air dried and crushed then the DTPA - extractable Cu or Ni was determined for each sample according to Marczenko (1976).

Washing (Leaching) Technique

Water acidified with phosphoric acid until pH 2 or water were used for soil leaching test. Also, two organic acids namely; oxalic and citric acids, were used for soil washing test. The pre-contaminated soil samples (portions of 1374 g) were carefully packed in Perspex columns of 70 cm height and 5 cm inner diameter. This column size permits to back the soil sample to 50 cm height and leaving 10 cm free head at the top for addition of the washing solution. The columns were provided at the bottom with perforated plates, glass wool and cheesecloth as filter. Also glass wool was placed on the top of the soil after packing the column to minimize surface disturbance of

soil particles during addition of the leaching solution.

Five liters of the required acid concentration (0.5, 1, 2 or 3%) were prepared then passed through the soil column and received individually at the bottom. Each liter was divided into four leachates. Volume of each leachate was 250 ml. The collected leachates were analyzed for copper or nickel determined according to Marczenko (1976).

RESULTS AND DISCUSSION

Immobilization using Immobilizing Agents

Stabilization of copper or nickel in the soils initially contaminated with 500 µg Cu or Ni /g soil was done using immobilizing agents of bitumen, K-humate, taflla or $CaCO_3$. The results of these experiments through DTPA extractable Cu or Ni from soil after immobilization were shown in Tables 2 and 3 and Figs. 1 and 2. It is worthy to mention that DTPA extractable Cu and Ni (control) for the pre-contaminated soil before the immobilization tests was 140 and 120 µg/g for copper and nickel respectively.

Table 2. DTPA – Extractable Cu in soil after treating with different immobilizing agents

Immobilizing agents	Rate of addition,%	DTPA -extractable copper in soil, µg/g	Decrease percentage of DTPA-extractable copper in soil
Control	0.0	140	--
Bitumen	0.5	73.4	47.5
	1.0	62.7	55.0
	2.0	34.6	75.0
Potassium Humate	0.5	95.0	32.0
	1.0	70.0	50.0
	2.0	47.0	66.0
Taflla	0.5	115.0	18.0
	1.0	80.0	43.0
	2.0	55.0	61.0
Calcium Carbonate	0.5	107.0	24.0
	1.0	75.4	46.0
	2.0	62.0	56.0

1. Note: Soil initially contained 13 µg Cu /g and contaminated with 500 µg Cu/g (total 513 µg Cu /g).

2. Decrease percentage of DTPA-extractable Cu in soil =

$$\frac{\text{Initial DTPA-extractable Cu in soil (control)} - \text{Final DTPA-extractable Cu in soil}}{\text{Initial DTPA-extractable Cu in soil (control)}} \times 100$$

Table 3. DTPA – Extractable Ni in soil after treating with different immobilizing agents

Immobilizing agents	Rate of addition, (%)	DTPA -extractable nickel in soil, µg/g	Decrease percentage of DTPA-extractable nickel in soil
Control	0.0	120	--
Bitumen	0.5	88.5	26.0
	1.0	74.0	38.0
	2.0	54.0	55.0
Potassium humate	0.5	99.0	17.5
	1.0	80.0	33.0
	2.0	64.0	47.0
Taflla	0.5	112.0	6.3
	1.0	103.0	14.0
	2.0	76.0	37.0
Calcium carbonate	0.5	113.0	6.0
	1.0	108.0	10.0
	2.0	80.0	34.0

1. Note: Soil initially contained 11 µg Ni /g and contaminated with 500 µg Cu/g (total 511 µg Ni /g).

2. Decrease percentage of DTPA-extractable Ni in soil =

$$\frac{\text{Initial DTPA-extractable Ni in soil (control)} - \text{Final DTPA-extractable Ni in soil}}{\text{Initial DTPA-extractable Ni in soil (control)}} \text{X } 100$$

Abd El-Megeed, *et al.*
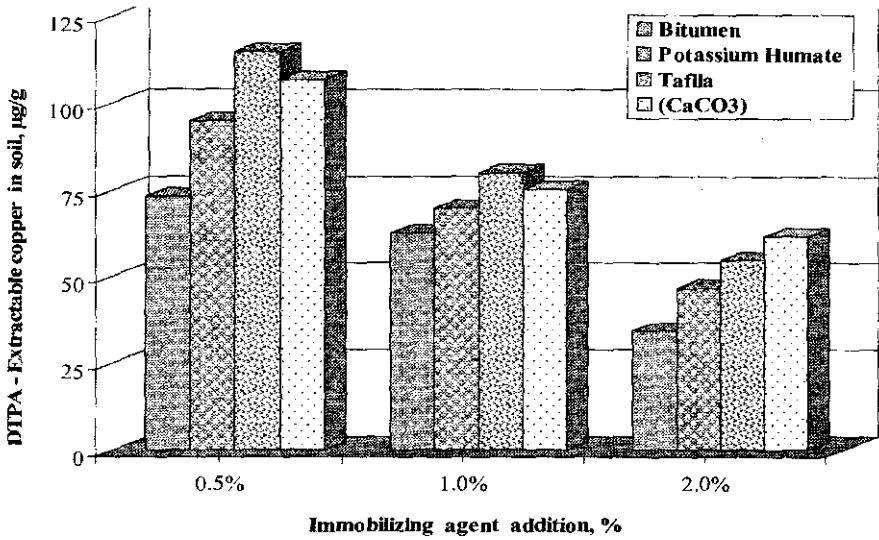
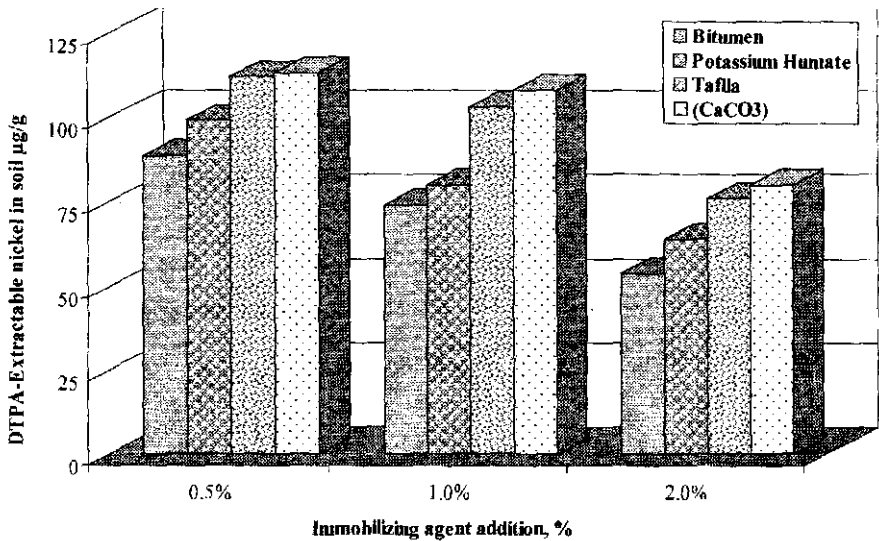**Fig. 1. DTPA – Extractable Cu in the soil samples after treating by the immobilizing agents**

Fig. 2. DTPA – Extractable Ni in the soil samples after treating by the immobilizing agents

From these results it is clear that, contents of DTPA - extractable Cu or Ni from soil after immobilization decreased at the end of the experiments to reach lower as compared with that at the start by increasing the added amount of the immobilizing agent. In this regard, DTPA - extractable copper in soil decreased to 34.6 and 73.4 µg/g for bitumen, 47 and 95 µg/g for potassium humate, 55 and 115 µg/g in taflla, and decreased to 62 and 107 µg/g for $CaCO_3$ in case of 2.0 and 0.5% additions respectively. It is clear also that, bitumen was the most effective immobilizing agent followed by potassium humate, taflla and the latest $CaCO_3$ and their effectiveness was increased by increasing the addition amount from 0.5 to 2%.

On the other hand, DTPA - extractable nickel in soil decreased to 54 and 88.5 µg/g for bitumen, 64 and 99 µg/g for potassium humate, 76 and 112 µg/g for taflla and 80 and 113 for $CaCO_3$ in case of using 2.0 and 0.5% additions of the immobilizing agent respectively. It is also clear that bitumen was the most effective immobilizing agent followed by potassium humate and in to a less extent (and similar) was taflla and $CaCO_3$. The effectiveness of immobilizing was increased by increasing the percent of its addition from 0.5 to 2%. However, these results are agreements with those obtained by El-Hady *et al.* (2000).

According to WHO (2001), the permissible level of copper and nickel in soil should to be 50 - 140 µg/g and 30 - 75 µg/g respectively.

Therefore the four studied immobilizing agents are effective in decreasing DTPA - extractable copper in soil but bitumen and potassium humate were only the effective for decreasing DTPA - extractable nickel in soil to the permissible limits. However, taflla and $CaCO_3$ may require more amounts of additions to reach the aforementioned nickel permissible level.

Removal of Heavy Metals from Soil by Leaching

Removal of copper and nickel heavy metals from soil by washing was studied to evaluate the effectiveness of this method as recommended by El-Khatib *et al.* (2007) and Polettini *et al.* (2008). Washing the soil by water or acidified water with phosphoric acid was firstly tested. Washing using solutions of the two weak organic acids namely citric and oxalic acid was then tested.

Results of soil washing by water or acidified water with phosphoric acid are shown in Table 4.

The results of washing efficiency reveal that less than 1% of the heavy metals contaminated the soil (Cu or Ni) were washed from the soil. This result indicated the strong retention of Cu and Ni by the soil.

With regard to leaching of the contaminated soil using the tested organic acids, the results were indicated in Fig. 3 to 6. The results show that oxalic acid leaching solution more effective for copper than that of citric acid. This result agrees with that found by Palma, and Mecozzi, (2007). In this regard, copper washing efficiency was increased from 17.3% in case of 0.5% oxalic acid solution and reached to 43.8% when the oxalic acid concentration was increased to 3%. In case of using citric acid solution, copper washing efficiency increased from 6.6% when the citric acid concentration was 1.0% and reached to 38.7% when the citric concentration was increased to 3%. However, results of copper washing through firstly wetting the contaminated soil using 3.0% citric acid (soaking), drying and finally washing with water reveal that the washing efficiency was greatly enhanced and increased to reach more than 90%.

The results of nickel washing from the contaminated soil using the weak organic acids, the data of Fig. 7 to 10 show that citric acid was more effective than the oxalic acid. Nickel washing efficiency was increased from 7% at the citric acid concentration 1% and reach to 93% at the citric concentration 3%. With regard to the results of nickel washing from the contaminated soil using oxalic acid, it is clear that the washing efficiency did not reach more then 9% at the oxalic acid concentration of 3%.

ACKNOWLEDGMENT

REFERENCES

Eid, M.K. (2004). Distribution of different fractions of heavy metals in desert sandy soil amended with composted sewage sludge International Conf. on Water Resources & Arid Environment, Cairo, Egypt.

Table 4. Washing of copper/nickel from contaminated soil using water and acidified water.

Leaching solution	Liter No.	Metal concentration in successive leachates , mg/l				Total, mg/l	Washing efficiency, %
		*1st	*2nd	*3rd	*4th		
Water + H₃PO₅ pH 2.0 (Cu-washing)	1	1.1	1.2	1.5	1.6	1.35	0.2
	2	1.8	2.0	2.4	2.7	2.2	0.3
	3	2.2	1.9	1.7	1.5	1.8	0.26
	4	1.2	0.9	0.7	0.5	0.8	0.12
	5	0.45	0.33	0.2	0.09	0.26	0.04
						$\sum 6.4$	$\sum 0.93$
Water (Cu-washing)	1	0.53	0.8	1.3	1.5	1	0.14
	2	1.4	1.8	1.9	2.0	1.8	0.26
	3	1.8	1.5	1.2	1.2	1.4	0.2
	4	0.9	0.73	0.68	0.58	0.7	0.1
	5	0.4	0.33	0.2	0.1	0.26	0.04
						$\sum 5.2$	$\sum 0.76$
Water (Ni-washing)	1	1.6	1.9	2.7	3.0	2.3	0.3
	2	3.3	2.8	1.2	0.8	2	0.29
	3	0.66	0.4	0.22	0.18	0.4	0.058
	4	0.09	0.05	0.03	0.02	0.045	0.006
						$\sum 4.7$	$\sum 0.68$

* Leachate volume 250 ml acid solution or water.

$$\text{Washing efficiency (WE)} = \frac{\text{amount of metal removed by leaching}}{\text{amount of metal present in the soil at start of leaching}} \times 100$$
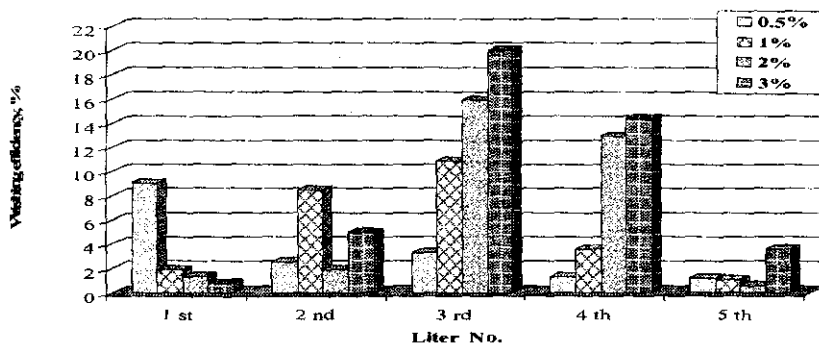
Abd El-Megeed, *et al.*

Fig. 3. Washing of copper from contaminated soil using oxalic acid solution
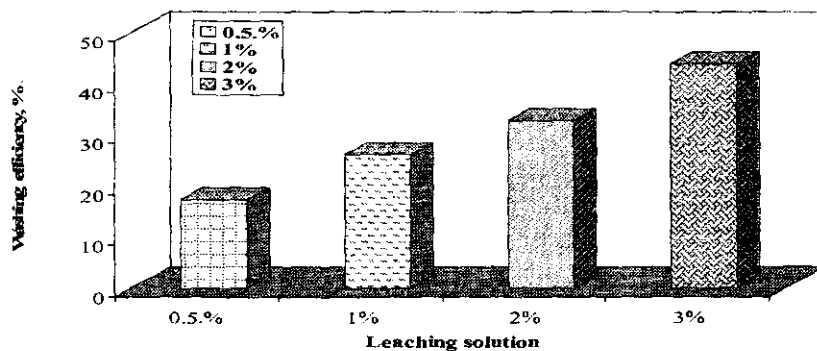

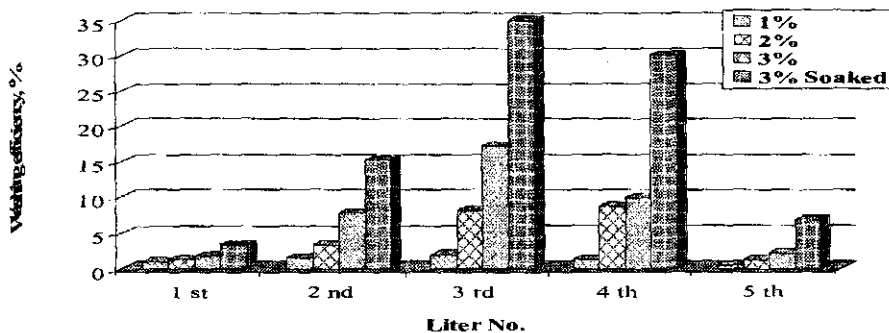**Fig. 4. Total washing of copper from contaminated soil using oxalic acid solution**

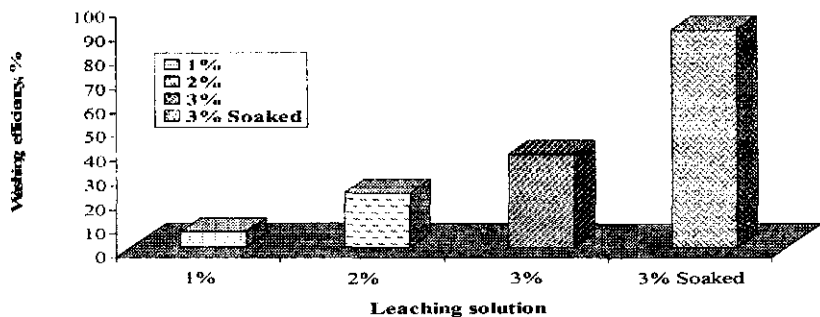**Fig. 5. Washing of copper from contaminated soil using citric acid solution**

Fig. 6. Total washing of copper from contaminated soil using citric acid solution
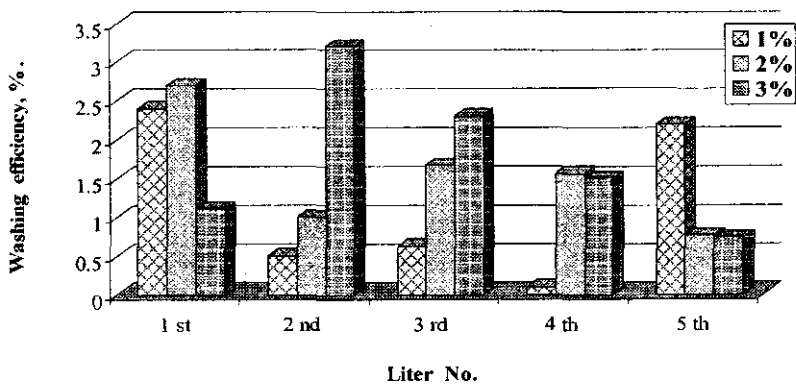
Fig. 7. Washing of nickel from contaminated soil using oxalic acid solution
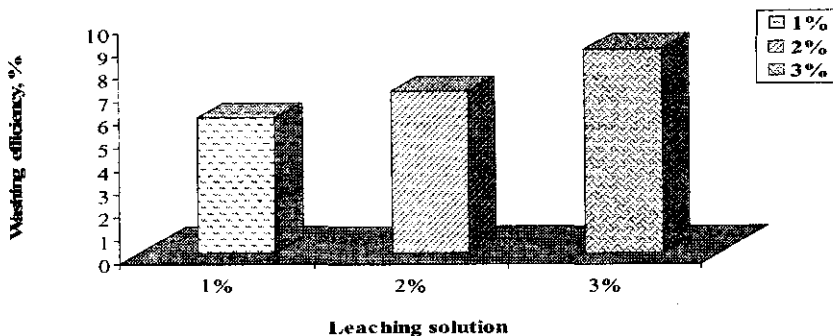
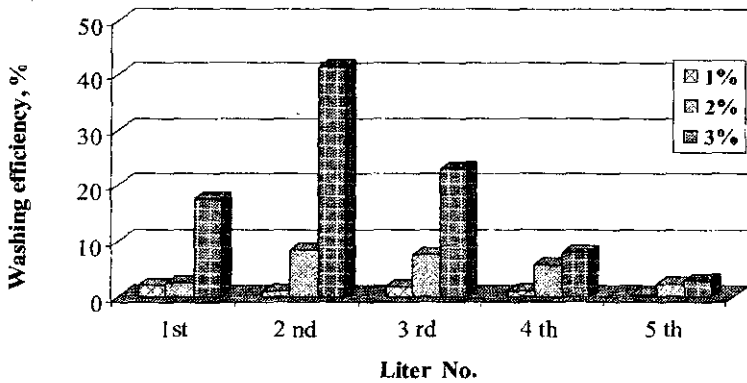**Fig. 8. Total washing of nickel from contaminated soil using oxalic acid solution**

Fig. 9. Washing of nickel from contaminated soil using citric acid solution
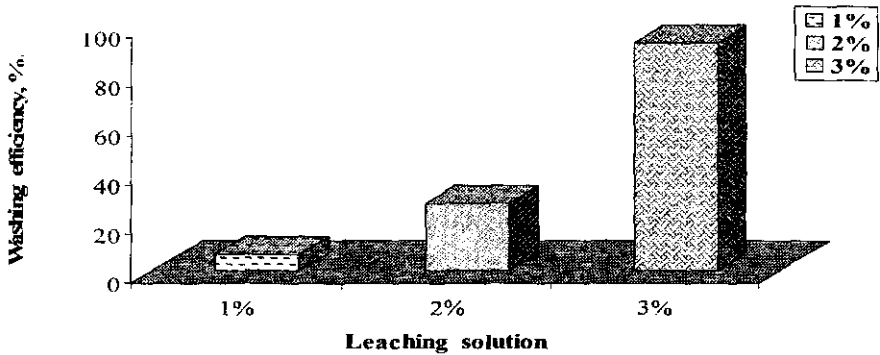

Fig. 10. Total washing of nickel from contaminated soil using citric acid solution

El-Hady, O.A., A.L. Saleh and N.F. Ghaly (2000). Minimizing the hazardous effects of heavy metals in contaminated soils using some locally prepared bitumen emulsions .Egypt J. Soil Science, 40: 223-244.

El-Khatib, E.A., A.M. Mahdy, M.E. Saleh and N.H. Barakat (2007). Kinetics of copper desorption from soils as affected by different organic ligands Int. J. Environ. Sci. Tech., 4 (3): 331-338.

Gad, N. and A.M. Zaghloul (2007). Minimizing the Health Hazard of Lettuce Cultivated in Some Heavy Metals Affected Soils Australian Journal of Basic and Applied Sciences, 1 (2): 79-86.

Jackson, M.L. (1967). Soil Chemical Analysis prentice Hall of India private. Limited New Delhi.

Manceau, A., B. Lanson, M.L. Schlegel, J.C. Harge, M. Musso, L. Eybert-Berard, J.L. Hazemann, D. Chateigner and G.M. Lamble (2000). Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy. Am. J. Sci., 300: 289–343.

Marczenko, Z. (1976). Spectrophotometric Determination of Elements, John Wiley& Sons Inc. New York. London. Sydney. Toronto.

Martinez, F., G.R. Cuevas and I. Walter (2003). Biowaste Effects on Soil and Native Plants in a Semiarid Ecosystem. J. Environ. Qual., 32: 472- 479.

Mcbride, M.B. (1999). Chemisorption and precipitation reactions. PB265–B302. In M.E. Sumner (ed.) Handbook of soil science. CRC Press, Boca Raton, FL.

Mcbride, M.B., S. Sauve and W. Hendershot (1997). Solubility control of Cu, Zn, Cd, and Pb in contaminated soils. Eur. J. Soil Sci., 48: 337–346.

Morin, G., J.D. Ostergren, F. Juillot, P. Ildefonse, G. Calas, and G.E. Brown Jr (1999). XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes. Am. Mineral., 84: 420–434.

Palma, L.D. and R. Mecozzi (2007). Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents Journal of Hazardous Materials., 147 (3) : 768-775.

Piper, C.S. (1950). Soil and Plant Analysis. Interscience pubi. Inc. New York. Plant and soil, 91(3):429-432.

Polettini, A., R. Pomil and G. Calcagnoli (2008). Assisted washing for heavy metal and metalloid removal from contaminated dredged materials, 196: 1 - 4.

World Health Organization (WHO) (2001). Proposed maximum heavy metal contents of soils beyond which the land application of sludge may be restricted, developing human health-related chemical guidelines for reclaimed waster and sewage sludge applications in agriculture, page 48.

دراســــات علـــى إزالـــة بعض الفلزات الثقيلة من تـــربة ملـــوثة

يـــاسر محمد عبد المجيد¹ - إبراهيم رمضـــان محمد²

نبيـــه عطيـــة عطيـــة² - محمـــد سيـــد عبدالغنى¹

١- هيئة المواد النووية – ص.ب. ٥٣٠ – المعادى – مصر.

٢- قسم علوم الأراضى– كلية الزراعة – جامعة الزقازيق.

أجرى هذا البحث لدراسة قدرة بعض المواد العضوية وغير العضوية على تثبيت أو إزاحة بعض الفلزات الثقيلة (كالنحاس والنيكل) من الأرض الملوثة بهم، ولهذا تم أختيارعينات سطحية (صفر– ٣٠ سم) من موقع تربة أنشاص بمحافظة الشرقية وخلطها، حيث تم تلويثها بتركيز ٥٠٠ ميكرو جرام نحاس أو نيكل/ جرام تربة فى صورة كبريتات نحاس أو كلوريد نيكل.

فى تجربة التثبيت تم أستخدام أربع مواد هى البيتومين، هيومات البوتاسيوم، الطفلة، كربونات الكالسيوم لتثبيت كلا من عنصرى النحاس والنيكل في الأرض وتحويلهما إلى صور غير صالحة للامتصاص بالنبات. حيث عوملت عينات التربة المدروسة بثلاثة تركيزات من المواد السابقة الذكر بمعدلات (٠,٥ ، ١ ، ٢٪) ثم تم تحضين التربة المعالجة مع تعريضها لدورات من الترطيب والتجفيف فى حضانة عند درجة حرارة ٤٠ درجة مئوية (٨ دورات ، ٢٨ يوم). فى نهاية فترة التحضين تم تحليل التربة لتقدير كلا من عنصرى النحاس والنيكل الكلى والمستخلص بواسطة مستخلص الـ DTPA.

ولقد أوضحت نتائج تجربة التثبيت أن ترتيب كفاءة المواد المستخدمة فى تثبيت كلا من عنصرى النحاس والنيكل فى التربة المدروسة كان كما يلى: البيتومين > هيومات البوتاسيوم > الطفلة > كربونات الكالسيوم، وأن قدرة هذه المواد على تثبيت كل من عنصرى النحاس والنيكل فى التربة إرتفعت بزيادة معدل الأضافة من ٠,٥ حتى ٢٪.

وفى تجربة الغسيل، وضعت عينات التربة الملوثة بفلزى النحاس والنيكل فى شكل أعمدة داخل أنابيب قياسية من البيرسبكس حيث تم غسيلها بحمض الستريك أو حمض الأوكساليك بتركيزات صفر، ١ ، ٢ ، ٣٪، ثم تم تجميع الراشح كل ٢٥٠سم³ حتى تمام الحصول على لتر مع تقدير تركيز كل من عنصرى النحاس ، والنيكل بالراشح.

ولقد أوضحت نتائج تجربة الغسيل أن حمض الأوكساليك أكثر قدرة من حمض الستريك على إزاحة النحاس من التربة، بينما كان حمض الستريك أكثر كفاءة من حمض الأوكساليك فى إزاحة النيكل من التربة.