

CONTENTS

	Page
Acknowledgment	I
List of tables	II
List of figures.....	III

CHAPTER (1) INTRODUCTION

1.1 Main sources of soil pollution by heavy metals.....	2
1.1.1. Crude oil	2
1.1.2. Impacts of roads.....	3
1.1.3. Mine tailing in the road.....	4
1.1.4. Waste and sewage water.....	5
1.2. Hazardous effects of heavy metals.....	7
1.2.1. Effects on human health	9
1.2.2. Effects on plants.....	10
1.2.3. Effects on soil properties	11
1.2.4. Soil – Plant – Man relations.....	11
1.3. Remediation techniques for polluted soils.....	13
1.3.1. Contaminated soil dilution	13
1.3.2. Ex-Situ remediation.....	13
1.3.3. In-Situ Immobilization.....	14
1.3.4. In-Situ or Ex-Situ bioremediation.....	14
1.3.5. In-Situ soil flushing.....	15
1.3.6. Soil washing streams.....	17
1.3.7. Factors affecting soil washing.....	17
1.4. Remediation of soils polluted by heavy metals	18
1.4.1. Applications of organic acids or its salts and chelating agents.....	18
1.4.2. Applications of synthetic amino poly carboxylic acids (APCAs) through phytoremediation.....	23

1.4.3. Applications of natural APCAs for polluted soils remediation	24
1.4.3.1. EDDs (ethylenediaminedisuccinate)	24
1.4.3.2. NTA (nitrilotriacetic acid).....	24
1.4.4. Applications of Natural low molecular weight organic acid... ..	25
1.4.5. Using Humic substances (Hs) for extraction of heavy metals during oil washing	27
1.4.5.1. Formation of Humic acid in soils.....	28
1.4.5.2. Structures of Humic acid	29
1.4.5.3. Application of Humic acid to remediate heavy metal contaminated soils	30
Aim of the work	33
CHAPTER (2) EXPERIMENTAL	34
2.1. Materials	34
2.1.1. Soil sampling.....	34
2.1.2. Organic compounds	34
2.2. Methods of analysis	37
2.2.1. Soil samples preparation	37
2.2.2. Particle size distribution (by international pipette method)	37
2.2.3. Estimation of organic matter	38
2.2.4. Soluble cations and anions	38
2.2.5. Electrical conductivity	39
2.2.6. Soil pH.....	39
2.2.7. Heavy metals	39
2.2.7.1. Available concentrations	39
2.2.7.2. Total concentrations	39
2.3. Soil treatments.....	40
2.3.1. Soil washing using organic acids and chelating agents	40
2.3.1.1. Removal of heavy metals at different pH values	40
2.3.1.2. Effect of organic acids and chelating agents concentrations... ..	41
2.3.1.3. Kinetic study of washing technique.....	41

2.3.2. Immobilization of heavy metals using humic acid	41
2.3.2.1. Effect of humic acid rate	41
2.3.2.2. Kinetic study of immobilization technique.....	41
CHAPTER (3) RESULTS AND DISCUSSION	43
3.1. Heavy metals in investigated soils.....	43
3.2. Removal of heavy metals	58
3.2.1. Effect of pH	58
3.2.2. Effect of extracting solution concentration	64
3.2.3. Kinetic study	67
3.3.3. Heavy metals immobilization	68
3.3.3.1. Effect of humic acid percent	68
3.3.3.2. Kinetic study.....	69
Summary.....	73
REFERENCES..	76
Arabic summary	

SUMMARY

The pollution problem is one of the most dangerous problems that face mankind in the last fifty years either in air, water or soil. There are enormous amounts of pollutions which contaminate the environment specially soils that arises from civilized development and industrial progress. As a result, pollution remediation and cultivated soil protection are very important two challenges that meet us in the 21st century especially in the heavily polluted areas in the world.

The aim of the present work is to study the Soil contamination by heavy metals which are one of the most serious problems due to its hazardous and toxic effects on soil, marine environment, plants and human health. These contaminants accumulate in plant tissues (as fruits and vegetables) that after eating cause many diseases in liver and kidney and may lead to cancer and death. In this work two soils contaminated by heavy metals were studied:

- 1- Sandy clay soil polluted with sewage sludge for long periods from El-Gabal El-Asfar, Kaliobiya Governorate, Egypt.
- 2- Clay soil adjacent to roads collected from Kalioub, Kaha and Tokh cities, Kaliobiya Governorate, Egypt.

Different organic compounds are investigated to remediate heavy metals contaminated soils throughout two strategies as follows:

- a. Heavy metals immobilization by using humic acid
- b. Heavy metals extraction by using EDTA and DTPA as synthetic chelating agents while citric and oxalic acid as natural low molecular weight organic acids. Both organic acids and synthetic chelating agents are used as extracting solutions with different concentrations at different pH values, while humic acid was added as stabilizing (immobilizing) agent to soil samples with percent 0, 2 and 4 % (w/w).The thesis comprises three main chapters.

The first chapter:

Deals with the introduction, which includes sources of pollution, Hazardous effects of Heavy metals, Available Remediation technologies and literature survey and aim of the present work.

The second chapter:

Deals with the experimental techniques, which include investigations of chemical properties of polluted soils, preparation of remediation solutions and instruments and procedures used for measurements of heavy metal ions concentrations.

The third chapter:

Deals with the results obtained and their discussion.

The results showed that Both the concentrations of DTPA extractable and total concentrations of the examined heavy metals Cd^{2+} , Pb^{2+} , Ni^{2+} , Cu^{2+} and Mn^{2+} showed a horizontal distribution with tendency to decrease with increasing distance from the pollution source at Kalioub, Kaha, Tokh and El-Gabal El-Asfar soils.

Available and total concentrations of the estimated heavy metals highly exceeded the normal levels of these metals in alluvial Nile Delta soils. The greater concentrations were found in soils at distance 3 m for soils of Kalioub, Kaha and Tokh. For samples of Kalioub, these concentrations were 15.45, 0.0944, 7.19, 8.28 and 122.97 ppm ($\mu\text{g/g}$) for Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} respectively. While the total concentrations were 45.19, 2.88, 13.99, 85.03 and 400.43 ppm for the same heavy metals respectively. For samples of Kaha, the greatest available concentrations were 12.22, 0.0384, 5.26, 4.88 and 97.34 ppm for Pb, Cd, Ni, Cu and Zn respectively, while the largest total concentrations were 45.94, 1.49, 19.24, 47.85 and 460.53 for the same heavy metals. For Tokh samples, the largest available concentrations for Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} were 15.60, 0.0216, 5.26, 2.88 and 70.10 ppm respectively, while the largest total concentrations for the same heavy metals were 49.1, 1.80, 53.10, 180.11 and 304.01 ppm respectively.

For El-Gabal El-Asfar samples, it was found that the largest of both available and total concentrations of the heavy metals were found in the oldest soil irrigated by

sewage sludge, and these concentrations decreased as the distance from the irrigation source increased. For the oldest irrigated soil samples (70 years), the available concentrations were 19.25, 0.0648, 6.74, 6.14 and 116.24 ppm for Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} respectively at distance of 10 m from the irrigation source. These concentrations decreased in 50 years old soil samples to be 10.95, 0.0402, 6.39, 2.59 and 78.49 ppm for the same heavy metals respectively. The smallest available concentrations were found in 20 years old samples to be 8.24, 0.0384, 5.26, 1.94 and 39.45 ppm for the same heavy metals. Also the greatest total concentrations of the heavy metals following the order of $70 > 50 > 20$ years sewage sludge irrigated soil samples.

Application of humic acid significantly decreased the available concentrations of Zn, Cd, Ni, Cu and Pb. The results showed that after three months of treatment, the estimated available concentrations of Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} were 5.3, 0.0031, 3.71, 1.32 and 29.31 ppm in the least contaminated samples (100 m distance).

While these values were 2.5, 0.0030, 2.88, 1.22 and 27.31 ppm for the same heavy metals when humic acid was used in 2 % percentage. But these values were decreased to 1.98, 0.0029, 2.66, 1.11 and 25.22 ppm for the same metals when humic acid was used in 4 % percentage.