Suez Canal University Faculty of Science Ismailia



Remediation of Soil and Water Contaminated by Cadmium and Lead using Humic Acid

A Thesis submitted by Rasha Atef Mohamed Mahdy Shoman B.Sc. in Chemistry (2004)

In Partial Fulfillment of the Requirements for the Degree of Master in Sciences (M.Sc. Chemistry)

IN Chemistry (Inorganic and Analytical Chemistry)

> To Chemistry Department Faculty of Science Suez Canal University Ismailia (2017)

ABSTRACT

The distribution and fate of heavy metal pollutants in soil and aqueous solution is strongly influenced by the presence of natural organic material. They are present in aqueous systems and can exist either in solution or as a precipitate mixed with sediments. Important characteristics of humic acid form waterinsoluble complexes with metal ions and sediments or suspended particulates.

The aim of this study remediation of soil and water contaminated cadmium and lead ion by using humic acid.

The extract of the humic acid was achieved from compost sample. The obtained humic acid was characterized using Fourier transform infrared (FTIR), Scanning electron microscopy and the elemental analysis(C, H, N, S and O %). Adsorption capacities of humic acid towards the different concentration of Cd²⁺and Pb²⁺. The effect of pH, metal concentration and ionic strength was evaluated and discussed. The obtained data go well with previous work. The concentration of metal ions was followed by using the atomic absorption Spectrophotometer (AAS) technique.

The ash content of the humic acid was measured by muffle furnace at $500C^{\circ}$ for two hour 0.1 6%. Remediation of water at pH = 6 is greater than pH= 4. The high adsorption ratio for Cd^{2+} and Pb^{2+} at pH= 6 are 92.25% and 99.02% respectively, Meanwhile at pH=4 for are 63.49% and 84.93% respectively. The hydrated humic acid appears to be significantly more reactive than the dried humic acid, Pb^{2+} bond strongly to humic acid more than Cd^{2+} . With the for Frindlich. application of adsorption equations Langmiur and Temkin.Langmiur's model was better for adsorption of Cd²⁺ on HA. Freundlich's model was better for adsorption of Pb²⁺ to HA. Study of the effect of ionic

strength on the adsorption of Cd^{2+} or Pb^{2+} on HA was found that the rate of adsorption decreased with increasing ionic strength.

Remediation of contaminated soil samples with Cd²⁺ or Pb²⁺:

The highest efficiency of bonding of Cd²⁺ or Pb²⁺ was on loam clay soils, calcareous loamy sand soil and loamy sand soil and when applying the adsorption models, Langmiur model was the best with the three soil samples. When soil samples were treated with dissolved humic acid in potassium hydroxide, the highest treatment was in loamy sand, then calcareous loamy sand and then clay loam.

These results indicate that soil properties (pH, organic matter, calcium carbonate) have a significant impact on the treatment process.

- The metal ions Cd^{2+} or Pb^{2+} had very similar kinetic adsorption.
- The rate law for a pesudosecond- order kinetic model best described the experimental data with the correlation coefficients (\mathbb{R}^2) of being over 0.995. Successful fitting of the data with the second order kinetic model suggests that chemisorption was the rate controlling step and $\mathrm{Pb}^{2+} > \mathrm{Cd}^{2+}$ according to the initial adsorption rate. The very fast sorption kinetics observed on humic acid and soil.

CONTENTS	page
ABBREVIATIONS	Ι
LIST OF TABLES	III
LIST OF FIGURES	V
Chapter One	
1 INTRODUCTION	1
	-
1.1. Background and identification of the problem	1
1.2. General remediation approaches	3
1.2.1 Isolation	3
1.2.2 Immobilization	3
1.2.2.1 Solidification/Stabilization	1
$1.2.2.\text{Tr} = \frac{1}{2} \frac{1}{2$	4
1.2.3. Toxicity and/or Mobility Reduction	5
1.2.3.1 Chemical Treatment	5
1.2.3.2 Permeable Treatment Walls	5
1.2.3.3 Biological Treatment	6
1.2.4 Physical Separation	6
1.2.5 Extraction	7
1.3 . Mobility and speciation of metals in water and soil	8
1.4.Cadmium	12
1.4.1.Some physical and chemical properties of cadmium	13
1.4.2. Origin of cadmium in soils	13
1.4.3. Health effects of cadmium	15
1.4.4. Amiloration and renabilitation of cadmium-contaminated soli	10
1.5.1 Some physical and chemical properties of lead	19
1.5.2. Health effects	20
1.5.3.Sources of lead in soils	21
1.5.3.1. Lead derived from vehicle exhausts	21
1.5.3.2. General atmospheric additions to soil and vegetation	22
1.5.3.3. Contamination from mining and smelting	22
1.5.3.4. Lead derived from agricultural materials	$\begin{vmatrix} 22\\ 22 \end{vmatrix}$
1.5.4. Lead in soil profiles	23

CONTENTS	Page
$1.5.5$ Associate little of local in social and for the manufacture Dh^{2+} such that	24
1.5.5. Availability of lead in soil and factors controlling PD uptake	24
1.6. Humic substances	25
1.6.1. Humic Acid (HA)	26
1.6.2. Physical properties of soil	28
1.6.3. Soil chemical and biochemical properties	29
Aim of the study	30
Chapter Two	
2. MATERIALS AND METHODS	31
2.1. Sampling and analysis	31
2.1.1. Soil analysis	33
	07
2.2. Compost analysis	3/
2.2.2. Extraction, purification and characterization of HA from	39
2.2.2.1. Extraction	39
2.2.2.2. Purification	40
2.2.2.3. Characterization	42
2.2.2.3.1. Total acidity	42
2.2.2.3.2. Carboxyl group	43
2.2.2.3.3. Phenolic hydroxyl groups	43
2.2.2.3.4. Elemental analysis (C, H, N, S and O %)	43
2.2.2.3.5. UV-Visible	44
2.2.2.3.6. Ash contents	44
2.2.2.3.7. Infrared spectrophotometer	44
2.2.2.3.8. Scanning Electron Microscopy (SEM)	44
2.2.2.3.9. ¹ H-Nuclear magnetic resonance spectra	45
2.2.2.3.10. Potentiometric titration measurements	45
2.2.3. Remediation of water from Cd²⁺ or Pb²⁺ using HA	48
2.2.3.1. Effect of ionic strength on adsorption of Cd ²⁺ or Pb ²⁺ ions	48
with HA at both pH = 6 and temperature = $30 ^{\circ}$ C	
2.2.3.2. Isothermal adsorption equation	48
The Langmuir equation	49
• The Freundlich equation	49
• The Temkin equation	50

CONTENTS	Page	
2.2.4 Dense \mathbf{l}^{i} of the set of \mathbf{f}^{i} is $\mathbf{l} \in \mathbf{U}^{2+}$ and \mathbf{D}^{i} is $\mathbf{L} = \mathbf{U}^{2+}$	51	
samples	51	
2.2.4.1. Artificial Cd^{2+} or Pb^{2+} contamination of the studied soil samples	51	
2.2.4.2 Remediation of the Cd^{2+} or Pb^{2+} contaminated soil samples 2.2.4.3. The Kinetics of the adsorption process	51 51	
Chapter Three		
3 RESULTS AND DISCUSSION	52	
5. RESULTS AND DISCUSSION	52	
3.1. Characterization of extracted humic acid	52	
► Total acidity	52	
Elemental analysis (C, H, N, S and O %)	52	
► UV-Visible	52	
Ash contents	53	
► Infrared spectrophotometer	54	
Scanning Electron Microscopy (SEM)	56	
H-NMR spectroscopy	5/	
Potentiometric titration measurements Eulyushima method	58 59	
Fukushima method	58 62	
Completin method Detentiometric studies of the free ligend(HA) at different	62	
temperatures (20, 30, 40 °C)	02	
Potentiometric measurements of the humic acid with Cd ²⁺ and Pb ²⁺ ions use 0.05 N HCl as titrant	62	
3.2. Remediation of both water and soil contaminated by Cd²⁺ or	65	
Pb ²⁺ using humic acid		
3.2.1. Remediation of water contaminated by Cd^{2+} or Pb^{2+} using humic acid	65	
$2.2.2 \text{ Lasthermal adaptation of } Cd^{2+} \text{ or } Dh^{2+} \text{ from water on humic acid}$	70	
5.2.2. Isomerinal adsorption of Cu or Pb from water on numic acid 2.2.2.1 Leather $1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 $	70	
3.2.2.1. Isothermal adsorption of Cd^{-1} ion on HA at pH = 4 and pH = 6	70	
3.2.3.2. Isothermal adsorption of Pb^{2+} ion on HA at $pH = 4$ and $pH = 6$	70	
3.2.3. Effect of ionic strength on adsorption of cadmium and lead	75	

ions on humic acid at pH = 6 and temperature = $30 ^{\circ}$ C	
3.3.1. Cadmium or lead ion adsorption and desorption on the	77
studied soil samples	
3.3.2. Isothermal adsorption of Cd ²⁺ or Pb ²⁺ ions on different soils	86
Isothermal adsorption of Cd ²⁺ ion on soil samples	86
Isothermal adsorption of Pb ²⁺ ion on soil samples	87
3.4. The Kinetics of the adsorption process	95
3.4.1. Effect of contact times on adsorption of cadmium ion	95
3.4.2. Effect of contact time on adsorption of lead ion	95
3.4.3. The pseudo first order model	98
3.4.4. The pseudosecond -order model	98
Recomendation	105
English summary	106
References	109
Arabic summary	ĺ