344

Egypt. J. Chem. **Vol. 64,** No. 7 pp. 3671 - 3679 (2021)

Determining Cadmium Activities and Predicting Solid- Phases Which Control Its solubility in the Soil irrigated with Sewage Water, in Egypt.

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Abstract

Solubility of heavy metal in contaminated soils is a key factor which controls the solubility and toxic effects of metals on soil environment. Hence, study aims to determination the active portion of Cadmium (Cd^{+2}) and predicting possible solid phases which controlling in soil irrigated consecutively with sewage water effluent collected from the farm of the Egyptian at El- Gabal El-Asfar which located in the eastern desert in the southeastern edge of Al Qaliobia governorate, for 100 years, as well as assessing contribution of some remedial materials. The results indicated that Cd^{2+} activities increased from ($8.1548E^{-10}$) in the control soil samples to ($8.11333E^{-9}$) in the sewage effluent soil samples, the data indicated that Cd activities were correlated negatively with soil pH.

On the other side, the tested remedial materials had a great influence on the values of Cd activities. The obtained Cd activities were ($4.65006E^{-9}$ and $6.89868E^{-9}$), ($3.7353E^{-9}$ and $6.00091E^{-9}$), and ($4.61439E^{-9}$ and $5.93551E^{-9}$) in C1, C2, and C3 Zero valent iron- and Rock phosphate amended soil, respectively, also determined Cd activities of the tested soil samples on the constructed stability diagram of the various cadmium minerals obtains that values of Cd were lie below all the established Cd- mineral diagrams, suggesting that there are possibility of other minerals could controlling the solubility of Cd in that soils. Furthermore the continual use of sewage effluent water in irrigation implying serious hazards on terrestrial ecosystem.

Keywords: Cadmium activity, soil remediation, competition chelation method, Stability diagram

1. Introduction

The shortage of fresh water in many part of the world as a result of rapid population, urbanization, climatic changes, and mismanagement of using water resources have been compelled many farmers to use low water quality. This water are often contain miserable quantities of heavy metal which eventually posing threads to human beings. It is generally recognized that the particular behavior of heavy metals in the environment is determined by their specific physicochemical forms rather than by their total concentration [1,2].

Moreover, It has been established that in most circumstances activity of free metal ion is the key factor in determining metal bioavailability and toxicity [3,4],Furthermore, The ion activity of metals can also be used in thermodynamics to describe the direction and impetus of chemical reactions such as precipitation, complexation and adsorption[5,6].The free metal ion concentration not only depends on the total metal content in soils, but also on the metal species that exist in the soil. In addition, some environmental conditions (e.g., pH, concentration of competing ions, concentration of complexing ligands in solution, and the soil colloid) and characteristics of organism in soil may play an important role [7].

2. There are several approaches that have been widely used to determine the free ion concentration (activity). Each method has its advantages and limitations and generally based on a more profound analytical back ground (e.g., pH, concentration of competing ions, concentration of complexing ligands in solution, and the soil colloid) and characteristics of soil biota, for instance, the ion selective electrometer (ISE) method, [8], voltammeter and polarography methods [9], and Donnan membrane

technique(DMT), [7]. Also, the competitive chelation method which proposed by[10] was used widely for determining activity of some metals[11]. They reported that this method was good sensitive and convenient for measuring metal activities in neutral to slightly alkaline soils, it's and provides estimates of ion.Stability diagrams are used as a convenient technique for illustrating how the solubility of metal compounds varies with soil pH and with metal concentration (or activity),[12,13,14].

3. Several technologies exist for the remediation of metals-contaminated soil and water. These technologies are contained within six categories of general approaches to remediation:1) ex-situ (excavation) or in-situ (on-site) soil washing with chemical agents, 2) chemical immobilization/stabilization method to reduce the solubility of heavy metals by adding some non-toxic materials into the soils, 3) electro kinetics (electro migration), 4) covering the original polluted soil surface with clean soils, 5) dilution method (mixing polluted soils with surface and subsurface clean soils to reduce the concentration of heavy metals), 6) phytoremediation by plants such as woody trees [15,16].As is usually the case, combinations of one or more of these approaches are often used for more cost-effective treatment of a contaminated site.

4. Immobilization technologies are the most commonly selected treatment options for metals-contaminated sites, these methods are simple, effective for heavy metals remediation and have the potential to provide significant cost savings [17].

5. Also used biocharto remediate industrial contaminated soil and their data showed that mobility factor of cadmium in untreated soil show that was higher in untreated soil than in treated soil [18].

6. Nanotechnology offers the possibility of an efficient removal of pollutants, Zero-valent iron is elemental metallic iron, and refers to the zero charge carried by each Fe atom. It acts a bulk reducing agent, converting oxidized materials – which may be toxic and soluble in water – into immobile solid forms, releasing soluble Fe^{+2} in their place, which further oxidizes to Fe^{+3}[19,20].In this study, we examined activities of cadmium in contaminated and non-contaminated soils additionally; the effect of ZVI ,RP application on the form of Cd in soils was investigated, and predicted the solubility cadmium minerals diagram.

7. The present study aims to assess the contribution of using sewage effluent water consequentially for 100 years in soil irrigation on Cd activities,identify the probable solid phases (minerals), which govern the solubility of Cd^{2+} as well as influence of some remedial materials.

Material and Method

Two composite surface soil samples(0 – 30cm)were collected from the farm of the Egyptian Wastewater Treatment Plant at El- Gabal El-Asfar , which located in the eastern desert in the southeastern edge of Al Qaliobia governorate .This plant received sewage effluent water from Great Cairo since 1911 . The first sample represent un-irrigated soil sample (as control), while the second sample represent soil consequentially irrigated with sewage effluent irrigated for more than 100 years. The soil samples were air-dried, sieved through 2-mm sieve. The general characteristics of the tested soils are present in Table (1).

Moreover, a portion of the tested soils were amended with three rates (C1,C2,andC3) of two remediation materials namely, Zero-valent iron and rock phosphate and then incubated with ionized water for 35 days , air- dried and passed through 2- mm sieve and stored for analysis.

Method of analysis

a) **Soil reaction (pH):-**It was measured in soil paste using combined electrode pH meter model 781 pH/ ion Meter)**.**[21].

b) **Soil salinity (EC):-** It was measured by electrical conductivity meter in saturated soil extract, dSm^{-1}(modelCDM210 Conductivity meter)**.**[22].

c) **Total metal content**: -One gram (dry weight) of the soil samples was digested as previous mentioned as described by [23].

d) **Determining active Cd concentration** : Cd^{+2}activitieswere measured using the competitive chelation method given in details by [6], this method depends on reacting soil with a series of chelate solution having different mole fractions of Cd and a competing metal (Pb)a series of chelating solution, having different mole fractions of chelate ligand (L),

That is (CdL / CdL+PbL),were prepared using reagent grade diethylenetriaminepentaacetic acid (DTPA),$Pb(NO_3)_2$ and $Cd(NO_3)_2$. The initial CdL/(CdL +PbL) mole fractions used varied from 0.0 to 0.3 and included six different mole fractions .

The procedure carried as follows:

Fifteen –gram subsamples of each soil were weighed in 125 ml Erlenmeyer flasks , and 30 ml of 0.01 M of $CaCl_2$ solution having a given CdL/(CdL+PbL) mole fraction was added along with 10 mg of $PbCO_3$ to maintain a known Pb^{2+} activity in solution . For each soil , a blank treatment without a chelating agent was prepared by shaking 15 g of soil with 30 ml of 0.01M $CaCl_2$ solution . The Erlenmeyer flasks were then covered with perforated parafilm to allow gas exchange with the atmosphere.
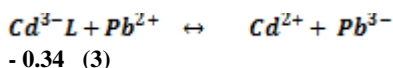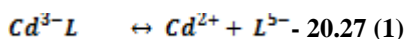
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The suspensions were shaken for 5 days, pH were measured, and then centrifuged, filtered and the clear solutions were analyzed for Cd and Pb using atomic absorption spectrophotometer.

Calculation:

The final mole fraction of Cd/ (CdL +PbL) for each soil was calculated from the total soluble Cd and Pb after subtracting Cd and Pb in the CaCl2 blank treatment . A graph relating initial and final CdL/(CdL +PbL) mole fractions was made for each soil , and the equilibrium CdL/(CdL +PbL) mole fractions were obtained (Figs.) which used to calculate Cd2+ activity in the soil.

Derivation of the equilibrium equation used to calculate Cd^{+2} activity is given as follows:

LogK$_m$0.01

$$Cd^{3-}L \leftrightarrow Cd^{2+} + L^{5-} - 20.27 \quad (1)$$

$$Pb^{2+} + L^{5-} \leftrightarrow Pb^{3-} + 19.93 \quad (2)$$

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$$Cd^{3-}L + Pb^{2+} \leftrightarrow Cd^{2+} + Pb^{3-}$$
$$- 0.34 \quad (3)$$

Rearranging Equation (3) gives:

$$[Cd^{2+}] \rightarrow \frac{[CdL^{3-}]}{[PbL^{3-}]} * 10^{0.34-} * [Pb^{2+}] \quad (4)$$

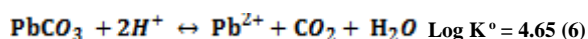**Since the activities of Cd^{2+} and Pb^{2+} and of CdL^{3-} and PbL^{3-} are equal equation (4) can be written in terms of activities .**

$$(Cd^{2+}) \rightarrow \frac{(CdL^{3-})}{(PbL^{3-})} * 10^{0.34-} * [Pb^{2+}] \quad (5)$$

Since PbCO$_3$ was added to the soil suspensions to control Pb^{2+}activities,   then it possible to calculate Pb activity as follows:

$$PbCO_3 + 2H^+ \leftrightarrow Pb^{2+} + CO_2 + H_2O \quad \text{Log K}^o = 4.65 \ (6)$$

$$(Pb^{2+}) \rightarrow 10^{4.65} * H^{2+}/ CO_2 \quad (7)$$

At0.03 Kpa(0.0003atm) CO$_2$

Then; Pb^{2+} = 10$^{8.17}$* H^{2+} (8)

**Substituting in Equation (8) into Equation (5) gives ;**

$$(Cd)^{2+} = (CdL) / (PbL) * 10^{7.83 - 2pH} \quad (9)$$

The pH value used in Eq.(9) was the pH of the suspension closest to the equilibrium point .

e) Constructing stability diagrams

Cadmium minerals that may control the level of Cd^{2+} activity in soils were plotted on an equilibrium solubility diagram in terms of Cd^{2+} activity and pH (Fig 9) using as the thermodynamic data reported by[12] which listed in in Table (1) as follows;

$$CdCO_3(c) + 2H^+ \leftrightarrow Cd^{2+} + CO_2 (g) + H_2O \quad (10)$$
$$(\text{Log K}^o = 6.16)$$
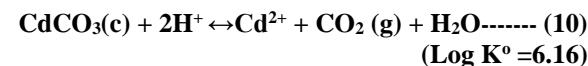
Log (Cd^{2+}) = 6.16 – Log CO$_2$ – 2pH

At CO$_2$ = 0.0003 atm, this equation becomes;

Log (Cd^{2+}) = 10.68 -2pH (11).

At CO$_2$ = 0.003 atm, this equation becomes;

Log (Cd $^{2+}$) = 9.68 -2pH (12).

The constants used to constructed solubility diagrams of Cd minerals are listed in Table (1).

Equilibrium reaction	logK°
$CdCO_3 + 2H^+ \leftrightarrow Cd^{2+} + CO_{2(g)} + H_2O$	6.16
$CdSiO_3 + 2H^+ + H_2O \leftrightarrow Cd^{2+} + H_4SiO_4^0$	7.63
$Cd_3(PO_4)_2 + 4H^+ \leftrightarrow 3Cd^{2+} + 2H_2PO_4^-$	1.00
$CdFe_2O_4 + 8H^+ \leftrightarrow Cd^{2+} + 2Fe^{3+} + 4H_2O$	11.37
$Fe(OH)_3(amorp) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	3.54
$Fe(OH)_3(soil) + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	2.70
$1/2\gamma Fe_2O_3(maghemite) + 3H^+ \leftrightarrow Fe^{3+} + 3/2H_2O$	1.59
$FePO_4.2H_2O9(strengite) + 2H^+ \leftrightarrow Fe^{3+} + H_2PO_4^- + 2H_2O$	-6.85
$CaHPO_4.2H_2O(brushite) + H^+ \leftrightarrow Ca^{2+} + H_2PO_4^- + 2H_2O$	0.63
$\beta Ca_3(PO_4)_2 + 4H^+ \leftrightarrow 3Ca^{2+} + 2H_2PO_4^-$	10.18
$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + CO_{2(g)} + H_2O$	9.74
$SiO_2(soil) + 2H_2O \leftrightarrow H_4SiO_4^0$	-3.10
$-SiO_2(quartz) + 2H_2O \leftrightarrow H_4SiO_4^0$	-4.00

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3. Result and Discussion

1. General properties of tested soils:

In Table (2) the sewage effluent irrigated soil samples , soil salinity (EC), soil acidity (pH), , soil organic matter (OM) increased by (7.04 , 1.08, 8.09 times) consequentially than their corresponding values in the control soil sample , referring that the continual use of sewage water has great influence on organic matter content , followed by soil salinity and soil acidity. These results ascribed to the composition of the sewage water [25, 26]. On the contrary that calcium Carbonate (CaCO$_3$%) decreased by 33.48% , which may contributed to the action of organic ligands exist in that water on increasing solubility of CaCO$_3$, also reveal that sewage water irrigation has resulted in significant build-up of total soil content of Cd (1286%), Cu (6153%), Zn (9139%), Fe (1491%), and Mn (10172%) over the control soil in investigated soils. These findings referred that contribution of sewage water on soil heavy contamination may ranked as follows ; Mn>Zn>Cu>Fe>Cd.

2-Measurement Cd activities in the tested soils :

The activities of Cd in the investigated soil samples were measured using the competitive chelation method as described by [24].

This procedure depends on the soil reacted with a series of chelating solutions containing different mole fractions of principal ion in our case, Cd and a competing ion in our case, Pb. Some soils gain the principal ion and lose the second; other solutions gain the counter and lose the principal.

The unique point where no gains or losses, represent the equilibrium point which use in calculation of the activity of the principal ion. A plot of the final CdL/(CdL+PbL) mole fraction of the filtrates against the initial mole fractions are presented from Figs.(1 - 8) , the intersected between them pointed out to the equilibrium point of mole fraction.

This equilibrium value was used in the following equation to calculate Cd activities by using the following formula; and the results are listed in Table (3).
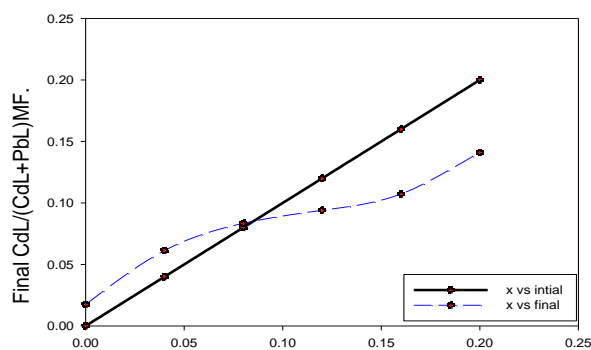
$$(Cd^{2+}) = (CdL) / (PbL) * 10^{\,(7.83 - 2pH)}$$

Table(2) General characteristics of the tested soils		
Variables	**0-yrs**	**100-yrs**
Ec(dms^{-1})	0.35	2.47
pH	7.35	7.96
OM.%	0.42	3.4
CaCO$_3$%	4.51	3.00
Total heavy metals content (mg/ kg)		
Cd	1.01	14.0
Cu	3.00	187.6
Zn	3.8	331.0
Fe	1140.3	18148.8
Mn	1.1	113.0
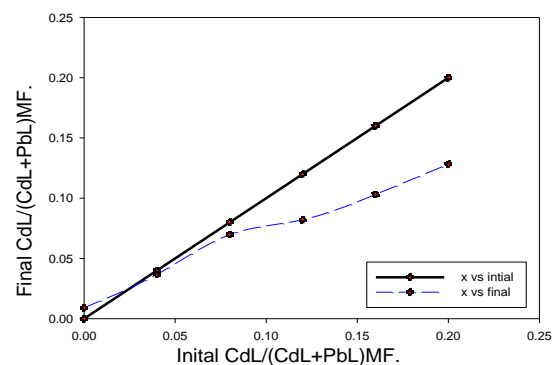
Fig(1) Change in CdL/ (CdL+PbL) mole fraction in control soil

Fig(2) Change in CdL/ (CdL+PbL) mole fraction in polluted soil

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It is obvious from the Figs that at low concentrations of initial mole fraction; Cd released from the soil sample to the equilibrium solution, whereas at high concentrations; the chelate lost Cd. Figs. (1 to 2) Changes in CdL/(CdL+PbL) mole fraction in the tested soil samples Equilibrium pH(Eq. pH) values, initial Cd MF ranges, equilibrium Cd MF, and calculated Cd^{2+} activities in the 0-yrs, 100-yrs and remediated soil samples are summarized in Table (3).

The measured Cd^{2+} activities were negatively correlated with pH values. For example the activity of Cd in the 0-yrs soil sample was 8.1548E-10 (pCd =9.0885871), with a pH of 7.75, and increased to 8.11333E-09 ((pCd^{2+}=8.090801) in the 100-yrs soil sample with pH 7.44.Similar conclusions were also reported by(El-Gendi et. al. 2017)[25] for Pb who indicates that Pb solubility in the soils decreased about 100 fold for each pH unit increase, in the same connections, the present data show that the coefficient of correlation between the Cd activities and equilibrium pH values in the tested soil samples was (r= 0.81)

The influences of soil contamination on the activities of Cd^{2+} in soils were also investigated in the present study,as shown from the Table (3), pCd^{2+} values were 9.08 and 8.09 in the 0-yrs and 100-yrs soil samples, respectively, indicating that the continual use of sewage effluent water in irrigation increased Cd^{2+} activity by 9.94 folds than the control soil sample.These results are consistent with results reported by [11] who computed the activity of some metals (M/L) in soil consecutive irrigated with sewage effluent water for more than 50-years concentration. (M/L) as follows, Cd^{2+}(1.61E-07), Ni^{2+}(5.96E-07), and Pb^{2+}(1.29E-08),they also added that continual use of sewage effluent in irrigation decreased the activity of both of Pb and Cd than the 0-yrs by (26% and 72%, respectively), meanwhile Cd^{2+} activity increased by about 8 times due to sewage effluent application.

The impact of sources of soil contamination on Cd^{2+} activities was studied by many authors ; [26] showed that Cd activities in the sludge – amended soil was higher than that in industrial contaminated soil by 63.71% , attributed that to the lowest of pH in the former one.

Also, It is clearly obvious from the Table (2) and Figs (3-8) that the tested remedial materials (Zero-iron and Rock phosphate) with the three rates of amending (1, 2, and 3% w/w) had great influences on the values of Cd activities, as shown from the Table(2), the values of Cd^{2+} activities varies widely among the tested soil, in the Zero valent iron– amended soil(M1), the activity of Cd was 4.65006E-09, 3.7353E-09, and 4.61439E-09 in C1 , C2, and C3 respectively, which represent , 57% , 46%, and 56 %, of its value in 100-yrs soil .

Meanwhile in rock phosphate – remediated soil samples(M2) , the Cd activities were ; 6.89868E-09 , 6.00091E-09 , and 5.93551E-09 for C1,C2, and C3 , soil sample, respectively, which represent only 85%, 73 % , and 73%, respectively, compared with Cd^{2+} activity in 100-yrs soil sample.
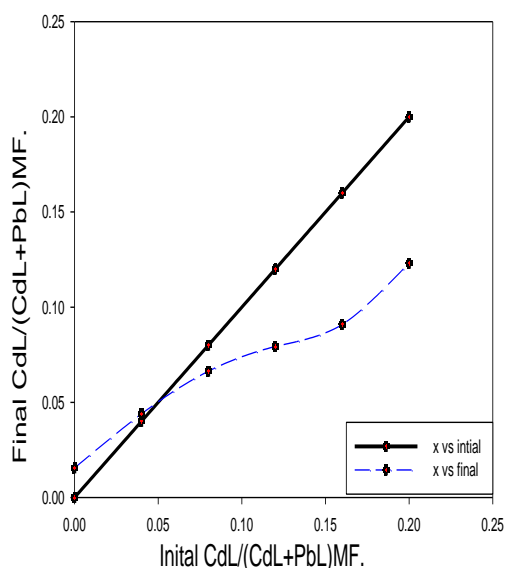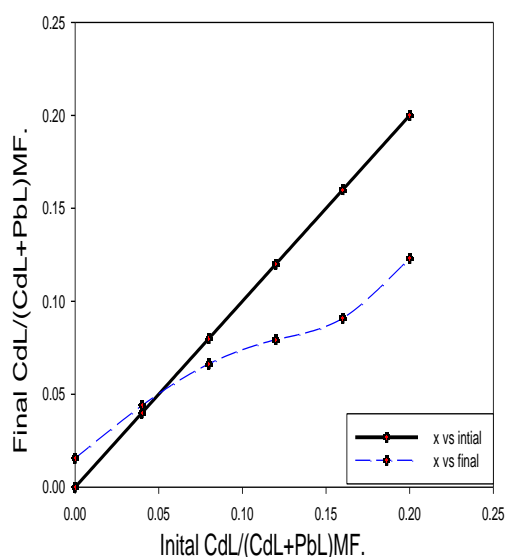

Fig.(3) Change in CdL/ (CdL+PbL) mole fraction in polluted soil under effect 1% by zero valent iron (ZVI)

Fig.(4) Change in CdL/ (CdL+PbL) mole fraction in polluted soil under effect 2% by zero valent iron (ZVI)
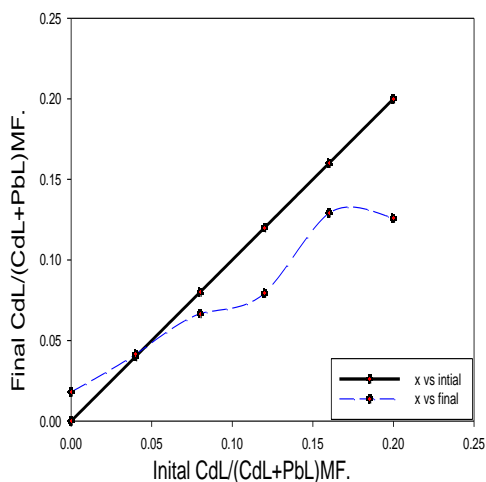
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Fig.(5) Change in CdL/ (CdL+PbL) mole fraction in polluted
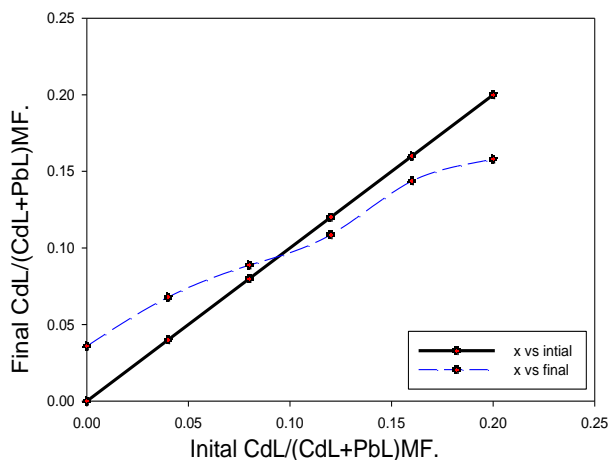soil under effect 3% by zero valent iron (ZVI)

Fig.(6) Change in CdL/ (CdL+PbL) mole fraction in polluted
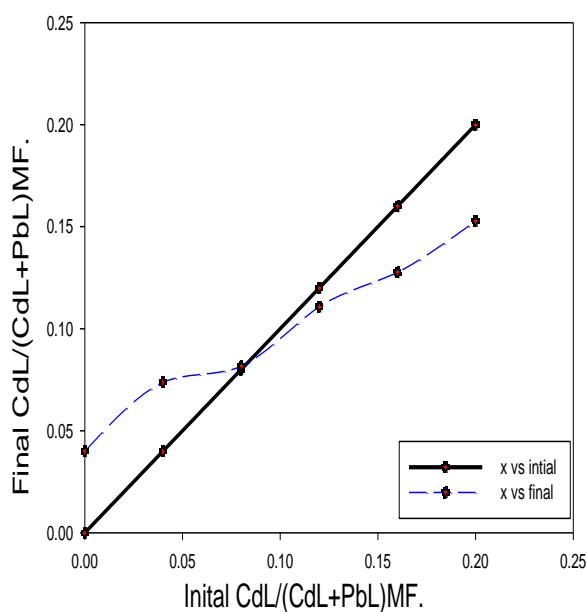soil under effect 1% by Rock Phosphate (RP)

Fig.(7) Change in CdL/ (CdL+PbL) mole fraction in
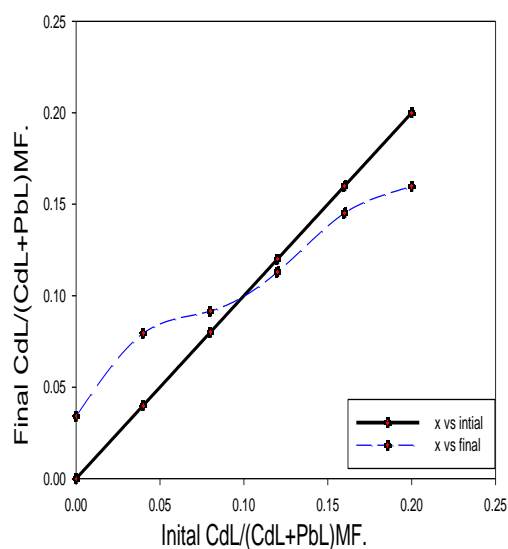polluted soil under effect 2% by Rock Phosphate (RP)

Fig.(8) Change in CdL/ (CdL+PbL) mole fraction in
polluted soil under effect 3% by Rock Phosphate (RP)

Table(3): Measured pH, equilibrium Cd mole fractions (MF) and pCd^{2+} activities in the tested soil samples

Soil			Eq. pH	Initial Cd MF	Equilibrium	
					(CdL/PbL)	pCd^{2+*}
0-yrs Soil			7.75	0.0-0.2	0.038143	9.088587
100-yrs soil			7.44	0.0-0.20	0.091033	8.090801
Remediated soils	M1	C1	7.51	0.0-0.20	0.072021	8.332542
		C2	7.46	0.0-0.20	0.045954	8.427675
		C3	7.51	0.0-0.20	0.071468	8.338600
	M2	C1	7.49	0.0-0.20	0.097446	8.161234
		C2	7.50	0.0-0.20	0.088760	8.221783
		C3	7.53	0.0-0.20	0.100799	8.226542

pCd^{2+*}= (-log Cd^{2+}).

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On mean basis , the present data revealed the reduction in Cd^{2+} activity due to amending the 100-yrs soil with Zero valent iron(M1) was 53%, whereas ,it was (x=77%) in Rock phosphate amended soil.

Concerning the rate of amending on the values of Cd activity, the data show that second rate of the tested amending materials (C2, 2%w/w) was more effective in reducing of Cd^{2+} activity in the tested soil sample.

Predicted solid- phases which controlling the solubility of Cd in the soils.

Solubility lines of M-ferrite were developed in equilibrium with Fe $(OH)_3$ (amorphous), $Fe(OH)_3$ (soil-Fe). Solubility lines of M-aluminate were developed in equilibrium with gypsite, or Al $(OH)_3$ amorphous .

Solubility line of M-silicate were developed in equilibrium with SiO_2 (quartz or soil), while for M-phosphate minerals were developed in equilibrium with gypsite and Ca-phosphate minerals as described by[12,14] and plotted in Fig(9).

By examining the proximity of the measured values of Cd^{2+} to solubility lines, the solid phases supposed to control the solubility of Cd in respective soils, could be identified.

It clearly shown from the Fig.(9) that CdO (monteponite) , β-Cd$(OH)_2$ are too soluble to form in soils . Also, $CdSiO_3$ is more soluble than activate, so it is not expected to form in the soil. Also, the Fig.(9) indicated that the solubility of $CdCO_3$ decreased with increasing CO_2 concentration. Moreover, $Cd_3(PO_4)_2$ which plotted in the Fig.(9) is controlled by $FePO_4-2H_2O$ (strengite) and $Fe(OH)_3$ (soil) and tricalcium phosphate (TCP) and CO_2,in pH range from 6-7.5 ,$Cd_3(PO_4)_2$ in equilibrium with TCP controls Cd activity at concentration of about $10^{-5.5}$ M.

Plotting the calculated values of Cd^{2+} on the Cd solubility mineral diagram indicated that Cd^{2+} value were lie below the constructing minerals. This suggested that other possible solid phase of cadmium may be controlling its activity in that soil. They added that No known Cd mineral has yet been identified whose solubility, reflecting low activity of Cd^{2+}.Meanwhile , [11] The data show that the solubility of Cd^{2+} in virgin soil was closed to the solubility of $CdCO_3$ (log CO_2=-2.52) and $CdSO_4-2Cd(OH)_2$ at (log SO_4=-2) , while in sludge soil ,the value of Cd^{2+} was under saturated with respect the constructed Cd minerals.
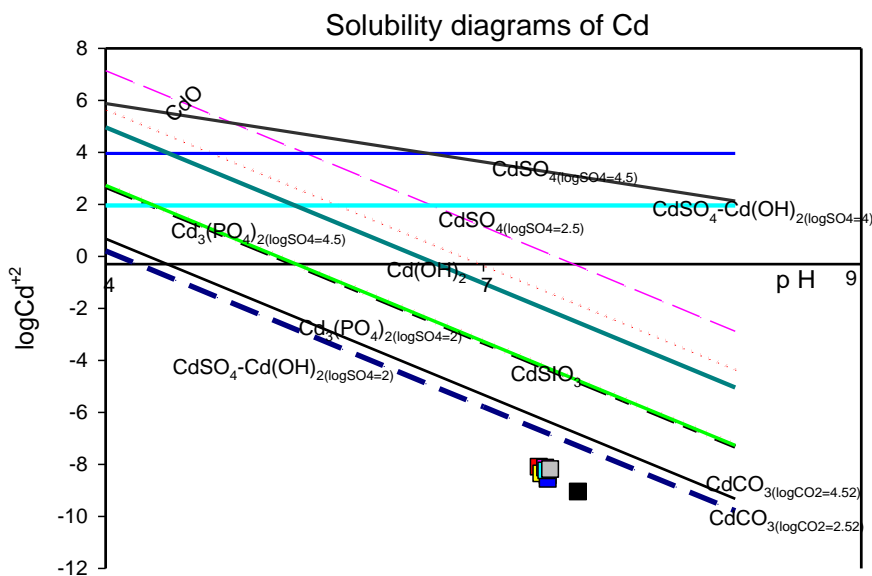

Fig.(9) Stability diagrams of various Cd- minerals

Conclusion:

Long-term irrigation with sewage effluent water resultedinto a significant increase in soil salinity (EC), soil acidity (pH) , soil organic matter (OM), whereas soil CaCO3 content declined.Also, significant build-up of total soilheavy metal contents was associated with the continual use of sewage water over the virgin soils and could be ranked as follows ; Mn>Zn>Cu>Fe>Cd.

Also, it can concluded that the continues use of sewage water in irrigation lead to appreciable increase in free ion activities of Cd^{2+} , thereby induce serious hazards on terrestrial ecosystem.

Zero valent iron- and Rock phosphate which evaluated as remedial materials declined Cd activities.

On mean basis, the present data revealed the reduction inCd^{2+} activity in soil amending with Zero valent iron(M1) was 53%, whereas ,it was 77% in Rock phosphate amended soil. Concerning the rate of amending on the values of Cd activity, the data show that second rate of the both tested amending materials (2%w/w) was more effective in reducing of Cd^{2+} activity in the tested soil samples.

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Determined Cd activities of the tested soil samples on the constructed stability diagrams of the various cadmium minerals obtained values of Cd activities were lie below all the established Cd- mineral diagrams, suggesting that there are possibility of other minerals could controlling the solubility of Cd in that soils.

References

1. Cances, B., Ponthieu, M., Castrec-Rouelle, M., Aubry, E., & Benedetti, M. F. Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma*, *113*(3-4), 341-355.(2003).

2. Yuan, GCopper, zinc, and nickel in soil solution affected by biosolids amendment and soil management. *Soil Research*, *47*(3), 305-310. (2009).

3. Candelaria, L. M., Chang, A. C., & Amrhein, C. Measuring cadmium ion activities in sludge-amended soils. *Soil science*, *159*(3), 162-175(1995).

4. Alloway, B. J. Heavy metals in soils. Blackie Academic and Professional. *An Imprint of Chapman & Hall. Glasgow*(1995)

5. Santillan-Medrano, J., & Jurinak, J. J. The chemistry of lead and cadmium in soil: solid phase formation. *Soil Science Society of America Journal*, *39*(5), 851-856(1975).

6. El-Falaky, A. A., Aboulroos, S. A., & Lindsay, W. LMeasurement of cadmium activities in slightly acidic to alkaline soils. *Soil Science Society of America Journal*, *55*(4), 974-979.. (1991).

7. Temminghoff, E. J., Plette, A. C., Van Eck, R., & Van Riemsdijk, W. H.. Determination of the chemical speciation of trace metals in aqueous systems by the Wageningen Donnan Membrane Technique. *Analytica Chimica Acta*, *417*(2), 149-157(2000)**.**

8. Mota, A. M. Trace metal speciation of labile chemical species in natural waters: electrochemical methods. *Metal speciation and bioavailability in aquatic systems*(1995).

9. Nordstrom, D. K. Trace metal speciation in natural waters: computational vs. analytical. *Water, Air, & Soil Pollution*, *90*(1), 257-267(1996).

10. Norvell, W. A., & Lindsay, W. L.. Estimation of the Concentration of Fe3+ and the $(Fe^{3+})(OH^-)$ 3 Ion Product from Equilibria of EDTA in Soil. *Soil Science Society of America Journal*, *46*(4), 710-715(1982).

11. El-Gendi, S., El-Desoky, A., & Khalafalla, M. Predicted Speciation and Mineral Solid Phases of some Heavy Metals in Sludge-amended Soil. *Journal of Soil Sciences and Agricultural Engineering*, *9*(11), 561-566.(2018).

12. Lindsay, W. L. *Chemical equilibria in soils*. John Wiley and Sons Ltd.(1979)..

13. Santillan-Medrano, J., & Jurinak, J. J. The chemistry of lead and cadmium in soil: solid phase formation. *Soil Science Society of America Journal*, *39*(5), 851-856(1975).

14. Sposito, G. The Chemistry of Soils Oxford Univ. *Press, New York, USA*(1989).

15. Wuana, R. A., Okieimen, F. E., & Imborvungu, J. A. Removal of heavy metals from a contaminated soil using organic chelating acids. *International Journal of Environmental Science & Technology*, *7*(3), 485-496(2010).

16. Zhang, Y. L., Dai, J. L., Wang, R. Q., & Zhang, J. Effects of long-term sewage irrigation on agricultural soil microbial structural and functional characterizations in Shandong, China. *European journal of soil biology*, *44*(1), 84-91(2008).

17. Aljlil, S. A., & Alsewailem, F. D. Adsorption of Cu & Ni on bentonite clay from waste water. *Athens Journal of Natural & Formal Sciences*, *1*(1), 21-30(2014).

18. Anegbe, B., Okuo, J. M., Ewekay, E. O., & Ogbeifun, D. E.. Fractionation of lead-acid battery soil amended with Biochar. *Bayero Journal of Pure and Applied Sciences*, *7*(2), 36-43(2014).

19. Bazdanis, G., Komnitsas, K., Sahinkaya, E., & Zaharaki, D.. Removal of heavy metals from leachates using permeable reactive barriers filled with reactive organic/inorganic mixtures. In *Proceedings of the 3rd international conference on environmental management, engineering, planning, and economics (CEMEPE) & SECOTOX conference, Skiathos island, Greece* (pp. 19-24).(2011, June).

20. Rathor, G., Adhikari, T., & Chopra, N. Management of nickel contaminated soil and water through the use of carbon nano particles. *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, *3*(2), 901(2013).

21. Black, C. A., Evans, D. D., White, J. L., Ensminger, L. E., & Clark, E. E., Methods of soil analysis, Part 2. *Chemical and microbiological properties: Madison, Wis., American Society of Agronomy Monograph*, (9) (1966).

22. Jackson, J. F. C., Nevissi, A. E. and Dervalle, F. B. "Soil Chemical Analysis". *Prentice Hall Inc. Engle Works Cliffs. New Jersey. .* (1984).

23. Tessier, A., Campbell, P. G., & Bisson, M. J. A. C.. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry*, *51*(7), 844-851(1979).

24. Workman, S. M., & Lindsay, W. L.. Estimating divalent cadmium activities measured in arid-zone soils using competitive chelation. *Soil Science Society of America Journal*, *54*(4), 987-993.(1990).

25. El-Gendi, S. A., Hassan, M. A., & El-Naka, E. A. Determining lead activity in an egyptian alluvial soil using competitive chelation method. *Zagazig Journal of Agricultural Research*, *44*(4), 1315-1323(2017).

26. Omnia, F. A. Chemistry of Some Heavy Metals in Polluted Soils. Ph.D. thesis in soil Science, Faculty of Agriculture Cairo University, Egypt.(2007).

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الملخض العربى

تحديد أنشطة الكادميوم والتنبؤ بالمراحل الصلبة التي تتحكم في قابليته للذوبان في التربة المروية بمياه الصرف الصحي في مصر

رباب احمد عمر 1 * سمير عبد الرحمن الجندي 1 جمال السيد عويس 2

معهد بحوث التربة والمياه والبيئة ، مركز البحوث الزراعية ، الجيزة ، مصر 1

كلية العلوم ، جامعة بنها ، بنها ، مصر 2*

يعتبر تلوث التربةعاملاًرئيسياً يتحكم في تاثير على قابلية الذوبان للمعادن السامةهتاثير على بيئة التربة. ومن هنا تهدف الدراسة إلى تحديد الجزء النشط من الكادميوم (Cd^{+2}) والتنبؤ بالمراحل الصلبة المحتملة التي تتحكم في التربة المروية بالتتابع بمياه الصرف الصحي المتدفقة المجمعة من مزرعة المصري بالجبل الأصفر الواقعة في الشرق. صحراء في الطرف الجنوبي الشرقي لمحافظة القليوبية لمدة 100 عام بالإضافة إلى تقييم مساهمة بعض المواد العلاجية.

أشارت النتائج إلى أن نشاط Cd^{2+} زاد من ($8.1548*10^{-10}$) في عينات التربة الضابطة إلى ($8.11333*10^{-9}$) في عينات تربة الصرف الصحي ، وأظهرت البيانات أن أنشطة الكادميوم كانت مرتبطة سلبًا بالرقم الهيدروجيني للتربة (ر 0.81).

من ناحية أخرى ، كان للمواد العلاجية المختبرة تأثير كبير على قيم أنشطة الكادميوم. كانت أنشطة الكادميوم التي تم الحصول عليها ($4.65006*10^{-9}$) و ($6.89868*10^{-9}$) و ($3.7353*10^{-9}$) و ($6.00091*10^{-9}$) و ($4.61439*10^{-9}$) و ($5.93551*10^{-9}$) في C1 و C2 و C3التربة تحت تاثير الحديد ذو الصفر التكافؤ والفوسفات الصخري ، على التوالي. حددت أيضًا أنشطة الكادميوم لعينات التربة المختبرة على مخطط الثبات المركب لمختلف معادن الكادميوم التي حصلت على أن قيم الكادميوم تقع أسفل جميع الرسوم البيانية للكادميوم المعدني ، مما يشير إلى وجود احتمال من معادن أخرى يمكن أن تتحكم في قابلية ذوبان الكادميوم في تلك التربة.

علاوة على ذلك ، فإن الاستخدام المستمر لمياه الصرف الصحي في الري قد يؤثر على النظام البيئي الأرضي.