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THE ROLE OF CEMENT DUST IN CHEMICAL REMEDIATION OF THE SLUDGE TREATED SOIL

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ABSTRACT :

Remediation of toxic metals has been considered as an important research subject for environmental studies. This study investigated the effect of cement dust (*CD*) applied with two levels i.e. 2.5 and 5% on the remediation of Pb, Cd, Ni and Cr in sludge treated soil using the kinetic approach represented by the modified Freundlich, Elovich, the first order, Z(t), and the parabolic diffusion equations through the electrical stirred flow unit (ESFU) technique. Field experiment was also carried out on El-Gabal El-Asfar region to evaluate and assess the potential effect of cement dust by using corn (*Zea maize L.*) as an indicator.

The obtained results showed that application of sludge significantly accumulated and showed increases in studied heavy metals especially in high applied level i.e. 20 m^3 .fed^{-1} compared with the low level one i.e. 10 m^3 fed^{-1}. The application of *CD* showed a significant decrease in the studied heavy metals represented by the decreasing order of the kinetic parameters of used equations. The fractionation of heavy metals showed that the residual fraction increased compared with other fractions with increasing the applied level of *CD* material. Also, the remediation success of the studied heavy metals represented by remediation index (RI), showed that application of *CD* led to a decrease in the heavy metal availability in the *CD* treated soils. Moreover, the RI showed that there is a priority of *CD* in minimizing Cr availability in the sludge treated soil followed by Pb, Cd and Ni which gave the highest RI value with respect of the available form of the studied metals. In the field experiment the results revealed that *CD* treatments generally led to a significant decrease in the uptake of heavy metals by corn, especially for Ni and Cr and less extent for Pb and Cd. The applied kinetic models are trusted technique for evaluating the remediation success of the applied material to contaminated soils because it was highly correlated with heavy metal uptake by corn. The remediation mechanisms of *CD* was discussed in more details.

INTRODUCTION:

There is an ever increasing awareness and concern about the environment and the extent of the interrelationships between the three basic resources; land, water and air. A seemingly for removed input into one of these resources can be detrimental to another. Because of the immensity of the environment and the heretofore relatively low level of use, interests have generally been centered on other aspects of daily activities. Recently, a considerable degree of worldwide concern has been developing regarding the effects of heavy metals on the environment. Because soils are heterogeneous,

numerous studies have been focused on the interaction of several heavy metals with different soil constituents. Thus, an accurate description of the complex interactions of heavy metals in soils is a prerequisite to predict their behavior in the contaminated soils and to build up a good strategy of soil remediation for such heavy metals. To predict the fate of heavy metals and minimize their hazardous in soils, one must account for understanding the mechanism of these pollutant reactions under Egyptian conditions. Such information is critical since heavy metals are used in a variety of industrial and manufacturing processes and are the most common contaminants found at hazardous waste sites (Reed *et al.,* 1996; Strawn *et al.,* 1998). Moreover, downward heavy metal migration is another way to contaminate ground water, especially after sludge applications where soluble metals are easy to leach down (Campbell and Beckett, 1988; Abou Seeda, 1997; Abou Seeda *et al.,* a, b and c 1997).

Heavy metals in soils can be involved in a series of complex chemical and biological interactions including oxidation-reduction, precipitation and dissolution, volatilization, and solution phase complexation. In addition, many soil chemical processes are time-dependent. To fully understand the dynamic interactions of heavy metals and their bioavailability and to predict their fate with time, and the final remediation technique in soils, knowledge of the kinetics of these reactions is important.

Fractionation technique is a fairly widely used for understanding the mechanisms of distribution and relatively available forms of metals in soils. Zaghloul and Abou Seeda (2003) studied lead (Pb) distribution in three Egyptian soils to understand Pb reactions as affected by their chemical characteristics and to predict the bioavailability of Pb in these soils. However, metals added as salts did not undergo the same

processes as those metals that were present in the sewage entering the treatment plant. For this reason the studies exists with simple metal salts is controversial, since there is no certainty that the added metals will be present in the same forms as those metals already present in the sludge. This is important because there is evidence that metals added to soils as metal salts may differ in their bioavailability from those added in non-spiked sewage sludge (Davis and Carlton-Smith, 1981; Coppola *et al.,* 1988; Abou Seeda, 1997).

In an attempt to overcome this problem, the primary objectives of this study are to:

I-Investigate the environmental risks of sewage sludge compost applied to the studied soil

II-Display distribution of heavy metals in different fractions of sewage sludge amended soils.

III-Demonstrate the most effective fraction that influences the uptake of heavy metals by corn plant.

IV-Evaluate the agrochemical efficiency of cement dust treated sewage sludge on the mobility and bioavailability of heavy metals in the soil through the kinetic studies.

MATERIALS AND METHODS:

I-Materials:

1- Soil:

Field trial was conducted on a sandy soil at El-Gabal Al-Asfar site, the investigated soil characterized by pH 7.34, EC 0.37 dsm^{-1}, organic matter content 2.79%, CEC 9.90 Cmol$^{(+)}$/kg soil and CaCO$_3$ of 0.45%. The particle size distribution of the studied soil is as follows, sand 89.59%, Silt 7.51% and clay 2.89%.

2-Sewage Sludge treatment:

The sewage sludge used in this study was prepared for application to field plots in an experiment designed to examine the effects of cement dust material (SiO_2 17.5%, Fe_2O_3 0.07%, Al_2O_3 5.24%, CaO 54.47%, MgO 0.50%, SO_3 3.46%, Cl 1.66% and L.O.I 11.95) on minimizing lead (Pb), cadmium (Cd), nickel (Ni) and chromium (Cr) release from the studied sludge. The chemical composition of the studied material is reported by Abou Seeda *et al.* (1997).

3-Plantation:

Corn plant (*Zea maize* L.) was chosen as an indicator plant to study the relationship between the studied heavy metal (Pb, Cd, Ni and Cr) distribution and its uptake by plant and to evaluate the cement dust in minimizing the mobility and availability of metals.

II-Treatments:

The experiment was carried out in a randomized complete block design with the following treatments:

T1: Sludge 10 m^3.fed^{-1}

T2: Sludge 20 m^3.fed^{-1}

T3: Sludge 10 m^3. fed^{-1}+ 2.5% cement dust.

T4: Sludge 20 m^3.fed^{-1} + 2.5% cement dust.

T5: Sludge 10 m^3.fed^{-1}+ 5.0% cement dust.

T6: Sludge 20 m^3. fed^{-1} + 5.0% cement dust.

1-Replication and Quality Assurance:

All analyses were carried out in duplicate and the mean values of the replications are reported in this paper.

2-Kinetic study:

Release experiments were carried out using Electrical Stirred Flow Unit (ESFU) method for all soil samples and for different incubation times i.e. 2, 8 and 16 weeks. A Diagram of ESFU

used in this paper, the modification of the new set up and the mechanism of the kinetic work were previously mentioned in details (Zaghloul, 2002). Exactly 20g of the sewage sludge treated soil were put in the kinetic part of the device with 100 ml of 0.1 N DTPA solutions. The system was vigorously shaken and the solution samples were received after different periods ranged between 1 min to 10080 min. at 25°C $\pm 2°$ C and analyzed for their concentrations of Pb, Cd, Ni and Cr using the atomic absorption (Cottenie *et. al.* 1982). The heavy metal release data were fitted, using the regression analysis to four kinetic equations reported by Sparks, (1989), (1995) and (1998). These equations were proved to be the best fitted ones under Egyptian conditions for both nutritional and non-nutritional elements (Zaghloul, 2001; Zaghloul and Abou-Seeda, 2003).

The linear forms of these equations are as follows:

● **Modified Freundlich equation (MFE)**

$$Log\ q = log\ b^{\backslash} + k_d\ log\ t$$

● **The Elovich equation in the form:**

$$q_t = 1/\beta\ ln\ \alpha\beta + 1/\beta\ ln\ t$$

● **The apparent first-order equation**

$$Log\ (1-k_t/k\varphi) =-k\ t$$

● **The parabolic diffusion model was also used to determine if transport was level limiting:**

$$q_t = b+ R\ t^{0.5}$$

Where:

q = the amount of the metal desorption in time t

k_d = desorption level coefficient in mg kg^{-1}soil min^{-1}

$b^{\backslash}$ = intensity constant in mg of pollutant kg^{-1}soil

α = constant related to the initial level of heavy metals release in mg.kg^{-1} min^{-1}

β = constant in (mg/kg)$^{-1}$soil

b = intensity constant in mg kg $^{-1}$soil

R = the apparent diffusion level coefficient in mg kg^{-1}soil min^{-1}

k_t = the maximum amount of metal release mg kg^{-1}soil

k_φ = the level constant of the reaction in sec^{-1}

The kinetic parameters in the four tested equations namely $k_{d,}$ b$^{\backslash}$ of modified Freundlich, α and β of Elovich, R of the parabolic diffusion and k of the first-order equations were calculated for the studied soils under different treatments. The regression analysis to test the conformity of metal release to the applied models and testing for significant differences in rate coefficients and cumulative quantity of heavy metals desorbed was done using the SAS software (SAS Institute, 1985).

3-Sequential extraction of investigated heavy metals:

Fractionation of heavy metals was carried out according to the method described by Tessier *et al.* (1979). One gram of each soil is weighted into 40 ml polycarbonate centrifuge tube and the following fraction obtained:

A-Water-soluble: Soil sample extracted with 15ml of deionized water for 2h.

B-Exchangeable: The residue from water-soluble fraction is extracted with 8 ml of 1M MgCl$_2$ (pH7.0) for 1h.

C-Carbonate-bound: The residue from exchangeable fraction is extracted with 8 ml of 1 M NaOAC (adjusted to pH 5.0 with HOAc) for 5h.

D-Fe-Mn Oxides-bound: The residue from carbonate fraction is extracted with 0.04M NH$_2$OH.HCL in 25% (v/v) HOAC at 96°C with occasional agitation for 6h.

E-Organic bound: The residue from Fe-Mn oxide fraction is extracted with 3 ml of 0.02M HNO$_3$ and 5ml of 30% H$_2$O$_2$ (adjusted to pH 2

with HNO$_3$). The mixture is heated to 85°C for 2h, with occasional agitation. A second 3-ml aliquot of 30% H$_2$O$_2$ (pH 2 with HNO$_3$) is added and the mixture heated again to 85°C for 3h with intermittent agitation. After cooling, 5 ml of 3.2M NH$_4$OAC in 20% (v/v) HNO$_3$ is added and the samples are diluted to 20 ml with deionized water and agitated continuously for 30 min.

F-Residual: The residues from organic fraction are digested using a HF-HCl/HNO$_3$.

After each successive extraction, centrifugation occurred for 30 min to get the supernatant. The supernatants were removed with a pipette, filtered and analyzed for the metal using the atomic absorption. The residue was washed with 8ml deionized water followed by vigorous hand-shaking, and then followed by 30 min of centrifugation before the next extraction.

4-Remediation index (RI):

In this study, the heavy metal remediation of the studied soil sample is judged by using a Remediation Coefficient (RC). This coefficient is represented is judged by the equation:

$$RI = [(WSF + EF) / R_f] \times 100$$

Where:

RC: remediation coefficient

WSF: water soluble fraction

EF: exchangeable fraction

R_f: residual fraction.

The lower value of the RC, the more successful is remediation material applied to minimize the hazardous of the studied pollutant(s).

RESULTS:

1-Effect of sludge and cement dust on heavy metal release from treated soils :

Figure (1) represents the effect of sewage sludge (*SS*) applied to the studied soil in two levels (10 and 20 m^3.fed^{-1}.) and treated with cement dust (*CD*) on the extractable amounts of Pb, Cd, Ni and Cr of the studied soil.

Generally, the data showed that the amounts of heavy metals desorbed from sewage sludge (*SS*) treated soil (T1 and T2) and *SS*-cement dust (*SS-CD*) treated soil (T3, T4, T5, and T6), take the following order:

<div align="center">

Pb > Cd > Cr > Ni

</div>

The high added level of sewage sludge (20 m^3/fed) showed more accumulation of all heavy metals in the soil than low one (10 m^3/fed). Moreover, the application of cement dust (*CD*), showed a significant decrease in Pb, Cd, Ni and Cr released compared with high level SS amended soil. In addition, in *CD* treated soil, the obtained results indicate that increasing the level of *CD* from 2.5 to 5% in SS treated soil led to an increase in the amount of Pb, Ni and Cr desorbed. Nevertheless, this trend was not observed in pollutant release regardless the level of SS applied.

The interaction between *CD* and the studied heavy metals detected a considerable variation according to the studied pollutant. Data of Pb released from the amended soil showed that all treatments with *CD* reduced Pb release compared with high level of SS applied to the soil; the higher decreasing order was observed in T3 (10 m^3 SS+2.5% *CD*). Increasing *CD* to 5% does not affect Pb extractability from the studied soil. However, no significant difference was found between the low level of SS and

different treatments of sewage sludge treated with cement dust (SS-*CD*). Concerning Cd and Ni release, data showed that no significant difference was observed among T4, T5 and T6 and again T3 gave the lower decrease in Cd extractability.

For chromium release from treated soil (Figure 1), data recorded a significant variation between T3 and T4 (sludge 10 and 20 m^3/f treated with 2.5% *CD* respectively) and T5, T6 (soil treated with sludge 10 and 20 m3/f treated with 5% *CD*). However, all showed a significant decrease as compared with the high level of SS-*CD* treated soil.

In the same figure represents an important trend related with enhancement of *CD* in increasing some metals release from SS-*CD* treated soil over the low added level of SS. Results of Pb show a significant increase in the amount of Pb desorbed from T4, T5 and T6 compared with T1 (Sludge, 10 m^3/fed). This significant difference is also observed in Cr desorption with respect to the native amounts of Pb and Cr in different treatments applied.

In some cases, data showed that T3 (SS, 10m^3/fed +2.5% *CD*) gave higher trend in decreasing Pb, Cd and Cr release compared with T5 (SS, 10 m^3/fed + 5% *CD*). In other words, increasing the level of *CD* from 2.5 to 5% does not affect reducing the three above named heavy metals. The same trend was also observed between T4 and T6. According to standard division analysis, data revealed that it is preferable to apply 2.5% *CD* with applying 10 or 20 m^3 SS (T3 and T4) to minimize Pb, Cd, Ni and Cr release from contaminated soils.
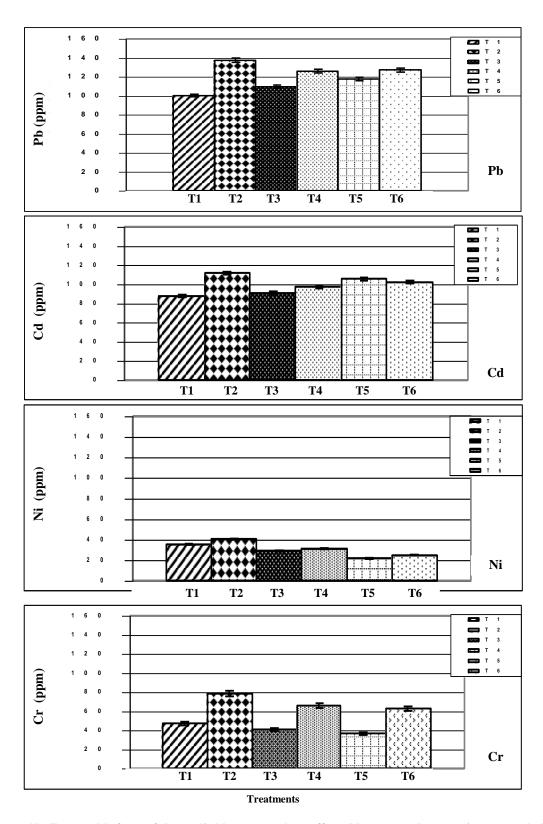
Figure (1): Extractable form of the studied heavy metals as affected by cement dust treating swage sludge

2-Fractionation of heavy metals in the studied soil as affected by different treatments:

Distribution of heavy metals through six fractions in SS and SS-*CD* treated soil samples is presented in Figs (2 and 3). In all soil treated with SS and amended with Cement Dust (*CD*), the increase in the residual is over the non-residual fraction (sum of all fractions except residual); all metals were presented in all fractions. In addition, most of Pb, Cd, Ni and Cr are concentrated in a residual fraction (F fraction), followed by organically bound fraction (E-fraction). However, the most retained metals were equally distributed between Fe-Mn and carbonate and then a small amounts of metals were showed to be as water soluble and exchangeable fractions (A and B fractions). Moreover, different metals did not show regular behavior in their distribution in different fractions, but according to different treatments applied in this study.

From sequential extraction, results of Pb distribution among six fractions indicate that residual fraction increased by about 20% compared with the control (20 m^3/fed SS). Using 10 m^3 SS that amended with 2.5% *CD* (T3) showed average increases of 8, 14 and 7% for T4, T5 and T6, respectively. The effect of different treatments were more pronounced in the organically bound fraction; Figure (2) showed that the concentration of Pb in the organically pound fraction decreased about 44% with adding 2.5% *CD* to the soil that treated with 10 m^3 SS. The increase was to 45.5% for T4 treatment; the respective increases were about 49.5 and 52% with increasing the level of CD (T5 and T6).

Concerning the Fe-Mn fraction, data showed that a high decrease was detected for T6

(about 54%), followed for T5 and T4. However, T3 (SS 10 m^3/F+2.5% *CD*) gave an equal value to T4~35% compared with control treatment (T2). Worth to mention that the same trend was also observed in the carbonate fraction (C faction).

Cadmium was mostly concentrated in the residual fraction with adding 5% *CD* to the soil treated with 10 and 20 m^3 SS/fed. (T5 and T6), although it was also present in other fractions (Fig. 2). The percentages of total Cd in the residual fraction increased about 18 and 11% over the control treatment (T2) for T5 and T6, respectively. All fractions showed decreases as compared to control treatments, for example, the decrease percentages of organically bound fraction (E-fraction) ranged between 18-32%, 24-34% for the Fe-Mn fraction and 36-52% for the carbonate fraction. The highest decrease was detected for SS treated soil and amended with 5% *CD*. The decrease percentage of water soluble and exchangeable fractions was very small but observed for the same treatment.

Like Pb and Cd, the residual fraction was the most important fraction in Ni distribution (Fig. 3). In all treatments applied, the residual fraction ranged between 55 to 68% for different treatments. The highest value was observed for T6 (SS 20 m^3+5% *CD*), followed for T5, T4 and T3, respectively. The organically bound Ni decreased when CD was applied at a level of 5% (T5 and T6) to the treated soil by about 45 and 41%, respectively. The same trend was also observed in Fe-Mn and carbonate fractions. Although Ni was found in all fractions, the lowest values was observed for the soil treated with 20 m^3 SS and 5% *CD* (T6). Both water soluble and exchangeable fractions, however, gave unclear trend for different *CD* treatments compared with control (zero *CD*).
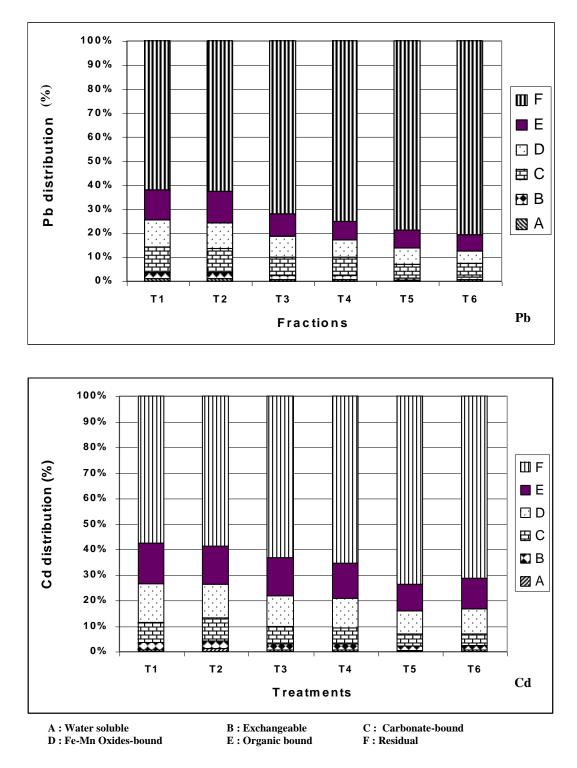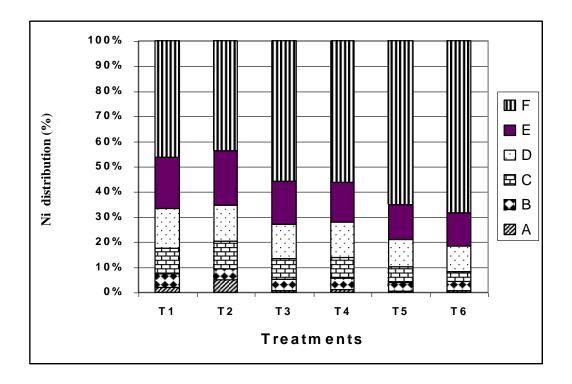
A : Water soluble   B : Exchangeable   C : Carbonate-bound
D : Fe-Mn Oxides-bound   E : Organic bound   F : Residual

Figure (2): Lead (Pb) and cadmium (Cd) fractionation as affected by different treatments.

A : Water soluble   B : Exchangeable   C : Carbonate-bound
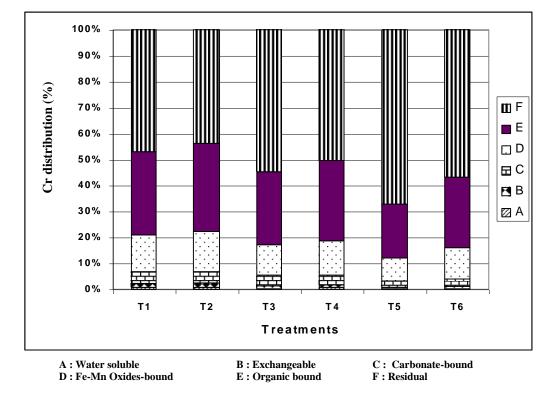D : Fe-Mn Oxides-bound   E : Organic bound   F : Residual

Figure (3): Nickel (Ni) and chromium (Cr) fractionation as affected by different treatments

Chromium distribution is present in Fig. (3), that showed that more than 47% of the total Cr was associated with the residual fraction for control treatment (T2). This value increased to about 54 and 50 % with adding 2.5 % *CD* to SS amended soil (T3 and T4). Increasing *CD* to 5% led to increase Cr in the residual fraction to 67% and 57% for T5 and T6, respectively. In contrast, data indicate that all other fractions were decreased compared with control treatment; for example, the organically bound fraction was decreased by about 52% for T3 and decreased to about 57% for T5.

The highest decrease was observed in the carbonate fraction (64%) for 10 m^3 SS treated soil and amended with 5% *CD* (T5). Again, no obvious trend was observed in water soluble and exchangeable fractions for different treatments.

In this study, remediation index (RI) was used as an indicator parameter and test technique for succession of remediation material applied to minimize the hazardous of heavy metals applied to SS treated soil. The decrease in RI value for different treatments applied represents an indication of the succession of remediation material applied.

Table (1): Effect of different applied treatments on RI of some studied heavy metals

Treatments	RI (%)			
	Pb	Cd	Ni	Cr
T1	5.60	6.17	15.5	4.73
T2	5.90	7.21	21.4	5.74
T3	3.10	4.49	9.46	2.69
T4	2.97	4.68	10.1	3.23
T5	1.71	2.87	5.92	1.19
T6	2.04	3.19	6.1	1.91

Table (1), gives the effect of *CD* applied to different treatments on RI of some studied heavy metals. Data showed that all *CD* treatments decreased the availability of heavy metals compared with the control treatment. The obtained results revealed that T5 (10 m^3/f SS+2.5%*CD*) was the best treatment in reducing Pb availability under low application of SS. However, under high application, data indicated that there is little tendency for high applied level of *CD* over the low one (2.5 %), whereas, the decrease in RI was only 2.04 for 5% *CD* treatment compared to 2.97 for 5% *CD* treatment.

Like Pb, all *CD* treatments decreased Cd availability in the treated soil. Moreover, T5 was the best treatment in decreasing Cd

availability in the soil treated with *CD* compared to other treatments even in high application of *CD* (5%). Also, the application of 5% *CD* gave higher decrease values for 20 m^3 SS treatment compared to low level of *CD* applied on the high level of the SS treated soil.

The remediation index (RI) of Ni gave the highest values compared to other heavy metals studied. It ranged between 21.4 and 5.92. The lowest value was also observed for both T5 and T6 using both high and low application of SS to the soil. Although the RI of Cr gave the lowest values compared to other heavy metals, data showed that T5 and T6 were the best treatments that could be applied to minimize heavy metals availability in soils treated with 10 and 20 m^3 SS.

3- Kinetic study:

All used equations showed high significance in describing the release of the studied heavy metals from different treatments applied. The modified Freundlich equation was the best fitted equation whereas it gaves the highest coefficient of determination (R^2) and the lowest standard error (SE); it was followed by Elovich equation and then parabolic diffusion and first-order equations. This result again emphasized the reliability of empirical equations over theoretical ones in describing the kinetics of soil chemical process (Zaghloul and Abou-Seeda, 2003).

In this study, the conformity of kinetic data was evaluated to the applied equation by meaning of Z(t) equation. Aharoni and Ungarish, (1976) suggested a generized empirical equation by examining the applicability of power function, Elovich, and first-order equations to experimental data. Writing these as the explicit functions of the reciprocal of the level, Z, which is $(dq/dt)^{-1}$, one can show that a plot of Z vs. t should be convex if the power-function equation is operational, linear if the Elovich equation is appropriate and concave if the first order equation is appropriate. However, Z vs. t for the soil system is usually S-shaped convex at small t, concave at large t and linear at some intermediate t. (Aharoni and Ungarish, 1976)

Figure (4) showed that all three shapes are present in the release of the studied heavy metals. For example, the power function equation represented by convex shape in the release of Ni, concave shape in the release of Pb, Ni and Cr and a straight line represented in dividing the entire reaction time into two periods for different heavy metals studied especially for Pb and Cd. However, for Cr, the results showed that Z vs. t plots for the applied treatments gave S-shaped, convex at small t, concave at large t, and linear at some intermediate t.

These findings suggested that the reaction rate can be the best described by the power function equation, Elovich and first order equations. The conformity of the kinetic data to diffusion models is expected in same cases when slow reactions at the soil particle/liquid take place.

Results in Table (2) represent the rate constant of the used equations, the slope of data plotted according to used equation(s), to describe the effect of applied treatments on heavy metals availability in the soil with and without application of cement dust (*CD*) as a remediation treatment. For the modified Freundlich equation, results indicate that rate of Pb release decreased from 6.5 mg kg^{-1} min^{-1} to 4.6 and 4.7 mg kg^{-1} min^{-1} with adding 10 *SS* and 2.5 % *CD* to T3 and T4, respectively; the decrease was also observed by adding 5% *CD* (T5 and T6). The priority of applying 2.5% *CD* instead of 5% was also observed in other studied heavy metals.

The β constant representing the bioavailability of the studied heavy metals, showed that application of 2.5% *CD* led to a decrease in the heavy metal bioavailability for T3 and T4. Application 2.5% *CD* led to a decrease in Ni release from 6.2 (mg/kg)$^{-1}$ to 4.6 and 4.8 (mg/kg)$^{-1}$ for T3 and T4, respectively. Although T5 and T6 were also decreased to 3.5 and 3.7 (mg/kg)$^{-1}$ by applied 5% *CD*, the decrease of Ni was not related to the high level of *CD* applied.
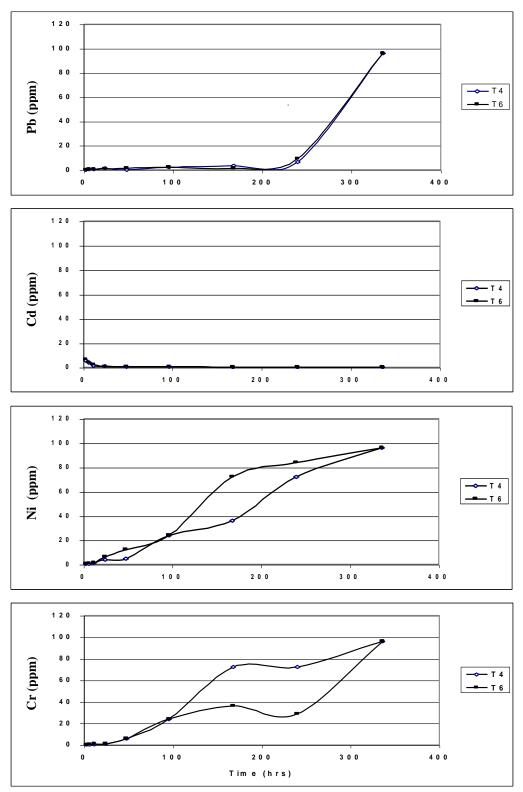
Figure (4):Level of heavy metal release from T4 and T6, the best treatments for remediation, is best represented by Z(T) equation.

Table (2): A comparison of the rate constants of the kinetic models used to describe heavy metal release from some applied treatments

Treat.	The first order				MFE*				Elovich				Diffusion			
	Pb	Cd	Ni	Cr	Pb	Cd	Ni	Cr	Pb	Cd	Ni	Cr	Pb	Cd	Ni	Cr
T1	7.7	5.9	4.6	6.2	5.8	4.8	3.9	4.3	17.7	14.9	5.6	7.8	5.47	4.7	1.7	2.2
T2	8.9	6.1	6.7	8.7	6.5	7.1	6.6	5.9	23.3	16.3	6.2	10.9	7.42	4.8	1.8	2.9
T3	5.7	5.6	5.2	6.3	4.6	4.4	4.1	4.6	19.0	15.3	4.6	6.9	5.93	4.7	1.3	1.9
T4	6.5	5.8	5.3	6.5	4.7	3.9	3.5	2.9	17.5	15.6	4.8	9..3	5.01	4.8	1.4	2.5
T5	7.6	6.4	4.9	6.1	4.8	3.3	4.4	5.2	20.3	16.2	3.5	6.4	6.41	4.8	1.0	1.8
T6	7.8	6.4	4.8	6.3	4.4	3.7	3.6	3.3	21.6	16.4	3.7	9.3	6.83	4.9	1.1	2.5

* Modified Freundlich Equation

Although the first order and diffusion equations proved to be suitable for describing the kinetic data and the rate constants of these equations (k and R), did not gave a specific trend for some studied heavy metals. In Cd release study, data showed that application of 10 and 20 m^3/fed SS did not influence the rate of release described by the diffusion equation (T1 and T2). Applying 2.5% to these treated soils (T3 and T4), no change was observed in the R constant, the rate of release. Moreover, increasing the application level of CD did not affect the rate of Cd release from SS treated soil.

Comparing the studied heavy metals the best fitted equation (MFE), showed that although the available form of the studied heavy metals was Pb > Cd >Ni > Cr, the rate of release of heavy metals took the order Pb>Cd >Cr > Ni.

In both SS and SS+*CD* treated soils, the same trend was also observed in other used equations. In some cases, however, this trend was varied especially in Cd.

Also in *CD* treated soils, data showed that the decrease in the rate of heavy metal (s) release was more influenced by the type of heavy metals studied over the rate of Cd applied. In the first order equation data showed that although the available Ni was higher than available form of Cr, results indicated that *CD* minimized the rate of Ni release more than Cr.

4-Correlation analysis :

a-Relationship between K_d of modified Freundlich equation and fractions of heavy metals for different treatments:

There is a closed relationship between heavy metal release from both SS treated soils or SS treated soils amended with *CD* and their forms found in the soil. In this study, correlation analysis was conducted between k_d, the constant of MFE, and the six forms of different heavy metals studied to represent the source(s) of bulk of heavy metals release in treated soils and subsequently the mode of action of *CD* in remediation of these heavy metals.

Table (3): Correlation analysis between k_d constant of Modified Freundlich Equation (MFE) and the fraction forms of the studied heavy metals.

Fractions	Pb	Cd	Ni	Cr
A	79[**]	0.96[**]	0.90[**]	0.89**
B	97[**]	0.95[**]	0.37[ns]	0.87**
C	93[**]	0.98[**]	0.74**	0.02 [ns]
D	96[**]	0.90[**]	0.43 [ns]	-0.09 [ns]
E	97[**]	0.97[**]	0.80**	-0.13 [ns]
F	-0.35[ns]	-0.34[ns]	-0.39 [ns]	-0.33 [ns]

Data in Table (3) showed that a high correlation was observed between rate of Pb release and all fractions except the residual fraction (F fraction), the high correlation was observed for the exchangeable and organically bound fractions. Although the same trend was observed in Cd release from different treatments of having high correlation coefficient, data showed that the highest value was observed for carbonate fraction.

The soluble water, carbonate and organically bound fraction were the most factions that had significant correlation with k_d. Results showed that the rate of Ni release had high correlation coefficient with these fractions reached to 0.90**, 0.74** and 0.80**, respectively. However, just soluble water and exchangeable fraction were significant correlated with Cr release from the SS and SS-CD treated soils. Finally, the Fe-Mn and carbonate fractions were almost the fractions that did not correlate with all studied heavy metals.

b-Effect of sewage sludge and cement dust on heavy metals uptake by corn:

Figure (5) represents the effect of both soil treated with sewage sludge SS (T1 and T2) and soil-sewage sludge system amended with cement dust (*CD*) on the heavy metal uptake by corn (*Zea maize* L.). Data indicated that increasing SS applied to soil from 10 to 20 m^3/fed, led to significant increase in the uptake of studied heavy metals by corn. The higher uptake was observed for Pb followed by Ni, Cd and Cr. Data showed that increasing the application level from 10 to 20 m^3/fed SS led to an increase of Pb uptake from 143 to 223 mg/plant; the respective values were 95 and 189 mg/plant for Ni; 55 and 78 mg/plant for Cd and 97 and 147 mg/plant for Cr, respectively.

The cement dust (*CD*) treatment generally led to a significant decrease in the uptake of heavy metals by plant regardless the type of metal or the level of *CD* applied on the SS treated soil. Results indicate that addition of 2.5% *CD* led to decreasing the amount of Pb release to 130 and 143 mg/plant for low and high level of SS applied respectively. The respective values were 115 and 140; 41.5 and 62.0 as well as 95 and 105 for Ni, Cd and Cr, respectively. Increasing the application level of *CD*, all treatments gave the same trend without significance differences between high and low level of *CD* applied for *SS* treated soil.

c- Correlation between the uptake of the studied heavy metals and rate constants of used equations

The kinetics of heavy metal desorption for the studied treated soils were fitted to different desorption models and the kinetic parameters of those models were calculated and correlated with plant heavy metal-uptake by Corn plant (*Zea maize* L.).

Table (4) indicated that β constant of Elovich equation had highly significant relationships with the uptake of all studied heavy metals by corn plant; the highest r value was observed for Pb followed by Ni, Cd and Cr. The k_d of the power function equation showed also a significant relationship with Pb and Ni uptake with having lower values of r compared with the β constant of Elovich equation. Regarding the theoretical equations represented by the first order and parabolic diffusion equations, only Ni and Cr uptake showed a high significance with k constant of the first order equation and a low significance with Cd and Cr for the parabolic one.
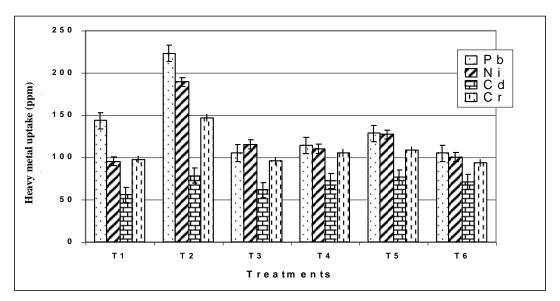
Figure (5): Effect of different applied treatments on heavy metals uptake by Corn plants

Table (4): Correlation analysis between rate constant of used equations describing heavy metal release and its uptake by corn plants grown on the different treated soils.

Kinetic model	Pb	Cd	Ni	Cr
The first order	0.54*	0.36 ns	0.96**	0.94**
MFE*	0.89**	0.03 ns	0.84**	0.62*
Elovich	0.98**	0.88**	0.90**	0.82**
Diffu. Equ	0.41 ns	0.64*	0.45 ns	0.62*

* Modified Freundlich Equation.

DISCUSSION:

All types of remediation can be classified in one or two categories: (1) decontamination or (2) isolation and/or containment. The in situ immobilization of the heavy metals in some insoluble form. The use of alkaline-stabilized biosolids as organic fertilizers or soil conditioners has become widespread in Egypt especially in land reclamation such as sandy soil (more than 95% of total area). Cement dust (*CD*) is an inorganic by-product or waste material from precipitators in cement factories (Burnham *et al.*, 1992; Wong *et al.*, 1997). This material consist of SiO_2 17.5%, Fe_2O_3 0.07%, Al_2O_3 5.24%, CaO 54.47%, MgO 0.50%, SO_3 3.46%, Cl 1.66% and L.O.I 11.95. The presence of calcium oxide and aluminum oxide in the *CD*

composition creates some kind of high adsorption sites for metals found in soils. Moreover, application of this by-product material may lead to increase the pH of the treated soils and subsequently decreasing the bioavailability of heavy metals in soils.

The obtained results indicated that using of *SS* as an organic amendment for sandy soils led to an increase in the availability of Pb, Cd, Ni and Cr. This increasing was related to the level of *SS* applied to the soil. The application of *CD* to this amended soil led to a decrease in the availability of these pollutants by far 10-20%, 30-40%, 25-30% and 35-40% from the total available Pb, Cd, Ni and Cr, respectively compared with control treatments (high application level of *SS* treatment). However, the

remediation treatment of *CD* was completely varied with the type of metals released in soil system. This result may be due to the formation of metal-oxides that vary in their solubility products and may be key controls on the mobility of these metals in natural environment. (Logan *et al.,* 1997).

The fractionation study of heavy metal distribution in both *SS*-contaminated and *CD* treated soils may explain the variation of remediation effects of the alkaline-stabilized materials on these studied metals. For Pb, although *CD* minimizing all fractions, the main effect of this material was observed in the organically bound-Pb and (Fe-Mn)-Pb fractions and subsequently increasing the residual one. However, for Cd, the effect of *CD* was on the carbonate-Pb fraction over the other studied fractions. The same observation was detected for Ni in decreasing the carbonate fractions. However, cement dust was also worked on organically bound and residual fractions. The residual fraction was the most effected for one on Cr. The kinetic study of heavy metal release agree with this trend in minimizing heavy metals by the *CD* material. The solubility products of metal oxides take the order:

$$Cr > Ni > Pb > Cd$$

Cement dust (*CD*) reduced the uptake of heavy metals by corn plant. That may be due to the adsorption capacity of *CD* (Peter Christie, *et al.,* 2001). The uptake of heavy metals decreased due *CD* application in the order of Pb > Ni > Cr > Cd. This result may explain the specific effect of *CD* in heavy metals remediation of soils. Moreover, in *CD* treated soil, the relative increase of pH in soil system may the second reason of minimizing heavy metals uptake by plant. However, the second point of increasing soil pH by *CD* application may be an important point should be take into consideration in application of such materials under Egyptian conditions.

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دور استخدام تراب الأسمنت فى المعالجة الكيميائية
للأراضى المعاملة بمخلفات الصرف الصحى

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تعتبر الدراسـات التى تجرى لمعالجـة العناصـر الثقيلـة الضـارة فى الأرضى المعاملـة بمخلفـات المجـارى مـن أهم الموضوعات التى تطبق فى الدراسات البيئية لتلافى الأضرار الناتجة من هذه الملوثات ، ولذلك أجريت دراسات معملية وأخرى حقلية بمزرعة الجبل الأصفر بالقاهرة تم فيها إضافة المخلفات الصلبة للصرف الصحى بمستويات ١٠ ، ٢٠ م٣ للفدان حيث عوملت بتراب الأسمنت بمعدلات ٢.٥، ٥% لمعرفة هذه المادة على خفض محتوى الأراضى من الكميات المتاحـة مــن كـل مــن الرصــاص، الكـادميوم، النيكــل والكـروم. وقـد تــم الاسـتعانة بالدراسـات الكينيتيكيــة Kinetic Studies إذ تعتبر الوسيلة التى يتم بها تقييم هذا الانخفاض من الكميات المتاحة من هذه العناصر. أيضاً تم إجراء تجربـة حقليـة تـم فيهـا الاستعانة بنبـات الـذرة الشـامية كدليل علـى تـأثير مخلفـات الصرف الصحى الصلبة المعاملـة بتراب الأسمنت فى خفض الأضرار الناتجة من إضافة هذه المخلفات .

وأوضحت النتائج المتحصل عليها ما يلى : –

– أن إضافة مخلفات الصرف الصحى الصلبة أدى إلى زيادة تراكم العناصر الثقيلة خاصة عند إضافة المستوى العالى من هذه المخلفات بالمقارنة بالمستوى المنخفض.

– أدى إضافة تراب الأسمنت إلى انخفاض مستوى العناصر الثقيلة للمستخلصات فى الكميات المتاحة من العناصر الثقيلة واتضح هذا الانخفاض من خلال نقص الثوابت الكينيتيكية للمعدلات المستخدمة فى الدراسة (فرندليش المعدلـة ، الوفيتش، الانتشار، الدرجة الأولى ومعادلة $Z(t)$.

– اتضح من خلال توزيع العناصر فى الأراضى المعاملة وكذلك ثابت المعالجة أن تأثير تراب الأسمنت أدى إلى تحول معظم المتاح من هذه العناصر إلى الصورة المتبقية الغير ذائبة وقد نوقش التأثير المعالج للمـادة المستخدمة خلال هذه الدراسة.