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Heavy Metals Immobilization in Sewage Sludge Using Some Amendments

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THE ENHANCEMENT of sewage sludge to decrease its toxic effects on living organisms due to the high content of heavy metals (Cd, Cr, Ni and Pb) was studied using some organic and inorganic materials. Four materials (Silica gel, Cement Bypass, Rock phosphate and Charcoal activated carbon) were mixed with the sewage sludge in three rates (5, 15 and 25%) and the mixture of each two materials at a rate of 15% of each. Results indicated that DTPA extractable Cd, Ni and Pb decreased from 0.895, 12.097 and 26.02 ppm in the control to 0.376, 3.13 and 9.06 ppm, respectively (58, 74 and 65% reduction , respectively, compared with the control) with 25% of rock phosphate application. The lowest extracted Cr was obtained by the application of 25% silica gel with a reduction of 67% compared with the control. The maximum reduction in extracted Cd, Cr and Pb resulted by the mixture of charcoal + silica gel (0.33 ppm Cd), rock phosphate + silica gel and cement By-pass + silica gel (0.04 ppm Cr) and rock phosphate + cement By-pass (9.98 ppm Pb), respectively. While, the mixture of silica gel with any other amendment under study always retained 100% of the extracted Ni.

Keywords: Silica gel, Cement Bypass, Rock phosphate and charcoal activated carbon, Stabilization, Sewage sludge

The growing population of Egypt demand growing production of food which makes the governorate encourage people to reclaim and use desert areas which are in great need for organic fertilizers. The most commonly heavy metals found in biosolid are Pb, Ni, Cd, Cr, Cu and Zn (Mattigod and Page, 1983). Clay, zeolite, minerals, phosphates, cement, organic compost, microbes (Fin Zgar *et al.,* 2006) and red mud (Lombi *et al.,* 2002) are mostly applied as amendments. Udeigwe *et al.* (2011) concluded that the immobilization mechanisms of contaminant could include: 1) Preciptaton as salts, 2) Co-precipitation 3) Surface precipitation 4) adsorption to mineral surfaces (ion exchange and formation of stable complexes). The dissolved organic carbon forms complexes with a large portion of Cd n soils containing large amounts of organic matter (Sauve *et al.*, 2000). A linear relationship was obtained by Hyun *et al.* (1998) between organic carbon and soluble Cd in solution forming metal-organic complex in sludge-treated soils. Chen *et al.* (2010) and Hua *et al.* (2009) reported a high adsorption capacity for heavy metals on bamboo charcoal due to its large negatively charged surface area and the high surface density of functional groups and metal oxides. They also concluded that Bamboo charcoal has five times greater porosity and ten times higher adsorption efficiency than that of wood charcoal. Studying the enhancement of heavy metals stabilization in sewage sludge, Chiang *et al.* (2007) reported that the increasing applied coal fly ash to sewage sludge (from 0 to 20%) decreased DTPA-Pb in sludge from 40 to 21%. While an insignificant decrease in DTPA-Cu, Zn and Ni were found with the same application. The surface of silica gel consists of inter connected particles forming a three dimensional skeleton. Silica gel has high surface area (Jiang *et al.*, 2007), porosity and rigid structure (Repo *et al.*, 2011), it is also characterized by highly porous texture (Fenglian and Wang, 2011).

Amin (2013) reported that the constituents of cement By-pass collected from Assiut cement company were 11.88% SiO_2, 2.97 % Al_2O_3, 2.60% Fe_2O_3, 47.8% CaO, 0.68% MgO, 12.13% SO_3, 2.28 Na_2O, 4.38% K_2O and 4.81% Cl. The total available Pb, Cd, and Ni were decreased by 10-20, 30-40 and 25-30%, respectively, with the application of cement dust to amended soil (Abou-Seeda *et al.*, 2005). Treating sludge with cement kiln dust reduced the solubility and increased the immobilization of heavy metals in the treated sludge matrix (Emmerich *et al.*, 1982). Kigel *et al.* (1994) showed that the application of cement kiln dust stabilized chromium in waste sludge. A reduction in Cu and Zn mobility andimmobilization of Pb were reported Ownby *et al.* (2005) when using phosphorus containing materials. Both ionic exchange and precipitation of poorly soluble products are the main reasons of Pb mobility reduction when Pb-impacted soil receives phosphste amendments (Scheckel *et al.*, 2005). Bolan *et al.* (2003) explained the induced immobilization of Cd by phosphate application by: 1) the adsorption of Cd^{2+} on phosphate 2) the precipitation of $Cd(OH)_2$ and $Cd_3(PO_4)_2$. They also reported that Cd^{2+} adsorption on phosphate were due to several mechanisms such as: 1) increasing of pH, 2) increasing of serface charge, 3) Co-adsorption of phosphate and Cd as an ion pair, and 4) surface complexes formation of Cd on the phosphate compounds. According to Naidu *et al.* (1996), the net negative charge of variable charge surfaces increases when a specific adsorption of anions occurs which increases the retention of metal cations such as Cd^{2+}, Cu^{2+} and Zn^{2+} (Boland *et al.*, 1999). McGowen *et al.* (2001) reported that high levels of diammonium phosphate (2300 mg kg^{-1}) application to a smelter-contaminated soil resulted in immobilizing Cd, Pb and Zn.

This study aims to evaluate the effect of some soil amendments (silica gel, rock phosphate, cement By-pass and Charcoal activated carbon on the in situ stabilization of certain heavy metals (Cd, Cr, Ni and Pb) in sewage sludge.

Material and Methods

Most of wastewater treatment plants in Egypt pumps wastewater into gravity thickeners leaving the remained sewage sludge to be naturally dewatered and air dried. Sewage sludge was collected from Elmadabigh Sewage Plant, Assiut, air dried and left in the Soil Laboratory for Analysis and Technical Consultations, Assiut University, Egypt. In order to minimize heavy metals availability from sewage sludge, four materials were used: Silica gel (100-200 Mesh), Cement Bypass (CB), Rock phosphate (RP) and Charcoal activated powder (AC). Three rates of each material (5, 15 and 25% w w^{-1} sewage sludge) and a mixture of 15% of each two compound were mixed thoroughly with the sludge and each treatment was replicated three times. Cement By-pass is an industrial byproduct produced from cement industry (Assiut Cement Company) in huge amounts (about 150 ton day^{-1}). This byproduct is a very fine powdered containing significant level of CaO, iron, silicon, aluminum oxides and some other oxides in small amounts (Zn, Cu, Mn and some heavy metals).

Sewage sludge was mixed with the different materials under study. Water was added to the samples when needed every day for three weeks to maintain the moisture content stable in the mixture. Sludge was found to contain 52.3% organic matter, 6% nitrogen, 1.9% P_2O_5, 0.72% K_2O, 11.9%CaO and 5.8% MgO. The total content of studied heavy metals in sludge was 3.1, 249, 0.9 ppm and 58.7 for Cd, Pb, Cr and Ni. Samples were left in the lab to dry for another week then extracted using 0.1M Diethylene Triamine Penta Acetic Acid (DTPA) according to Lindsay and Norvell (1978). Cadmium, Ni, Cr and Pb were determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICAP 6200). For statistical analysis results were conducted in a simple experiment and the treatments were arranged in a complete randomized block design with three replicates. The MSTATC 2.10 computer program written by Freed (1992) was used to perform analysis of variance. The obtained data were subjected to statistical analysis of variance according to Gomez and Gomez (1984), the means of treatments were tested using the least significant difference method (LSD) at P= 0.05.

Results and Discussion

Effects of different amendment types and rates on DTPA extractable heavy metals:

The application of silica gel always increased the extractable Cd, Ni and Pb significantly with a gradual decrease in extracted metals with increasing silica gel rates (Fig. 1). Kosmulski (2000) reported that silica shows a significant solubility exceeding 1mmol dm^{-3} in acidic and neutral aqueous solutions and that the dissolved silica species in solution can be comparable with or higher than the concentration of active surface sites at a sufficiently low solid- to- liquid ratio. Due to silica solubility in basic pH values, the same researcher concluded that heavy metals adsorption on silica may be affected by 1) the silica species in solution that can compete with the surface sites for heavy metal cations 2) The silica species can interact with adsorbed metal cations to build phases of springly soluble metal silicates. While, extracted Cr reached its lowest value with a reduction by 67% compared with the control. To explain the effect of silica on Cr adsorption, Kosmulski (2000) reported that sorption of some heavy metal cations on silica is significantly depressed when the concentration of alkaline-earth metal cations is comparable with the concentration of surface hydroxyl groups but sorption of some other heavy metal cations remains unaffected.

Cement By-pass (CB) application at any rate resulted in significant reduction in DTPA extractable Pb, Ni and Cr. The highest reduction occurred with the application of 15% CB which resulted in decreasing DTPA extractable Pb, Ni and Cr by 44, 47 and 56%, respectively, compared with the control. Applying 100-2000 mg L^{-1} of cement kiln dust to solutions containing 100-800 mg L^{-1} of Zn^{2+}, Al^{3+}, Co^{2+} and Cd^{2+} removed 95% of the metals with a gradual decrease in removed ions with increasing concentrations above 800 mg L^{-1} (Waly *et al.,* 2010). While Cd increased gradually with the application of CB to reach 96 % higher than the control with the application of 25% CB. The application of 2% cement By-pass to El-Gabal El-Asfar contaminated soil increased the exchangeable form of Zn, Cu, Pb and Cd to reach 634, 74, 14 and 77%, respectively, compared with the control, while a decrease in soluble Zn by 77.3%, compared with the control, was observed (Amin, 2013).

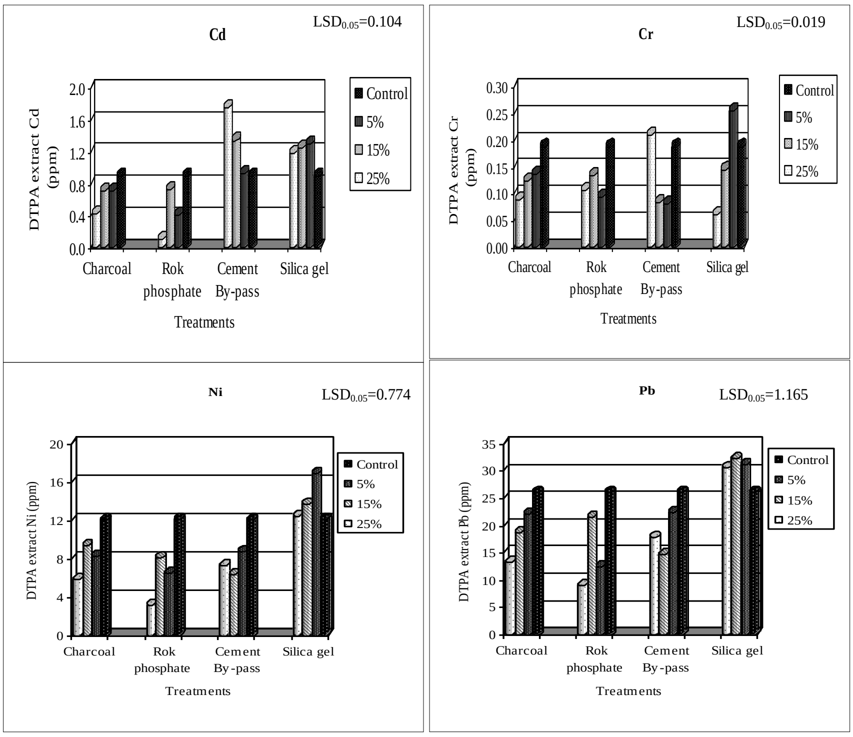

Fig. 1. Effect of charcoal active carbon (AC), cement By-pass (CB), silica gel (SI) and rock phosphate (RP) application on DTPA extractable Cd, Cr, Ni and Pb (ppm).

All rock phosphate treatments (RP) significantly decreased all extracted metals under investigation. The decrease in extracted Cd, Cr, Ni and Pb were 54, 50, 47 and 52% with 5% RP, 18, 29, 33 and 17 with 15%RP and 58, 43, 74 and 65% with 25%RP application, respectively, compared with the control. These numbers shows that the amounts of stabilized metals were higher with the application of 5 and 25% RP compared with 15%RP. The explanation of this behavior according to Sen *et al.* (2002) who found a physical effect between the individual particles having a high solid-to-solution ration which lead to coagulate and flocculate into larger particles with less available surface for adsorption. This explanation is correct when the applied RP increased from 5 to 15% leading to decrease the retention of metals on RP particles. On the other hand, increasing the applied RP up to 25% resulted in increasing the total surface area (compared with 5 and 15% RP application) wither in large particles or in small ones leading to increase all the reaction processes that stabilize metals. The main mechanisms in immobilizing metals such as Pb and Zn by phosphate compounds are precipitation as metal phosphate (Pierzynski and Schwab, 1993) and surface complexation of metals by hydroxyapatite (Xu *et al.,* 1994).

Charcoal activated carbon (AC) application gradually and significantly decreased almost all discussed elements having the maximum effect with the application of 25% AC with a decrease of 52, 52, 51 and 49% for Cd, Cr, Ni and Pb, respectively, compared with the control. Active carbon (black carbon and charcoal) is used as adsorbent materials for filtration and water treatment for its high surface area (Day and Vlassopoulos, 2010).

Combined effect of different amendment types on DTPA extractable heavy metals

Figure 2 shows a comparison between the DTPA extractable metals in the untreated sludge samples and after application of each treatment alone in a ratio of 15% and the mixture of each two treatments in a ratio of 15% of each. Generally, mixing any two amendments together with the sludge resulted in significant reduction in DTPA extractable metals. The maximum reduction in extracted Cd, Cr and Pb were found when silica gel was mixed with AC (0.33 ppm Cd), CB (0.04 ppm Cr) and RP (9.98 and 0.04 ppm Pb and Cr, respectively). Contaminants may be physically bound in nano-to microscale inclusions or chemically bound as sorbed or precipitated nanoparticles within another resistant medium in a mechanism called "Microencapsulation", silica and cement-based amendments provide an example of Microencapsulation that reduces contaminant partitioning into pore water (Day and Vlassopoulos, 2010). Dissolved toxic divelent cations, such as Pb^{2+} in contaminated soils can be immobilized using phosphate due to the precipitation of pure or substituted phosphate phase of the apatite group (Miretzky and Fernandez-Cirelli, 2008). The formation of secondary metal phosphate precipitates resulted in the decrease in the solubility of a range of metals in the presence of hydroxyapatite (Seaman *et al.,* 2001).

On the other hand, mixing silica gel with any of the other amendments under discussion always resulted in 100% reduction of extracted Ni. Charlet and Manceau (1994) suggested formation of clay minerals upon sorption of Co and Ni on silica; this phenomenon is accompanied by a slow change from a tetrahedral to an octahedral co-ordination. Also, Hayes and Leckie (1987) reported that heavy metal cations form inner sphere complexes with the surface of silica, while alkaline earth metal cations form outer sphere complexes.

The effect of silica gel on heavy metals stabilization that appears when mixing it with other substances needs further attention and studies for explanation.

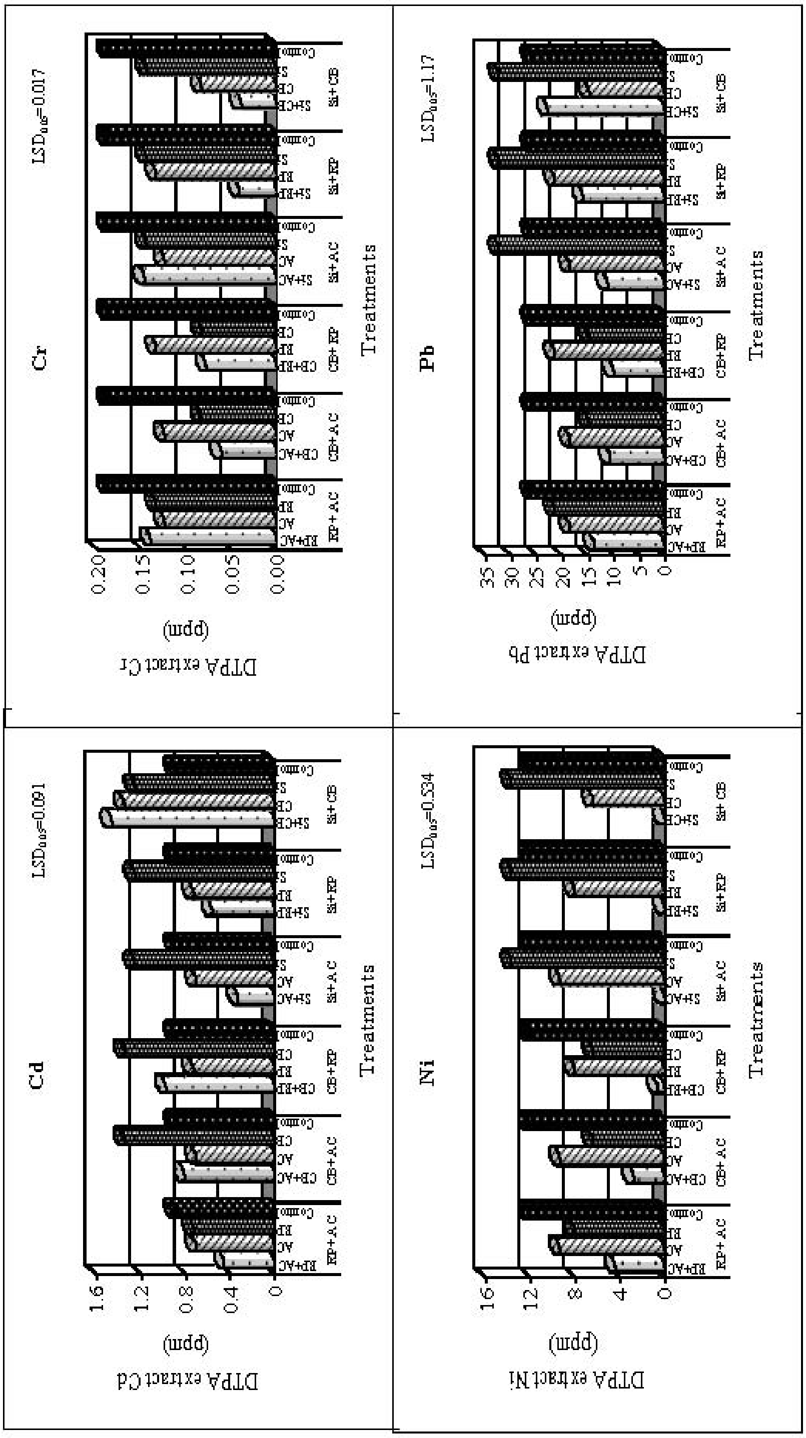

Fig 2. Effect of mixed charcoal active carbon (AC), cement By-pass (CB), silica gel (Si) and rock phosphate (RP) application on DTPA extractable Cd, Cr, Ni and Pb (ppm).

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تثبيت العناصر الثقيلة في مخلفات المجارى الصلبة (الحمأه) باستخدام بعض محسنات التربة

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هذا البحث يناقش خفض محتوى مخلفات المجارى الصلبة (الحمأه) من العناصر الثقيلة الميسرة (نيكل – رصاص – كادميوم – كروم) لتقليل تأثيرها السام على الكائنات الحية فى التربة باستخدام بعض المحسنات العضوية والغير عضويه. تم خلط أربع مركبات بالحمأه وهى السليكا جيل – مخلفات صناعة الاسمنت (cement By-pass) – صخر الفوسفات – الكربون النشط فى ثلاث معدلات وهى 5 – 15 – 25% بالإضافة إلى معاملات أخرى عبارة عن خلط كل نوعين من المحسنات معا بنسبة 15% لكل محسن ثم خلطهم مع الحمأه.

أظهرت النتائج انخفاض الكميه المستخلصة من الكادميوم – النيكل – الرصاص من 0.895 – 12.097- 26.02 جزء في المليون في الكنترول الى 0.376 – 3.13 – 9.06 جزء في المليون على التوالي بما يوازى 58 – 74 – 65% انخفاض بالمقارنة بالكنترول وذلك عند إضافة 25% صخر فوسفات والذي يعتبر أفضل معامله في التجربة. بينما كانت ادني كميه من الكروم المستخلص عند معاملة الحمأه بـ 25% سليكا جيل بانخفاض يعادل 67% مقارنة بالكنترول. اكبر انخفاض فى الكميات المستخلصة من الكادميوم – الكروم – الرصاص ظهرت عند خلط الكربون النشط + السليكا (0.33 جزء فى المليون كادميوم) – صخر الفوسفات + السليكا جيل – مخلفات الاسمنت + السليكا جيل (0.04 جزء في المليون كروم) – مخلفات الاسمنت + صخر الفوسفات (9.98 جزء فى المليون رصاص) على التوالي. بينما أدى خلط السليكا جيل مع أي محسن أخر إلى انخفاض النيكل المستخلص بنسبة 100%.