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In-Situ Remediation of Heavy Metals in Sewage Sludge Using Some Pesticides and Inorganic Amendments

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THE AIM of this study was to investigate the effect of some pesticides (Methomyl, Deltamethrin and Chlorpyrifos), zeolite, silica gel and ferric oxide on the immobilization of some heavy metals (Cd, Ni, Cr and Pb) in sewage sludge. The results indicated that the application of 3 g of Deltamethrin $100g^{-1}$ sludge decreased the DTPA- extractable content of Cd, Ni, Cr and Pb by 25, 21, 46 and 16%, respectively. Adding 1.5 ml Chlorpyrifos$100g^{-1}$ sludge caused significant increase in extractable Cd, Ni and Pb by 39, 38 and 16%, respectively, compared with the control treatment.

Application of 15% (w w^{-1}) zeolite to the sludge resulted in the maximum decrease in both extractable Cd (from 0.90 ppm in the control to 0.33 ppm) and Pb (from 26.7 ppm in the control treatment to13.4 ppm). Application of 25% silica gel decreased DTPA extractable Cr from 0.19 ppm in the untreated sludge to 0.05 ppm by 74%. Application of a mixture of silica gel with zeolite or with ferric oxide completely retained all the extractable Ni.

Keywords: Sewage sludge, Zeolite, Pesticides, Ferric oxide, Silica gel.

The main cause of high concentrations of cadmium, selenium, arsenic and mercury in cultivated soils were due to the long term usage of pesticides and chemical fertilizers which were absorbed and accumulated into clay minerals as a result of ion exchange processes (Yargholi and Azarneshan, 2014). On the other hand, Bansal (2014) found that there was almost no effect of pesticides application on heavy metals content in the vegetative parts of any of the studied vegetables. Gomah and Ezzeldin (2003) reported an increase in DTPA extractable Cd, Ni, Cr, Pb, Cu and Zn with the application of any of the tested pesticides (Mancozeb, Copper hydroxide, Carbofuran, Chlorpyrifos and Aldicarb).

Zeolite is one of the class minerals known as "tectosilicates" which naturally occur as hydrated aluminosilicate minerals (Erdem *et al.,* 2004), three-dimensional tetrahedral frame works of SiO_4 and AlO_4 (Villasenor *et al.,* 2011). The ion exchange capacities resulting from the replacement of Al^{3+} instead of Si^{4+} in tetrahedral sheets are the reason of the adsorption properties of zeolites (Bailey *et al.,* 1999). Zorpas *et al.* (2000) reported that zeolite can improve the biodegradability and the composting process of the organic matter by increasing the porosity of the substrate and can also take almost all bounded metal to the exchangeable and carbonate fractions. Villansenor *et al.* (2011) found that 100% of Ni, Cr and Pb were retained when applying zeolite to the sludge. The addition of 25% w w^{-1} zeolite in compost removed 12, 27, 14, 30, 40, 55 and 60% of Co, Cu, Cr, Fe, Zn, Pb and Ni, respectively (Zorpas *et al.*, 2002). They also indicated that increasing the particle size of clinoptilolite resulted in increasing the metals concentration taken up by it. Stylianou *et al.* (2008) concluded that ion exchange and adsorption processes are the main mechanisms of zeolite for trapping metals which caused a decrease by 94.1, 59.5, 82.2 and 69 % of Zn, Cu, Cr and Ni, respectively. The use of small particles of zeolite gave the high rates of ion exchange process (Helfferich, 1995). Zorpas *et al.* (2002) reported that parts of the pore openings in zeolite structures are clogged by surface dust leading to slower ion exchange kinetics for smaller particles than for larger ones. Grinding process causes structure damage in smaller particles which may result in the same effect for smaller particles (Malliou *et al.*, 1992).

The nanoparticles of iron oxide magnetite have a unique superparamagnetism and high surface area (Yuan *et al.*, 2009) which offers more multiple sites for adsorption or interaction (Paljevac *et al.*, 2007) that makes it an innovative immobilization carrier (Sulek *et al.*, 2010). Xu *et al.* (2012) concluded that iron oxide magnetite nanoparticles can be considered as immobilization carriers. Sen *et al.* (2002) found that the higher adsorption of Ni^{2+} on iron oxides compared with Cu^{2+} adsorption is due to the relatively smaller size of Ni^{2+} ions and that iron oxide is a better adsorbent compared with kaolin due to the specific adsorption that occurs on iron oxide which is due to both chemical and electrostatic forces of attraction that gives higher amount of adsorption.

Silica gel is known for its large specific surface area and fast adsorption kinetics (Jiang *et al.*, 2007), it is also characterized by highly porous texture (Waseem *et al.*, 2011). The surface of silica gel consists of inter connected particles forming a three dimensional skeleton. Repo *et al.* (2011) reported that silica gel has high surface area, porosity and rigid structure.

The main objective of this study is to conclude either a recommendation or restriction for using specific pesticide or specific dose for treating sludge or contaminated soils with heavy metals due to its side effect on the stability of heavy metals. Also, to evaluate the effect of iron oxide, zeolite and silica gel on the immobilization of heavy metals.

Materials and Methods

A laboratory experiment was conducted in the Soil Laboratory for Analysis and Technical Consultations, Assiut University, Egypt in order to minimize heavy metals availability from sewage sludge by using three pesticides (mostly used for controlling a wide range of insects), zeolite, silica gel and ferric oxide. Three rates of the pesticides were used, the recommended dose, twice and triple the recommended dose. The first pesticide used was Methomyl 90% S.P., dissolving 1.5, 3 and 4.5 g in 1 liter of distilled water and 150 ml of each concentration were applied to 100 g sewage sludge. The second pesticide was Deltamethrin 25% E.C. (1.5, 3 and 4.5 ml were diluted in 150 ml of distilled water and each concentration was applied to 100 g sewage sludge). The third pesticide was Chlorpyrifos 48% E.C., diluting 0.75, 1.5 and 2.25 ml in 150 ml of distilled water and each concentration was applied to 100 g sewage sludge. Zeolite (clinoptilolite 1-3 mm), silica gel (100- 200 Mesh) and ferric oxide red (Fe_2O_3) were used in three rates (5, 15 and 25% w w^{-1} sewage sludge). Each treatment was replicated three times. A mixture of each two compounds of Zeolite, silica gel and ferric oxide were prepared by applying 15% of each compound to the sludge.

Sewage sludge samples were taken from Elmadabigh Sewage Plant, Assiut, which only separates the solid colloidal in huge sieve plates and leave it to dry in the open air without any treatment. The tested sludge contained 51.7 % organic matter, 6% N, 1.7% P_2O_5, 0.6%, 0.63% K_2O, 11.2% CaO and 6 % MgO. The total content of discussed heavy metals in sludge was 3.1, 249, 0.9 and 58.7 for Cd, Pb, Cr and Ni. Hundred grams of sewage sludge were mixed thoroughly with each treatment then 80 ml of distilled water were added to each treatment and mixed again. Samples were weighted every day to add the amount of water lost due to the vibration, mixed again and lift in the lab. After three weeks, samples were air dried for another week and then they were extracted using 0.1M Diethylene Triamin 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). The work was 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 the analysis of variance. The obtained data were subjected to statistical analysis of variance according to Gomez and Gomez (1984), means of treatments were tested using the least significant difference method (LSD) at P= 0.05

Results and Discussion

Effect of pesticides application on extractable heavy metals in sludge

All pesticide treatments decreased the amounts of DTPA extractable Cd, Ni, Pb at all rates, compared with the control treatment, except for chlorpyrifos at the rate of 1.5 ml $100g^{-1}$ sludge (twice the recommended dose) which increased the extractable Cd, Ni and Pb by 39, 38 and 16%, respectively (Fig. 1). Such increase may be due to heavy metals content in the used pesticide or due to the formation of new complexes that may occur in an extractable form.

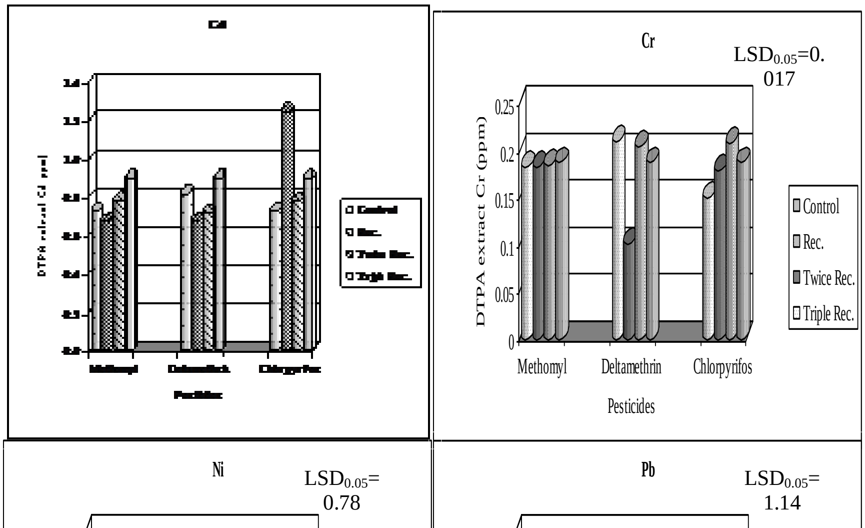


Fig .1. Effect of pesticides application on DTPA extraclable Cd, Cr, Ni and Pb (ppm).

Gomah *et al.* (2003) reported that the total content of heavy metals were 0.30, 0.19, 3.99 and 1.71 ppm in methomyl pesticide, 0.32, 9.00, 9.36 and 4.22 ppm in deltamethrin pesticide and 0.08, 2.05, 2.05 and 3.99 ppm in chlorpyrifos pesticide. The application of methomyl pesticide at a rate of 3 g $100g^{-1}$ sludge (twice the recommended dose) had highly significant effects on decreasing the availability of Cd, Ni and Pb by 25, 23 and 12%, respectively, while there was almost no effect on Cr content. The same effects were found with the application of 3 ml deltamethrin pesticide$100g^{-1}$ sludge (twice the recommended dose) with a decrease of DTPA extractable Cd, Ni, Cr and Pb by 25, 21, 46 and 16%, respectively. The lowest DTPA extractable elements were obtained with the application of 3ml deltamethrin$100g^{-1}$ sludge for both Cd (0.68 ppm) and Cr (0.10 ppm), 3 g methomyl $100g^{-1}$ sludge for both Cd (0.68 ppm) and Ni (9.9 ppm) and 1.5 ml deltamethrin $100g^{-1}$ sludge for Pb (22.0 ppm). The decrease of heavy metals mobility and availability may be due to the formation of insoluble organic compounds with the pesticide itself of its degrade. Wang *et al.* (2005) reported that the content of organic complex- bounded heavy metal in compost or sewage sludge, speciation and chemical composition could affect metals mobility in the compost or sewage sludge.

Effect of ferric oxide, zeolite or silica gel application on extractable heavy metals in sludge

A highly significant decrease in all extracted heavy metals occurred with increasing the rate of Fe_2O_3 application (Fig. 2). Comparing between iron oxide treatments, the application of 25% iron oxide had the most significant effect on decreasing extracted Cd and Ni by 42 and 34%, respectively. While, Cr was almost the same (32%) with the application of 15 or 25% iron oxide. On the other hand, the application of 15% Fe_2O_3 had the highest effect on extracted Pb with a decrease of 25% compared with the control. This decrease may be due to a strong bound initiated between heavy metals and ferric oxide. Sen *et al.* (2002) used preliminary kinetic experiments to explain the adsorption of Ni^{2+} and Cu^{2+} metal ions on iron oxide and reported that the adsorption is a two- step process: an adsorption on the external surface which is a rapid adsorption of metal ions followed by slow intraparticle diffusion in the interior parts of the particles.

The application of 15% zeolite to the sludge was the most effective treatment and resulted in the lowest values for both Cd (from 0.90 ppm in the control to 0.33 ppm) and Pb (from 26.7 ppm in the control to13.4 ppm) among all other tested amendments (mixed or unmixed), the decrease in DTPA extractable Cd, Cr, Ni and Pb were 64, 53, 58 and 50%. Sprynskyy *et al.* (2007) reported a decrease in the mobile forms of Cd, Cr, Cu and Ni by 87, 64, 35 and 24%, respectively, with the addition of 9.09% clinoptilolite to sewage sludge. They clarified that the immobilization was due to their bound into the pseudo residual fraction in a firmly sorbed forms. On the other hand, the application of 5 or 25% zeolite either had no significant effect or significantly increased the extractable heavy metals under discussion. Sen *et al.* (2002) explained the increase of extractable Ni^{2+} and Cu^{2+} with increasing iron oxide amendment content by:1) the particle- particle interactions which occur in systems with higher solids content due to the physically blocking of some adsorption sites, 2) an electrostatic interference may occur between the surface of individual grains and the adsorbing solutes, 3) 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.

As shown in Fig. 2, silica gel generally increased the content of extractable heavy metals under study. The only significantly reducing effect of silica gel application was with the application of 25% silica gel which decreased DTPA extractable Cr from 0.19 ppm in the control to 0.05 ppm with a ratio of 74% which is the lowest value of extracted Cr in all treatments. While in almost all other cases, silica gel increased the amount of extractable metals significantly. Kosmulski (2000) reported that silica is a weak adsorbent of heavy metal cations compared with metal oxides and that in natural system, uptake of heavy metal cations by iron or manganese oxides is often more significant than adsorption on silica even when the latter is much more abundant.

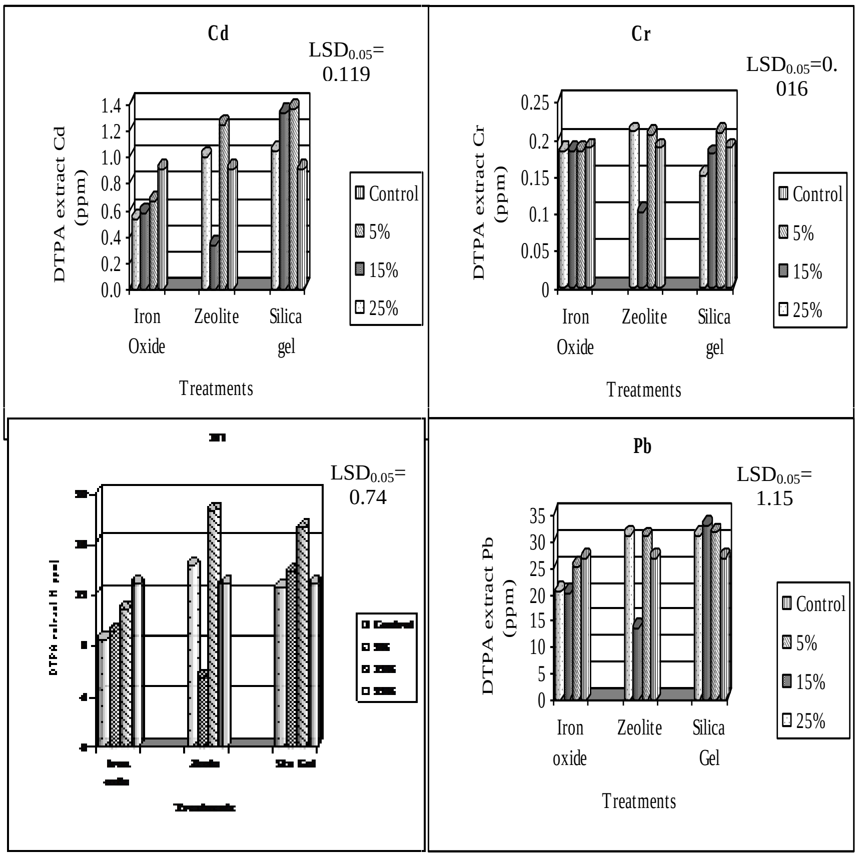
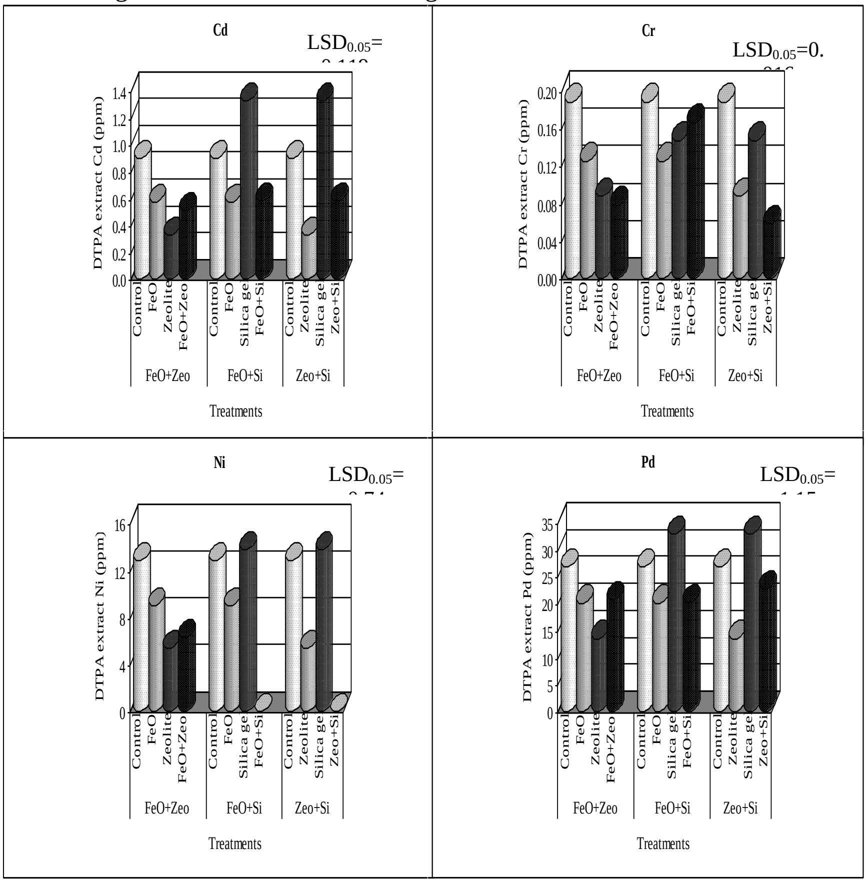


Fig. 2. Effect of Iron oxide, Zeolite and silica gel application on DTPA extractable Cd, Cr, Ni and Pb (ppm)

As shown in Fig. 2, silica gel generally increased the content of extractable heavy metals under study. The only significantly reducing effect of silica gel application was with the application of 25% silica gel which decreased DTPA extractable Cr from 0.19 ppm in the control to 0.05 ppm with a ratio of 74% which is the lowest value of extracted Cr in all treatments. While in almost all other cases, silica gel increased the amount of extractable metals significantly. Kosmulski (2000) reported that silica is a weak adsorbent of heavy metal cations compared with metal oxides and that in natural system, uptake of heavy metal cations by iron or manganese oxides is often more significant than adsorption on silica even when the latter is much more abundant.

Effect of mixed amendments on extractable heavy metals in sludge

Mixing each two amendments together in a ratio of 15% of each and



applying the mixture to the sludge always resulted in a decrease in the extractable amount of all discussed elements compared with the control (Fig. 3). Mixing silica gel with any of the two other amendments decreased 100% of the extracted Ni. Using 15% zeolite alone was more effective in reducing most of the extractable metals except of Ni which decreased by 100% when zeolite was mixed with silica gel. This effect of silica gel when mixed with some amendments should get more attention and investigation. Generally, the mixture of any two amendments with a ratio of 15% each always resulted in a decrease in the extractable amount of all discussed elements. Sen *et al.* (2002) explained the different types of binding sites on the adsorption particles by two- stage metal uptake: 1) interparticle diffusion that occurs in kaolin through the space between latic layers, 2) an interaparticle diffusion occurs in iron oxide in the micropores of the particles.

Fig 3. Effect of Mixing Iron oxide, Zeolite and silica gel application on DTPA extractable Cd, Cr, Ni and Pb (ppm)

Conclusion

Some pesticides may be used as heavy metals stabilizers while other pesticides should be forbidden at some rates to use such as chlorpyrifos at the rate of 1.5 g $100g^{-1}$ sludge (twice the recommended dose). The application of 15% zeolite to the sludge may be considered as the best treatment for Cd and Pb stabilization in sludge among all other treatments. The decrease in DTPA extractable content of Cd, Cr, Ni and Pb with the application of 15% zeolite were 64, 53, 58 and 50%, respectively, compared with the control. The application of 25% silica gel decreased DTPA extractable Cr to the lowest value in all treatments (74% reduction). Mixing silica gel with any other amendment completely retained the extracted Ni. Generally, the mixture of amendments with a ratio of 15% each always resulted in a decrease in the extractable amount of all discussed elements.

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معالجة مخلفات الصرف الصحي الصلبة (الحمأه) من العناصر الثقيلة في الموقع باستخدام بعض المبيدات و المحسنات غير العضوية

هاله حسنين جمعه
قسم الأراضى والمياه – كلية الزراعة جامعة اسيوط- اسيوط – مصر .

الهدف من هذه الدراسة هو التحقيق فى تأثير بعض المبيدات (الميثوميل – دلتامثرين – كلوربيريفوز)، الزيوليت، سليكا جيل، أكسيد الحديد على تثبيت بعض العناصر الثقيلة (كادميوم – كروم – نيكل – رصاص) في الحمأ.

أظهرت النتائج أن إضافة 3 جم من مبيد دلتامثرين/100جم حمأه أدى إلى نقص الكميه المستخلصه من الكادميوم – النيكل - الكروم – الرصاص بمقدار 25 – 21 – 46 – 16٪ على التوالي مقارنة بالكنترول. بينما أظهرت النتائج ان استخدام 1.5جم كلوربيريفوز/100جم حمأه أدى إلى زيادة معنوية في الكميه المستخلصة من الكادميوم، النيكل، الرصاص بمقدار 39 و38 و16٪ على التوالي.

أدت إضافة 15٪ زيوليت للحمأه إلى أقصى انخفاض فى كل من الكادميوم المستخلص (من 0.9 جزء في المليون في الكنترول إلى 0.33 جزء فى المليون) و الرصاص المستخلص (من 26.7 جزء في المليون في الكنترول إلى 13.4 جزء فى المليون) وكان الانخفاض في الكادميوم – الكروم – النيكل-الرصاص المستخلص بنسبة 64 – 53 – 68 – 50 على التوالي مقارنه بالكنترول. أدت إضافة السليكا جيل بنسبة 25٪ إلى انخفاض الكروم المستخلص بنسبة 74٪. أدى خلط السليكا جيل مع إي من المركبات الأخرى إلى انخفاض النيكل المستخلص بنسبة 100٪ عند خلط السليكا جيل مع إي من المركبات الأخرى.