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Assessment the phytoextraction efficacy of phosphate minerals and their granulometry on metal immobilization in contaminated urban soil

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Abstract The efficiencies of different grain sizes (< 63 , $63-93$, $93-106$ and $106-125 \mu\text{m}$) of mined rock phosphate (RP), in addition to the vital role of different phosphate sources ($< 63 \mu\text{m}$ rock phosphate, processed and biogenic) as an effective remedial technology (based on solubility, percentage of metal/metalloid impurities and availability of impurity metal/metalloids) were assessed in contaminated urban soil. The results demonstrate that the application of RP substrate with smaller grain size (< 63) was significantly more effective than larger grain size for Cu, Co, Cd and Pb immobilization. Depending on phosphate solubility, the reduction of metals availability were highest in biogenic and processed phosphates than mined rock phosphate, while the lower dissolution of rock phosphate may be advantageous for long term maintenance.

environmentally friendly remediation technologies has generally become one of the key research activities in environmental science and technology. In selecting the most appropriate soil remediation methods for a particular polluted site, it is of paramount importance to consider the characteristics of the soil and the contaminants to consider the characteristics of the soil and the contaminants. (Leštan et al., 2007).

Stabilization involves fixing up the contaminants in stable sites by mixing or injecting inorganic or organic soil amending agents (e.g., liming agents, organic materials, aluminosilicates, phosphates, iron and manganese oxides, coal fly ashes, etc.). Due to the effects of a change in pH, such agents are effective at decreasing the bioavailability of metals by introducing additional binding sites for toxic metals. Stabilized metals then become less available for plants, and their bioconcentration through the food chain is reduced (Guo et al., 2006). However, the toxic metals remain in the soil and can be harmful when soil dust is ingested or inhaled. Many of the amendments used in soil stabilization are by-products of industrial activities, and are therefore inexpensive and available in large amounts. Overviews on previously successfully applied amending agents and their effectiveness for different metals have been given by Knox et al. (2001) and Puschenreiter et al. (2005). In the last few years, significant research has focused on this topic. Several soil additives have been tested: eight substrates (calcium carbonate, bentonite, kaolinite, charcoal, manganese oxide, iron oxide, zeolite, phosphate) to reduce metal availability and to study the change of metals speciation in different forms (Fawzy, 2008), zeolites (Rebedea and Lepp, 1994; Chlopecka and Adriano, 1996b; Boisson, et al., 1999), beringite (Vangronsveld et al., 1991, 1995a,b, 1996; Mench et al., 1994a), and steel shots (Mench et al., 1994b; Sappin-Didier et al., 1997). Ma et al. (1993); Laperche et al. (1996) showed that the application of synthetic hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) led to immobilization of dissolved Pb in contaminated soils. In aqueous solutions HA led to an immobilization of Al, Cd, Cu, Fe (II), Ni and Zn as well (Suzuki et al., 1981; Takeuchi and Arai, 1990; Middelburg and Comans, 1991; Ma et al., 1994b; Xu et al., 1994). HA seems therefore a promising soil additive for immobilizing metals in polluted soils.

Many studies have been conducted to understand the mechanism of this immobilization (Suzuki et al., 1981; 1993, 1994a, 1994b; Xu et al., 1994; Laperche et al., 1996). However, a chemical and physical evaluation of the efficiency of HA application as a remediation technique is not sufficient. Biological evaluation methods are necessary to assure that immobilization results in lower soil to plant transfer and phytotoxicity. Moreover, these methods can give indications about possible adverse effects (toxicity, deficiency of other elements) of HA application. Chlopecka and Adriano (1996a,b) showed that the addition of apatite (0.4% by weight) to a Zn, Cd and Pb polluted soil led to an increasing yield and lowered

the Zn, Cd and Pb content in three week-old maize plants (*Zea Mays*), in mature maize tissues (roots, young leaves, old leaves, stems, grains) and in barley (*Hordeum vulgare*). The addition of HA (0.6%, 1.16%, 1.74%, and 2.32% by weight) to Pb polluted soils led to a strong decrease of the Pb concentrations in shoots of sudax (*Sorghum bicolor* L. Moench) while the Pb concentrations in the roots decreased only at low application rates of HA.

Rock phosphates (RP) are natural inexpensive sources of phosphorus but their solubilization rarely occurs in non-acidic soils. However, microbially mediated processes involving chelation and exchange reactions are able to solubilize inorganic P forms (Rodríguez et al., 1999)

The main objectives of this study were:

- (1) To evaluate the effectiveness of grain size fractions of rock phosphate in decreasing heavy metals (Pb, Cd, Co and Cu) mobility,
- (2) Quantifying of Purity of Different Phosphate Sources,
- (3) Comparing of suitability of different Phosphate sources for remediation of contaminated soil by determine the total metals concentration in different phosphate sources, the tendency of these trace impurities to leach, and the apparent amendments for stabilizing contaminants.

Experimental

Quality Assurance

During sampling and laboratory analysis of heavy metal contaminated soils, care should be devoted to prevent sample contamination and to ensure the reliability and quality of analytical results. First of all, the use of metallic tools should be avoided whenever possible. Soil samples should be collected using tools made of stainless steel and stored in nonmetallic containers, such as glass bottles or polyethylene bags. For all analysis the standard samples were run during and end of the measurements to ensure continued accuracy.

For analytical precision the samples were run in triplicates. The blank were run all the time. All chemicals used were of analytical grade. Concentrated acids were provided by BDH Chemicals Ltd. (Poole, UK), while salts were provided by Sigma (Missouri, USA). All glassware's were cleaned in 10% HNO_3 (w/v) prior each experiment.

Samples Collection

Surface soils (0–30 cm in depth) were collected from an urban area (ca 20 samples), in Aswan city, in southeastern Egypt. The soils are enriched with heavy metals, including Pb, Cd, Co and Cu; due to the population densities are high.

We also studied three types of phosphate: mined, processed, and biogenic. Mined phosphate referred to as rock phosphate (31%), Processed rock phosphate fertilizers were in granular form (125 μm) and

the biological phosphate (*Tilapia nilotica*). Lake Nasser, Egypt (i.e., ground fish bones, 125 μ m).

Analysis of Soil Chemical Properties

The soil samples were air-dried and then ground to pass through a 2-mm sieve prior to use. Soil pH (soil: water; 1:2.5) using a pH-meter (Orion Research, Model SA520, U.S.A.). Electrical conductivity was measured in the sample suspension obtained in the pH determination using conductivity meter (HANNA Instruments, HI 8033 Italy). Calcium carbonate and organic matter contents were determined by back-titrating an excess of 0.5M HCl added to 1 g of the sample (Nelson, 1986), and wet oxidation (Nelson and Sommers, 1982), respectively. Particle size analysis was carried out using the Particle size distribution (percent sand, silt, and clay) was determined by the micro-pipette method. The physicochemical properties of the studied soil are listed in Table (1).

Phosphate Analysis

Mined rock phosphate (RP) was sieved through < 63, 90-63, 106-90, 125-106 μ m, respectively. Each phosphate source (rock phosphate, processed, and biogenic) was analyzed for pH (in 1:1 mineral/water equilibration solution), solubility, total metal content and toxicity characteristic leaching technique (TCLP).

Experimental design

Sequential extraction procedure:

Mobility of metal in contaminated (T0), treated soil with mined RP of grain size 125-106 μ m (T1), 106-90 μ m (T2), 90-63 μ m (T3) and < 63 μ m (T4), processed (T5) and biogenic (T6) was evaluated using sequential extraction scheme. This scheme is used to operationally define heavy metal into different geochemical phases, usually in order of increasing stability. A five-step sequential chemical extraction procedure was proposed for harmonization and validation the methods used to speciation studies in soils and sediments. It was designed based on MgCl₂, pH7 (step1), hydrogen peroxide oxidation and ammonium acetate extraction (step2), sodium acetate, pH5 (step3), 0.175M ammonium oxalate and 0.1M acetic acid (step4) and conc. Acids mixture, HCl/HNO₃/HF (3:1:2, v/v/v). These extractions have been associated with the exchangeable, organic-bound, acidic, amorphous Fe/Al oxides-bound and the residual form, respectively. It is acknowledged that the reactivity and potential bioavailability of heavy metals generally increases with increasing solubility. Thus, the first form is usually considered the most mobile form of metals in soils and the other three fractions are relatively immobile and more stable, but may sometimes become mobile and bioavailable with changes of soil conditions.

All the steps and the operationally fractions of metal are displayed in the Table (2). The sequential extraction was carried out, in triplicates, on 1 g of soil, in 85 ml polyethylene tubes. After each extraction step, the suspensions were centrifuged at 8000 rpm for 15

min. The supernatants were carefully removed and stored in polyethylene bottles at 4 C°. The residues were washed with ultrapure water before the addition of the next extracting agent.

Chemical Analysis of Phosphate Sources

The measured metal solubility of each phosphate source was tested in 25 mL polyethylene tubes with 1 g of well mixed phosphate sample and 10 mL of dis. water. The samples were placed on a shaker for 12 days, centrifuged and decanted. Consequently metal concentrations in the decanted solutions will be referred to as the apparent solubility of these elements. The samples were placed on a shaker for 12 days, centrifuged, and decanted. Total metal concentrations were determined using complete acids attack (digestion of 0.6 g of phosphate material with concentrated acids, 10 mL of HNO₃, 4 mL of H₂SO₄ and 2 mL of HCl). The same elements were also extracted from the phosphate materials with the standardized TCLP; (U.S. EPA, 1992). The TCLP leaching solution consisted of 0.1 M glacial acetic acid and 0.0645 M NaOH and had a final pH of 4.93. Forty milliliters of leaching solution were added to 2 g of phosphate material; the mixture was agitated on a shaker for 18 h at 25 °C and then centrifuged. All tests were duplicated.

Elemental Analysis and Instrumental Technique

Metal concentrations in all extracting solutions of contaminated and amended soil samples were determined by atomic absorption spectrophotometer (Model Solaar 969, ATI Unicam Comp.) equipped with a digital and direct concentration read out and air - acetylene burner was used. The standard addition calibration method and extraction blanks were employed to avoid interferences in the measurements.

Results and Discussion

The effect of grain size of rock phosphate as amendment Sequential extraction procedure:

The percent distribution of measured metals in contaminated (T0) and amendments soil (T1-T6) with RF were displayed in Fig (1). Metal levels indicate relatively high metal contamination of the study area because it subject to urban and wastewater effect. The application of the sequential extraction technique can help to investigate the metal distribution in the various soil compartments. To illustrate the results in more detail, we compared the extraction forms as a function to determine the efficiency of different grain size for remediation of the contaminated soil.

The leached metals concentrations in different forms are in the order: residual > amorphous Fe/Al oxides-bound > organic bound > acidic > exchangeable (Fig1). The residual metals content is significantly high as compared with the available metals in exchangeable phase or that bond to Fe/Mn oxides fraction. Total metal content is still used as an important index in the long run, which, together with the changing

environmental condition (both soil and plant factors), determines the bioavailability of heavy metals (Haiyan and Stuanes, 2003). Elevated concentrations of heavy metals in soils are of potential long-term environmental and health concerns because of their associated toxicity to biological organisms (Wong and Li, 2003).

In general, the analytical results of the sequential chemical extraction indicate that all measured metals were primarily associated with residual and amorphous Fe/Al oxides fraction and secondary with the organic fraction, and the Pb, Cd, Co and Cu in the exchangeable fraction represented small percentage of the total metal content (Fig.1). Although results suggest that high percentages of measured metals were relatively significant associated with the non-residual fractions (Table2), that the contaminated metals in these fractions might be moderately soluble and potentially bioavailable (with changes of different soil characteristics that influence the heavy metals solubility e.g. pH, organic matter, CEC, carbonate and clay mineralogy), representing a potential environmental concern.

Fawzy, et al (2006) studied the relation of the mobility and distribution of metals between Tamarix parts and their crystal salts - soil system and applied sequential extractions on the different soil samples to obtain a better understanding of the geochemistry of heavy and trace metals in soil. They concluded that, the hydrous Fe and Mn oxides may hold significant proportions of some heavy metal ions. These oxides are known to exist as separate phases, and there is evidence from electron microprobe analysis of surface soils that

Cl, SO₄²⁻, CO₃²⁻, PO₄³⁻, organic acids, and fulvic acid. Immobilization or transformation of soil metals especially Pb to low soluble species that reduces metals dissolution and leachability in soil system may be a remedial strategy for metal contaminated soil, which safeguards human and ecosystem from the contamination (Yang and Mosby, 2006). The real effectiveness of in situ remediation of metal-contaminated soils can be assessed using a fractionation scheme (Chen et al, 2006). Among the four treatment Rock phosphate RP, T4 (< 63µm) was the most effective in transferring metals from the non-residual fractions to the residual fraction, while T1 (125-106 µm) was the least effective, indicating that the potential bioavailability of Pb, Cd, Co and Cu in RP treatments decreases with increasing rock grain size.

Comparing of Suitability of Different Phosphate Sources for Remediation of Contaminated Soils

As Above processed (T5), phosphate fertilizers-treated soil and biogenic (T6) showed markedly reduces contaminant metals concentrations compared to the control (Table 3), a similar trend were observed in these substrates. All determined metals decreased in the following order: mobile < acidic organic bound < Amorphous Fe/Al oxides-bound < residual (Fig 2).The difference in extraction efficiency of metals concentrations between the six substrates (T1-T6) reflect that, biogenic phosphate is the most effective amendment for contaminated soil (Fig. 3). This ability of biogenic phosphates to readsorption of metals from the contaminated soil may be result from the capacity of

Available metal concentrations reflected relatively high lead and copper levels (Table 4). Elevated lead in soil has been identified as a threat to human health and ecosystem (Cotter-Howells and Thornton, 1991; US Environmental Protection Agency, 1998). The ecological threat is associated with Pb mobility in soil system (Yang and Mosby, 2006), which is controlled by the chemical or mineralogical associations of soil Pb and their solubility (Ruby et al., 1992; Davis et al., 1993). Immobilization of soil Pb can be achieved by formation of pyromorphite through phosphate amendments. Based on the results, a pronounced mobilization of Pb, Cd, Co and Cu was observed high in mined phosphate compared with other phosphate sources (Table 4). This characteristic points the release of mobile constituents into aqueous phase during solubility test. The solubility of phosphate materials is important because dissolution may be, depending on the contaminant, a necessary step in the immobilization of contaminants (Knox et al., 2006).

Total concentration of impurities in phosphate sources

As in the solubility test, the results (Table 4) showed markedly higher Cd, Co, Pb and Cu concentrations in mined and processed phosphate sources than those in uncontaminated soils. The finding concentration of measured metals in the mined, processed and biogenic phosphate sources was higher than measured concentrations in the soluble form. These elevated concentrations of metals in some phosphate materials were expected because of

The TCLP was designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. This test reflects the availability of contaminants under extreme environmental conditions, such as low pH, that could cause the release of contaminants that would otherwise be stable. Displaying the data in Table (4), it was found that metal concentrations in the TCLP extracts were much lower than concentrations in the total digestion extracts and similar to or slightly higher than concentrations in the water soluble extract. The TCLP is a regulatory test used widely to classify solid waste materials as hazardous or nonhazardous (U.S. EPA, 1992) based on their potential to leach certain toxic elements. Measured metals in mined and processed showed relatively higher concentrations than corresponding values in biogenic phosphate (Table 4). However, even in this case measured metals content in different phosphate sources still under EPA regulatory levels (U.S. EPA, 1992).

Knox et al., (2006) studied the suitability of Phosphate sources for remediation of contaminated soils. They concluded that rapid phosphate release would be advantageous when a rapid immobilization of contaminants is necessary. Conversely, a slow-release phosphate source may be preferred for long-term treatment. Combining phosphate sources with high and slow dissolution rates may provide a rapid immobilization of contaminants while providing a slow release of phosphate for continued long-term treatment and maintenance.

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Table (1) Some Chemical Soil Properties

Mechanical Analysis%			CaCO ₃ mgg ⁻¹	O.M mgg ⁻¹	CEC (μS cm ⁻¹)	pH	Item
Sand	Silt	Clay					
35	36	38	2.5	23	920	6.8	Urban Soil

Table (2) Procedure of the five-step Sequential Extraction of Metals from the Urban Soil and Corresponding Phases.

Phase/Association	Abbreviation	Operational Definition
Exchangeable	EX	16 ml MgCl ₂ , pH7.0, shaking 1h
Organic-bound	OB	10 ml 30 % H ₂ O ₂ (PH2), then 10 ml 30 % H ₂ O ₂ (PH2) cool, add 50 ml mol/lammonium acetate (PH2)
Acidic	AC	16 ml 1M NaOAC, pH5.0 with HOAC, shaking 5h
Amorphous Fe/Al oxides-bound	OX	40 ml 0.175M (NH ₄)C ₂ O ₄ /0.1M H ₂ C ₂ O ₄ , shaking 4h in the dark
Residual	RES	Acid mixture ^a

^a the residual from step 4 was digested in 15 ml HCl/HNO₃/HF (3:1:2, v/v/v) at 150 °C

Table (3) Measured Metals Percentage in the Non-Residual (EX+OB+AC+OX) and Residual Fractions (RES).

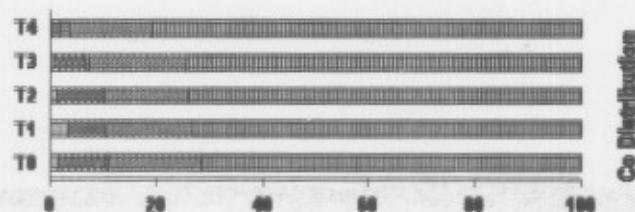
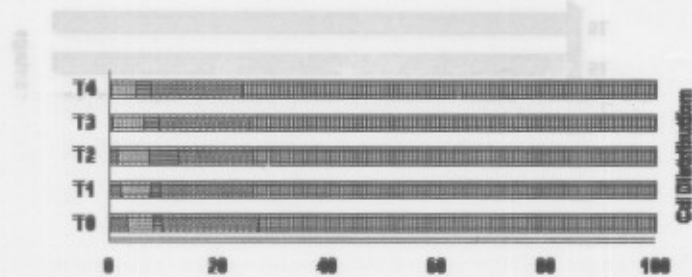
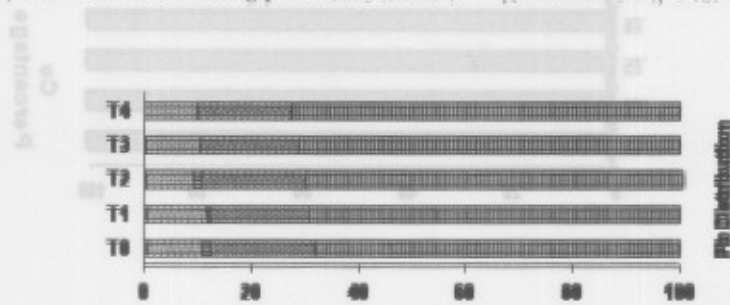
Cu	Co	Cr	Pb	Element



Table (4) Display of Total, Water Soluble and TCLP Mean Concentrations ($\mu\text{g/g}$) of Impurities in Different Sources of Phosphate Materials.

TCLP regulatory limit	Average Shale, 1961	Biogenic Mean	Processed Mean	Mined Mean	Element
		6.98	6.41	8.89	pH
		0.02	0.05	0.03	Pb
		0.0	0.02	0.011	Cd
		0.005	0.22	1.12	Co
		0.017	2.01	0.005	Cu
					Total Digestion
	20.0	1.15	3.93	2.15	Pb
	00.3	0.021	0.09	0.13	Cd
	19.0	0.021	0.76	16.23	Co
	45.00	2.3	3.6	45	Cu
					TCLP
5.0a		0.23	0.27	1.0	Pb
1.0a		0.01	0.01	0.067	Cd
		0.11	0.52	0.087	Co
		0.088	1.2	3.0	Cu

TCLP: Toxicity characteristic leaching procedure limits (a - 40 CFR 261.24, U.S. EPA, 1999).



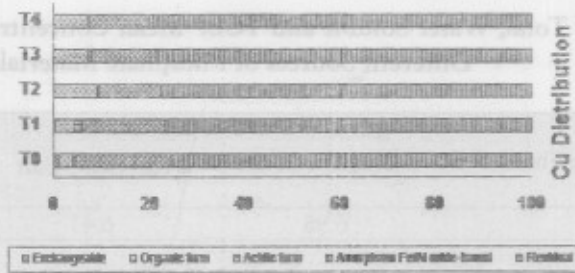
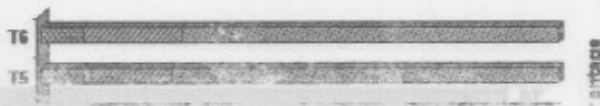
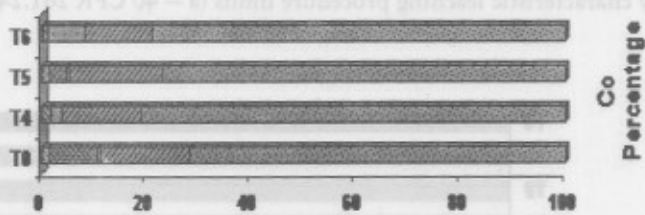
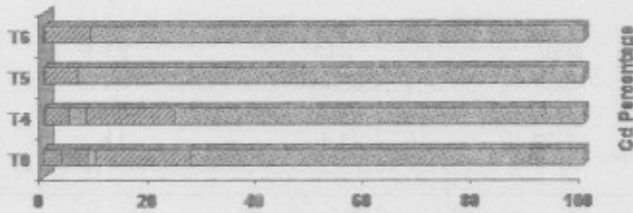
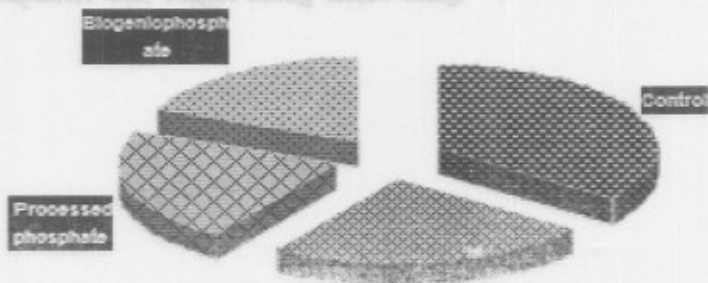
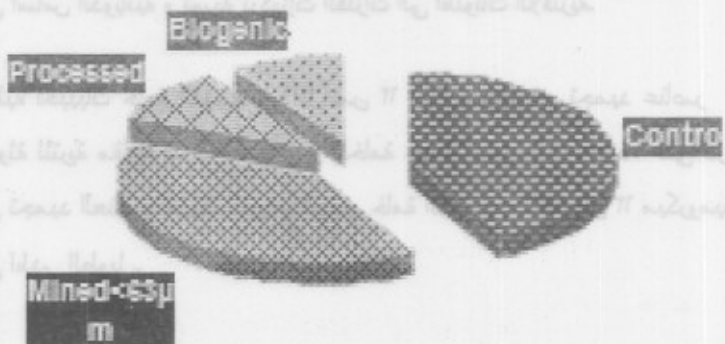
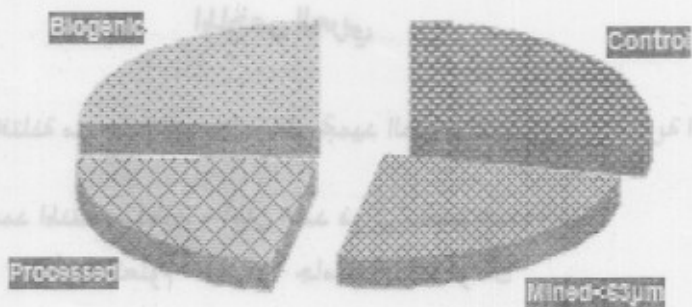


Fig (1) Percentage of Pb, Cd, Co and Cu in Contaminated and Treated Soil.





الملخص العربي

تقييم فعالية أنواع وأحجام مختلفة من خامة الفوسفات على تجميد الفلزات المعدنية الملوثة لتربة المناطق الحضرية

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تعرض الدراسة لتقييم فاعلية أحجام مختلفة من خامة الفوسفات الصخرية (أقل من ٦٢ & ٦٢-٩٢ & ١٠٦-١٦ & ١١٥ ميكروميتر) كمعالج للفلزات المعدنية الملوثة لتربة المناطق الحضرية، كما تم كذلك اجراء مقارنة عملية لتحديد الدور الحيوي لمصادر مختلفة من الفوسفات (خامة الفوسفات الصخرية > ٦٢ ميكروميتر، سماد فوسفات & فوسفات حيوي) وذلك لتجميد العناصر الملوثة للتربة على أساس الذوبانية و نسبة تركيزات الفلزات الى الملوثات اللافلزية.

وقد اظهرت النتائج كفاءة عالية لحبيبات خامة الفوسفات (أقل من ٦٢ ميكروميتر) في تجميد عناصر النحاس ، الكوبلت، الكاديوم و الرصاص الملوثة للتربة مقارنة بالأحجام الأخرى للخامة بينما اثبتت النتائج وبناء على درجة الذوبانية قدرة عالية للفوسفات الحيوي على تجميد العناصر الملوثة للتربة أكثر من خامة الفوسفات (أقل من ٦٢ ميكروميتر) والتي قد تفيد في معالجة التربة الملوثة على المدى الطويل.

الكلمات المفتاحية:

معالجة التربة، مصادر الفوسفات، حجم الحبوب، المعادن الثقيلة، التخليل،