

Modern Technologies in Remediation of Heavy Metals in Soils

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Abstract: Environmental pollution becomes an important paradigm in our society to reservation of the environment. Worldwide, concerns have been voiced about numerous soil and water contaminants. The concern comes from the fact that the magnification of very small amounts of these pollutants have resulted in adverse effects on bio-systems. The increasing use of heavy metal-contaminated sewage sludge as agricultural fertilizer, these elements may pass into the soil solution where plant uptake or leaching to groundwater can contaminate the food chain. Several cleanup methods have been investigated, which can be divided into two groups: those that remove contaminants and those that transform pollutants into harmless forms (immobilization) by fixation, oxidation, etc. These cleanup technologies can be applied on- or off-site, utilizing three kinds of remediation treatments: biological, physical, and chemical techniques. It is most convenient to divide them into three major categories: first, electro kinetic methods, second chemical methods such as solidification, precipitation, or ion exchange, and third, biological methods, which use plants or microorganism to remove heavy metals. In the past few years, innovative approaches such as passive treatment technologies for soil and groundwater contaminations have been developed. The following state of art introduces the various remediation technologies applied in contaminated soil systems with comments about the best of these technologies should be applied under Egyptian conditions to minimize their injures.

Keywords: Soil, Environmental Pollution, heavy metals, Remediation technologies

INTRODUCTION

Metals can be found in all parts of the lithosphere. Most of them are dispersely distributed, only small portions are concentrated in ores. Beside these geogenic concentrations, human use of metals has led to significant changes in the circulation of metals. Many metals are of great importance for biological processes. These metals needed as nutrients by organisms are called essential metals. Some of them are needed in higher amounts (macro-elements), others in smaller amounts (trace-elements). Shortage, but also surplus of essential metals has negative influence on biomass growth. Non-essential metals however can cause toxic effects at low concentrations.

Generally, heavy metals are not degraded biologically and persist in the environment indefinitely. Once accumulated in the soil, the toxic metals inversely affect the microbial compositions, including plant growth promoting rhizobacteria (PGPR) in the rhizosphere, and their metabolic activities. In addition, the elevated concentration of metals in soils and their uptake by plants adversely affect the growth, symbiosis and consequently the yields of crops by disrupting the physiological process, such as, photosynthesis, or by inactivating the respiration, protein synthesis and carbohydrate metabolism.

Several cleanup methods have been investigated, which can be divided into two groups: those that remove contaminants and those that transform pollutants into harmless forms (immobilization) by fixation, oxidation, etc. These cleanup technologies can be applied on- or off-site, utilizing three kinds of remediation treatments: electrical, biological, and chemical techniques.

This article aims to precise and evaluate the recent technologies applied in remediation of heavy metals contaminated soils in literatures to gain the suitable technique(s) should be applied in contaminated soils and to minimize the hazards of such toxic metals under Egyptian conditions.

ELECTRO KINETIC REMEDIATION

Electrokinetic (EK) remediation is an in-situ process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil. As a result of the application of this electric field, heavy metal contaminants may be mobilized, concentrated at the electrodes, and extracted from the soil ^[1].

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Figure 1. A diagram of field-processing configuration depicting transport of the process fluid and ionic species under an electric field

The electrodes can be placed in either a vertical or horizontal array.

When DC current is applied to the electrodes, an electrical field develops between the anodes and cathodes.

The application of the electric field has several effects on the soil, water, and contaminants. These effects include electromigration, electroosmosis, changes in pH of the system, and electrophoresis.

Electromigration refers to the movement of cations and anions under the influence of the electrical field. These ions concentrate in the solutions near the electrodes or may undergo reactions at the electrodes, which may plate the metals onto the electrodes or liberate gaseous compounds.

Electroosmosis is the movement of liquid containing ions relative to a stationary charged surface **or** a bulk transport of water, which flows through the soil as a result of the applied electrical field.

pH changes occur under the influence of the current as a result of electrolysis reactions at the electrodes. Oxidation of water occurs at the anode and generates hydrogen (H^+) ions; H^+ ions generate an acid front, which migrates to the cathode.

Electrophoresis is the movement of a charged particle in a liquid, caused by an electric field

In contrast, reduction of water occurs at the cathode and generates hydroxyl (OH-) ions (Equation 2), which migrate as a base front towards the anode

$2H_2O - 4e^- \rightarrow O_2 + 4H^+$	(Equation 1)
$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$	(Equation 2)

The transport of the H^+ ions is approximately two times faster than the OH⁻ ions. Thus, the acid front moves at a greater rate than the base front. Unless the transport of the proton (H^+ ion) is retarded by the soil buffering capacity, the soil between the electrodes will be acidified. This acidification, results in solubilization of contaminants due to desorption and dissolution of species from soil. Once contaminants are present in ionic form in the soil pore fluid, they migrate to the electrode opposite in polarity under the applied electric field and/or via electroosmosis, leading to their extraction from the soil at the electrodes.

Extraction and removal of the contaminants may be accomplished by electrodeposition, precipitation or co-precipitation at the electrode.

EK remediation heavy metal extraction rate and efficiency is dependent upon many subsurface characteristics such as soil type and grain size, contaminant concentration, ionic mobility, total ionic concentration, types of contaminant species and their solubility, etc. Additional complications with the application of EK remediation can arise from the presence of organic contaminants and possibly the organic material in the soil.

Zhemin, et al. (2008) ^[2] tried to evaluate the effect of adsorption, desorption mechanisms on successful of EK remediation technique. Adsorption data obtained in this study for four soil samples were fitted to Freundlich equation. The influencing soil characteristics significant to Cd EK removal order were total organic carbon, clay contents of these soils; cations exchange capacity, soil pH parameters. According to the rate constants of used model, fast reactions are attributed to H⁺-M²⁺ exchange processes occurring on the surfaces of different inorganic phases and to the dissolution of the water-insoluble precipitates. Slow irreversible reactions refer to H⁺ ions exchanging with metal ions bound in the internal lattice sites and organic matters being oxidants produced by electrochemical reactions. Slow reactions limit the EK remediation effect,

Solar cell could be used to drive the Electromigration of cadmium in contaminated soil. This procedure generally involved two steps, desorption from soil to pore solution and the subsequent electromigration ^[3].

Compared with traditional DC power supply, using solar cell as a power supply for EK remediation can greatly reduce energy expenditure. Evaluation of the using of a solar cell, instead of direct current (DC) power supply was investigated by ^[4], to generate electric field for EK remediation of cadmium-contaminated soil. In their study, they evaluate three EK tests; one was conducted on a cloudy and rainy day with solar cell, the second was conducted on a sunny day with solar cell and the third was conducted periodically with DC power supply. Their results indicated that the output potential of solar cell depended on daytime and was influenced by weather conditions; the applied potential in soil was affected by the output potential and weather conditions, and the current achieved by solar cell was very cheaper compared to that achieved by DC power supply.

Enhancement of EK remediation for removal of heavy metals in soils was investigated by several researchers. Ching and Chiang (2008) ^[5] concluded that the arsenic removal could be enhanced by selecting suitable chemical reagents and increasing potential gradient. After 5-day EK treatment under potential gradient of 2.0 V/cm, the removal efficiency of As (V) in enhanced EK systems was 1.2–1.3 times greater than that in EK-ground water (GW) system. The enhanced removal of As(V) was resulted from the characteristics of chemical reagents, included counter ion binding, chelating and solubility enhancement in acid environment. A better EK removal of 44.8% for As (V) was found in EK-EDTA system with higher potential gradient. The quantity of As(V) collected in anode reservoir was 1.4, 1.6–1.8, 2.3–2.4, and 2.2–2.5 times greater than that in cathode reservoir in EK-GW, EK-cetylpyridinium chloride, EK-EDTA, and EK-Citric Acid system, which was reasonably inferred that most of As(V) was existed as anionic form of HAsO4 and consequently, it migrated to the anode by electrical force. Their data also indicated that As (V) removal was directly related to the electromigration rather than electro-osmosis mechanism in EK systems.

Applying of EDTA as enhancement material for EK remediation was investigated by ^[6]. The soil sample selected in this study was affected by Cu pollution followed by electrochemical advanced oxidation process. The released Cu was removed from the solution mostly as an electro-deposit on the cathode. Results indicated also that two consecutive additions of 10 mmol kg⁻¹ EDTA removed 26% of Cu from the soil, mostly from carbonate and oxide soil fractions (58% and 40% Cu reduction). The soil Cu oral availability was reduced after remediation by 42% and 51% in the simulated stomach and intestinal phases.

Decreasing pH by Nitric acid for enhancing EK- remediation was applied by [7]. In this study, removing of Ni and Zn from contaminated soil by applied acidic solution at various pH conditions was increased.

PHYTOREMEDIATION

With the high costs of site remediation, it is important to develop and refine innovative low-cost methods for cleaning the environment. Advances in soil remediation continue to lead to a better understanding of the many processes by which plants can have a positive impact on contamination in the environment. This realization has provided impetus to studies in an emerging field of interest, which employs certain plants possessing the natural ability to take up heavy metals for an inexpensive means of environmental cleanup. This method is referred to as plant-assisted remediation or phytoremediation, and it also has the benefit of contributing to site restoration when remedial action is ongoing.

Phytoremediation has many advantages compared to other remediation techniques of soil extraction, incineration, chemical treatment, and land filling. It can be used to decontaminate large areas, can be carried out with little environmental disturbance and is applicable to a broad range of contaminants. It is cost-effective, the topsoil is left in usable condition and may be reclaimed for agricultural use, and plant uptake of contaminated groundwater can prevent off-site migration ^[8].

Types of phytoremediation

• Phytofiltration

Plant roots/shoots absorb/ adsorb pollutants. Precipitate/ concentrate toxic metals

• Phytostabilization

Reduce bioavailability of pollutants (e.g. by leaching/erosion)

• Phytovolatilization

Using of plants to volatilise pollutants. Extract from soil, volatilise to foliage (e.g. selenium, mercury)

• Phytodegradation

Use of plants (& associated microbes) to degrade organic pollutants

• Phytoextraction- plant characteristics

• Tolerant to and accumulated high levels of the metal

• Rapid growth rate and accumulate 10-500 times more elements than other crop plants with high biomass in the field.

- Remove from soil via uptake capabilities of plant
- accumulate for growth & development + random

Enhancing phytoextraction by different chemicals applied becomes one of the recent technologies applied. Lesage, et al. (2005)^[9] suggested that EDTA able to increase heavy metals bioavailability and uptake in plant parts. The effect of increasing doses of EDTA from 0.1 to 1 and 10 mmol/kg dry soils and citric acid from 0.01 to 0.25 and 0.5 mol/kg dry soil was beneficially observed on bioavailable fractions of Cu, Zn Cd and Pb.

Johnson, et al. (2009) ^[10] indicated that chemical amendments can be added to increase the uptake and translocation of metals to aerial biomass. In their study, they tested a range of amendments of various types for increasing the copper uptake with the test species Indian mustard and ryegrass. These materials included citric acid (an organic acid); histidine (an amino acid); EDTA, Nitrilotriacetic acid, and ethylenediaminedisuccinic acid (aminopolycarboxylic acids); rhamnolipid (a biosurfactant); and Triton X-100 (a synthetic surfactant). The results indicated that EDTA was the most effective amendment for enhancing copper uptake and translocation into the shoots of Indian mustard and ryegrass, with respective shoot tissue copper levels.

Ericka Nehnevajova (2007) ^[11] tries to improve the very low biomass and low heavy metals concentration accumulated in hyper accumulated plants. They found that in Sunflowers- hybrid cultivar treated with the chemical mutagen ethyl methane sulfonate, led to directly assess heavy metals Cd Zn and Pb concentrations inside plant reached to 2-3 times metal shoot concentration than the control plant besides increasing plant biomass.

The effect of temperature on HM phytoextraction, in polluted soils was examined by ^[12], they found that Pre-rooted weeping Willows (*Salix babylonica L.*), exposed to hydroponic solution spiked with potassium cyanide and undergone to 10 temperature regimes ranging from 11-32°C, significantly removed from hydroponic solutions. The highest cyanide metabolism rate for weeping willows was found at 32° C, where as the lowest value was observed at 11° C.

Concerning the effect of genotypes, ^[13] studied the practical capability of five common crop plants, i.e. maize (*Zea mays*), sunflower (*Helianthus annuus*), canola (*Brassica napus*), barley (*Hordeum vulgare*) and White lupine (*Lupinus albus*) for their absorption and accumulation of Pb, Zn, and Cu in six polluted soil samples taken from mine tailings, pasture and arable soils around an old Pb-Zn mine in Spain. With the exception of the highest polluted sample, soil total metal concentration did not influence significantly biomass yields of each crop for the different growth substrates. The order found for the total metal accumulation rate (TMAR) in the crops was Zn>>Pb > Cu, with maize reaching the highest metal concentrations. Pb root concentrations were markedly higher than those of shoots for all the crops, while Zn and Cu were translocated to shoots more efficiently. Concentrations of metals extracted by EDTA and BCR sequential extraction were well correlated, in general, with both root metal content and TMAR. CaCl₂-extracted Zn was well correlated with root concentrations, TMAR and, in some cases, with shoot contents.

Sarah, et al (2005) ^[14] showed that siderophores may have a very important impact on Pb and Cd mobility. In their study they showed that the primary impact is decreased adsorption at intermediate to high pH. At pH >6, siderophores decreased Pb adsorption to kaolinite by 5-75% according to the type of siderophores, the respective values for Cd were 5-80%. Their results also indicated that molecular charge and pH of the media are very important factors controlling adsorption characteristics of Pb and Cd. Generally they suggested that siderophores have the ability to either enhance or inhibit metal mobility in porous media.

In the study of ^[15] they indicated that plant biomass and metal shoot accumulation are key factors for efficient phytoextraction. They found that chemical mutagenesis improved the phytoextraction potential of sunflowers towards Cd, Zn and Pb. The best sunflower mutants showed either higher metal accumulation in shoots or enhanced metal accumulation in roots, suggesting to improved phytoextraction or rhizofiltration efficiency, respectively.

BIOREMEDIATION

Sharda and Adholeya (2007) ^[16] defined Bioremediation as the utilization of microorganisms to reduce or eliminate environmental hazards by mediating desired chemical reactions or physical processes. The most important principle of bioremediation is that microorganisms (mainly bacteria) can be used to destroy hazardous contaminants or transform them to less harmful forms. The microorganisms act against the contaminants only when they have access to a variety of materials— compounds to help them generate energy and nutrients to build more cells. In a few cases the natural conditions at the contaminated site provide all the essential materials in large enough quantities that bioremediation can occur without human intervention—a process called intrinsic bioremediation. More often, bioremediation requires the construction of engineered systems to supply microbestimulating materials—a process called engineered bioremediation. Engineered bioremediation relies on accelerating the desired biodegradation reactions by encouraging the growth of more organisms, as well as by optimizing the environment in which the organisms must carry out the detoxification reactions.

A critical factor in deciding whether bioremediation is the appropriate cleanup remedy for a site is whether the contaminants are susceptible to biodegradation by the organisms at the site (or by organisms that could be successfully added to the site). Although existing microorganisms can detoxify a vast array of contaminants, some compounds are more easily degraded than others.

The suitability of a site for bioremediation depends not only on the contaminant's biodegradability but also on the site's geological and chemical characteristics. The types of site conditions that favor bioremediation differ for intrinsic and engineered bioremediation. For intrinsic bioremediation, the key site characteristics are consistent ground water flow throughout the seasons; the presence of minerals that can prevent pH changes; and high concentrations of oxygen, nitrate, sulfate, or ferric iron. For engineered bioremediation, the key site characteristics are permeability of the subsurface to fluids, uniformity of the subsurface, and relatively low (less than 10,000 mg/kg solids) residual concentrations of nonaqueous-phase contaminants.

When deciding whether a site is suitable for bioremediation, it is important to realize that no single set of site characteristics will favor bioremediation of all contaminants. For example, certain compounds can only be degraded when oxygen is absent, but destruction of others requires that oxygen be present. In addition, one must consider how the bioremediation system may perform under

variable and not perfectly known conditions. A scheme that works optimally under specific conditions but poorly otherwise may be inappropriate for in situ bioremediation.

Principles of Bioremediation

Microbial transformation of organic contaminants normally occurs because the organisms can use the contaminants for their own growth and reproduction. Organic contaminants serve two purposes for the organisms: they provide a source of carbon, which is one of the basic building blocks of new cell constituents, and they provide electrons, which the organisms can extract to obtain energy.

Microorganisms gain energy by catalyzing energy-producing chemical reactions that involve breaking chemical bonds and transferring electrons away from the contaminant. The type of chemical reaction is called an oxidationreduction reaction: the organic contaminant is oxidized, the technical term for losing electrons; correspondingly, the chemical that gains the electrons is reduced. The contaminant is called the electron donor, while the electron recipient is called the electron acceptor. The energy gained from these electron transfers is then "invested," along with some electrons and carbon from the contaminant, to produce more cells. These two materials—the electron donor and acceptor—are essential for cell growth and are commonly called the primary substrates.



Figure 2. Microbes degrade contaminants because in the process they gain energy that allows them to grow and reproduce. Microbes get energy from the contaminants by breaking chemical bonds and transferring electrons from the contaminants to an electron acceptor, such as oxygen. They "invest" the energy, along with some electrons and carbon from the contaminant, to produce more cells.

Khan, et al (2009) ^[17] showed that contaminated soils are often nutrient poor or sometimes nutrient deficient, due to the loss of beneficial microbes. However, such soils can be made nutrient rich by applying metal-tolerant microbes, especially the plant growth promoting rhizobacteria, which would provide not only the essential nutrients to the plants growing in the contaminated sites but would also play a major role in detoxifying heavy metals.

Kova, et al., (2006) ^[18] studied the effect of arbuscular mycorrhiza (AM) on the phytoextraction efficiency of transgenic tobacco with increased ability to tolerate and accumulate cadmium (Cd) in a pot experiment. The tobacco plants bearing the yeast metallothionein CUP1 combined with a polyhistidine cluster were compared to non-transgenic tobacco of the same variety at four Cd concentrations in soil, non-inoculated or inoculated with two isolates of the AM fungus Glomus intraradices. Mycorrhizal inoculation improved the growth of both the transgenic and non-transgenic tobacco and decreased Cd concentrations in shoots and root to shoot translocation.

Sharda and Adholeya (2007) ^[16] stated that Bioremediation is an integrated management of a polluted ecosystem where different organisms are employed to catalyze the natural processes that decontaminate the environment. The potential role of bioremediation, particularly higher terrestrial plants. They also showed that Arbuscular mycorrhizal fungi are soil microorganisms that establish mutual symbiosis with the majority of higher plants, providing direct links between fungi and roots. In their reviews, indicated that high metal concentrations in soil are toxic to bacteria and fungi.

CHEMICAL REMEDIATION

Chemical treatments include all techniques involving reagents or external compounds. Soil washing is one. In this technique different reagents able to solubilize toxic elements are coupled with

the removal of leaching solutions and added chelators that make cations less labile, thus allowing them to immobilize toxic elements in a less bioavailable form. For instance, EDTA is one of the proposed complexing reagents. In addition, adding solid phases should also be mentioned. Solid phases can fix (irreversibly) toxic elements, and they can sometimes be used to reduce remediation costs.

The extraction of heavy metals by chelating agents becomes the most recent technologies in chemical remediation. Hauser, et al (2005) ^[19] used biodegradable chelant EDDS in remediation by chemical extraction of Cu, Zn and Pb from three contaminated soils in both batch and columns techniques. Their data showed that a total of 53-80% of Cu was extracted in batch and 18-26% in column extraction. For Zn, the extractability was 16-50% in batch and 20-64% in columns and for Pb 25-52 and 18-91%, respectively.

Using of especial kinds of material for stabilize heavy metals like coal ash was become an important recent technique for remediation. Terzano, et al, $(2005)^{[20]}$ deals with the process of zeolite formation in an agricultural soil artificially polluted by high amounts of Cu (15 mg of Cu/g of soil dry weight) and treated with fused coal fly ash at 30 and 60 °C and how this process affects the mobility and availability of the metal. Micro XRF (X-ray fluorescence) tomography showed direct evidence that Cu can be entrapped as clusters inside the porous zeolitic structures while X-ray absorption near edge structure spectroscopy determinations revealed Cu to be present mainly as Cu(II) hydroxide and Cu(II) oxide.

Walker, et al. (2003) ^[21] studied the effects of two contrasting organic amendments (fresh manure and mature compost) and the chelate ethylene diamine tetraacetic acid (EDTA) on soil fractionation of Cu, Fe, Mn, Pb and Zn, their uptake by plants and plant growth. In the Murcia soil, heavy metal bioavailability was decreased more greatly by manure than by the highly-humified compost. EDTA (2 mmol kg⁻¹ soil) had only a limited effect on metal uptake by plants.

Tomoyuki et al. (2007) ^[22] developed a new, three-step soil-wash method to remediate Cd contaminated paddy fields. The method comprises (1) chemically washing the field soil with a CaCl₂ solution; (2) washing the treated soil with water to eliminate residual Cd and CaCl₂; and (3) on-site treatment of wastewater using a portable wastewater treatment system. Cd concentrations in the treated water were below Japan's environmental quality standard (0.01 mg Cd L⁻¹), and the removal of Cd from the exchangeable fraction was 55% and from the acid-soluble fraction 15%. While soil fertility properties were affected by the soil washing, adverse effects were not crucial and could be corrected. The washing had no affect on rice growth, and reduced the average Cd concentration in rice grains by about two-thirds compared to a control plot. These results confirmed the effectiveness of the soil-wash method in remediating Cd-contaminated paddy fields.

The mobilization of chromium and nickel from an industrial soil was investigated by ^[23] using two biodegradable chelants (citric acid and histidine), compared with a persistent one (EDTA). Successive metal mobilizations were carried out in batch experiments. For a single mobilization, citric acid was the most effective for Cr mobilization and EDTA for Ni. Their effectiveness could be explained by their ability to solubilize the mineral matrix and by the competition for the surfaces sites to desorb Cr (VI).

Shi-Bao Chen (2006) ^[24] investigated the effects of bone char (BC) application on the bioavailability of Pb in a polluted soil from Hunan Province, China. The Pb-contaminated soil was treated with two types of bone char, one from the UK and the other from China. The bioavailability of Pb was determined in terms of the uptake by Chinese cabbage (*Brassica chinensis L*.). The results indicate that the Pb concentrations in both shoots and roots decreased with increasing quantities of added bone char, and the application of BC from the UK had the largest effect. Lead Pb concentrations in the shoots and roots decreased by 56.0% and 75.9%, respectively, whereas the application of BC from Zhejiang Province, China reduced Pb concentrations in the shoots and roots to 2.04 mg kg⁻¹ and 8.42 mg kg⁻¹, respectively, only 45.8% and 30.2% compared to the control treatment. Sequential extraction results indicate that the addition of bone char, as a metal-immobilizing agent, substantially transforms soil Pb from non-residual fractions to the residual fraction.

Rene et al (2007) ^[25] examined the use of two composts derived from green waste and sewage sludge, amended with minerals (clinoptilolite or bentonite), for the remediation of metal-contaminated Brownfield sites to transform them into green space. Soils contaminated with high or low levels of metals were mixed with the mineral-enhanced composts at different ratios and assessed by leaching tests, biomass production and metal accumulation of ryegrass (Lolium perenne L.). The results showed

that the green waste compost reduced the leaching of Cd and Zn up to 48% whereas the composted sewage sludge doubled the leachate concentration of Zn. However, the same soil amended with composted sewage sludge showed an efficient reduction in plant concentrations of Cd, Cu, Pb or Zn by up to 80%. The results suggest that metal immobilization and bioavailability are governed by the formation of complexes between the metals and organic matter.

Zn accumulation in *Solanum nigrum* grown in naturally contaminated soil in the presence of different types of organic amendments was assessed by ^[26]. Under the experimental conditions, the response of the plant to inoculation with two different isolates of arbuscular mycorrhizal fungi (AMF) (*Glomus claroideum* and *Glomus intraradices*) was also evaluated. *S. nigrum* grown in the non-amended soil always presented higher Zn accumulation in the tissues, with the addition of amendments inducing reductions of up to 80 and 40%, for manure and compost, respectively, and enhancing plant biomass yields. The establishment of *S. nigrum* in the Zn contaminated soil combined with the application of amendments led to a 70-80% reduction in the amount of Zn leached through the soil. The use of *S. nigrum* in combination with manure appeared as an effective method for reducing the effects of soil contamination, diminishing Zn transfer to other environmental compartments via percolation.

Phosphate-induced lead immobilization from different Pb minerals in soils under varying pHs was studied by ^[27]. This study clearly demonstrated the importance of the form of Pb contamination and soil pH in determining the effectiveness of Pb immobilization in soils. In this study, one Pb-contaminated soil (NC-Soil) and three soils spiked with litharge (PbO), cerrusite (PbCO₃), or anglesite (PbSO4), referred to as PbO-soil, PbCO₃-soil, and PbSO₄-soil, respectively. Their results indicated that P addition can effectively transform various Pb minerals into insoluble chloropyromorphite in soils. This transformation was more significant at acidic condition (e.g., pH - 5). Among the three Pb minerals tested, PbSO₄ was the most effectively immobilized by P, followed by PbO and PbCO₃.

Compost application for remediation of heavy metals contaminated soils is also recent technique to minimize HM desorption. Susan, et al (2009) ^[28] compared two strategies for immobilizing trace elements (Cu, Pb, Zn, and As) in mine spoil: (1) co-composting contaminated soil with organic wastes and (2) conventional incorporation of mature compost into contaminated soil. Sequential chemical extraction of the soil was also performed to determine temporal changes in trace element fractionation and bioavailability during composting and plant growth. They conclude that for remediating trace-element-polluted soil incorporation of compost with polluted soils becomes an active technique in remediation.

Comments about recent technologies in remediation of heavy metals contaminated soils

A successful remediation plan has to be based on the information gained during the preliminary diagnostic works, which are done before taking the decision to start a remediation project. The following checklist should be worked out and carefully studied before starting with the actual design of the technical work.

- 1. What are the types and chemical nature of the pollutants determined at the site?
- Organics Inorganic substances
- 2. What are the dimensions and scale of pollution?
- Is the pollution localized? Is it of the dispersed type?
- How urgent is the remediation plan?
- 3. What is the risk level?
- Low risk level Medium level High risk level
- 4. Which technical measures are thought to be most suitable for carrying out this project?
- In place (in situ)?

- Ex situ? And if yes, should the soil be transported to a special facility? Should the remediation be carried out in a prepared bed system, or in a tank?

5. Are there any financial restrictions on choosing the technical method of remediation?

6. Which method is technically suitable and financially fitting in the economic framework of the project?

The EK remediation technique of contaminated soils mentioned before is not suitable under Egyptian conditions for many reasons.

• In Egypt the contaminated soils are common distributed in narrow areas. Under such conditions and from economic point of view, using of such technique will be useless.

• The presence of naturally occurring ions and organic material as well as organic contaminants can result in the development of potentially hazardous by-products (i.e. chlorine, trihalomethanes, acetone, etc.) when an electric field is applied to the soil. The addition of ions to the soil as a result of the amendment addition to the cathode well may also result in the formation of hazardous by-products during operation of the technology.

• The impact that EK extraction will have on the soil's physical, chemical, and biological characteristics has not been addressed.

However, the application of EK remediation technique in waste, saline or even low quality of irrigation water will be very effective especially in new reclaimed areas to elevate soil degradation.

Bioremediation techniques could be used and will be more suitable to treat heavy metals contaminated soils, beside other materials that are susceptible to metabolism by microorganisms. In situ remediation will be cheaper than ex situ bioremediation. The first technique, sometimes known as aerobic bioremediation, is accomplished by introducing oxygen and nutrients to the soil in order to enhance biodegradation of the contaminants. Both are applicable for a wider range of contaminants, yet they are more expensive and may, in some cases, need pre-treatment as well as post treatment measures, in order to achieve the optimum effectiveness.

In phytoremdiation technique, marginally contaminated agricultural soils provide the most likely land use where phytoextraction can be used as a polishing technology ^[29]. An alternative and more useful practical approach in many situations currently would be to give more attention to crops selected for phytoexclusion: selecting crops that do not translocated high concentrations of metals to edible parts. Soils of urban and industrial areas provide a large-scale opportunity to use phytoremediation, but the focus here should be on the more realistic possibilities of risk-managed phytostabilization and monitored natural attenuation. An additional focus on biomass energy, improved biodiversity, watershed management, soil protection, carbon sequestration, and improved soil health is required for the justification and advancement of phyto-technologies

As a general point of view, economically under Egyptian conditions, transform pollutants into harmless forms (immobilization) by different materials applied in chemical remediation is the best suitable technique should be applied to have safety food from these contaminated soils. Zaghloul and Abou-Seeda, (2005) ^[30] found that application of humic acid (HA), Roch phosphate (PR) and polyvinyl acetate butyl acrylate (PVAc) emulsion, all led to decrease heavy metals release from Pb contaminated soils varied in their properties. However, application of OM effectively was the best material minimized HM desorption from contaminated soils.

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