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Analytical study on methods for remediation of heavy metals contaminated soils

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In front of the committee consisting of:

Mrs. Zaoui Manel	MCA at U.K.M.O	President
Mr. Douadi Ali	Professor at U.K.M.O	Examiner
Mrs. Chaouche Khaoula	MCB at U.K.M.O	Supervisor

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Dedication

I am thankful to those who supported and motivated me throughout my journey of this work. Thereby, I dedicate this work:

TO MY BELOVED MOTHER (may she rest in peace)
Who has offered me the inspiration of success and keenness in my life

TO MY DEAR FATHER
For your sacrifices and encouragements. Thank you for being present at every moment of my life. May Allah bring you health, happiness and long life.

TO MY FAITHFUL SISTERS AND BROTHERS
Who have always helped me and believed that I could do it

TO MY TWO BEST FRIENDS "HOUDA" AND "DARRYN"
Thank you for being present in my life

TO OUSSAMA
Thank you for being with me and for helping me in this work

Last but not least, I want to dedicate this work to ME
I want to thank ME for believing in ME, for doing all this hard work and for having no days off

NOUR ELHOUDA

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Eh: oxidation-reduction potential**.**

MTE: Metalic trace element.

PTEs: Potentially toxic elements.

WHO: World Health Organization.

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General Introduction

General introduction

Since the 1960s, environmental pollution has been a major concern of our modern societies. The United Nations conference on the environment that was held in Stockholm, June 1972, was the event that shed light on the seriousness of environmental pollution turning it as a major issue at the international level, recognizing the protection of the environment and the effective management of natural resources as major issues. This conference led to the creation, in many countries, of ministries of the environment as we know them today [1].

Among the different types of pollution (organic and/or mineral), the problem posed by heavy metals pollution is quite unique. The presence of heavy metals in soils is particularly problematic because of their non-biodegradability compared to part of the organic pollution and their toxicity [2].

They can migrate and accumulate in the various components of natural ecosystems and possibly pose a risk to human health through contamination of the food chain [1].
Soil pollution by heavy metals is considered as a long-term threat to the environment [3].

Thus, numerous studies have focused on the remediation of heavy metals in soil [4].

Heavy metal remediation in soil can apply physical, chemical, and biological techniques depending on land use, pollution level, and time/labor availability [4].

In our study, we will focus on 5 heavy metals, which are among the most present metals in the soil, which are: Cadmium (Cd), Lead (Pb), Copper (Cu), Zinc (Zn) and Mercury (Hg).

In this study we have analyzed some previous studies to investigate the appropriate methods for remediation of contaminated soil by each metal.

So this study included 3 chapters:

Chapter 01: Present basic principles about soil, pollution, heavy metals (Cd, Pb, Cu, Zn and Hg) and its toxicity and impacts.

Chapter 02: Studied methods for remediation of heavy metals contaminated soils.

Chapter 03: We analyzed and discussed results from previous studies.

Finally, we stamped our work with general conclusion.

We have analyzed many previous studies, so what's the best method for remediation of contaminated soils by each studied metal?

Chapter I

Basic principals

Preface:

Heavy metal pollution has become a global environmental problem. The most important sources of these minerals are the chemical nature of the earth's crust and some human activities.

This chapter is a bibliographical summary of the soil, its pollution and its impact by heavy metals. We tried to explain the general information necessary to explain the concept of soil contamination with heavy metals.

I.1. Soil:

Soil can be defined as “the collection of natural bodies occupying parts of the Earth’s surface that is capable of supporting plant growth and that has properties resulting from the integrated effects of climate and living organisms acting upon parent material, as conditioned by topography, over periods of time” or, in a simplest way, as “a dynamic natural body composed of mineral and organic solids, gases, liquids, and living organisms”. Thus, soil is a dynamic resource formed by an abiotic and a biotic component. The abiotic component includes different sized mineral particles (sand, silt, and clay) and the organic matter. The biotic components are living organisms, including populations of plants, animals, and microorganisms (bacteria and fungi), which differ in size, number, habits, life-cycles, food sources, etc. Thus, soil has biological, chemical, and physical properties, which are in general, dynamic and respond to changes that may occur [5].

I.2. Soil pollution:

A soil should be considered contaminated when it is unfit for its use due to the presence of contaminants, i.e., when it is not performing the soils services expected for that land use. The simple presence of compounds with an anthropogenic origin or of levels above the background does not necessarily mean that the soil is polluted. It is important to assess the degree of contamination and whether the risk is acceptable or not [5].

I.2.1. Types of contaminants:

There are several chemicals that may pollute soils, ranging from simple inorganic ions to complex organic molecules, and two major groups of pollutants may be defined: inorganic and organic. The inorganic contaminants include metals (e.g., Cd, Cr, Cu, Hg, Mn, Ni, Pb, V, and Zn), metalloids (e.g., As, Bo, and Sb), non-metals (e.g., Se), actinoids (e.g., U), and halogens (e.g., I and F). Some of these elements are essential for life and they are considered micronutrients (beneficial in small quantities, but toxic when exceeding certain thresholds e.g., B, Cl, Cu, Fe, Mn, Mo, and Zn); while others are considered toxic elements (toxic at all concentrations, e.g., Hg, As, and Tl). Some elements tend to form organometallic compounds which are lipophilic and highly toxic (e.g., methylmercury and tributyltin oxide). All these elements are ubiquitous in the environment and most of them occur at concentrations less than 100 mg/kg, and in this case, they are considered trace elements. Other elements typically occur at higher concentrations and they are named major elements (e.g., Al, Ca, Fe, and Na). However, in geochemistry the limit to distinguish a trace element from a major element is 1000 mg/kg. Considering this, it is easy to understand that call these contaminants heavy metals, toxic metals, trace metals, or even trace elements may be inaccurate. Thus, these elements are often referred as potentially toxic elements (PTEs). PTEs are natural substances which are present on the Earth since its formation [5].

I.2.2. Origin and sources of soil pollution:

The origin of contaminants in the ecosystems may be natural or anthropogenic. Natural processes that result in an input of pollutants can be the weathering of orebodies (inorganic pollutants), volcanic activity or forest fires (inorganic and organicpollutants). Nevertheless, in most cases, soil pollution is a result of human activity (deliberate or accidental). Deliberate soil pollution includes mining, smelting, disposal of wastes, fossil fuel combustion, gas works, industries, sports shooting, military training, and application of agrochemicals or sewage. Accidental pollution can occurdue to nuclear accidents, flooding by rivers or seas, leaks from landfills, or accidental spills [5].

I.3. Heavy metals:

I.3.1. Definition:

Although the term "heavy metals" is widely used, even in the scientific literature, it has no real scientific or unanimously recognized legal definition. From a purely chemical point of view, the elements of the periodic table that form cations in solution are metals. From a physical point of view, the term "heavy metals" refers to natural metallic elements, metals or in some cases metalloids, characterized by a high density greater than 5 g/cm^3 [6]. From another biological point of view, we distinguish two types according to their physiological and toxic effects: essential metals and toxic metals:

I.3.1.1. Essential metals: They are essential trace elements for many cellular processes and are found in very low proportions in biological tissues. Some can become toxic when the concentration exceeds a certain threshold. This is the case of Cu, Ni, Zn, Fe. For example, Zn, at a concentration of one mill molar, is a trace element which is involved in numerous enzymatic reactions (dehydrogenases, proteinase, and peptidase) and plays an important role in the metabolism of proteins, carbohydrates and lipids [1].

I.3.1.2. Toxic metals: They have a polluting nature with toxic effects for living organisms even at low concentrations. They have no known beneficial effect for the cell. This is the case of Pb, Hg and Cd [1].

The term heavy metals also implies a notion of toxicity. However, the term “metallic trace elements” is also used to describe these same elements, because they are often found in very small quantities in the environment [7].

I.3.2. Origins of heavy metals:

The main problem with heavy metals like lead, cadmium, copper and mercury is that they cannot be biodegraded, and therefore persist for long periods in soils. Their presence in soils can be natural or anthropogenic (Figure 01) [8].

In comparison to the natural flow of metallic trace elements in the environment, the anthropogenic flow is of the same order of importance (Table 01). However, the natural flow is carried out across the globe while the anthropogenic flow is more geographically concentrated [1].

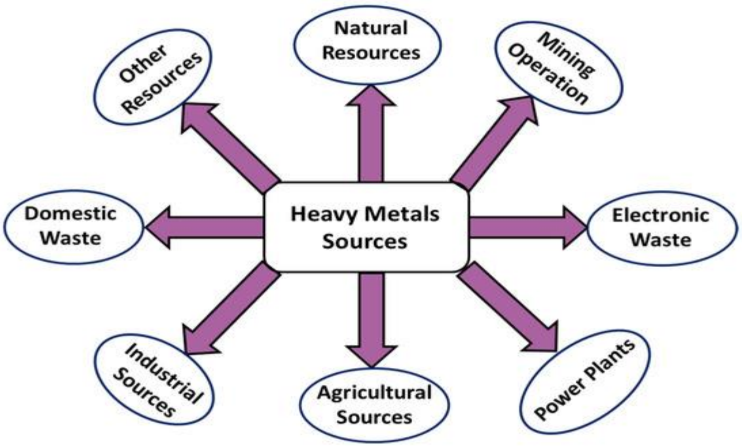

Figure 1: Sources of heavy metals in soils.

Table1: Flux of trace elements in the environment (tonne/year) [9].

Element	Anthropogenic flow	Natural flow
As	150	80
Cd	43	4.5
Cr	7810	810
Cu	9162	375
Pb	3665	180
Hg	17.8	0.9
Ni	1134	255
Zn	7467	540

I.3.2.1. Natural origin:

Heavy metals are naturally present in rocks, they are released during the alteration of these to constitute the geochemical background [10]. The natural concentration of these heavy metals in the soil varies according to the nature of the rock, its location and its age [1].

Important natural sources include volcanic activity, continental weathering and forest fires. The contribution of volcanoes can be in the form of emissions voluminous due to explosive activity, or continuous low-volume emissions, resulting in particular from geothermal activity and the degassing of magma [11].

I.3.2.2. Anthropogenic origin:

The concentrations measured in the soil are mainly linked to emissions of anthropogenic origin. Over the past few decades, the input of heavy metals to soil around the world has increased; at present it is estimated at 22,000 tons of cadmium, 939,000 t of copper, 783,000 t of lead, and 1,350,000 t of zinc. However, it should be noted that between 1990 and 2007, the emissions of certain heavy metals fell sharply, in particular lead (-97%) due to its suspension in gasoline, chromium (-90%), Zinc (-86%) and Mercury (-70%). Only copper emissions have decreased by only 4.5% due to the road and rail traffic which continues to increase [1].

I.4. The behaviour of metallic trace elements in the soil:

MTEs are bound to different soil constituents and are present in different chemical forms. They can change form (more or less soluble) or migrate to other soil constituents or to the liquid phase depending on the physico-chemical conditions [1].

These changes make MTE more or less mobile in soils and more or less available for the biosphere [1].

I.4.1. Speciation:

The term speciation has been used in soil and sediment chemistry and refers to the chemical and structural form in which a metallic element is found. Speciation has been defined as the determination of a specific form (monoatomic or molecular) or the configuration according to which an element can be present in a group of atoms corresponding to different matrices. In the environment, MTEs are found in different chemical forms and measuring the total concentration of these MTEs is not sufficient to determine their reactivity, mobility, bioavailability and toxicity. These facts explain the major interest that is given to the quantification of certain bioavailable or very toxic chemical forms of MTE [1].

I.4.2. Mobility:

The mobility of an element is characterised by its ability to pass through soil compartments where it is less and less strongly retained. MTEs are associated with soil constituents that control their mobility. They can be adsorbed on the hydroxide phases of iron, aluminium and manganese, or included in the crystal lattices of primary minerals and constituents secondary, or adsorbed on organic matter. The distribution of metals and metalloids in these different soil compartments and all the forms available do not necessarily present environmental risks. Variations in physico-chemical conditions (pH, temperature, ionic strength, etc.) can directly affect the mobility of elements by changing the metals present in a soil from one form to another. This change therefore involves biogeochemical mechanisms of mobilisation, immobilisation and transport. These mechanisms depend on dissolution/precipitation, desorption/adsorption and complexation processes which involve biological, chemical and physico-chemical reactions. Indeed, the mobility and bioavailability of MTE strongly depend on their chemical speciation in soils. However, the exact determination of chemical speciation is often difficult and in most cases impossible [1].

I.4.3. Bioavailability:

Bioavailability refers to the ability of a quantity of an element present in the soil to be absorbed by a living organism. Bioavailability is a tool for assessing toxicity and the risk of pollution. A change in the bioavailability of a pollutant corresponds to a change in toxicity. The phytoavailable quantity of an element in a soil corresponds to the MTE capable of going into solution and being absorbed by the plant. Indeed, the ion in free form (Zn^2+, Cu^2+, Pb^2+, Cd^2+, etc.) is one of the most reactive forms, with neutral species and the most easily assimilated by living organisms. The risks associated with MTEs for the environment and human health will therefore have to be assessed through their speciation, their mobility and their bioavailability, which are the main factors conditioning their toxicity [1].

I.5. Factors influencing the mobility of heavy metals in the soil:

The chemical forms of trace elements (speciation), their interactions and associations with the various constituents of the soil (pH, clays, oxy-hydroxides, carbonates, cation exchange capacity and organic matter) determine their bioavailability for plants as well as their mobility by transfer to the soil solution [12].

I.5.1. pH: The influence of pH on the mobility of metallic elements in the soil has been highlighted by numerous studies. The majority of metallic elements is more mobile in acidic conditions than in alkaline conditions: lowering the pH promotes the mobility of metallic elements, in particular by dissolving metallic salts, whereas, on the contrary, increasing the pH causes the immobilisation of metallic elements by the formation of insoluble compounds. In soils with acidic pH, most of the potential binding sites are occupied by protons, so the metals are free and mobile. On the other hand, when the pH increases to become alkaline or even basic, the competition of the metallic elements with the protons, in lower numbers, decreases: the binding sites are occupied by the metallic elements and therefore immobilised [1].

I.5.2. The oxidation-reduction potential (Eh): Soils are subject to variations in oxidation-reduction potential which mainly affect the major elements but also certain TEs. Oxidation-reduction reactions can have an important action on certain elements whose toxicity varies greatly with the chemical form (speciation). The mobility of trace elements increases in reducing conditions, such as in poorly aerated soils. For example, under reducing conditions, Mn is present in the Mn(II) form which is the most soluble form. Under oxidative conditions, Mn(II) is oxidised to Mn(III) and Mn(IV), which are present mainly in insoluble hydroxides and oxides, thus decreasing the mobility of Mn. Under reducing conditions, the mechanisms involved are the conversion of soluble species into gaseous species (denitrification or methanization), the dissolution of soil matrix components (such as Mn and Fe oxides) and the modification of speciation elements. The solubility of Cd, Pb and Zn is affected indirectly by Eh and pH, especially with the dissolution of Fe and Mn oxy-hydroxides under reducing conditions. At stable pH, reducing conditions have been shown to lead to the dissolution of Fe-Mn oxides, which increased the mobility of Cd, Pb and Zn [1].

I.5.3. Biological activity: The overall understanding of biological phenomena affecting the solubility of metals in soils is made difficult by the multiplicity of actions and interactions at all levels. The main phenomena of action on the mobility of metallic pollutants are [1]:

- Solubilization: comes from the production of acidic compounds such as carboxylic, aliphatic, nitric and sulfuric acids. Certain chemolithotrophic bacteria (Thiobacillus, Leptospirillum) oxidise the reduced forms of iron and sulphur contained in the sulphides and produce sulfuric acid, capable of dissolving the silicates, phosphates, oxides and sulphides, thus releasing the metals contained. Fungi and plant roots also excrete acids to increase their nutrient uptake, or simply as metabolic waste. This acidification also promotes the mobility of other elements that are not essential for plant metabolism [1].

- Insolubilization is the opposite phenomenon. Although the phenomenon of external detoxification of metals by root exudates has never been demonstrated. certain organic acids of low molecular weight, such as oxalic, citric or fumaric acids which are involved in the intracellular complexation of nutrient elements, can be secreted into the external environment. They would thus limit transfers by complexation processes [1].

- Volatilization: based on the direct action of certain microorganisms on the degree of oxidation of the metallic species. This is the case of mercury, arsenic and selenium. Bio methylation allows the transfer of methyl groups directly to the atoms, Pb (lead), Sn (tin), Sb (antimony), allowing their volatilization in the atmosphere [1].

I.5.4. Temperature: The soil's temperature depends primarily on the meteorology, and therefore of the climate, but it is also linked to biological activity and retroactively influences the formation of complexes with inorganic ligands, by modifying the activity of the element in solution. Temperature has a direct impact on the mobility of elements metals by shifting the equilibria of dissolution reactions - precipitation and co-precipitation, and an indirect impact, by modifying the water content of the soil, the pH or the redox potential (Eh) [1].

I.6. Toxicity of Heavy Metals:

Heavy metals become toxic when they are not metabolised by the body and accumulate in the soft tissues. Toxicity of heavy metals refers to the harmful effects that result from exposure or consumption of excessive amounts or more than the daily recommended limits. Although individual metals exhibit specific signs of toxicity, the general signs associated with cadmium, lead, arsenic, cobalt, Nickel, zinc, copper, and aluminium poisoning include gastrointestinal disorders, diarrhoea, stomatitis, tremor, hemoglobinuria, ataxia, paralysis, and vomiting, and convulsion, depression, and pneumonia when vapours and fumes are inhaled [13] (Table 2).

Table2: Classification of some heavy metals according to their density and toxicity [6].

HMs	**Plants**	**Animals**	**Density (g/cm^3)**
Cd	T	T	8.65
Cr	-	E	7.20
Cu	E	E	8.92
Ni	T	E	8.90
Pb	T	T	11.34
Zn	E	E	7.14
Mn	E	E	7.20

T : toxic**, E :** essential**.**

I.7. Presentation of the heavy metals considered in this study:

I.7.1. Cadmium:

Cadmium is located at the end of the second row of transition elements with atomic number 48, atomic mass 112.4. Cadmium is a silver-white metal (slightly bluish), very malleable and ductile (Figure 2). It is a fairly rare chemical element in nature. It is found in the soil in the following chemical forms: Cd^{2+}, $CdSO_4$, $CdCl^{+}$, $dHCO^{3+}$, CdO, CdCO3, d(PO4)2, CdS [1].

Anthropogenic sources add 3–10 times more cadmium to the atmosphere than natural sources. Chronic exposure to the metal can lead to kidney disorders, anaemia, emphysema, anosmia (loss of sense and smell), cardiovascular diseases, renal problems, and hypertension[12].

Figure 2: Cadmium element.

I.7.2. Lead (Pb):

Lead is a metal belonging to group iv and period 6 of the periodic table with atomic number 82, atomic mass 207.2 (Figure 3). Indeed, in the soil, it is found in the following chemical forms: Pb^{2+}, $PbHCO^{3+}$, $PbOH^{+}$, $PbSO_4$, $Pb(OH)_2$, $PbCO_3$, PbO, $Pb(PO_4)_2$, $PbO(PO_4)_2$, $PbCl^{+}$ [1].

The main sources of Pb in the environment include, dust from leaded paints from older houses, leaded and tap water from soldered pipes [1]. Lead is probably the least mobile of the heavy metal and has low bioavailability, but due its long residence time in the soil it can be of environmental concern if the levels are high [12]. Lead has a negative influence on humans, as it reduces physical growth and mental growth. The intelligent quotient of children is diminished. Pregnant woman exposed to Pb can affect physical growth and can cause anaemia, kidney damage and headache [12].

Figure 3: Lead element.

I.7.3. Copper (Cu):

Copper is a transition metal that belongs to period 4 and group IB of the periodic table with atomic number 29, atomic mass 63.5 (Figure 4). Indeed, their chemical forms present in thesoil are: Cu^2+; $CuOH^+$; $Cu(OH)_2$; CuO; $CuCO_3$; Cu-O-Fe; Cu-O-Al; Cu-O-Mn [1].

This metal usually comes from the corrosion of distribution pipes. Also from industrial pollution and agricultural treatment [1].

At the toxicological level, soluble copper salts are toxic by ingestion. They can cause severe poisoning with vomiting and dysenteric syndrome resulting in collapse. The inhalation of copper fumes is responsible for the "smelter fever" which is accompanied by fatigue, diffuse pain and headaches [1].

Figure 4: Copper element.

I.7.4. Zinc (Zn):

Zinc is a transition metal with the following characteristics: period 4, group IIB, atomic number 30, atomic mass 65.4 (Figure 5). It is found in the following chemical forms: Zn^{2+}, $ZnSO_4$, $ZnHCO^{3+}$, $ZnCO_3$, $ZnFe_2O_4$, Zn_2SiO_4, $Zn_3(PO_4)_2$ Zn^{2+}, $ZnSO^4$, $ZnHCO^{3+}$, $ZnCO_3$, $ZnFe_2O_4$, Zn_2SiO_4, Zn_3 $(PO_4)_2$ [1].

Zinc is used in many fields. In metallurgy, printing, dyeing, matches, pesticides and animal feed. Zinc poisoning occurs especially during exposure to strong zinc vapours. In this case, one can contract “metal fever” which is characterized by irritation of the respiratory tract, a flu-like state, skin lesions and a dysregulation of the immune system. The bioaccumulation potential of zinc is quite low and no data on chronic toxicity, carcinogenic potential or possible reproductive effects in humans have been collected [1].

Figure 5: Zinc element.

I.7.5. Mercury (Hg):

Mercury is a metal belonging to group 12and period 6 of the periodic table with atomic number 80, atomic mass 200.59. it found in the following chemical forms: Hg^{2+}, $HgCl_2$. Mercury is known as quicksilver and was named hydrargyrum. It is usually used in thermometers, barometers, manometers. Mercury (Hg) is naturally ubiquitous in the earth's crust, present in rocks, soils and sediments. An unpolluted soil may contain up to 200 µg/kg Hg [14]. Mercury possess high toxicity, bioaccumulation and non-degradability (Figure 6).

Figure 6: Mercury element.

Chapter II

Methods for remediation of heavy metals in contaminated soils

Preface

At many sites around the nation, heavy metals have been mined, smelted, or used in other industrial processes. The waste (tailings, smelter slag, etc.) has sometimes been left behind to pollute surface and ground water. The heavy metals most frequently encountered in this waste include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which pose risks for human health and the environment. Clean up (or remediation) technologies available for reducing the harmful effects at heavy metal-contaminated sites include excavation (physical removal of the contaminated material), stabilization of the metals in the soil on site, and the use of growing plants to stop the spread of contamination or to extract the metals from the soil (phytoremediation) [15].

II.1. Remediation of Heavy Metals in Contaminated Soils:

Heavy metal in soil readily accumulates in plants and then transported through the food chain, thus becoming a major threat to human health. The overall objective of any soil remediation approach is to create a final solution that is protective of human health and the environment. Remediation is generally subject to an array of regulatory requirements and can also be based on assessments of human health and ecological risks where no legislated standards exist or where standards are advisory. For heavy metal-contaminated soils, the physical and chemical form of the heavy metal contaminant in soil strongly influences the selection of the appropriate remediation treatment approach. Information about the physical characteristics of the site and the type and level of contamination at the site must be obtained to enable accurate assessment of site contamination and remedial alternatives [12].

II.2. Methods for remediation:

The contamination in the soil should be characterized to establish the type, amount, and distribution of heavy metals in the soil. Once the site has been characterized, the desired level of each metal in soil must be determined [13]. These techniques are often used in combination with each other for more economical and efficient remediation of a contaminated site [12].

II.2.1. Physical Remediation: The physical remediation mainly includes soil replacement method and thermal desorption. The former relies on the use of clean soil to fully or partly replace the contaminated soil with the aim of diluting the pollutant concentration and increasing the soil environmental capacity for the remediation [16].

II.2.1.1. Soil Excavation: the process involves replacing the contaminated soil with new soil. This method is suitable for treatment of small-scale contamination. Excavation and physical removal of the soil is perhaps the oldest remediation method for contaminated soil. It is still in use at many locations, including residential areas contaminated with heavy metals. Advantages of excavation include the complete removal of the contaminants and the relatively rapid cleanup of a contaminated site. Disadvantages include the fact that the contaminants are simply moved to a different place, where they must be monitored; the risk of spreading contaminated soil and dust particles during removal and transport of contaminated soil; and the relatively high cost. Excavation can be the most expensive option when large amounts of soil must be removed or disposal as hazardous or toxic waste is required [12].

II.2.1.2. Soil spading: The process involves deeply digging the contaminated soil, inducing the pollutant spread into the deep sites to achieve dilution and natural degradation [12].

II.2.1.3. New soil importing: Involve adding a large amount of clean soil into the contaminated soil, covering the surface (or mixing) to reduce pollutant levels. Soil replacement can effectively isolate the soil and ecosystem, thus decreasing the effect of pollutants on the environment. This technology is costly and suitable just for soil in small areas [12].

II.2.1.4. Soil isolation: Soil isolation means to separate the heavy metals contaminated soil from the uncontaminated soil, but for complete remediation it still needs other auxiliary engineering measures. Isolation technologies are generally designed to prevent off-site movement of heavy metals and other contaminants by restricting them within a specified area. Soil isolation technology is used to avoid further contamination of groundwater by heavy metals when other remediation methods are not economically or physically feasible. In some cases, contaminated sites are isolated temporarily in order to avoid transport during site assessment and remediation [12].

II.2.2. Thermal desorption: The process involves heating the contaminated soil using steam, microwaves, and infrared radiation to volatilize the pollutants such as mercury (Hg) and Arsenic (As) [17].

II.2.2.1. Vitrification Remediation: The mobility of heavy metals inside soil can be reduced by applying high temperature treatment at the contaminated site that leads to the formation of vitreous material. During vitrification, some metal species (Hg) may be volatilized under high temperature that must be collected for further disposal or treatment. Vitrification is not considered a classical metal remediation technique but the process is comparatively easy to apply compared to other physical remediation methods. Vitrification can be applied to majority of soils contaminated with inorganic (heavy metals) and organic contaminants. During in situ vitrification, electric current is passed through the soil by vertically inserting an array of electrodes into the contaminated area. However, dry soil may not provide enough conductances for vitrification. The process may not be appropriate for sites where contaminated soil exists directly to buildings, other structures, or the property line [12].

II.2.2.2. Electrokinetic Remediation: Soil electrokinetic remediation is a new and cost effective physical method for the remediation of heavy metals. Soil electrokinetic remediation operates on the principle that the electric field gradient of suitable intensity is established on two sides of the electrolytic tank containing saturated contaminated soil. Heavy metals present in the soil are separated via electrophoresis, electric seepage or electro migration, and thus decrease the contamination. The method performs well in the soil with low permeability, while being advantageous to easily install, operate, and undestroyed the original natural environment at low cost [12].

II.2.3. Chemical Remediation: Chemical remediation involves the use of chemicals to extract or stabilize pollutants in contaminated media. There are several chemical remediation methods including chemical leaching (soil washing), immobilization techniques and stabilization method [12].

These techniques either remove risk by chemically degrading hazardous substances or achieve stabilization of the contaminants within the bulk matrix by breaking pollutant linkages [12].

II.2.3.1. Soil washing: The principle of soil leaching is to wash the heavy metal contaminated soil with specific reagents and thus remove the heavy metal complex and soluble irons adsorbed on the solid phase particles. By using this method, heavy metals are separated from the soil and heavy metals are then recycled from extracting solution. Chemical leaching consists of washing the contaminated soil with fresh water, reagents and other fluids (or gas) to leach pollutants from the soil. The process is cost effective because it can reduce the quantity of material that would require further treatment [12].

II.2.3.2. Immobilization Techniques: Chemical fixation is adding reagents or materials into the contaminated soil to form insoluble or hardly movable, low toxic matters; it can thus decrease the migration of heavy metals to water, plant, and other environmental media. If the soil immobilization technique is employed, simplicity and rapidity (besides high public acceptability) will be achieved. This method is relatively inexpensive, while covering a broad spectrum of inorganic pollutants. However, immobilization is only a temporary solution (contaminants are still in the environment), the activation of pollutants may occur when soil physicochemical properties change. Hence, the reclamation process should be applied only to the surface layer of the soil (30–50 cm), and permanent monitoring is necessary. Heavy metals immobilization in soil is generally carried out by using organic and inorganic amendment to soils [12].

II.2.3.3. Solidification/Stabilizing: Heavy metals can be left on site and treated in a way that reduces or eliminates their ability to adversely affect human health and the environment. This process is sometimes called stabilization. Eliminating the bioavailability of heavy metals on site has many advantages over excavation. One way of stabilizing heavy metals consists of adding chemicals to the soil that cause the formation of minerals that contain the heavy metals in a form that is not easily absorbed by plants, animals, or people. This process does not disrupt the environment or generate hazardous wastes. Instead, the heavy metal combines with the added chemical to create a less toxic compound. The heavy metal remains in the soil, but in a form that is much less harmful [12].

II.2.4. Biological Remediation: Bioremediation is a technology that uses microorganisms to treat contaminants through natural biodegradation mechanisms (intrinsic bioremediation) or through the enhancement of such capacity with the addition of microbes, nutrients, electron donors, and/ or electron acceptors (enhanced bioremediation). The microorganisms cannot degrade or destroy the heavy metals but can affect the migration and transformation by changing their physical and chemical characterizations. The process is ecologically safe and natural, and is generally 60–70% less costly than other technologies. Bioremediation is vulnerable to variables such as temperatures, oxygen, moisture, and pH value. Its applications can also be limited to some microorganisms that can only degrade special contaminants [18].

II.2.4.1. Phytoremediation: Phytoremediation basically refers to the use of plants and associated microorganisms to partially or completely remediate selected contaminants from soil, sludge, sediments, wastewater and groundwater. It can be used for removal of radionuclides, organic pollutants as well as heavy metals. Phytoremediation utilizes a variety of plant processes and the physical characteristics of plants to aid in remediation of contaminated sites. Over the recent years, a special emphasis has been placed on phytoremediation since this property can be exploited for remediation of heavy metal polluted soils [12].

II.2.4.2. Phytoextraction: The initial step of phytoremediation is phytoextraction, the uptake of contaminants from soil or water by plant roots and their translocation to and accumulation in biomass, i.e., shoots. Translocation of metals to shoots is an important biochemical process and is desirable in an effective phytoextraction. Some plant species can take up heavy metals and concentrate them in their tissue. The plants can be harvested and the contaminated plant material disposed of safely. Sometimes soil amendments are added to the soil to increase the ability of the plants to take up the heavy metals [12]. Phytoextraction is done with plants called hyper accumulators, which absorb unusually large amounts of metals in comparison to other plants. Phytoextraction is no doubt a publicly appealing green technology [12].

II.2.4.3. Phytostabilization: The process involves reducing the mobility and bioavailability of metals in the environment and thus prevents their migration into groundwater or the food chain. The plants are used to reduce wind and water erosion that spread materials containing heavy metals. If all of the ground could be re-vegetated, sediment loss could be cut by approximately 70%. However, it would be necessary to find plants that could tolerate high levels of heavy metals [12].

II.2.4.4. Phytofiltration: The next important process of phytoremediation is phytofiltration, which includes rhizofiltration (use of plant roots), blastofiltration (use of seedlings) or caulofiltration (use of excised plant shoots). In this, the metals are absorbed or adsorbed and thus their movement in underground water is minimized. Heavy metals are removed directly from water by plant roots. The plants are grown directly in water or in water rich materials such as sand, using aquatic species or hydroponic methods [12].

***Chapter* III**

Analyzing and discussing previous studies

Preface

Soil is the most important ecosystem because it affects the rest of the systems. Soil contamination, especially with heavy metals, is a concern because it may enter the food chain and harm humans. Heavy metals may enter the soil through soil-forming rocks, or from some human activities such as industrial waste, transportation or agricultural practices. This led to a quest for innovation and development of methods for the disposal of these heavy metals. Where we proposed the analysis of some previous studies that study methods of treating soils contaminated with heavy metals.

By searching for previous studies that include methods for remediation of heavy metals contaminated soils , we have found that science has a growing interest in this field. This is due to the dangerous of these metals in the soil. This histogram shows the increase in the number of publication over the past years regarding the remediation of heavy metals contaminated soil (Figure 7).

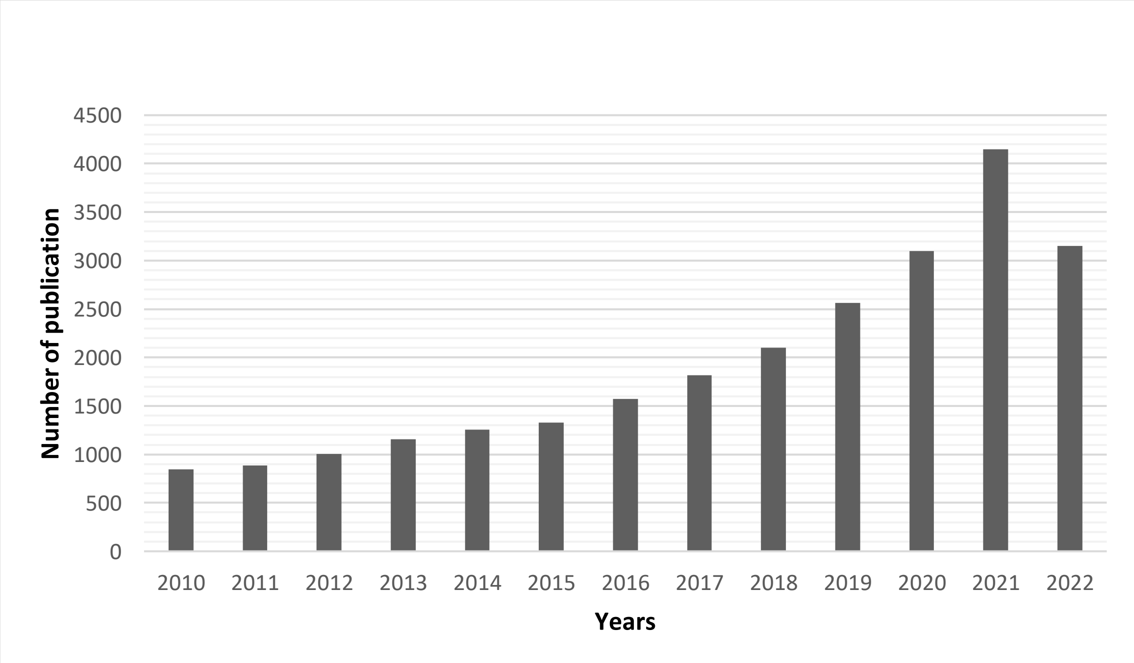

Figure 7: A histogram showing the number of publications on methods for remediation of heavy metals-contaminated soil during the last years (science-direct)[19].

III.1. Analysis and discussion of previous studies:

III.1.1. Cadmium (Cd):

Analytical study N° (01): Scientific article entitled:

"Effectiveness and longevity of amendments to a cadmium-contaminated soil" [20].

This study investigated the long-term effectiveness of amendments in Cd-contaminated soil. The results obtained are in the following table:

Table3: Method for remediation of lead-contaminated soil in Dezhou (DZ) City, Shandong Province, China.

Journal	Journal of Integrative Agriculture.
Authors	ZHAO Rui, LÜ Yi-zhong, MA Yi-bing, LI Ju-mei.
Article history	Accepted 11 September, 2019.
Study site	Dezhou (DZ) City, Shandong Province, China.
Treatment method	In situ remediation.
Soil type	Agricultural soil.
Ways to sample	0–20 cm depth.
Content of metal in the soil	0.11 mg/kg.

Abstract:

Evaluation of the effectiveness and longevity of amendments in the reduction in cadmium (Cd) bioavailability by in situ remediation techniques. Different amendments, including red mud (RM), corn straw (CS), rape straw (RS), and their combinations with zinc (Zn) fertilizer, were evaluated based on a long-term field experiment. It was resulted that RM, CS, RS, and their combinations with Zn fertilizer as effective amendments can have a profound and lasting positive impact on Cd-contaminated soils.

Analytical study N° (02): Scientific article entitled:

"Effects of inorganic and organic amendments on physiological parameters and antioxidant enzymes activities in Zea mays L. from a cadmium-contaminated calcareous soil" [21].

This essay aimed to evaluate the mechanisms and efficacies of emerging amendments on cadmium immobilization in a contaminated calcareous soil. The results obtained are in the following table:

Table4: Method for remediation of lead-contaminated soil in Northeast of Iran.

Journal	South African Journal of Botany.
Authors	S. Sefidgar Shahkolaie, M. Baranimotlagh, E. Dordipour, F. Khormali.
Article history	Available online 14 November 2019.
Study site	Northeast of Iran.
Treatment method	Chemical stabilization.
Soil type	Calcareous soil.
Ways to sample	0-20 cm depth.
Content of metal in the soil	150 mg/kg.

Abstract:

Investigating the effectiveness of various amendments and selected low cost amendments on Cd stabilization through testing their potential to decrease soil Cd bioavailability. The result showed that there is a good potential for using various inexpensive amendments to remediate a calcareous soil that is highly polluted with Cd.

Analytical study N° (03): Scientific article entitled:

" Physiological stress responses, mineral element uptake and phytoremediation potential of Morus albaL. in cadmium-contaminated soil" [22].

This dissertation examined the role of using Morus alba L. for remediation of Cd contaminated soil. The results obtained are in the following table:

Table5: Method for remediation of lead-contaminated soil in Changsha city, Hunan Province, China.

Journal	Ecotoxicology and Environmental Safety.
Authors	Peng Zeng, Zhaohui Guo, Xiyuan Xiao, Chi Peng, Lingqing Liu, Demei Yan, Yalei He.
Article history	22 November 2019.
Study site	Changsha city, Hunan Province, China.
Treatment method	Phytoremediation method.
Soil type	Agricultural soil.
Ways to sample	0 and 20 cm depth.
Content of metal in the soil	1.56 mg/kg.

Abstract:

Application of Fast growing woody plants for phytoremediation of contaminated soil. The results indicated that M. alba L. can be regarded as a potential Cd accumulator for phytoremediation in contaminated sites.

Analytical study N° (04): Scientific article entitled:

" In-situ immobilization of copper and cadmium in contaminated soil using acetic acid-eggshell modified diatomite" [23].

This monograph strived to illuminate the idea of immobilization of Cd in contaminated soil by AEMD. The results obtained are in the following table:

Table6: Method for remediation of lead-contaminated soil in Changsha city, China.

Journal	Journal of Environmental Chemical Engineering.
Authors	Chiyue Huang, Hongli Huang, Pufeng Qin.
Article history	Accepted 3 April 2020.
Study site	Changsha city, China.
Treatment method	Immobilization method.
Soil type	Agricultural soil.
Ways to sample	A depth of 20 cm.
Content of metal in the soil	1.83 mg/kg.

Abstract:

Industrial purified diatomite modified for in-situ immobilization of cadmium in contaminated soil. The results showed that AEMD can be applied for the immobilization of HMs in contaminated soil.

Analytical study N° (05): Scientific article entitled:

"A novel remediation method of cadmium (Cd) contaminated soil Dynamic equilibrium of Cd^{2+} rapid release from soil to water and selective adsorption by PP-g-AA fibers-ball at low concentration" [24].

This paper aimed to eliminate the risk of Cd(II) in soil by using PP-g-AA fibers-ball. The results obtained are in the following table:

Table7: Method for remediation of lead-contaminated soil in Hunan province, China.

Journal	Journal of Hazardous Materials.
Authors	Kaijian Zou, Junfu Weia,c, Di Wanga,e, Zhiyun Kong, Huan Zhang, Huicai Wang.
Article history	Available online 24 April 2021.
Study site	Hunan province, China.
Treatment method	Adsorption method.
Soil type	/
Ways to sample	0–20 cm depth.
Content of metal in the soil	/

Abstract:

Preparing Carboxylated polypropylene PP-g-AA fibers-ball with high selectivity by irradiation grafting methods. After PP-g-AA fibers-balls were added to the contaminated soil-water system, a migration pathway of the acid-extractable fraction Cd(II) to be released from soil to water and simultaneously adsorbed on the surface of PP-g-AA fibers-ball. The results showed that More than 90% the acid- extractable fraction Cd(II) could migrate to the surface of PP-g-AA fibers-ball by the pathway.

Analytical study N° (06): Scientific article entitled:

"Immobilization of cadmium in contaminated soils using sulfidated nanoscale zero-valent iron Effectiveness and remediation mechanism" [25].

This treatise investigated in the efficiency of sulfidated nanoscale zero-valent iron in reducing of Cd in the soil. The results obtained are in the following table:

Table8: Method for remediation of lead-contaminated soil in Guangzhou, China.

Journal	Journal of Hazardous Materials.
Authors	Yiqing Guo, Xiaoqin Li, Li Liang, Zhang Lin, Xintai Su, Wenchao Zhang
Article history	Available online 7 July 2021.
Study site	Guangzhou, China.
Treatment method	Immobilization method.
Soil type	/
Ways to sample	/
Content of metal in the soil	49.5 mg/kg.

Abstract:

Evaluating the effectiveness of S-nZVI for the remediation of Cd in soil through sequential extraction procedures (SEP). it found that S-nZVI was a promising amendment to remediation Cd contaminated soil.

Analytical study N° (07): Scientific article entitled:

"Novel agricultural waste-based materials decrease the uptake and accumulation of cadmium by rice (Oryza sativa L.) in contaminated paddy soils" [26].

This thesis examined the role of using organic amendments in immobilization of cadmium in paddy soils.The results obtained are in the following table:

Table9: Method for remediation of lead-contaminated soil in Taizhou, Zhejiang province, China**.**

Journal	Environmental Pollution.
Authors	Guofei Liu, Jun Meng, Lingzao Zeng, Xingmei Liu, Zhongmin Dai, Caixian Tang, Jianming Xu.
Article history	Available online 26 July 2021.
Study site	Taizhou, Zhejiang province, China.
Treatment method	Immobilization method.
Soil type	Agricultural soil.
Ways to sample	0–20 cm depth.
Content of metal in the soil	3.75 mg/kg.

Abstract:

Using the raw sugarcane bagasse (SB) and two sugarcane bagasse materials modified with citric-acid (SSB) and citric-acid/Fe_3O_4 (MSB) to study their effects on plant uptake and the immobilization and transformation of Cd in soil. The results showed that the functional groups in the amendments (-OH, –COOH, C–O, -COO- and Fe–O) and precipitates [$Cd(NO_2)_2K(NO_2)_2$, $Cd(OH)_2$ and $Cd_{75}Zn_{25}Fe_2O_4$] played active roles in Cd immobilization.

Analytical study N° (08): Scientific article entitled:

"Plant microbial fuel cells with Oryza rufipogon and Typha orientalis for remediation of cadmium contaminated soil" [27].

This study tested the idea of using plant microbial fuel cell (PMFC) to treat Cd contaminated soil. The results obtained are in the following table:

Table10: Method for remediation of lead-contaminated soil in Taiwan.

Journal	Environmental Technology & Innovation.
Authors	Natagarn Tongphanpharn, Chih-Huang Chou, Chung-Yu Guan, Chang-Ping Yu.
Article history	Available online 19 October 2021.
Study site	Taiwan.
Treatment method	Biological treatment.
Soil type	Agricultural soil.
Ways to sample	/
Content of metal in the soil	/

Abstract:

The wetland plants, cattail (Typha orientalis), and wild rice (Oryza rufipogon) were utilized in PMFCs to compare the effects of different plants under closed and open-circuit during 150 days. It was resulted that The cattail PMFCs and wild rice PMFCs can achieve 30.2% and 22.8% of Cd removal in the soil, respectively, and wild rice PMFCs containing 5% of biochar achieved the highest removal efficiency (31.7%).

Discussion:

Cadmium (Cd) is a very toxic element to life and has been involved in historic poisoning episodes of human and animal populations, as known it impacts to many organs including liver, kidney, lung and testis. Because of industrial waste and sewage sludge fertilizers Cd has become everywhere in the biosphere and it can enter the food chain. Therefore, scientists have strived to apply several techniques to remediate Cd contaminated soil.

We summarized the most important results of previous studies related to the treatment of Cd contaminated soil in this table below:

Table11: Summary of the most important previous studies for Cd.

	Study number	**Study site**	**Study history**	**Treatment method**	**Soil type**	**Removal rate (%)**
Previous studies	**01**	China	2019	In situ remediation	Agricultural	83.5
	02	Northeast of Iran	2019	Stabilization	Calcareous	/
	03	China	2019	Phytoremediation	Agricultural	/
	04	China	2020	Immobilization	Agricultural	66/65
	05	China	2021	Adsorption	/	90
	06	China	2021	Immobilization	/	97.6
	07	China	2021	Immobilization	Agricultural	/
	08	Taiwan	2021	Biological treatment	Agricultural	31.7

Through the results of previous studies studying Cd contaminated soil:

Scientific article N° 01: The results proved that this method was not very effective as it requires a very long time (may reach several years) to reach a medium removal rate.

Scientific article N° 02: This method showed that application of amendments can be effective but it should choose the cost-effective amendments.

Scientific article N° 03: The results indicated that M. alba L. can be regarded as a potential candidate for phytoremediation in Cd-contaminated sites but in a long period.

Scientific article N° 04: It was resulted that even if Cd in the soil got effective immobilization by this method but in a long period little bit.

Scientific article N° 05: We found that this method was so effective, because it can remove high concentration within a very short period.

Scientific article N° 06: We noticed great effectiveness in applying this method, especially since the used product changed to iron oxides which are excellent cadmium adsorbent. But the remediation takes a little bit long period.

Scientific article N° 07: The results showed that not all amendments were effective, despite the effectiveness of SSB, however, the addition of SB and MSB had inhibited the growth of rice plants.

Scientific article N° 08: We noticed that the cattail PMFCs and wild rice PMFCs used in this method it has not been very effective in removing cadmium.

Result:

As seen in (Table 11) we found that most studied soils were agricultural soils. Therefore, we had easily compared between the studied treatment methods and now we can conclude that the most effective treatment method was the adsorption method using PP-g-AA fibers-ball at low concentration, because removal rate reached 90% during just 12 hours.

III.1.2. Lead (Pb):

Analytical study N° (01): Scientific article entitled:

"Popular wood and sugarcane bagasse biochars reduced uptake of chromium and lead by lettuce from mine-contaminated soil" [28].

This study investigated the influence of biochar on mine-contaminated agricultural soil.The results obtained are in the following table:

Table12: Method for remediation of lead-contaminated soil in Pakistan.

Journal	Environmental Pollution.
Authors	Amir Zeb Khan, Sardar Khan, Tehreem Ayaz, Mark L. Brusseau, Muhammad Amjad Khana, JavedNawab, Said Muhammad.
Article history	Available online 2 April 2020.
Study site	Pakistan.
Treatment method	Immobilization method.
Soil type	Agricultural soil.
Ways to sample	0 to 20 cm depth.
Content of metal in the soil	44 mg/kg.

Abstract:

This study examined the efficacy of biochar for contaminated soil remediation. The results showed that the amendments of sugarcane bagasse biochar SCBB and poplar wood biochar PWB have significant impacts on mine contaminated agricultural soils.

Analytical study N° (02): Scientific article entitled:

"Removal of lead and other toxic metals in heavily contaminated soil using biodegradable chelators GLDA, citric acid and ascorbic acid" [29].

This research investigated the level of contamination of agricultural soil near an old recycling lead smelter in Vietnam and proposed an effective treatment for the remediation of the soil.The results obtained are in the following table:

Table13: Method for remediation of lead-contaminated soil in Van-Lam district, Hung-Yen province, northern Vietnam.

Journal	Chemosphere.
Authors	Nguyen Van Thinh, Yasuhito Osanai, Tatsuro Adachi, Bui Thi Sinh Vuong, Ippei Kitano, Nguyen Thuy Chung, Phong K. Thai.
Article history	Available online 19 August 2020.
Study site	Van-Lam district, Hung-Yen province, northern Vietnam.
Treatment method	Soil washing
Soil type	Agricultural soil.
Ways to sample	Four surface soil samples (0-10 cm) and two soil profiles (0-100 cm) were collected.
Content of metal in the soil	>3000mg/g.

Abstract:

Identify and optimize the combination of organic chelating agents for soil washing with the purpose of remediating the contaminated soil. Single and multiple chelating agent combinations that consist of citric acid (CA), ASC and GLDA are investigated.

The washing experiments using biodegradable chelate agents indicated that the order of Pb removal effectiveness was: GLDAASC>GLDA CA>GLDA>CA>ASC.

Analytical study N° (03): Scientific article entitled:

"Remediation of lead polluted soil by active silicate material prepared from coal fly ash" [30].

This paper analysed using of coal fly ash on the remediation of heavy metal polluted soils.The results obtained are in the following table:

Table14: Method for remediation of lead-contaminated soil in Guangdong, China.

Journal	Ecotoxicology and Environmental Safety
Authors	Chang Lei, Tao Chen, Qin-Yi Zhang, Lai-Shou Long, Zhou Chen, Zhi-Ping Fu.
Article history	Available online 01 October 2020.
Study site	Guangdong, China.
Treatment method	Immobilization method.
Soil type	Agricultural soil.
Ways to sample	The sampling depth is 0–20 cm.
Content of metal in the soil	1359.9 mg/kg.

Abstract:

Application of the active silicate material (ASM) prepared from coal fly ash in the remediation of lead polluted soil. The results showed that The Pb(II) removal efficiency by ASM reached 88.1%.

Analytical study N° (04): Scientific article entitled:

"Remediation of lead (II)-contaminated soil using electrokinetics assisted by permeable reactive barrier with different filling materials" [31].

This essay developed a new-type switchable-array-electrode electrokinetics for remediation of Pb^{2+}-contaminated soil. The results obtained are in the following table:

Table15: Method for remediation of lead-contaminated soil in Beimo Industry, China.

Journal	Journal of Hazardous Materials.
Authors	Haidong Zhou, Zhiyong Liu, Xin Li, Jiahui Xu.
Article history	Available online 18 December 2020.
Study site	Beimo Industry, China.
Treatment method	Electrokinetic method.
Soil type	/
Ways to sample	/
Content of metal in the soil	/

Abstract:

Exploring the performances of the new-type switchable-array-electrode electrokinetics by permeable reactive barrier SAE/EK-PRB on the remediation of Pb2+ -contaminated soil, focusing on the influences of different PRB filling materials. The kaolin was used as a simulated soil. The results showed that the highest removal of Pb^{+2} reached 92.6%.

Analytical study N° (05): Scientific article entitled:

"Influence of biochar and EDTA on enhanced phytoremediation of lead contaminated soil by Brassica juncea" [32].

This monograph investigated the synergistic effects of EDTA and biochar on phytoremediation of Pb contaminated soil. The results obtained are in the following table:

Table16: Method for remediation of lead-contaminated soil in Kalippatti, Tamil Nadu, India.

Journal	Chemosphere.
Authors	R. Rathika, P. Srinivasan, Jawaher Alkahtani, L.A. Al-Humaid, Mona S. Alwahibi, R. Mythili, T. Selvankumar.
Article history	Available online 31 December 2020.
Study site	Kalippatti, Tamil Nadu, India.
Treatment method	Phytoremediation technology.
Soil type	Agricultural soil.
Ways to sample	Topsoil.
Content of metal in the soil	100 mg/kg.

Abstract:

Evaluating the synergistic effect of biochar (BC) and EDTA to enhance phytoextraction of heavy metal lead (Pb) from artificially polluted soil by Brassica juncea. The results from this work showed that the combined use of BC and EDTA effective for the treatment of Pb contaminated soil.

Analytical study N° (06): Scientific article entitled:

"Choline-based deep eutectic solvent combined with EDTA-2Na as novel soil washing agent for lead removal in contaminated soil" [33].

This treatise aimed to remediate lead- contaminated soil using choline chloride and ethylene glycol. The results obtained are in the following table:

Table17: Method for remediation of lead-contaminated soil in Shanghai, China.

Journal	Chemosphere.
Authors	Kaiyou Huang, Yingjie Shen, Xiaoyan Wang, Xiaolong Song, Wenyi Yuan, Junying Xie, Shenyang Wang, Jianfeng Bai, Jingwei Wang.
Article history	Available online 20 April 2021.
Study site	Shanghai, China.
Treatment method	Washing soil.
Soil type	Agricultural soil.
Ways to sample	0-20 cm depth.
Content of metal in the soil	14,074.38 mg/kg.

Abstract:

Using ethylene-diamine-teraacetic acid disodium salt (EDTA-2Na) combined with diluted deep eutectic solvent (DES) which was prepared by mixing choline chloride with ethylene glycol for the remediation of Pb-contaminated soil. It found that the lead leaching rate reached 95.79%.

Analytical study N° (07): Scientific article entitled:

"Immobilization of high-Pb contaminated soil by oxalic acid activate incinerated sewage sludge ash " [34].

This thesis tested the idea of using ISSA and OA for effective remediation of high-Pb Contaminated soil.The results obtained are in the following table:

Table18: Method for remediation of lead-contaminated soil in Hong Kong.

Journal	Environmental Pollution.
Authors	Jiang-shan Li, Qiming Wang, Zhen Chen, Qiang Xue, Xin Chen, Yanhu Mu, Chi Sun Poon.
Article history	Available online 23 April 2021.
Study site	Hong Kong.
Treatment method	Immobilization method.
Soil type	A silty soil.
Ways to sample	/
Content of metal in the soil	5000 mg/kg.

Abstract:

The feasibility of reusing incinerated sewage sludge ash (ISSA), a waste rich in phosphorus, under activation by oxalic acid (OA) for the remediation of highPb contaminated soil was investigated. The results showed that achieving over 94% removal rates within the pH range of 3.0-9.0.

Analytical study N° (08): Scientific article entitled:

"Simultaneous extraction and recovery of lead using citrate and micro-scale zero-valent iron for decontamination of polluted shooting range soils " [35].

This dissertation investigated a modified chemical soil washing technique to decontaminate Pb-contaminated soil from a shooting range. The results obtained are in the following table:

Table19: Method for remediation of lead-contaminated soil in Japan.

Journal	Environmental Advances.
Authors	Marthias Silwamba, Mayumi Ito, Carlito Baltazar Tabelin, Ilhwan Park, Sanghee Jeon, Masao Takada, Yasushi Kubo, Naohiro Hokari, Masami Tsunekawa, Naoki Hiroyoshi.
Article history	Available online 14 September 2021.
Study site	Japan.
Treatment method	Soil washing
Soil type	A pistol shooting range.
Ways to sample	A depth of 5 cm.
Content of metal in the soil	1243–3994 mg/kg.

Abstract:

This study investigated Pb removal from polluted shooting range soil by simultaneous extraction-recovery using citrate and mZVI. Lead removal from the soil increased to 99.5% and the recovery through cementation onto mZVI increased to 99%.

Discussion:

The World Health Organization (WHO) has designated lead as one often chemicals of major public health concern. Lead can cause acute and chronic illnesses of various organ systems, affecting both children and adults. Chronic lead poisoning is more common than acute poisoning. Lead exposure can come from various sources (e.g.lead mines, smelters, refineries). Contaminated soil is often an important source of lead exposure. The remediation of lead-contaminated soil aims to minimize or eliminate the hazard, and a range of soil remediation techniques exists [36].

We try to summarize the most important results of previous studies related to the treatment of Pb contaminated soil in this table below:

Table20: Summary of the most important previous studies for Pb.

	Study number	**Study site**	**Study history**	**Treatment method**	**Soil type**	**Removal rate (%)**
Previous studies	**01**	Pakistan	2020	Immobilization	Agricultural	57
	02	Northern Vietnam	2020	Soil washing	Agricultural	42.1
	03	China	2020	Immobilization	Agricultural	88.1
	04	China	2020	Electrokinetic	/	92.6
	05	India	2020	Phytoremediation	Agricultural	/
	06	China	2021	Soil washing	Agricultural	95.79
	07	Hong Kong	2021	Immobilization	Silty	94
	08	Japan	2021	Soil washing	From shooting range	99.5

Through the results of previous studies studying Pb contaminated soil:

Scientific article N° 01: Results of the study indicated that application of SCBB at 7% rate to mine impacted agricultural soil effectively increased plant biomass and reduced bioaccumulation [28].

Scientific article N° 02: The results showed that the mixture of GLDA-ascorbic can be considered as a potential candidate for Pb removal. So this method was effective.

Scientific article N° 03: The percentage of lead inhibition was rather high and in a very short period. In addition, this study can provide a novel active silicate material for the application of coal fly ash in heavy metal pollution treatment.

Scientific article N° 04: Even if this method had a high removal rate on simulated soil but we still not sure about its effeciniety on natural contaminated soil.

Scientific article N° 05: It was resulted that combined amendments was more effective for the treatment of Pb contaminated soil as compared to individual amendments.

Scientific article N° 06: We noticed that this method was the most rapid, efficient, and eco-friendly method.

Scientific article N° 07: We found that this method was so effective but design of mix proportions must be considered.

Scientific article N° 08: We found that Lead removal from the soil the recovery through cementation onto mZVI were very high. It means that this method was so effective.

Result:

From analyzing those previous studies, and because most soils were agricultural, we can conclude that washing soil using choline chloride and ethylene glycol was the best method compared with other methods for remediation and reducing lead from contaminated soil. And that's because it was the one which has the highest removal rate at a short period, and also it was eco-friendly method. So it can uptake lead without changing the soil's characteristics.

III.1.3. Copper (Cu):

Analytical study N° (01): Scientific article entitled:

"Remediation of copper-contaminated soil by Kocuria flava CR1, based on microbially induced calcite precipitation" [37].

This dissertation examined the purpose of remediation of copper-contaminated soil. The results obtained are in the following table:

Table21: Method of remediation of copper-contaminated soil in Urumqi, China.

Journal	Ecological Engineering.
Authors	Varenyam Achal, Xiangliang Pan Daoyong Zhang.
Article history	Available online 2 July 2011.
Study site	Urumqi, China.
Treatment method	Bioremediation.
Soil type	From mining area.
Ways to sample	/
Content of metal in the soil	/

Abstract:

An extensive copper bioremediation capacity of this isolate was studied based on microbially induced calcite precipitation (MICP). And it found The introduction of this indigenous bacterium provides a potential bioremediation process to highly copper contaminated soils.

Analytical study N° (02): Scientific article entitled:

"Application of an electrochemical treatment for EDDS soil washing solution regeneration and reuse in a multi-step soil washing process Case of a Cu contaminated soil" [38].

This research tested the idea of an electrochemical treatment for soil washing. The results obtained are in the following table:

Table22: Method of remediation of copper-contaminated soil in Castel San Giorgio, Italy.

Journal	Journal of Environmental Management.
Authors	Alberto Ferraro, Eric D. van Hullebusch, David Huguenot, Massimiliano Fabbricinoc, Giovanni Esposito.
Article history	Available online 22 August 2015.
Study site	Castel San Giorgio (Italy).
Treatment method	Soil washing.
Soil type	/
Ways to sample	/
Content of metal in the soil	18 mg/l.

Abstract:

This paper investigated the application of an electrochemical process. Results from this work showed the feasibility of electrochemical treatment for recovery of spent biodegradable washing solutions and their reuse in soil washing.

Analytical study N° (03): Scientific article entitled:

"Potassium lignosulfonate as a washing agent for remediating lead and copper co-contaminated soils" [39].

This dissertation investigated the purpose of remediation of soil contaminated by lead and copper by Applying potassium lignosulfonate (KLS). The results obtained are in the following table:

Table23: Method of remediation of copper-contaminated soil in Guangzhou and Guangdong Province in China.

Journal	Science of the Total Environment.
Authors	Qianjun Liu, YuDeng, Jiepeng Tang, DiChen, Xiang Li, Qintie Lin, Guangcai Yin, Min Zhangb, HuawenHu.
Article history	Available online 15 December 2018.
Study site	Guangzhou and Guangdong Province in China.
Treatment method	Soil washing.
Soil type	Simulated soil and soil from mining area.
Ways to sample	30–60 cm depth.
Content of metal in the soil	Soil (S): 827.03 mg/kg. Soil (M): 2135.80 mg/kg.

Abstract:

It was adopted washing soil method in two soils a simulated soil and in mining area soil. The result was in the batch washing experiment the removal ratios in the simulated and mining area soils were 73.42% and 55.20%, respectively, for copper.

In the column leaching experiment, the removal ratios were 39.74% and 22.76% for Cu, respectively.

Analytical study N° (04): Scientific article entitled:

"Remediation of soil co-contaminated with decabromodiphenyl ether (BDE-209) and copper by enhanced electrokinetics-persulfate process" [40].

This essay developed a new EK remediation technology for Decontaminate the Cu co-contaminated soil. The results obtained are in the following table:

Table24: Method of remediation of copper-contaminated soil in Xuzhou, China.

Journal	Journal of Hazardous Materials.
Authors	Fu Chen, Xiaoxiao Li, Jing Ma, Junfeng Qu, Yongjun Yang, Shaoliang Zhang.
Article history	Available online 13 February 2019.
Study site	Xuzhou, China.
Treatment method	A new EK remediation technology.
Soil type	/
Ways to sample	/
Content of metal in the soil	1000 mg/kg.

Abstract:

Investigating the influences of citric acid and methyl-β-cyclodextrin (MCD) as enhancing agents during the electrokinetics (EK)-persulfate process on the remediation of soil artificially contaminated with copper (Cu) with an initial concentration of 1000 mg/kg. The result shows that compared with MCD, citric acid better facilitated the migration of Cu in soil.

Analytical study N° (05): Scientific article entitled:

"Removal of Cu and Pb from contaminated agricultural soil using mixed chelators of fulvic acid potassium and citric acid" [41].

This thesis explored the removal efficiency of MC for Cu and its influencing factors. The results obtained are in the following table:

Table25: Method of remediation of copper-contaminated soil in Dabaoshan area of Shaoguan, Guangdong Province, China.

Journal	Ecotoxicology and Environmental Safety.
Authors	Yupeng Wang, Qintie Lin, Rongbo Xiao, Shuailong Cheng, Haoyu Luo, Xiaoqing Wen, Libin Wu, Quanfa Zhong.
Article history	Available online 27 August 2020.
Study site	Dabaoshan area of Shaoguan, Guangdong Province, China.
Treatment method	Washing soil.
Soil type	Agricultural soil.
Ways to sample	0–50 cm depth.
Content of metal in the soil	/

Abstract:

Application of a specific soil washing method to remove Cu from contaminated agricultural soil. a mixed chelator (MC) was prepared using potassium fulvic acid (PFA, 3.2%) and citric acid (CIT, 0.16 M) in a volume ratio of 4:1. The result was MC is a potential washing agent to remediate agricultural soils containing Cu.

Analytical study N° (06): Scientific article entitled:

"Remediation of artificially contaminated soil and groundwater with copper using hydroxyapatite/calcium silicate hydrate recovered from phosphorus-rich wastewater" [42].

This essay tested the idea of using HAP/CeSeH derived from phosphorus recovery from P-rich wastewater for Copper immobilization in soil. The results obtained are in the following table:

Table26: Method of remediation of copper-contaminated soil in Shanghai, China.

Journal	Environmental Pollution.
Authors	Yiyang Liu, Rongbin Zhang, Zhenjie Sun, Qin Shen, Yuan Li, Yuan Wang, Siqing Xia, Jianfu Zhao, Xuejiang Wang.
Article history	Accepted 30 October 2020.
Study site	Shanghai, China.
Treatment method	Immobilization method.
Soil type	/
Ways to sample	/
Content of metal in the soil	/

Abstract:

The feasibility of remediation of heavy metal pollution in soil and groundwater was investigated using hydroxyapatite/calcium silicate hydrate (HAP/CeSeH) recovered from phosphorus-rich wastewater in farmland. The result shows that HAP/CeSeH synthesized with P recovered from wastewater is an effective and eco-friendly amendment in the remediation of copper-contaminated soil.

Analytical study N° (07): Scientific article entitled:

"Accelerating Cu and Cd removal in soil flushing assisted by regulating permeability with electrolytes" [43].

This monograph strived to illuminate the idea of soil flushing assisted by regulating permeability with electrolytes. The results obtained are in the following table:

Table27: Method of remediation of copper-contaminated soil in Wuxi, China.

Journal	Chemosphere.
Authors	Jingyi Feng, Qi Yu, Anfei He, G. Daniel Sheng.
Article history	Available online 17 May 2021.
Study site	Wuxi, China.
Treatment method	Soil flushing (in-situ remediation).
Soil type	Agricultural soil.
Ways to sample	A surface soil.
Content of metal in the soil	/

Abstract:

Extraction heavy metals from soil by using deionized water as a flushing solution to enhance the solubility of the metals. it found that EDTA effectively improved the extraction efficiency, to the highest when together with electrolytes.

Analytical study N° (08): Scientific article entitled:

"A holistic approach to remediation of soil contaminated with Cu, Pb and Zn with sewage sludge-derived washing agents and synthetic chelator" [44].

This research investigated the purpose remediation of soil contaminated with Cu by application of washing agents (WAs) derived from organic waste sources. The results obtained are in the following table:

Table28: Method of remediation of copper-contaminated soil in Troszkowo, North Poland.

Journal	Journal of Cleaner Production.
Authors	Barbara Klik, Zygmunt M. Gusiatin, Dorota Kulikowska.
Article history	Available online 27 May 2021.
Study site	Troszkowo, North Poland.
Treatment method	Green soil washing.
Soil type	Agricultural soil.
Ways to sample	0–30 cm depth.
Content of metal in the soil	7874.5 mg/kg.

Abstract:

Comparison for the first time between the efficiency of sewage sludge-derived WAs (SS_WAs) extracted from sewage sludge with water or a NaOH solution. The WAs were used to remove Cu from soil during double batch washings. the result shows that sewage-sludge derived WAs possess great potential for remediating highly polluted soils with recovery of soil function and limited toxicity.

Discussion:

Copper in soil has a high degree of toxicity for the environment and can enter the food chain which it affects the human health. Therefore, copper contaminated soil remediation had become a necessary in environment protection. There is a lot of methods for remediation of these contaminated soils so We try to summarize the most important results of previous studies related to the treatment methods of Cu contaminated soil in this table below:

Table29: Summary of the most important previous studies for Cu.

	Study number	**Study site**	**Study history**	**Treatment method**	**Soil type**	**Removal rate (%)**
Previous studies	**01**	China	2011	Bioremediation	Mining area	95
	02	Italy	2015	Soil washing	/	99
	03	China	2018	Soil washing	Simulated and mining area	73.42/55.20
	04	China	2019	Electrokinetics	/	92.5
	05	China	2020	Soil washing	Agricultural	42.92
	06	China	2020	Immobilization	/	76.3
	07	China	2021	Soil flushing	Agricultural	/
	08	North Poland	2021	Green soil washing	Agricultural	/

Through the results of previous studies studying Cu contaminated soil:

Scientific article N° 01: The results demonstrated possibility of this method for bioremediation of highly Cu contaminated soils.

Scientific article N° 02: Multi-step soil washing method showed a very high effect on Cu removal from contaminated soil. This gave us a possibility for an economically sustainable soil remediation.

Scientific article N° 03: According to the results we found that the used agent in this study was harmless and degradable compared with used agents in other soil washing experiments. but it has only medium removal efficiency.

Scientific article N° 04: Results demonstrated that this method has a high removal rate for decontaminating the Cu co-contaminated soil. In addition, we considered it as a green efficient technology.

Scientific article N° 05: We concluded that this method wasn't effective for remediation of Cu contaminated soil even though it did not exhibit big loss for soil and its elements.

Scientific article N° 06: The results showed that the used amendment was effective and eco-friendly in the remediation of Cu contaminated soil.

Scientific article N° 07: We found that flushing soil was so effective for reducing Cu in contaminated soil in a short period.

Scientific article N° 08: Although this method resulted a high efficiency Cu removal. but it impacts the soil organic matter.

Result:

Our analyzing and discussing show that the multi-step soil washing has the highest Cu removal rate. So we have considered this method as the effective Cu contaminated soil remediation method and also an economically sustainable soil remediation method.

III.1.4. Zinc (Zn):

Analytical study N° (01): Scientific article entitled:

" Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium" [45].

This dissertation examines the purpose of decreasing the content of available Zn (DTPA extraction) whilst increasing the concentrations of nutrients. The results obtained are in the following table:

Table30: Method of remediation of zinc-contaminated soil in Minas Gerais, Brazil.

Journal	Journal of Environmental Management.
Authors	A.P. Puga, C.A. Abreu, L.C.A. Melo, L. Beesley.
Article history	Accepted 28 May 2015.
Study site	Minas Gerais, Brazil.
Treatment method	In situstabilization.
Soil type	From mining area.
Ways to sample	0 to 20 cm depth.
Content of metal in the soil	60 mg/kg.

Abstract:

Application of biochar to a metal contaminated mine soil to reduce the availability of Zinc in soil. The results indicate that it is practicable to amend metal contaminated soils with biochars to reduce metals in soil-water solution and mitigate against leaching risks to proximal waters.

Analytical study N° (02): Scientific article entitled:

"Evaluation of modified chitosan for remediation of zinc contaminated soils" [46].

This essay evaluates using Chitosan as an amendment for remediation of Zn toxicity in contaminated and wasteland soils. The results obtained are in the following table:

Table31: Method for remediation of zinc-contaminated soil in Redland Bay, Queensland, Australia.

Journal	Journal of Geochemical Exploration.
Authors	Nimisha Tripathi Ph.D., GirishChoppalaPh.D., Raj S. Singh Ph.D.
Article history	Accepted 17 August 2016.
Study site	Redland Bay, Queensland, Australia.
Treatment method	Immobilization method.
Soil type	Ferrosol soil.
Ways to sample	0–10 cm depth.
Content of metal in the soil	/

Abstract:

Examination the potential of pure and modified chitosan beads to immobilise Zn in contaminated soils. The results showed that the chitosan beads modified with molybdenum MoCB amendment is effective in reducing Zn bioavailability and shoot uptake, where as pure chitosan beads PCB effectively decreased Zn root uptake.

Analytical study N° (03): Scientific article entitled:

"Remediation of cadmium, lead and zinc in contaminated soil with CETSA and MAAA" [47].

This monograph tests the idea of using CETSA and MAAA remediation of zinc in contaminated soil. The results obtained are in the following table:

Table32: Method for remediation of zinc-contaminated soil in Hanyuan, Sichuan, China.

Journal	Journal of Hazardous Materials.
Authors	Zhenhua Xia, Shirong Zhang, Yaru Cao, Qingmei Zhong, Guiyin Wang, Ting Li, Xiaoxun Xu.
Article history	Available online 01 December 2018.
Study site	Hanyuan, Sichuan, China.
Treatment method	Soil washing.
Soil type	Mining area.
Ways to sample	0–20 cm depth.
Content of metal in the soil	1175.63 mg/kg.

Abstract:

Investigating whether carboxyalkylthiosuccinic acid CETSA or copolymer of maleic and acrylic acid MA/AA could remove heavy metals from soil while destroying as few soil nutrients as possible. They found that the three agents also effectively reduced the potential risks of Zn in contaminated soil, but only CETSA and MA/AA produced no significant changes in chemical properties.

Analytical study N° (04): Scientific article entitled:

"Effective remediation of cadmium and zinc co-contaminated soil by electrokinetic-permeable reactive barrier with a pretreatment of complexing agent and microorganism" [48].

The treatise strives to illuminate the electrokinetic-permeable reactive barrier (EK-PRB) technology for the remediation of zinc co-contaminated soil. The results obtained are in the following table:

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Table33: Method for remediation of zinc-contaminated soil in Shanghai, China

Journal	Chemical Engineering Journal.
Authors	Chiquan He, Anni Hu, Feifei Wang, Pu Zhang, Zhenzhen Zhao, Yanping Zhao, Xiaoyan Liu.
Article history	Accepted 2 September 2020.
Study site	Shanghai, China.
Treatment method	EK technology.
Soil type	Agricultural soil.
Ways to sample	a depth of 20 cm.
Content of metal in the soil	320.61 mg/kg.

Abstract:

This study aimed to provide a potential efficient technology for remediating Zn (Ⅱ) contaminated soils. It was resulted that Zn (Ⅱ) was reduced after EK-PRB remediation.

Analytical study N° (05): Scientific article entitled:

"Isolation and studies on zinc removal using microorganism from contaminated soil" [49].

This study developed a new technology using living microbes for zinc removal. The results obtained are in the following table:

Table34: Method for remediation of zinc-contaminated soil in India.

Journal	Materials Today: Proceedings
Authors	Neethu Jayan, M. Laxmi Deepak Bhatlu.
Article history	Available online 22 January 2021.
Study site	India.
Treatment method	Bioremediation.
Soil type	Industry area.
Ways to sample	/
Content of metal in the soil	/

Abstract:

Using bioremediation to remove heavy metals even at lower concentration with the help of living microbes which is not possible using conventional chemical methods. The spectral analysis before and after Zinc ion binding clearly indicated that alkenes, nitro compounds, amino groups are the predominant contributors in lead uptake by microorganisms.

Analytical study N° (06): Scientific article entitled:

"Bone-derived biochar improved soil quality and reduced Cd and Zn phytoavailability in a multi-metal contaminated mining soil" [50].

This thesis looks for the potential of bone-derived biochar as a promising material for metals immobilization in contaminated mining soils. The results obtained are in the following table:

Table35: Method for remediation of zinc-contaminated soil in Fengxian County, China.

Journal	Environmental Pollution.
Authors	Muhammad Azeema, Amjad Ali, Parimala Gnana Soundari Arockiam Jeyasundar, Ph.D, Yiman Li, Hamada Abdelrahman, Abdul Latif, Ronghua Li, Nicholas Basta, Gang Li, Sabry M. Shaheen, Jorg Rinklebe, Zenqqiang Zhang.
Article history	Available online 22 February 2021.
Study site	Fengxian County, China.
Treatment method	Immobilization method.
Soil type	Mining area.
Ways to sample	20 cm depth.
Content of metal in the soil	/

Abstract:

Cow bone-derived biochar (CB) produced at low (500°C) and a high (800°C) temperature was applied with different doses (0, 2.5, 5, and 10%; w/w) to a contaminated soil. The reported results demonstrate that bone biochar; particularly produced at low-temperature pyrolysis can be an efficient immobilizing agent for Zn in contaminated soils.

Analytical study N° (07): Scientific article entitled:

"Efficiency of CH_4N_2S-modified biochar derived from potato peel on the adsorption and fractionation of cadmium, zinc and copper in contaminated acidic soil" [51].

This study aims to increase the adsorption and reduce the bioavailability and mobility of heavy metals in acidic soil. The results obtained are in the following table:

Table36: Method for remediation of zinc-contaminated soil in Guilan province in north of Iran.

Journal	Environmental Nanotechnology, Monitoring & Management.
Authors	Leila Gholami, Ghasem Rahimi.
Article history	Available online 18 April 2021.
Study site	Guilan province in north of Iran.
Treatment method	Immobilization method.
Soil type	Acidic soil.
Ways to sample	0-30 cm.
Content of metal in the soil	/

Abstract:

Investigation the characteristics of potato peel biochar (PPB) and modified potato peel biochar (MPPB), and their effects on the adsorption and fractionation of some heavy metals in contaminated acidic soil. The results showed that the maximum adsorption of Zn in soil amended with 8 % MPPB was 3508.44 mg/kg.

Analytical study N° (08): Scientific article entitled:

"In-situ remediation of zinc contaminated soil using phosphorus recovery product Hydroxyapatitecalcium silicate hydrate (HAPC–S–H)" [52].

This research aims to identify the importance of HAP/C–S–H, the product of phosphorus recovery by C–S–H to remove Zn(II) from in-situ and immobilize Zn(II) in contaminated soil. The results obtained are in the following table:

Table37: Method for remediation of zinc-contaminated soil in Tongji, China.

Journal	Chemosphere.
Authors	Meng Yuan, Zaoli Gu, Siqing Xia, Jianfu Zhao, Xuejiang Wang.
Article history	Available online 23 July 2021.
Study site	Tongji, China.
Treatment method	In-situ immobilization.
Soil type	Agricultural soil
Ways to sample	/
Content of metal in the soil	/

Abstract:

Utilizing C–S–H phosphorus recovered products, HAP/C–S–H, to remove Zn (II) from aqueous solution and in-situ immobilize Zn (II) in contaminated soil. They found that the removal rate of Zn (II) by HAP/ C–S–H raised with the increase of pH value, reaching the highest (99.47%) at pH of 8.

Discussion:

With industrial development, soil contamination with heavy metals, especially zinc, has increased. Because of its danger to human health and the environment, scientists have sought to develop methods for treating zinc-contaminated soil.

Here we summarized the most important results of previous studies related to the treatment of Zn contaminated soil in this table below:

Table38: Summary of the most important previous studies for Zn.

	Study number	Study site	Study history	Treatment method	Soil type	Removal rate (%)
Previous studies	**01**	Brazil	2015	In situ stabilization	Mining area	50
	02	Australia	2016	Immobilization	Ferrosol	/
	03	China	2018	Soil washing	Mining area	/
	04	China	2020	Electrokinetics	Agricultural	/
	05	India	2021	Bioremediation	Industry area	/
	06	China	2021	Immobilization	Mining area	40-55
	07	North of Iran	2021	Immobilization	Acidic	/
	08	China	2021	In situ immobilization	Agricultural	99.47

Through the results of previous studies studying Zn contaminated soil:

Scientific article N° 01: We noticed that this method had medium zinc removal rate. So we cannot say that it was effective cause it steals plants can still accumulate large concentrations of metals in their tissues.

Scientific article N° 02: The results indicated that MoCB amendment was effective for reducing zinc bioavailability and uptake, but the effect of this amendment on the environment has not studied yet.

Scientific article N° 03: This study demonstrated that the applied washing agents were suitable for remediation of Zn contaminated soil. However, there is a shortage of economical and environmentally friendly washing agents with high removal efficiency.

Scientific article N° 04: The study showed the effectiveness of this method in removing zinc from contaminated soil over a little bit long period of time.

Scientific article N° 05: The results showed that Zn removal was obtained maximum at a time of 60 min. So we can say that Zn uptake by microorganisms was so effective and eco-friendly.

Scientific article N° 06: We can consider the used product as a potential fertilizer. But also we resulted that this method reduced the Zn in soil with low efficiency.

Scientific article N° 07: The results showed that MPPB can be used as a low-cost and eco-friendly adsorbent for the immobilization of Zn in only acidic contaminated soil.

Scientific article N° 08: We noticed that the removal rate was so high, and only in a short period. It means that the analysed method which depends on using HAP/ C–S–H was so effective for the remediation of Zn contaminated soil.

Result:

After analyzing and discussing previous studies we found that in situ immobilization method using HAPC–S–H was the best method for reducing zinc bioavailability and remediation of Zn contaminated soil. Because it can uptake Zn with high removal rate and only in a short period.

III.1.5. Mercury (Hg):

Analytical study N° (01): Scientific article entitled:

"Mercury uptake by Silene vulgaris grown on contaminated spiked soils" [53].

This dissertation examines the purpose of evaluate the effectiveness of Silene vulgaris to uptake Hg from artificially polluted soils. The results obtained are in the following table:

Table39: Method of remediation of mercury-contaminated soil in Madrid Region, Spain.

Journal	Journal of Environmental Management
Authors	Araceli Pérez-Sanz, Rocío Millán, M. José Sierra, Remedios Alarcón, Pilar García, Mar Gil-Díaz, Saúl Vazquez, M. Carmen Lobo.
Article history	Available online 12 August 2010.
Study site	Madrid Region, Spain.
Treatment method	Phytostabilization.
Soil type	Agricultural soil.
Ways to sample	0-20 cm depth.
Content of metal in the soil	0.6 and 5.5 mg/kg.

Abstract:

The objective of this study was to evaluate the effectiveness of Silene vulgaris, to uptake Hg from artificially polluted soils. The result showed that S. vulgaris a good candidate to phytostabilization technologies.

Analytical study N° (02): Scientific article entitled:

"Phytoremediation of mercury in pristine and crude oil contaminated soils Contributions of rhizobacteria and their host plants to mercury removal" [54].

This research investigates the purpose of using the rhizobacterial partners in the phytoremediation. The results obtained are in the following table:

Table40: Method of remediation of mercury-contaminated soil in Al-Khaldyah area, Kuwait City, Kuwait.

Journal	Ecotoxicology and Environmental Safety.
Authors	N.A. Sorkhoh, N. Ali, H. Al-Awadhi, N. Dashti, D.M. Al-Mailem, M. Eliyas, S.S. Radwan.
Article history	Available online 15 September 2010.
Study site	Al-Khaldyah area, Kuwait City, Kuwait.
Treatment method	Phytoremediation.
Soil type	Oily soil.
Ways to sample	/
Content of metal in the soil	10, 20 and 40 $mg.l^{-1}$ of $HgCl_2$.

Abstract:

This study deals with the bioremediation of mercury in oily soils via rhizopshere technology. They found that Rhizobacteria associated with conventional crop plants contribute almost equivalently to their host plants to mercury removal from soil.

Analytical study N° (03): Scientific article entitled:

"Mercury removal from contaminated soil by thermal treatment with $FeCl_3$ at reduced temperature" [55].

This research developed a method for remediation of mercury-contaminated soil by thermal treatment with $FeCl_3$ at reduced temperature. The results obtained are in the following table:

Table41: Method of remediation of mercury-contaminated soil in Tongren, Guizhou Province, China.

Journal	Chemosphere.
Authors	Fujun Ma, Qian Zhang, Duanping Xu, Deyi Hou, Fasheng Li, Qingbao Gu
Article history	Accepted 2 August 2014.
Study site	Tongren, Guizhou Province, China.
Treatment method	Thermal treatment.
Soil type	Agricultural soil.
Ways to sample	/
Content of metal in the soil	69 mg/kg.

Abstract :

In this study an agricultural soil was treated by a developed method. The result showed that this method reduced the content of mercury in the soil to a lower limit at a reduced temperature (400°C).

Analytical study N° (04): Scientific article entitled:

"Simultaneous removal of PCDDFs, pentachlorophenol and mercury from contaminated soil" [56].

This essay aims the purpose of remediation of the soil simultaneously contaminated with mercury. The results obtained are in the following table:

Table42: Method for remediation of mercury-contaminated soil in Taiwan.

Journal	Chemosphere.
Authors	Pao-Chen Hung, Shu-Hao Chang, Chia-Chien Ou-Yang, Moo-Been Chang.
Article history	Accepted 17 August 2015.
Study site	Taiwan.
Treatment method	Thermal treatment.
Soil type	/
Ways to sample	/
Content of metal in the soil	/

Abstract:

The work aimed to remove mercury from heavily contaminated soil. It found that mercury was significantly desorbed from contaminated soil due to the high operating temperature of the CPTS and 97.8% of input mercury rate is discharged through the exhaust.

Analytical study N° (05): Scientific article entitled:

"Bioremediation of Hg-contaminated soil by combining a novel Hg-volatilizing Lecythophora sp. fungus, DC-F1, with biochar: Performance and the response of soil fungal community" [57].

This thesis investigates the role of a novel fungal strain, Lecythophorasp for reducing Hg content and bioavailability in soil. The results obtained are in the following table:

Table43: Method for remediation of mercury-contaminated soil in Dongchuan, Yunnan Province, China.

Journal	Science of the Total Environment.
Authors	Junjun Chang,YijunDuan, Jia Dong,ShiliShen, Guangzheng Si, Fang He, Qingchen Yang, Jinquan Chen.
Article history	Available online 27 March 2019.
Study site	Dongchuan, Yunnan Province, China.
Treatment method	Bioremediation.
Soil type	From a mining area.
Ways to sample	5–10 cm depth.
Content of metal in the soil	29.3 mg/kg.

Abstract:

Reducing Hg contamination in soil using eco-friendly by a novel multi-metal-resistant Hg-volatilizing fungi belonging to Lecythophora., DC-F1. the result showed that the lowest uptake of Hg by lettuce shoots was obtained when both DC-F1 and biochar were added.

Analytical study N° (06): Scientific article entitled:

"In situ remediation of mercury-contaminated soil using thiol-functionalized graphene oxide/Fe-Mn composite" [58].

This monograph investigated the immobilization effectiveness and mechanisms of SGO/Fe-Mn for in situ remediation of mercury-contaminated soil. The results obtained are in the following table:

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Table44: Method of remediation of mercury-contaminated soil in Tianjin, China

Journal	Journal of Hazardous Materials.
Authors	Yao Huang, Mengxia Wang, Zhanjun Li, Yanyan Gong, Eddy Y. Zeng
Article history	Available online 01 April 2019.
Study site	Tianjin, China.
Treatment method	In-situ immobilization.
Soil type	/
Ways to sample	0–30 cm depth.
Content of metal in the soil	195.0 mg/kg.

Abstract:

In this study, a novel thiol-functionalized graphene oxide/FeMn (SGO/Fe-Mn) composite was prepared and investigated for in situ immobilization of Hg in contaminated soil. Tests showed that application this method reduced the leachability, and so the environmental risk of Hg in the soil was greatly reduced.

Analytical study N° (07): Scientific article entitled:

"Green remediation of Cd and Hg contaminated soil using humic acid modified montmorillonite: Immobilization performance under accelerated ageing conditions" [59].

This essay tests the idea of using A green immobilization amendment, humic acid modified montmorillonite for Immobilization of Hg in the soil. The results obtained are in the following table:

Table45: Method for remediation of mercury-contaminated soil in Beijing, China.

Journal	Journal of Hazardous Materials.
Authors	Liuwei Wang, Xuanru Li, Daniel C.W. Tsang, Fei Jin, Deyi Hou.
Article history	Available online 02 January 2020.
Study site	Beijing, China.
Treatment method	Immobilization method.
Soil type	Agricultural soil.
Ways to sample	30 cm depth.
Content of metal in the soil	0.025 mg/kg.

Abstract:

This study intends to investigate the Hg and Cd stabilization efficiency in the long term by a novel method based on conditional probability theory. It was resulted that a dosage of 5 % HA-Mont could effectively reduce the leachate Hg concentrations significantly.

Analytical study N° (08): Scientific article entitled:

"Mercury removal using modified activated carbon of peat soil and coal in simulated landfill leachate" [60].

This monograph strives to illuminate the idea of producing an adsorbent material which can reduce mercury content in contaminated soil at different pH conditions. The results obtained are in the following table:

Table46: Method for remediation of mercury-contaminated soil in Jambi Province, Indonesia.

Journal	Environmental Technology & Innovation.
Authors	Mochammad Arief Budihardjo, Yudha Gusti Wibowo,Bimastyaji Surya Ramadan, Muhamad Allan Serunting, Eflita Yohana, Syafrudin.
Article history	Available online 18 October 2021.
Study site	Jambi Province, Indonesia.
Treatment method	Physical activation and chemical activation.
Soil type	Coal and peat soil.
Ways to sample	/
Content of metal in the soil	/

Abstract:

This research focuses on producing an adsorbent material which can reduce mercury content at different pH conditions. And it shows that the adsorbents produced were able to reduce mercury content by up to 81%.

Discussion:

Mercury is a global pollutant, highly toxic, which can cross international borders. The toxicity varies depending on the element speciation, from the least toxic elemental form that is less bioavailable, to the highly toxic organomercurial compounds that can become concentrated as they move up the food chain the natural sources of mercury, independent of man's action, occur as a general cycle [53]. So we try to analyse some studies to investigate in methods for remediation of Hg contaminated soils.

We summarized the most important results of previous studies related to the treatment of Hg contaminated soil in this table below:

Table47: Summary the most important previous studies for Hg.

	Study number	**Study site**	**Study history**	**Treatment method**	**Soil type**	**Removal rate (%)**
Previous studies	**01**	Spain	2010	Phytostabilization	Agricultural	/
	02	Kuwait	2010	Phytoremediation	Oily	/
	03	China	2014	Thermal treatment	Agricultural	/
	04	Taiwan	2015	Thermal treatment	/	97.8
	05	China	2019	Bioremediation	Mining area	26.1
	06	China	2019	In situ immobilization	/	97.6
	07	China	2020	Immobilization	Agricultural	65.9
	08	Indonesia	2021	Physical/chemical activation	Coal and peat	81

Through the results of previous studies studying Hg contaminated soil:

Scientific article N° 01: We resulted that the ability of S. vulgaris to absorb large amounts of mercury makes it a good candidate for phytostabilization techniques in Hg contaminated soils.

Scientific article N° 02: Results indicated the valuable role played by used plant in the phytoremediation of Hg in soils.

Scientific article N° 03: We noticed that Hg in soil was successfully reduced when treated with this method. also this analysed method can be considered as a green and sustainable remediation method.

Scientific article N° 04: Results demonstrated that Hg can be removed via appropriate thermal treatment technology. But the possibility of air pollution should not be neglected.

Scientific article N° 05: We found that this method showed a low efficiency for remediation of Hg contaminated soil. although it has long-term efficiency, it should be studied more.

Scientific article N° 06: This method can in situ immobilize Hg in contaminated soil. in addition, it has the ability of improving soil properties besides remediating Hg-contaminated soil.

Scientific article N° 07: Results showed that the analysed method could immobilize Hg but only in the long term. in addition, we found that the HA-Mont stabilization performance should be examined at the field scale.

Scientific article N° 08: Results demonstrated that the produced adsorbent materials can reduce mercury in contaminated soils, where it showed a high removal efficient in a short period.

Result:

According to the results showing in (Table 47), and the discussion we have concluded that the efficacious method for the remediation of Hg contaminated soil is the thermal treatment. But the possibility of air pollution should be considered.

General Conclusion

General conclusion

Industrial and agricultural development in recent years has caused many environmental problems, including soil contamination with heavy metals, and because of their high toxicity and danger to the environment and humans, it has become necessary to develop methods to get rid of these metals and treat contaminated soil.

This study investigated the methods for remediation of heavy metals contaminated soil. Where through analyzing previous studies we can conclude the following:

- For Cadmium (**Cd**) the best remediation method is adsorption method.
- About Lead (**Pb**) we found that soil washing method is the effective method for reducing lead from contaminated soil.
- Copper (**Cu**) can be reduced with high efficiency remove by multi-step washing soil.
- In situ immobilization method is the appropriate method for remediation of zinc (**Zn**) contaminated soil.
- Results showed that the most efficient way for uptake of mercury (**Hg**) from contaminated soil is the thermal method.

This work focused on just some heavy metals (Cadmium, Lead, Copper, Zinc and Mercury). However, there are other heavy metals that are no less dangerous than the studied minerals, so attention should be paid to studying them in the future.

Future research should also take into account the safety of the environment so that all remediation methods are eco-friendly.

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Abstract:

This study aimed to research in the methods for remediation of heavy metals contaminated soils.

Where we had chosen the most studied metals (Cadmium, Lead, Copper, Zinc and Mercury), and we studied and analysed 08 scientific articles for each metal (40 scientific articles). The previous studies were from different areas and studied different soils (agricultural, acidic, calcareous and mining soil).

We evaluated and compared all the remediation methods for each studied metal. Results showed that the effective methods for remediation: adsorption method for **Cd** contaminated soil remediation **(90%)**, washing soil for treating **Pb** contaminated soil **(99.5%)**, multi-step soil washing for reducing **Cu** from soil **(99%)**, in situ immobilization to remove **Zn** from soil **(99.47%)** and thermal treatment for **Hg** contaminated soil **(97.8%)**.

Key words: soil, heavy metals, methods for remediation, contaminated soil, chemical remediation.

الملخص:

هدفت هذه الدراسة إلى البحث في طرق معالجة التربة الملوثة بالمعادن الثقيلة. حيث اخترنا أكثر المعادن المدروسة (الكادميوم، الرصاص، النحاس، الزنك والزئبق).

قمنا بدراسة وتحليل 08 مقالات علمية لكل معدن (40 مقالة علمية). كانت الدراسات السابقة من مناطق مختلفة ودرست أنواع التربة المختلفة (التربة الزراعية والحمضية والكلسية والتعدينية).

قمنا بتقييم ومقارنة جميع طرق المعالجة لكل معدن تمت دراسته. أظهرت النتائج أن الطرق الفعالة للمعالجة: طريقة الامتزازبالنسبة لمعالجة التربة الملوثة بالكادميوم (90%)، غسل التربة لمعالجة التربة الملوثة بالرصاص (99.5%)، غسل التربة متعدد الخطوات لتقليل النحاس في التربة (99%)، التثبيت في الموقع لإزالة الزنك من التربة (99.47%) والمعالجة الحرارية بالنسبة للتربة الملوثة بالزئبق (97.8%).

الكلمات المفتاحية: التربة، المعادن الثقيلة، طرق المعالجة، التربة الملوثة، معالجة كيميائية.