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Chapter

Metal-Contaminated Soil Remediation: Phytoremediation, Chemical Leaching and Electrochemical Remediation

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Abstract

Soil contamination has led to serious land tenure problems, reduction in land usability for agricultural production; as a consequence, food insecurity is nowadays a global challenge. Indeed, with rapid population growth across the world, the food demand for consumption has drastically increased and traditional ways of producing food cannot meet with the actual demand. Industrialization has been acknowledged as a way out to sustain humanity with food. Unfortunately, the later has further turn into a threat to the environment. In effect, several potentially toxic elements (PTE) are being released in the environment and soil systems; and arable or agricultural lands are getting restraint, limited and scarce. Nowadays, there is a consensus on remediating contaminated lands with PTE, mainly inorganic contaminants, metals. The state at which a metal is found in the soil greatly influences its bioavailability, interaction with plants and the level at which it will threaten (toxicity) the environment and thus human. It even defines the remediation approaches to be applied for the soil restoration. This chapter will provide an insight on the occurrence of PTE in the soil, bioavailability and remediation approaches namely phytoremediation, chemical leaching and electrochemical remediation; and finally highlight the future research direction on this topic.

Keywords: metals, bioavailability, soil, contamination, decontamination

1. Introduction

Soil is a balanced and complex system, where plants and microorganisms live and co-operate, thus ensuring, crops and food necessary to sustain life [1]. Natural erosion and human activities are enemies of the soil ecosystem. It has been reported that 25% of the global soils are highly degraded and 44% are significantly degraded [2]. Inorganic and organic pollutants are enemies of soils responsible of its contamination. The contamination of soil by a mixture of

organic and non-organic pollutants due to various anthropogenic and natural causes is one of the most important issues in soil pollution [3]. It threatens humans and the ecosystem via: direct inhalation or through contaminated soil, food chain, or consumption of contaminated surface and ground water, reduction agricultural land (arable land) and in the food's quality; otherwise, there occur an issue related to the reduction of the marketability of farm products as result of safety concern (phytotoxicity) [4].

Among several pollutants threatening soil are: metals [5, 6], through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes like e-wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation [7, 8]; and metalloids [9–11] from industrial waste [12] or mine ores [13]. To be noticed, there are also organic contaminants among which persistent organic pollutants (POP) such as chlorinated [14] and polycyclic aromatic compounds (PAHs) [15], pesticides and herbicides [16] that threaten soil and environment system. Particularly, potentially-toxic elements (PTE) in water and soil have been of great environmental concern due to their non-biodegradable nature, toxicity, bioaccumulation in the food chain, persistence in the environment, and adverse effects on organisms and humans. Chromium (Cr), copper (Cu), nickel (Ni), mercury (Hg), cadmium (Cd), and lead (Pb) are among the environment most concerned toxic PTE. The presence of toxic metals in soil can severely inhibit even the biodegradation of organic contaminants [17]. The treatment thus, protection and remediation of soil are of paramount importance nowadays.

Overwhelming numbers of soil remediation technologies have been developed and tested in both field and controlled environment experiments. Among many, bioremediation (use of microorganism) [18], phytoremediation (use of plants species) soil washing (use of inorganic and organic acids or organic chelators or surfactants), solidification, stabilization, excavation, and electroremediation techniques [19, 20] approaches are commonly used for the treatment of contaminated soil. However, these approaches seem limited and not efficient and effective under severe contamination such as metallic elements and POPs co-contaminated site (e.g. e-waste disposal site or industrial contaminated sites) as microorganisms and plants growth is severely inhibited [17]. Electrokinetic remediation approach which consists in applying direct low level current between two electrodes is nowadays widely used for soil treatment due to its many advantages. The latter shows promising in the future of soil remediation mainly its combination with other technologies; it being under intense investigation. In this chapter of the book we are going to give an insight on the functioning of each of these three approaches during soil treatment, its advantages and limits; and then the direction to explore for a better future of soil remediation.

2. Main sources of metals in the soil

Soil, originally, acts as both source and reservoir of metallic elements [21]. PTE are naturally occurring throughout the earth's crust. However, when talking of soil contamination, nowadays, it refers to the contamination related to anthropogenic activities which led to the increase of contaminants in the soil system; even beyond the threshold concentrations stated in regulations for the safe use of soil in agricultural productions. As consequence, due to its severe contamination, soil represents a major main through which metals are spread in different environment compartments including groundwater, plants, river etc.

Several sources can contribute to soil contamination by metallic elements. Indeed, with the rapid development and industrialization in many countries around the world, there occur an excessive use of various chemical based pesticides and fertilizers in agricultural fields, which results in to the accumulation of PTE in soil and the emerging of serious soil contamination issue [22]. The application of mineral and organic fertilizers can introduce PTE into the soil-plant system. It is commonly known that phosphate rock fertilizers often contain potentially toxic trace elements including copper (Cu), zinc (Zn), manganese (Mn), lead (Pb), and cadmium (Cd) [23, 24]. Several PTE, such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Lead (Pb), Nickel (Ni), Zinc (Zn), and the metalloid Arsenic (As), are widely used by industries, agriculture and consequently released into the environment [25]. Mining is considered to be one of the most significant sources of PTE [26, 27]. In China, it was reported that 1.5 million ha of waste land was the result of PTE contamination caused by mining. Furthermore, area of polluted land keeps increasing at a rate of 46,700 ha/year [26].

Otherwise, with the rapid industrialization and urbanization, the world is facing growing environmental issues [28] with respect the production and disposal of huge amounts of sewage sludge. Indeed, it is noteworthy that huge amount of sewage sludge is being produced yearly and its management remains challenging. Nowadays, one of the mains for the disposal of this matter, is through land application as soil amendment; because the matter is a rich source of phosphorous and nitrogen, and could be value-added as fertilizer [29]. Unfortunately this matter is generally loaded with various pollutants among which metallic elements at a high concentration; which threatens the safety of the receiving soil [30], with its adverse impacts on human and other living organisms when their bioavailability exceeds the concentration. These metals mainly originate from the aqueous phase of the wastewater, and then concentrate in the sludge during the treatment processes like precipitation, coagulation, adsorption etc. Recently, a studied was conducted in China by [31], and over 50 metallic elements including industrial commonly used PTE, rare earth elements and precious metals; were investigated in sewage sludge from different wastewater treatment plants from different region. Results revealed broad range of concentrations of the elements ranging from >125 – $53,500 \text{ mg kg}^{-1}$ dry sludge (DS) for commonly used industrial metals, 1.22 – 14.0 mg kg^{-1} DS for precious metals, and 1.12 – 439.0 mg kg^{-1} DS for rare earth elements. The application of such material to soil as amendment would lead to the accumulation and spreading of metals in the soil; mainly with a long-term soil application. Similar result on the occurrence of broad range of metals in the sewage sludge has been reported by [32] with over 60 metals detected in the sewage sludge from different states in US. Overwhelming numbers of reports can be found in the literature regarding the occurrence of metallic elements in the sewage sludge. For example, in 2006, a survey was carried out in china by [33] during which sludge samples collected from over 107 urban wastewater treatment plants (WWTPs) from 48 different provinces across China. Results revealed broad range concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (20.2 , 1.97 , 93.1 , 218.8 , 2.13 , 48.7 , 72.3 , and $1058 \text{ mg}\cdot\text{kg}^{-1}$, respectively). Another study carried out by [34] reported the present of Cr, Cu, Ni, Pb and Zn in sewage sludge, with concentrations ranging 293.7 , 181.7 , 114.8 , 40.3 , $1453.9 \text{ mg kg}^{-1}$ DS, respectively. One of the drastic concentration of PTE in the sludge, is the one reported by [35]. Indeed, the author reported higher concentrations up to $172,300$, 237 , 2225 , and 1700 mg kg^{-1} DS for Cd, Cu, Ni and Zn, respectively in an industrial sludge. In addition, [36, 37] recently reported concentration of 64 , 73.1 , 604.1 , 1102.1 , 483.9 , and $2060.3 \text{ mg kg}^{-1}$ DS for Cd, Co, Cu, Cr, Ni and Zn, respectively, in an urban sewage sludge. As can be seen, sewage sludge represent a great sink of metallic pollutants which deserves peculiar attention; as its land application would

lead to a drastic soil contamination and metals spreading. This was in accordance with a reported from [38] with respect the application of sewage sludge as soil fertilizer and the risk of metals spreading. To be noticed, aside sewage sludge, poultry and livestock manures from concentrated feeding operations can also, contain PTE and their application to agricultural land can lead to environmental problems and concerns over crop safety.

3. Metal bioavailability, mobility and transport in the soil

It is very important to highlight the fact that potentially-toxic elements (PTE) are not biodegradable elements and can be teratogenic, mutagenic, endocrine disruptors. This means that a metal can only change state of form in the soil; and depending to its forms, it can be transported from soil to another compartment of the environment, and cause serious adverse effects on the environment and human. The behavior and the transportability of a given metal in soil or from the soil to another environment compartment are strongly linked to the state at which the metal is mainly found in the soil. In another word, metal mobility in the soil is strongly linked to their bioavailability. The bioavailability of a metal in the soil is often determined by proceeding a sequential extraction of the metal using various extracting solution. The commonly used sequential extraction procedure is that of Tessier et al. [39]. It consists in to extracting metals in soil in five different fractions including ion exchanges fraction (F2), Carbonate bound-fraction (F3), organic matter-bound fraction (F4) and iron and manganese-bound fraction (F5), and silicate bound/residual fraction (F6). The method has further been modified by introducing a sixth fraction known as water soluble fraction; which normally should be the first fraction (F1) [40]. To be noticed, there are several sequential extraction protocols with various extracting solvents which can be found in the literature. However, following the chemical sequential extraction, metals in soil are generally been extracted in six different fractions (F1–6); which permit to appreciate the state or forms in which a given metal is found and predominate in the soil. Otherwise, the sequential extraction technic permits to evaluate the bioavailability of a metal and thus its mobility in the soil; and finally forecast it potential hazard and toxicity in the environment.

It is widely accepted that the sum of the first three fractions (F1, F2, F3) represents the minimum amount of labile/ bioavailable a given pollutant in the soil that could be easily be mobilized, spread and contaminate the environment [41]. As Result, it is bioavailable for plants uptake. These three fractions are environmental conditions-sensitive [42]. In addition, in the soil system, reactions that often take place are likely to be anaerobic which would lead to the degradation of organic matter in the soil system. As a consequence, the organic matter-bond metals would be released and be redistributed in the soil. This suggests that during the redistribution, the bioavailable fraction of metals could increase, thus increasing their mobility and the risk of environmental contamination. The higher S is for a given metal, the higher are its bioavailability and mobility. It can thus be easily transported in the soil towards the groundwater or be available for plants uptake or washed by runoff and then be transported towards the natural surface water reservoir. So, it can clearly be seen that the more a metal is bioavailable, the lesser its stability in the soil and the higher its toxicity would be. It thus very important to control the bioavailability and mobility of metals in the soil or at some extent, proceed to soil treatment and metals removal.

Otherwise, the bioavailability of a metal in the soil greatly influence it removal. As a consequence, the bioavailability of the metal greatly affects the efficacy and efficiency of soil treatment or remediation technologies [36]. As matter of fact, it is

recommended to first take this factor into account before any choice of the treatment or remediation approach. In the following sections, we are going to introduce three main technologies commonly used for soil remediation. It includes phytoremediation, chemical leaching and electrokinetic remediation.

4. Remediation technologies

4.1 Phytoremediation

Phytoremediation refers to the technologies that use living plants including herbs (e.g. *Thlaspi caerulescens*, *Brassica juncea*, *Helianthus annuus*) and woody (e.g. *Salix spp.*, *Populus spp.*) species, to clean up soil, air, and water contaminated with hazardous contaminants using their ability to either contain, remove, uptake, or render harmless various environmental contaminants like potentially-toxic elements, organic compounds and radioactive compounds in soil or water, thanks to their transport capacity and accumulation of contaminants [42, 43]. The use of plants for in situ treatment of contaminated soils was suggested for first time in the early 1990s [44]. The term phytoremediation was then introduced early in the same year to describe the use of plants for extracting PTE from soils [45]. Phytoremediation can be applied to inorganic as well as organic contaminants. As stated by [46], plants are kind of “chemical factories” that exercise great influence on their environment not only by uptake of substances but also by exudation of many molecules that are produced in primary and secondary metabolism. This lively chemical and physical interaction of plants with their environment are of great utility often use for the remediation of contaminated sites; refers to as phytoremediation.

The successful application of phytoremediation techniques is dependent on many parameters among which, contaminants must be bioavailable and ready to be absorbed by roots. The bioavailability of metals depends from solubility of the metals in soil. Nevertheless, mechanisms and efficiency of the phytoremediation depend not only on the bioavailability of metals but also on several others factors such as the nature of contaminant, soil properties, and plant species [47]. The plants which are generally considered for this purpose are those that exhibit great efficiency in phytoremediation processes. They are commonly named as “hyperaccumulator”, macrophytes capable of tolerating and accumulating metals present in the soil $\geq 10 \text{ g kg}^{-1}$ (1%) Mn or Zn, $\geq 1 \text{ g kg}^{-1}$ (0.1%) As, Co, Cr, Cu, Ni, Pb, Sb, Se or Tl, and $\geq 0.1 \text{ g kg}^{-1}$ (0.01%) Cd of the dry mass of shoots on soils rich in PTE in the aerial organs from soils without suffering phytotoxic damage [48]; while yielding low biomass [49]. The List of hyperaccumulators plant species for phytoextraction and phytostabilization has been already in a previous review by Mahar and his co-workers [50].

Otherwise, the extraction efficiency of the pollutants also depends on the biomass produced by the plant. Indeed, the bigger is the biomass the higher the ability of the plant to uptake big quantity of metals. However, more harvests, time and effort will be required to remove the plants after treatment. This will determine the total cost of the entire operation, including disposal, incineration or composting of biomass [51]. Phytoremediation is a reliable reclaiming treatment, because it does not interfere with the ecosystem, it requires less manpower and therefore cost-effective compared to traditional physicochemical methods. This technic knew some significant advancement in recent years thanks to the use of modern biotechnology such as phytoextraction and phytodegradation [51, 52]. Phytoremediation techniques could be applied for the recovery of the industrial sites heavily contaminated with low to moderate concentration.

4.1.1 Mechanisms of phytoremediation

The removal of inorganic pollutants and even organic using phytoremediation is made possible following diverse mechanisms summarized in the **Figure 1** below.

Phytoextraction: metals are extracted from the soil by the plant and transferred to the plant's shoot and leaves. Plants which are often used in this process are selected based on their ability to accumulate contaminants and produce a high biomass [51, 52].

Phytoimmobilization/Phytostabilization: in this process, pollutants are absorbed and immobilized in the root system and it reduces their mobility. It has been used for the removal of Pb, As, Cd, Cr, Cu and Zn [70, 71].

Phytovolatilization: pollutants are absorbed at root level and converted in a less toxic forms as a result of metabolic modification and released in atmosphere from the aerial parts of plant. We can thus state that this mechanism only relocate the pollutants from the soil to the air [46]. However, in anyway, the soil has been sanitized.

Phytodegradation: this mechanism is mainly for the sequestration of organic contaminants in the soil. It involves Plant enzymes to degrade organic contaminants [51, 52]. Various enzymes are involve in the mechanism among which: (i) dehalogenase (sequestration of chlorinated compounds); (ii) peroxidase (sequestration of phenolic compounds); (iii) nitroreductase (sequestration of explosives and other nitrate compounds); (iv) nitrilase (sequestration of cyanated aromatic compounds); (v) phosphatase (transformation of organophosphate pesticides) [53, 54]. At this

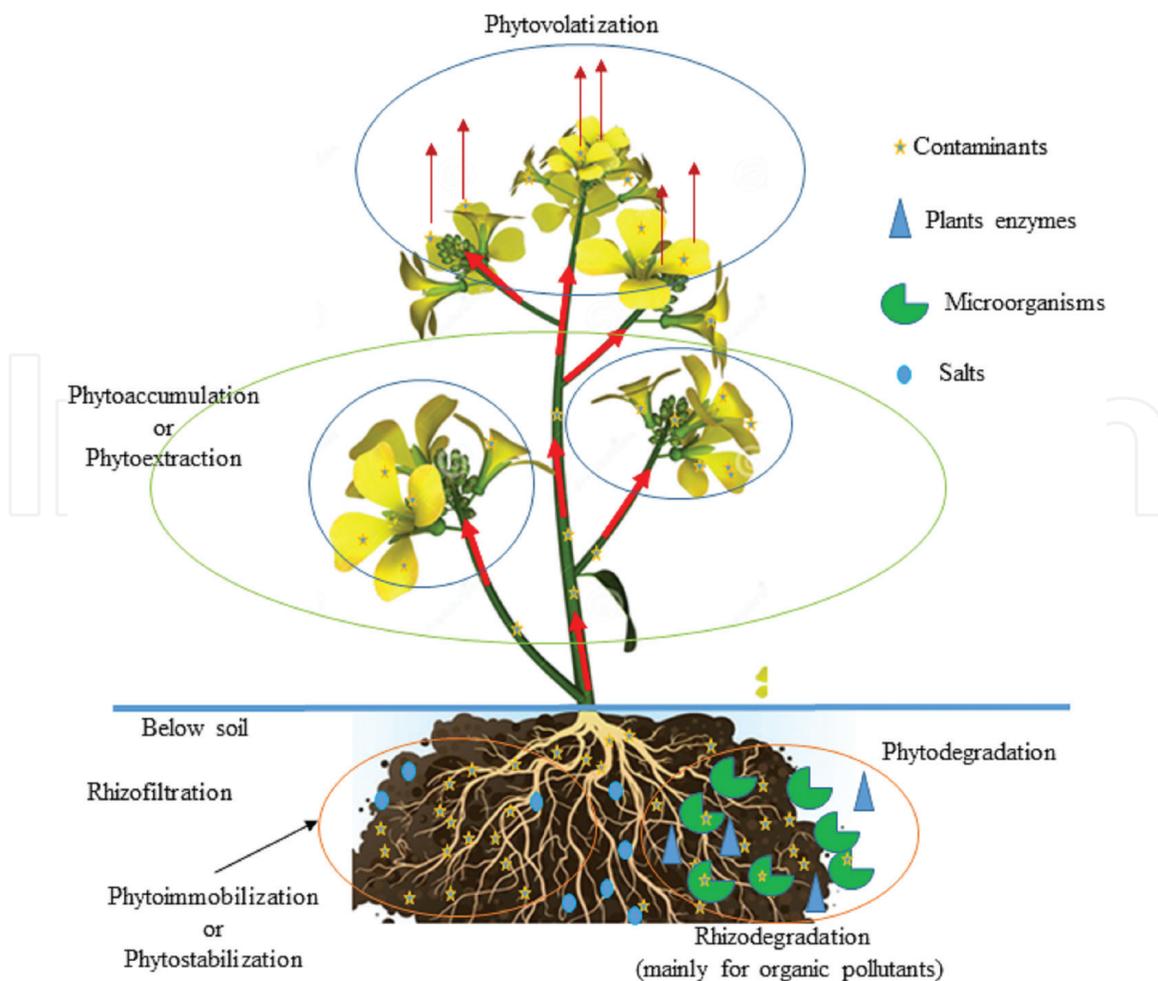


Figure 1.
Different mechanisms involve in phytotechnology.

level, phyto and bioremediation cannot be separated from one another, as microorganisms play an important role in these phytotechnologies. In fact, plants are in continuous interaction with microorganisms, some of which form close associations or symbiotic relationships. This phenomena is what explain the symbiosis that form mycorrhizal fungi with almost all land plants [55] and nitrogen-fixing rhizobia with legumes [56].

Rhizofiltration: this mechanism is commonly applied for the removal of pollutants from surface water or wastewater through adsorption or precipitation on the roots. It has been used for metals and even radioactive elements removal from soil, wastewater and contaminated water with satisfactory results [57]. This technique requires the adjustment of the pH of the medium a better efficiency of the operation; this is seen as a disadvantage of the technique.

Rhizodegradation: just like phytodegradation, this mechanism permit to degradation of organic pollutants in the rhizosphere through rhizospheric microorganisms. It involves a continuous interaction between plants and microorganisms; and thus it cannot be separated from bioremediation. Overwhelming number of research studies has already demonstrated the fact that the number of microorganisms in the rhizosphere is 100 times greater than present on the surface. The latter fetch their nutrients from the root exudates of the plant, which acts as carbon source.

Phytodesalination: this technique is really not used for remediation of contaminated-soil with PTE or persistent organic pollutants but used for the removal of salt from salt-affected soil; it is made possible using halophyte plants (*Artemisia argyi*, *Limonium bicolor*, *Melilotus suaveolens* and *Salsola collina*). Halophytes are plants with great ability to tolerate high concentrations of Na^+ and Cl^- ions; making them able to reclaim excessive saline soil [58]. To be noticed, it is reported that saline soils cover about 6% of the world's land [59] and it well known that salinity is the main environmental factor limiting plant growth and productivity.

4.1.2 Advantage and disadvantage of phytoremediation

In comparison to many other remediation technologies, phytoremediation is found to be of low costs, it protects the soil from erosion (reduction of erosion rate), improves the chemical, physical and biological soil properties, and enhances land esthetic. Phytoremediation is a technology that meets consensus and is highly accepted by the population. It is suitable for sites with low to moderate contamination and where contaminants diffused over large areas, and where there are no temporal limits to the intervention, and finally, it requires less human power. However, despite all this advantages, phytoremediation presents also some limitations which are worth to be mentioned. Indeed, it is time consuming, strong dependence upon: climatic conditions, contaminant(s) concentration and bioavailability, plant tolerance to contaminants, contamination area extent and depth (limited by the rhizosphere or the root zone). The disposal of harvested wastes is another challenge of phytoremediation. It is also not suitable for severely contaminated site such as e-waste contaminated site where potentially-toxic elements and persistent co-exist (the growth of plant would be inhibited), it is also not suitable when arable land (usable land for agricultural production is limited) [60]. Therefore, at this stage, another technology would be need to tackle the remediation of the site. For a better performance of phytoremediation, it could also be combined to electrochemical process. However, the challenge is that the combination would somehow inhibit some phytoremediation processes such as phytodegradation, rhizodegradation which only take place with continuous soil's microorganisms. Indeed, the electrochemical process which includes the induction of low level direct current in the soil

via electrodes, would provoke the rising of soil's temperature and the change of soil pH; and thus disturb or inhibit the activity of bacteria. As a consequence, the performance of plant to remove the contaminants will be affected. The detail about electrochemical process, would later be discussed, as it is part of our goal in this chapter.

4.2 Chemical leaching

4.2.1 Chemical leaching and leaching agents

Chemical leaching is one of the traditional remediation technologies used for contaminated soil remediation; and it involves dissolution, extraction and separation of the pollutants. Chemical leaching is one of the common and widely used methods for soil and sludge's PTE removal. Through the precipitation, ions exchange, chelation or adsorption, the PTE in soil are transferred from soil to liquid phase, and then separated from the leachate [61]. The separated pollutants are then converted to the appropriate form before disposal or can be reinserted in the recycling circle. For the dissolution and extraction process, there must be a step of breaking the bound between metals and soil constituents. The success this operation requires the use of acids, oxidants and complexants. Originally, contaminated soil is treated with strong inorganic acids such as HCl, HNO₃, H₂SO₄, H₃PO₄ [62]. Unfortunately, the application of the above-strong acids have been found to be environment and ecological disastrous. Indeed, strong acids have a strong capacity of destroying soil structure, and killing soil's microorganisms. Otherwise, in the process of sanitizing the soil using strong acids, there also occur the loss of soil constituent which is of great concern for the ecological consideration. Such situation is not in line with the protection of the environment on one hand, and does inhibit the productivity of the treated soil on the other hand. As a consequence, the use of strong acids is not environmental friendly. Thus, the integrated utilization of acids or reagents should be deliberately selected to fulfill the requirement of target contaminants removal on one hand, and soil ecological protection on the other hand. This justifies the introduction of Low molecular weight organic acids such as acetic acid, oxalic acid, which constitute a group of weak organic acids [63] and chelating reagents such as nitrilotriacetic acid (NTA) [33], sodium tripolyphosphates (STPP) and ethylenediaminetetraacetic acid (EDTA) [33, 63]. The use of weak acids showed mitigated results even though promising. On the other hand, chelating agents develop great affinity with the metals ions and possess prominent properties of oxidizing and forming complexes with metals cations; which could improve their extraction efficient. The use of the mentioned organic chelators has been widely investigated and results are satisfactory; mainly EDTA is well known for its excellent ability to recover metals from soil (25–80%) depending on the type of soil [64, 65]. However, these chelators seem to be refractory to the environment, and not easily biodegradable and thus can pose a secondary pollution via leaching to the groundwater [66]. As a consequence, there is a need to find more suitable chelators for the replacement of the refractory ones. In line with this objective, the use of organic acids and new generation of chelating agents are increasingly been investigated as an alternatives to above-mentioned washing reagents. N, N-bis(carboxymethyl) glutamic acid (GLDA), a chelator with excellent biodegradability [67], more than 60% degradable within 28 days. According to the OECD 301D test [68] with lowest 'eco-footprint' characteristics in comparison to EDTA and STPP; has been suggested due to it exceptional chelating capacity towards different divalent metal ions [69]. It was successfully used by [35] and [36] for the recovery of Cd Co, Cr, Cu, Ni and Zn from dewatered sewage sludge. The

removal efficacy was comprised between 60 and 86% and 70–94% for both studies, respectively. In addition, its comparison with citric acid during the work of [36] showed great efficacy and efficiency of GLDA compared to citric acid. The more a chelator possesses a carboxyl group (-COOH), the higher its performance would be during soil washing process. However, to be noticed, the overwhelming number of research work carried out on this topic which can be found in the literature are lab scale experiments, which is much easier to proceed comparing to field demonstration, mainly *in situ* application. It is only used in an *ex-situ* remediation technology, which create too much disturbance of soil system and its microorganisms. Here below (**Table 1**) are some organic chelators used in soil washing technology.

4.2.2 Challenges related to field application of chemical leaching

During chemical leaching, the use of significant amount of chelating agent is essential for the mobilization of PTE within the soil system. The addition of chelants to soils not only promote metals mobilization and transfer from the soil to the chelants' solutions but it also increases the total concentration of the soluble metals. A better mobilization of metals in the soil, requires up to hundreds of mill molar per liter concentration of the chelating agents in the soil solution. The issue is that the process can recover only part of the concentration of the dissolved metals, and leaching will be unavoidable [70]; which could lead to the possible contamination of the ground water and slow (several weeks or months) decomposition of the synthetic organic acids. Following the application of chelate forming agents, the removal of metals may continue for a long time. Besides, the use of chelating agents could exercises adverse effects on the soil microorganisms [71].

Otherwise, except the fact that during the soil washing/leaching process, soil minerals and other constituents are washing away together with the target pollutants, the *in situ* application of this technology at the large scale would be very challenging. Indeed, the injection of washing reagent in the soil is really challenging as it would not be easy to control the flow direction; and the solution will tend to flow vertically (leaching towards ground water) rather than in the desired direction, generally horizontal. As a consequence, the *in situ* field applicability of the technology at the large scale is limited; only *ex-situ* application are widely known. Otherwise, the technology is solvent consuming and involve longue processes and post treatments of the treatment waste and thus time consuming with high requirement of human power. Otherwise, it is soil generate too much soil disturbance (soil returning). One of the alternative to make valuable this technology is to combine it with other technology which permit the control of the solvent flow with less soil disturbance such as electrochemical process. This combination has given birth to the electrokinetic remediation technology.

4.3 Electrokinetic remediation

4.3.1 Principles and mechanisms of inorganic contaminants removal in soil

Electrokinetic remediation is a technique that consists in displacing or moving pollutants in contaminated soil from their contaminated points towards a specific controlled extraction points which are generally the electrodes cells. This technique is made possible by the application of a direct low current between electrodes well-disposed in the soil in order to optimize the electric field. The principle of pollutants cleanup is controlled by some key processes such as electroosmosis, electromigration and electrophoresis [72]. These mechanisms involve different mechanism. **Electroosmosis** knows as electroosmotic flow, consists of the

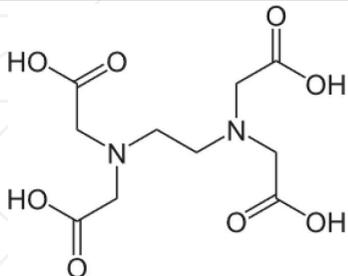
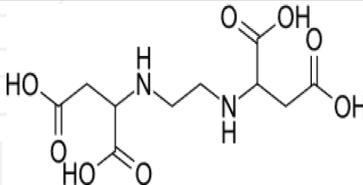
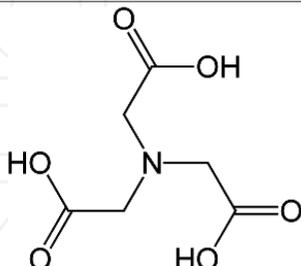
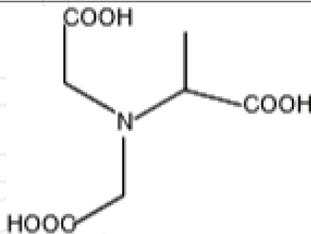
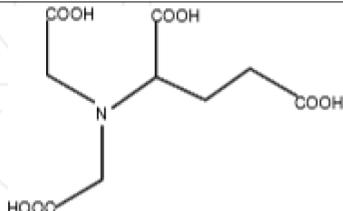
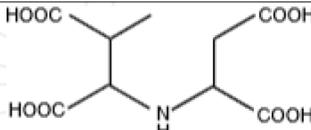
Name	Molecular structure	Name	Molecular structure
Ethylenediaminetetraacetic acid (EDTA) Molecular weight: 292.24 g/mol, appearance: colorless crystal, density: 0.860 g/mL at 20°C, solubility in H ₂ O: in any ratio biodegradability: moderate		Ethylenediaminedisuccinic acid (EDDS) Molecular weight: 358.1 g/mol, appearance: colorless to yellowish, pH: 9.2 density: 1.26 g/mL, solubility in H ₂ O: in any ratio biodegradability: > 60%	
Nitrilotriacetic acid (NTA) Molecular weight: 191.14 g/mol, appearance: white crystal, density: 1.6 g/mL solubility in H ₂ O: insoluble (<0.01 g/100 mL), biodegradability: easily biodegradable		Methylglycinediacetic acid (MGDA) Molecular weight: 271.0 g/mol, appearance: clear yellowish, pH: 11.0 density: 1.31 g/mL, solubility in H ₂ O: in any ratio biodegradability: > 68%	
N, N-bis(carboxymethyl) glutamic acid tetra sodium salt (GLDA) Molecular weight: 351.1 g/mol, appearance: colorless to yellowish pH: 13.5, density: 1.38 g/mL, solubility in H ₂ O: in any ratio biodegradability: > 83%		N-(1,2dicarboxyethylene)D,L-asparagine acid (IDS) Molecular weight: 337.1 appearance: colorless to light yellow pH: 10.3–11.4 density: 1.32–1.35 g/mL solubility in H ₂ O: in any ratio biodegradability: > 80%	

Table 1.

Some organic chelators often used for soil washing, EDTA and NTA are commonly used, while others in the table are known as new generation of chelators [69].

displacement of the liquid in the porous soil as result of the application of the electric field. During this movement, the pore fluid carries along organics and neutral molecules. **Electromigration** consists of the transport of charged particles (anions and cations) towards the opposite electrode cell. As for the **electrophoresis**, it is the movement of dispersed particles in the medium relative to a fluid as result of a spatially uniform electric field. These mechanisms are of great importance in pollution remediation (soil and sediment treatment) when using electrokinetic approach.

During electrokinetic remediation, there occur electrochemical reactions of which, electrolysis of water represents one of the most important and influential reactions. These reactions take place on the surface of the electrodes as the result of the application of low direct electric current. During electrolysis process, there occur a generation of protons (H^+) on the anodic surface and hydroxyl ions (OH^-) on the cathodic surface; which lead to an important pH gradient (**Figure 2**). These ionic species are mobilized through the soil at a rate determined mainly by the electromigration and diffusive processes and the soil's buffering capacity [73].

The pH profile is a key parameter during soil treatment with electrokinetic approach. Indeed, the changes of pH induce beside electrokinetic processes, physicochemical processes among which precipitation/dissolution of minerals and metals, adsorption/desorption of pollutants and ion exchange between the soil solid and the pore water. As it is well known, pH exercises strong influence on the chemical speciation of the compounds mainly inorganic present in the soil system. It determines the state or ionic forms in which a compound is found in the soil. This will indirectly condition the predominant transport mechanism by which this compound will move during the treatment.

Especially the change in pH affects the surface charge of soil particles and metal ions mobility. The generated acidic conditions help mobilize sorbed metal ions, prevents formation of metal hydroxide and carbonate precipitates; and thus facilitate their electromigration via the electroosmotic flow of the liquid. However, highly acidic conditions cause electroosmotic flow to stop or reverse, whereas alkaline condition results in PTE precipitation and increases electroosmotic flow.

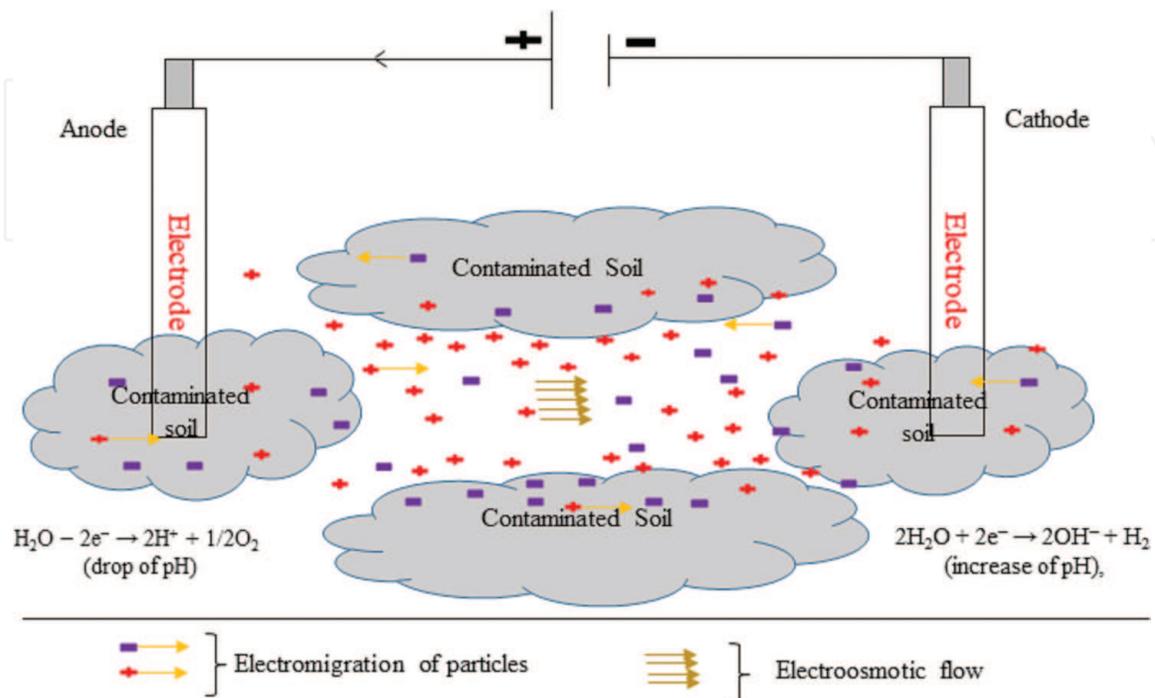


Figure 2.
Mechanism of electrokinetic remediation approach.

Thus, to maintain this parameter within a suitable range, pH control is often performed in both anode and cathode by adding sodium hydroxide (0.1 and 1 M) and acetic acid/citric acid (0.1 and 1 M) respectively [74, 75]. The in-situ acidification, however, may not be adequate if the soil possesses high buffering capacity. Moreover, the generated base front causes metal ions to precipitate, impeding their final arrival at the cathode [76]. Consequently, external/artificial acidification is often required even necessary during electrokinetic soil remediation [77]. However, the use of strong inorganic acids such as HCl, HNO₃ is not recommended as it can damage the soil structure. In addition, it would be costly and is not environmentally acceptable. Generally, water or chemical solutions [(0.1 M) EDTA or acetic acid, citric acid, etc.] are continuously injected at the anode to maintain optimal remediation conditions; contaminated water is removed at the cathode by pumping [78].

This technology has been successfully used in single for the treatment of various wastes/sites such as wastewater, sewage sludge, soil and sediments contaminated with inorganic and organic pollutants [76, 77, 79]. However, to optimize its efficacy, it has also been used in the combinations with other technologies [80–82]. The combination of electrokinetic remediation method with other technologies has been tested and is still on the hotspot of scientific research in environmental field. It includes electrokinetic-microbe joint remediation, electrokinetic-chemical joint remediation [82], electrokinetic-oxidation/reduction joint remediation [83], coupled electrokinetic-phytoremediation [81], electrokinetics coupled with electro-spun polyacrylonitrile nanofiber membrane [80], and electrokinetic remediation conjugated with permeable reactive barrier [79].

4.3.2 Electrodes and electrolytes

Various inert electrodes made of ceramic, carbon, graphite, titanium, stainless steel, are generally used during electrokinetic remediation of contaminated-soil. Each electrode has its level of stability, the choice of electrode depends on the use and purpose. The electrode are configured in order to optimize the electrical field in the treated area. Generally, they are disposed in the contaminated soil at 1.0–1.5 m spacing, with imposed DC current at 1.0–3.0 V cm⁻¹ or 100–500 kWh m⁻³ [84].

Electrokinetic extraction of PTE involves desorption/dissolution followed by transport. When the concentration of PTE in the soil solution becomes below the soil sorption capacity, chemical additives are typically needed to help mobilize and sorb metals. Also poor conductivity-pollutants (in the form of sulfides) or present in metallic form (Hg) cleanup involve a primary step of dissolution. This step generally involves the use of some appropriate electrolytes such as distilled water, organic acids or synthetic chelates; which aims to enhance the efficiency of the remediation. Several chemical have been tested as additives and include acetic acid (CH₃COOH), citric acid ((HOOC-CH₂)₂C(OH)(COOH)), nitrilotriacetic acid (NTA), ethylene-diamine-tetra-acetic acid (EDTA), ethylenediaminedisuccinic acid (EDDS), diethylenetriaminepentaacetic acid (DTPA), and potassium iodide (KI). These additives also known as enhancement fluids mobilization efficiencies varies from one to another and depending on the type of metal species in soil [85–87]. It is worth to mention that the removal efficiency varies not only depending on the type of the chemical used (anolyte) and metal remediated [88] but also on the type of electrode. Indeed, the use of KH₂PO₄ as an anolyte permitted to enhance the removal efficiencies of As species by >50% and ~ 20% for Cu species. Meanwhile, it did not enhanced the removal of the Pb and Zn (< 20%) [89, 90]. Also reported that adding ethylene diamine disuccinate (EDDS) in the anolyte enhanced Pb and Cd removal efficiencies in the contaminated soil.

4.3.3 Advantages and limitations

Electrokinetic technology has many advantages among which, its applicability for in-situ/ex-situ remediation, applicable to low-permeability soils and a mixture of contaminants where other technologies cannot be applied, applicable to a wide range of pollutants, and applicable to heavy and severely contaminated sites. However, the main limiting factor for direct electrokinetic remediation is the fluctuation in soil pH; because it cannot maintain soil pH value. Therefore there is a need to control the soil pH by external intervention through the addition of buffer solutions in cathode and anode cells. In fact, controlling the pH in the electrode cells remains the main challenge of this technology. Electrokinetic remediation has shown promising results and is still under development stage [91].

5. Comparison of the three technology

The comparison of the three technologies involved in the present chapter is summarized in the **Figure 3** below.

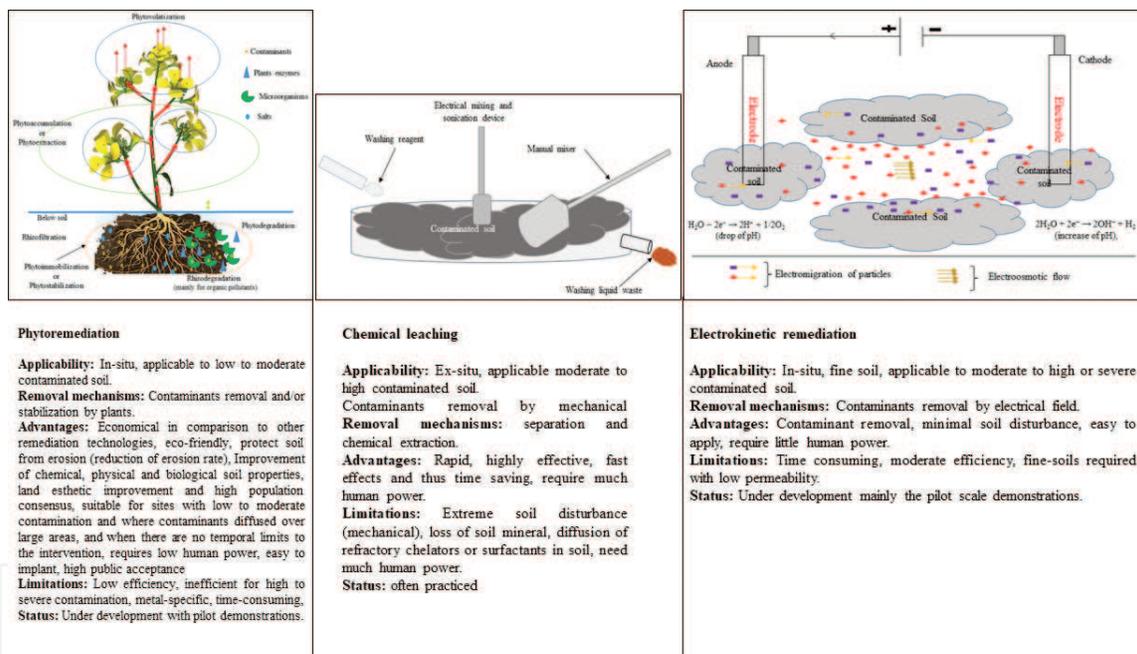


Figure 3. Comparison of phytoremediation, chemical leaching and electrokinetic technologies.

6. Conclusion

Soil contamination is one of the greatest challenges threatening the world as it lowers soil productivity and compromises food security. Contaminated soil/sites remediation or restoration is among the top list objectives of Food and Agriculture Organization's (FAO) agenda. Phytoremediation, chemical leaching and electrochemical remediation are three techniques commonly used for the remediation of contaminated sites. Each of these techniques has its advantages and limitations. Due to the non-availability of enough arable land, the use of phytoremediation, though it is eco-friendly, would lead to food insecurity as it takes long period to clean a target site. Moreover, it takes too much agricultural space for its implementation. As for chemical leaching, it is an *ex-situ* treatment technique, it thus disturbs too

much the soil and its microorganisms; it leads to the loss of much soil minerals and reducing soil fertility (non-suitable for agricultural land). In addition, it introduces much chemical into the soil, some of which may be refractory to biodegradation and leach to underground water. Electrokinetic approach is less time consuming and less disturbs the treated site; the main challenge is how to control the pH during the process; this could be monitored by external intervention. However, additives which include surfactants, chelants and organic acids must be carefully chosen having in mind their biodegradability and the protection of the soil structure and ecosystem. None of these techniques, when applied in single, is able to properly achieve the soil depollution; thus their combination is highly recommended. The combination of these technologies still suffers some lack of information which needs to be explored in order to appreciate their feasibility. In order to enhance the efficiency of soil remediation, it is recommended to investigate and develop more environmental friendly flushing reagents to replace refractory existing ones on one hand; and to promote phyto-electrokinetic remediation approach on the other hand.

Conflict of interest

None.

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