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Review

Remediation of Metal/Metalloid-Polluted Soils: A Short Review

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Abstract: The contamination of soil by heavy metals and metalloids is a worldwide problem due to the accumulation of these compounds in the environment, endangering human health, plants, and animals. Heavy metals and metalloids are normally present in nature, but the rise of industrialization has led to concentrations higher than the admissible ones. They are non-biodegradable and toxic, even at very low concentrations. Residues accumulate in living beings and become dangerous every time they are assimilated and stored faster than they are metabolized. Thus, the potentially harmful effects are due to persistence in the environment, bioaccumulation in the organisms, and toxicity. The severity of the effect depends on the type of heavy metal or metalloid. Indeed, some heavy metals (e.g., Mn, Fe, Co, Ni) at very low concentrations are essential for living organisms, while others (e.g., Cd, Pb, and Hg) are nonessential and are toxic even in trace amounts. It is important to monitor the concentration of heavy metals and metalloids in the environment and adopt methods to remove them. For this purpose, various techniques have been developed over the years: physical remediation (e.g., washing, thermal desorption, solidification), chemical remediation (e.g., adsorption, catalysis, precipitation/solubilization, electrokinetic methods), biological remediation (e.g., biodegradation, phytoremediation, bioventing), and combined remediation (e.g., electrokinetic–microbial remediation; washing–microbial degradation). Some of these are well known and used on a large scale, while others are still at the research level. The main evaluation factors for the choice are contaminated site geology, contamination characteristics, cost, feasibility, and sustainability of the applied process, as well as the technology readiness level. This review aims to give a picture of the main techniques of heavy metal removal, also giving elements to assess their potential hazardousness due to their concentrations.

Keywords: heavy metals and metalloids; removal techniques; contaminated soil

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1. Introduction

Soil contamination by heavy metals and metalloids is a problem that all countries in the world are facing. In recent years, the attention to heavy metal pollution has increased since they are non-biodegradable; they accumulate in soil causing damage to the environment, animals, and humans for a long time [1]. Multiple health effects are associated with exposure to heavy metals and metalloids: kidney and bone problems, neurobehavioral and developmental disorders, blood pressure problems, and tumor formation.

The problem becomes relevant when the concentration of heavy metals in the soil is high. Around the world, it is estimated that the number of sites with soil contaminated by heavy metals and metalloids is around five million [2], and anthropological activities are usually the origin of this pollution. Most of these heavy-metal-contaminated sites are in developed countries, such as the United States of America, Australia, the European Union State Members, and China. For example, in the USA, around 6000 km^2 have been contaminated by heavy metals/metalloids; 250,000 sites are polluted in the European Union; and

810,000 km^2 of farmland in China have been contaminated by heavy metals/metalloids [3]. The study of Cheng et al. [4] reports that more than 30,000 tons of chromium and 800,000 tons of lead have been released into the environment globally in the past half-century. Different studies have focused on determining the concentrations of heavy metals and metalloids in the European Union [5], China [6–8], and Brazil [9,10]. The amounts of these pollutants in soils are different and worldwide average concentrations depend on the type of soil, environmental conditions, and the distance from the contamination source.

In this review, the aim is to give information about the elements (metals and metalloids) that contribute to environmental pollution, due to their toxicity, persistence in the environment, and bioaccumulation in nature, and depict the main techniques that have demonstrated efficacy to remove these elements so far.

This review is focused on the removal of heavy metals, analyzing: (1) the toxicity effects of these pollutants on living organisms; (2) the legislation in force in some developed countries; and (3) the main remediation processes for contaminated soils.

Over the years, many authors have studied this topic, due to its great importance at the global level. Among the existing reviews, one was published by Dhaliwal et al. in 2020 [11]. However, it was mainly focused on biological remediation techniques at the laboratory level, and did not give detailed information on the other issues, which are important matters. To overcome this limitation, these issues have been developed in the current review. In addition to this, the last section of this review provides some case studies, and this constitutes a novelty compared to previous reviews, which have usually been limited to experimental studies and data, with limited (or without) links to their application.

These techniques are based on physical, chemical, and biological processes [12], and they can be classified as:

- physical methods (landfilling and leaching, excavation, soil washing, calcination) that permit high removal efficiency and the treatment of large quantities of soil, but are expensive;
- chemical methods (soil washing, electrochemical remediation, adsorption) that are very effective, but can be a source of new chemical contaminants introduced into soils, for example, in soil washing;
- physical–chemical processes (ion-exchange, precipitation, reverse osmosis, evaporation, and chemical reduction) which are simple and easy to apply, but have a high-cost burden;
- bioremediation processes (bioventing, biosparging, bioaugmentation, biostimulation) which are environmentally friendly and cost-effective, but the degradation time is slower than in other treatments.

2. Origin, Characteristics, and Properties of Heavy Metals and Metalloids

The term “heavy metals” is used to refer to metals and metalloids present in the environment and having a density higher than 5000 kg·m^{-3} and an atomic mass higher than 20. Based on this definition, 51 elements of the periodic table are considered heavy metals/metalloids [13].

Their mobility and bioavailability in soil are due to their chemical characteristics and those of soil. The pH, surface properties of the adsorbents, presence of cations, and anions affect the interactions between soil components and metals/metalloids [14].

The most common heavy metals and metalloids in the environment are chromium, manganese, nickel, copper, zinc, cadmium, lead, and arsenic. Chromium, copper, zinc, cadmium, lead, mercury, and arsenic are the most toxic [15].

Usually, they found in the weathering of underlying bedrock, and they are present as ores (sulfides of Pb, Co, Fe, As, Pb, Zn, Ag and Ni, and oxides of Se, Al, Mn, and Sb). In soils, normally, sulfides of arsenic, mercury, lead, cadmium naturally occur together with sulfides of copper (chalcopyrite, $CuFeS_2$) and iron (pyrite, FeS_2) [3].

The environmental problem is mainly due to the anthropological activities that cause an increase in heavy metal and metalloid concentrations, especially in the refining and mining of ores, pesticide applications, fertilizer industries, and solid wastes [16]. The anthropogenic sources of metals and metalloids can be dived into five groups, as shown in Figure 1.

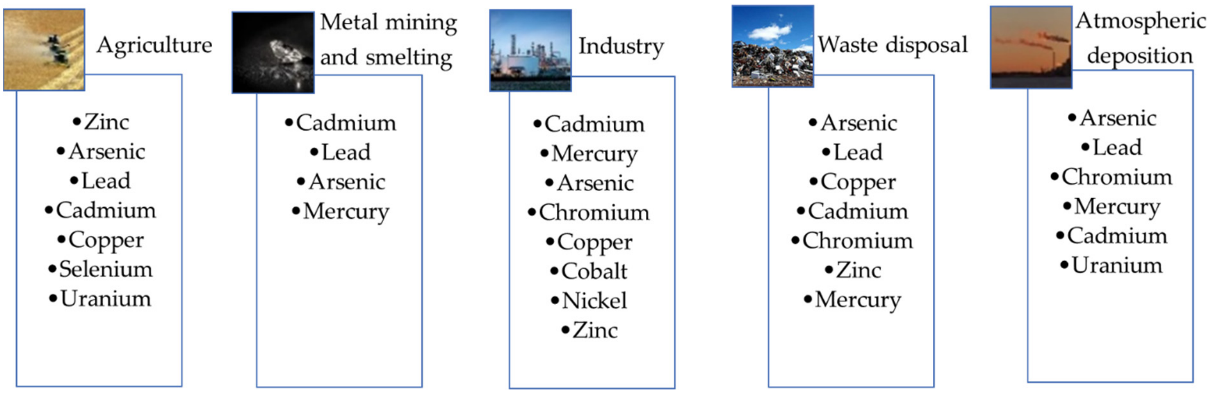

Figure 1. Anthropogenic sources of polluting metals and metalloids.

Heavy metals and metalloids are used in different sectors, increasing market demand and world production. Copper, selenium, zinc, iron, vanadium, and manganese, in trace amounts, are essential for various biological processes, such as in respiration systems, biosynthesis of complex compounds, nervous system, regulation, and functioning of enzymes. Iron, zinc, tin, lead, copper, and tungsten have an important role in electronic devices, especially in the realization of semiconductors [17]. In Table 1, the characteristics of the most toxic heavy metals and metalloids are summarized [18,19].

Table 1. Heavy metals and metalloids characteristics.

Element	Chemical and Physical Properties	Application	World Production (ton·y^{-1})
Chromium (Cr)	Density: 7190 kg·m^{-3} Atomic mass: 51.99 Heat of fusion: 21.00 kJ·mol^{-1}	Industrial application, alloys, tanning agents, paint pigments, catalysts, photography.	15,000,000 (year: 2017)
Copper (Cu)	Density: 8960 kg·m^{-3} Atomic mass: 63.55 Heat of fusion: 13.26 kJ·mol^{-1}	Electrical and electronics, transport equipment, construction, industrial machinery, pesticides.	20,000,000 (year: 2017)
Zinc (Zn)	Density: 7140 kg·m^{-3} Atomic mass: 65.38 Heat of fusion: 7.32 kJ·mol^{-1}	Paints, rubber, cosmetics, pharmaceuticals, plastics, inks, soaps, batteries, textiles, and electrical equipment	13,500,000 (year: 2019)
Cadmium (Cd)	Density: 8650 kg·m^{-3} Atomic mass: 112.41 Heat of fusion: 6.21 kJ·mol^{-1}	Electroplating, paint pigments, plastics, silver–cadmium batteries, coating operations, machinery and baking enamels, photography, television phosphors.	24,670 (year: 2019)
Lead (Pb)	Density: 11,340 kg·m^{-3} Atomic mass: 207.2 Heat of fusion: 4.77 kJ·mol^{-1}	Electrical accumulators and batteries, building construction, cable coatings ammunition.	11,600,000 (year: 2018)
Mercury (Hg)	Density: 13,530 kg·m^{-3} Atomic mass: 200.59 Heat of fusion: 2.29 kJ·mol^{-1}	Dental preparations, thermometers, fluorescent and ultraviolet lamps, pharmaceuticals, fungicides, industrial process waters, seed dressings.	4000 (year: 2019)
Arsenic (As)	Density: 5730 kg·m^{-3} Atomic mass: 74.92 Heat of fusion: 24.44 kJ·mol^{-1}	Pesticides, pharmaceuticals, alloys, semiconductors.	33,000 (year: 2019)

It is evident that these elements are used in all fields and that annual production around the world is very high, especially chromium, copper, zinc, and lead. The major producing countries are China, Peru, Australia, the United States of America, Russia, and Mexico.

3. Toxicology

The heavy metals and metalloids accumulate in the environment where anthropogenic sources increase the background quantity, and this effect becomes risky when the natural concentrations are such that they cause damage to living organisms. Their toxicity is relevant at low concentrations, as demonstrated by the limit concentrations imposed by legislative acts (Table 2).

Table 2. Limit concentrations of heavy metals and metalloids in the soil.

Country/ Organization	Type of Soil	Hg	Cd	Pb	Cr(VI)	Ni	Unit	Ref.
WHO	Agricultural soil	0.08	0.003	0.1	0.1	0.05	ppm	[20]
China	Agricultural soil	0.3–1.0	0.3–0.6	80	150–300	40–60	ppm	[20]
US	Agricultural soil	1.0	0.43	200	11	72	ppm	[21]
Italy	Residential soil	1	2	100	2	120	$mg \cdot kg^{-1}$	[22]
	Industrial soil	5	15	1000	15	500	$mg \cdot kg^{-1}$	
Finland	Threshold value	0.5	1	60	100	50	$mg \cdot kg^{-1}$	[23]
	Lower guideline value	2	10	200	200	100	$mg \cdot kg^{-1}$	
	Higher guideline value	5	20	750	300	150	$mg \cdot kg^{-1}$	
Canada	Agricultural soil	0.8	3	200	250	100	$mg \cdot kg^{-1}$	[24]
Germany	Agricultural soil	5	5	1000	500	200	$mg \cdot kg^{-1}$	[2]
Spain	Soil $pH < 7$	1	1	50	100	30	$mg \cdot kg^{-1}$	[25]
	Soil $pH > 7$	1.5	3	300	150	112	$mg \cdot kg^{-1}$	

The concentration limits vary from country to country as there is no international regulation. For example, in the European Union, this topic is not ruled by a directive, enforcing different threshold limits in the 27 countries. Furthermore, the limit value depends on the element type and the land use of the soil. The mobility of these elements in soil makes them available to plants and consequently, they enter the food chain [26]. For this reason, it is important to evaluate the diffusion of toxic elements in soil.

3.1. Presence and Distribution into the Environment

Several studies report on the distribution of heavy metals and metalloids in soil [9,10,27,28]. Some soil properties facilitate the accumulation of these pollutants and increase their concentrations. pH controls the adsorption and solubilization; if the soil pH is acidic, the solubility and the bioavailability of heavy metals/metalloids increase [29]. Organic matter content (OMC) is another factor that influences their presence since organic substances with a high molecular mass have a high affinity with heavy metals and form water-insoluble metal complexes [30]. In general, the distribution of heavy metals and metalloids is high in topsoil and decreases as the depth increases [31].

Some studies evaluated their concentrations in soils close to industrial activities, and some examples are reported in Table 3.

Table 3. Concentration of heavy metals/metalloids in polluted sites.

Country	Proximity to Activity Sources	Soil	Element	Concentration ($mg \cdot kg^{-1}$)	Ref.
China (Feng County)	Pb/Zn smelter	A = County Seat (pH 8.5) B = River basin (pH 8.0–8.5) C = Smelter area (pH 8.6)	Cd	A: 6.7 B: 0.8–2.7 C: 57.6	[31]
			Cu	A: 25.0 B: 21.9–30.2 C: 36.9	
			Ni	A: 46.0 B: 39.4–46.3 C: 49.3	
			Pb	A: 50.0 B: 30.0–70.0 C: 148.0	
			Zn	A: 900.0 B: 300.0–400.0 C: 2079	
China (Shuozhou)	Pingshuo open pit mine		Cd	0.117	[8]
			Hg	0.03	
			As	9.629	
			Pb	21.328	
			Cr	55.609	
China	Pb smelter	Distance from smelter D = 1 km E = 3 km F = 6 km	Cd	D: 4.5 E: 2.0 F: 1.0	[6]
			Cu	D: 45.0 E: 35.0 F: 32.0	
			Pb	D: 350.0 E: 180.0 F: 175.0	
			Zn	D: 128.0 E: 82.0 F: 80.0	
China (Changshu City, Jiangsu Province)	Primary, secondary, and tertiary industries	Gleyic clayey paddy soil	Mg	0.22	[32]
			K	1.64	
			V	82.77	
			Se	0.12	
			Mn	347.77	
			Fe	1.16	
			Co	12.76	
			Sb	4.14	
			Pb	31.41	
			Cu	31.60	
			Zn	61.13	
			As	7.46	
			Cr	86.38	
			Cd	0.11	
			Ni	34.93	

Table 3. *Cont.*

Country	Proximity to Activity Sources	Soil	Element	Concentration (mg·kg^{-1})	Ref.
Pakistan (Swabi)		G = Depth (cm) 0–15 Organic matter (%) 0.35–2.30 pH 7.21–9.21 EC (dS·m^{-1}) 0.13–0.56 $CaCO_3$ (%) 5.89–16.65 H = Depth (cm) 15–30 OMC (%) 0.21–1.52 pH 7.32–8.88 EC (dS·m^{-1}) 0.18–0.86 $CaCO_3$ (%) 6.56–17.81	Cu	G: 2.33–19.15 H: 1.32–14.11	[33]
			Fe	G: 8.23–36.89 H:8.22–30.95	
			Zn	G: 8.26–26.55 H: 7.77–24.20	
			Cd	G: 0.01–0.16 H:0.01–0.08	
			Co	G: 0.8–6.99 H: 0.33–5.46	
			Ni	G: 0.46–22.21 H:0.42–21.9	
			Cr	G: 0.23–8.02 H:0.54–5.11	
			Pb	G: 0.4–2.23 H:0.08–1.99	
Colombia (Sinú River Basin)		Agricultural soil	Cu	1149	[29]
			Ni	661	
			Pb	0.071	
			Cd	0.040	
			Hg	0.159	
			Zn	1365	
Greece (Argolida)		Agricultural soil	Cu	28.64	[34]
			Pb	13.96	
			Zn	45.26	
			Ni	253.7	
			Co	25.05	
			Mn	665	
			As	5.89	
			Cd	0.26	
			Cr	138.4	
			Fe	2.90	
			P	0.039	
			K	0.239	

Very often, in industrial areas, the concentrations of heavy metals and metalloids are higher than the threshold limits allowed by national legislation. Some authors compared the concentration values of the same soil, before and after the presence of anthropological sources. They demonstrated that an increase of concentration was precisely due to these activities [8]. In agricultural soils, high concentrations are due to the use of fertilizers and pesticides [29].

Regarding the European Union, an interesting study was done by Tòth et al. [5]; where they monitored As, Cd, Cr, Cu, Hg, Pb, Zn, Sb, Co, and Ni concentrations. Results showed that, in most soil samples taken from various regions, concentrations were above the threshold limits, both on their entire land area and on agricultural lands. In Western Europe and Mediterranean regions, the concentrations were higher than those in North-Eastern Europe and Eastern-Central Europe. The measured values of arsenic exceeded threshold values by 10% to 90%, and the most polluted regions were France, Italy, and Spain. For cadmium, the values were 10% to 70% above threshold values, and the highest concentrations were found in Ireland and Greece. A few European regions were found with cobalt values higher than the threshold values, among them, France and Greece. Zinc, mercury, and copper values were not higher than 10% of guideline values and most regions had concentrations below 2% of the threshold limits. Nickel and antimony contaminations were significant, especially in Italy and Greece since the concentrations exceeded 90% of the admissible values.

3.2. Health Impacts Over Short, Medium, and Long Term

The high amounts of these elements in soil lead to the deterioration of agricultural land, eutrophication, and the absorption of toxic substances. Direct effects of contamination are a reduction in the quality of agricultural soils, including phytotoxicity at high concentrations, the preservation of soil microbial processes, and the transfer of zootoxic elements to the human diet [35].

The health of living organisms is damaged, especially in the long term. The principal effects on health can be reduced growth and development, cancer, organ damage, nervous system damage, and, in extreme cases, death [36]. Toxicity depends on the type and form of the element, dose, route of exposure, age, genetics, and nutritional status of the exposed individuals [37].

The United States Environmental Protection Agency (EPA) establishes limits for some heavy metals and metalloids; surpassing these values has toxic effects on human health [38].

It is possible to summarize the principal effects of the most toxic metals/metalloids when the admissible concentration is exceeded:

- Chromium (Cr): it is found in the environment in different oxidation states (−2 to +6), but the most stable forms are trivalent (III) and hexavalent (VI). Chromium(VI) is more absorbed than chromium(III) by the human body through inhalation, ingestion, and dermal contact, due to its high solubility and mobility. Chromium(VI) enters into the cell via a nonspecific anion channel via facilitated diffusion, while chromium(III) enters by passive diffusion or phagocytosis. The main organs that are influenced are the liver, kidney, spleen, and bone. The hexavalent form can easily penetrate red blood cells [39]. The main toxic effects of chromium for humans are ulcers, dermatitis, perforation of the nasal septum, and respiratory cancer. In soil, chromium alters the structure of microbial communities and reduces their growth [40].
- Copper (Cu): this element is essential in many biological processes (oxidation, photosynthesis, and carbohydrate, protein, and cell wall metabolism) [41]. Excessive concentration of copper leads to the formation of free radical species that damage the cell and inactivate some enzymes, threatening the environment, microbes, and human health [42]. In particular, the accidental ingestion of copper may cause nausea, vomiting, and abdominal pain, whereas a prolonged exposure leads to chronic effects, involving the liver and kidneys [36]. In the plants, copper accumulates in the roots, reducing their growth and the ability to absorb other trace elements useful for plant development [43].
- Zinc (Zn): is a trace element essential for all organisms, important in nucleic acid and protein metabolism, in cell growth, division, and function [44]. Excessive concentration in food or potable water may cause vomiting, muscle cramps, and renal damage [45]. In plants, a high concentration of zinc leads to a decrease in growth (both roots and shoots) and development of the plant, chlorosis, alteration in metabolism processes, and induction of oxidative damage [46].
- Cadmium (Cd): has eight stable isotopes, the most common are ^{112}Cd and ^{114}Cd. Cadmium forms various complexes with amines, sulfur, chlorine, and chelates. Depending on the form, it has different clinical manifestations and toxic effects. Cadmium interferes with cell proliferation, differentiation, apoptosis, and DNA repair mechanism. The common clinical effects are skeletal demineralization, kidney, and liver problems [47]. Excess accumulation in plants can influence both photosynthesis and respiration, transport, and assimilation of mineral nutrients, affecting plant growth and development [48].
- Lead (Pb): lead poisoning occurs mainly by the ingestion of food and water. It is quickly absorbed into the bloodstream, damaging various systems [49]. Different studies have reported the dangerous effects of lead on the neurologic system, such

as irritability, agitation, headaches, confusion, ataxia, drowsiness, convulsions, and coma, and has an effect on renal functions, the body development, and the lymphatic system [50].

- Mercury (Hg): in the environment, mercury can be present in the form of both organic and inorganic (Hg, Hg_2^{2+}, Hg^{2+}) compounds. Mercury tends to deposit in many parts of the human body, damaging the brain, thyroid, breast, myocardium, muscles, liver, kidneys, skin, and pancreas. Among them, the nervous system is the most affected [51]. Inorganic mercury can inhibit the activity of enzymes in the body and destroy the normal metabolism of cells. The organic form has a great negative effect on brain function and can enter through the food chain [52].
- Arsenic (As): it is present in the environment in organic and inorganic forms, the most common and toxic forms are arsenate and arsenite. Arsenate can cause damage to the plant since it affects phosphate metabolism, while arsenite binds to sulfhydryl groups of proteins, interfering with their structures and functions [53,54]. Chronic exposure to this metalloid causes cutaneous lesions, such as melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation); lung, bladder, liver, and kidney cancers; ischemic heart diseases, impaired cognitive abilities, motor functions, and hormonal regulations [55].

If the heavy metal and metalloid concentrations in soil are known, some methods to assess the associated risks are available in the scientific literature. For example, the Hakanson method permits to calculate the potential ecological risk index (RI) [56–58]:

$$RI = T_r \cdot C_f = T_r \cdot \frac{C}{C_n} \tag{1}$$

where:

T_r is the toxic response factor of the element, which reflects the toxicity level and sensitivity of organisms to it [59]. This factor is calculated with an empirical formula, considering the effects that the element can cause in microorganisms. For Cr, Ni, Cu, As, Cd, and Pb, T_r is equal to 2, 6, 5, 10, 30, and 5, respectively;

C_f is the pollution index of the element, the ratio between the measured concentration of an element in the tested area, C, and the background (to say, natural) concentration of an element in the tested area, C_n.

The RI value reflects the state of the soil under examination, according to these assessments:

- $RI < 150$: the ecological risk is low;
- $150 \leq RI \leq 300$: the ecological risk is moderate;
- $300 \leq RI \leq 600$: the ecological risk is considerable;
- $RI \geq 600$: the ecological risk is very high.

Another method that defines the hazard quotient (HQ) [58] is expressed as:

$$HQ = \frac{C}{C_b} \tag{2}$$

where:

C is the measured concentration of an element in a study area;

C_b is the benchmark concentration of the element (the limit value concentration given by current legislation).

If the hazard quotient for the test is lower than 1 ($HQ < 1$), negative effects and ecological risks are highly unlikely. Vice versa, if $HQ > 1$, the soil must be remediated.

4. Removal Techniques

The removal techniques developed over the years can be divided into three categories: physical, chemical, and biological processes [60,61]. Their aim is the complete removal of contaminants or the transformation of contaminants into less dangerous forms [62]. They differ by in terms of the mechanism applied to remove/degrade the pollutants from soil.

The techniques can be also characterized by the location where they are applied, namely:

- *in situ*: the treatment is carried out directly on the site where the pollution is present, and there is no need to move/excavate the soil;
- *on site*: the soil is removed and processed on site surrounding the polluted area. The technique can be carefully monitored and kept under control;
- *ex situ*: the remediation occurs at a site far from the polluted area, and this entails soil excavation, its transport to a processing plant, and often transport back to the original site.

For some techniques, the operation can be carried out at all kinds of locations, whereas for others it can occur only *in situ*. Each location involves different features and impacts that are typical of the considered polluted site. Therefore, a detailed discussion with an assessment of pros and cons is impossible.

Table 4 reports a summary of the techniques and their main characteristics.

Table 4. Removal techniques for heavy metals/metalloids.

Technique	Studies	Maximum Removal	Advantages	Disadvantages	Location
Physical processes Removal through physical operations	Physical separation [63–66] Thermal treatment [67,68] Vitrification [69]	95%	High efficiency Simplicity Rapidity	Cost	A, B, C A, B, C A
Chemical processes Removal through chemical operations	Stabilization [70,71] Treatment with nanoparticles [72–81] Stabilization/solidification [82] Chemical soil washing [83–85] Electrochemical remediation [86–90]	90%	High efficiency Simplicity Rapidity	Cost Changes in the physicochemical soil properties	A, B, C B, C A B, C A
Biological processes Removal of pollutants by the microbial activity of microorganisms, or plants, or their combination	Biosorption [91–99] Bioleaching [100,101] Phytoremediation [102–117]	96%	Cheapness Ecofriendly Simplicity	Slow High efficiency only with low pollutant concentration	A, B, C B, C A

A: *in situ* treatment; B: *on site* treatment; C: *ex situ* treatment.

4.1. Physical Processes

Physical technologies permit removal through physical mechanisms such as physical separation, soil replacement, thermal treatment, or vitrification (Figure 2). These methods allow us to have a high removal efficiency, but they are rather expensive.

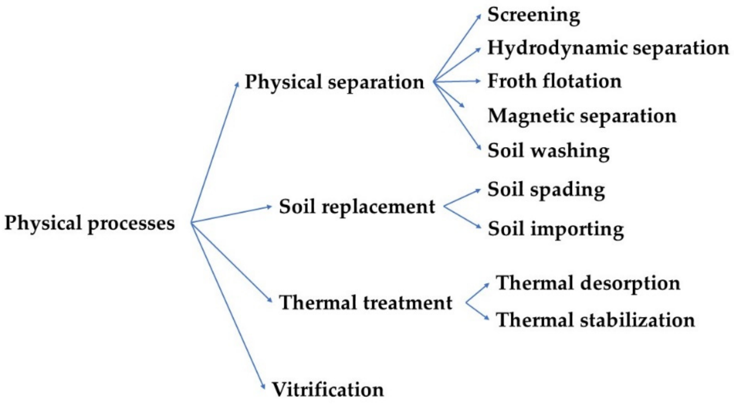

Figure 2. Physical processes to remove heavy metals and metalloids.

4.1.1. Physical Separation

Physical separation permits the removal of heavy metal/metalloid particles from contaminated soils at a large scale [64]. This technique exploits the differences in certain physical characteristics between metal particles and soil, such as size, density, magnetism, and hydrophobic surface properties [118]. Physical separation does not alter the chemical properties of soil, such as pH, elemental composition, and OMC [63].

Depending on the particle properties, physical separation can be done by [118]:

- Screening: the particle separation occurs on the basis of particle size, by passing (or not) through screen holes.
- Hydrodynamic separation: this operation exploits the different settling velocities of particles in a water flow; as an alternative, the different effects of centrifugal force can be applied.
- Froth flotation: the method exploits the differences in hydrophobic properties to separate metal-bearing particles from the soil matrix through air bubbles injected in a soil slurry.
- Magnetic separation: separates particles based on their different magnetic properties.
- Soil washing: the contaminates are desorbed and extracted from soil with an extractant solution.

Boente et al. [63] applied physical techniques to separate arsenic, copper, mercury, lead, and antimony from a brownfield affected by pyrite ash disposal. The used methods were high-intensity magnetic separation and hydrodynamic centrifugal separation. Magnetic separation was tested both under wet conditions, this is to say that the soil was mixed with water to form a slurry, and under dry conditions, with dried soil. The tests were carried out by changing the soil granulometry. They found that dry magnetic separation was more appropriate for large particle sizes (>250 μm), while the wet process was suitable for all particle sizes, except for clay soils (particle size lower than 63 μm). Hydrodynamic centrifugal separation was efficient for a wide fraction of sand (63–500 μm).

Liao et al. [64] found that the concentrations of heavy metals such as Pb, Cd, and Zn in soil increase with decreasing particle size and when soil has a high content of organic matter or clays. The use of mechanical mixing in soil washing promotes physical contact between contaminated soil particles and the washing liquid. To increase the efficiency of heavy metals removal, ultrasonic mechanical soil washing was also studied [65].

The advantages of physical methods are their high efficiency, simplicity, and rapidity of application, but they have a high cost, and they can change some soil properties; for example, soil texture or particle size, causing a deterioration in soil fertility [66].

4.1.2. Soil Replacement

This technique is indicated for treatment in small-scale applications. The method involves the total or partial replacement of contaminated soil with an uncontaminated one [119]. The replaced soil is treated as waste. It is also possible to decrease heavy metals/metalloid concentration with soil spading or new soil imports. With soil spading, contaminated soil is dug deeply, spaded, and then substituted with clean soil. With importing new soil, clean soil is added and mixed with polluted soil to reduce the heavy metal and metalloid concentrations [120]. Before replacement, the polluted soil area must be isolated from its surroundings through physical barriers to prevent the contamination of the neighboring areas and groundwater. Soil replacement is onerous and expensive but suitable for small areas that are severely contaminated.

4.1.3. Thermal Treatment

Thermal desorption, such as calcination, is the process of heating a medium under controlled temperature to eliminate a volatile substance. The main techniques for heating soil are conductive heating, electrical resistive heating, steam-based heating, and radiofrequency heating [60]. Volatile pollutants are desorbed from soil and are collected using vacuum-negative pressure or a carrier gas. The process can occur at high-temperature desorption (320–560 °C) or low-temperature desorption (90–320 °C), depending on the pollutant boiling point [11]. For example, this technique is widely used to treat contaminated soils with mercury. This metal boils at 357 °C, therefore thermal desorption is a good option to remove this metal from soil [68].

Wang et al. [67] studied thermal stabilization to reduce the mobility and availability of zinc and copper in contaminated soils. The metals are fixed in the treated soil. They found that the residual concentrations in tested soils decreased as the temperature increase to 700 °C.

The advantages of using this method are safety, little secondary pollution production, and less energy consumption compared with other processes [68]. However, it requires high capital costs and gas emission control, but it is only really effective high pollutant concentrations and it can damage soil structure.

4.1.4. Vitrification

Vitrification is a thermal technique at high temperatures (>1500 °C) to reduce the mobility of heavy metals and metalloids by fixing them into vitreous material. During the process, contaminated soil is heated with high-voltage electricity, an external heat source, or via electrical discharge-induced gas plasma. The soil is melted into molten lava, which, after cooling, is transformed into a vitrified structure. The heavy metals/metalloids are encapsulated in this glassy matrix, while the other contaminants are destroyed [69]. Vitrification is an efficient technique, but it is destructive for soil, expensive, and very complex. Moreover, it is not applicable to soil with high organic matter content, high moisture content, and soil contaminated by volatile or flammable organics.

4.2. Chemical Processes

Chemical techniques exploit chemical phenomena such as ion exchange and chemical reactions to stabilize and fix heavy metals and metalloids into less toxic forms. For these processes, chemical reagents are required. The main chemical processes are shown in Figure 3.

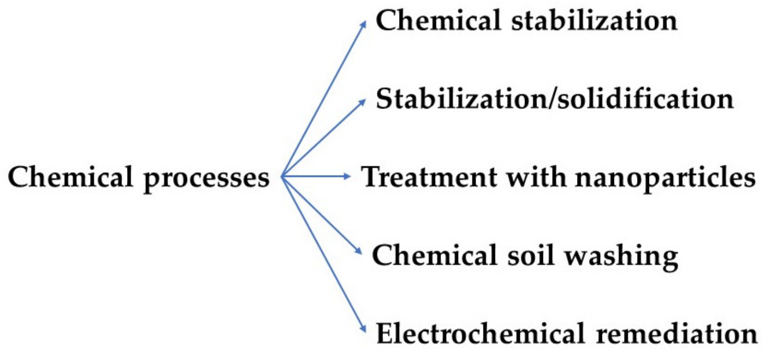

Figure 3. Chemical processes to remove heavy metals and metalloids.

4.2.1. Chemical Stabilization

Chemical stabilization reduces the mobility, bioavailability, and bioaccessibility of heavy metals and metalloids in soil. It consists of adding specific immobilizing agents. These agents promote precipitation, complexation, or adsorption to immobilize the pollutants.

In general, chelating agents with functional groups able to donate nitrogen, oxygen, sulfur, or phosphorus atoms can more likely react with heavy metal ions [82].

As a low-cost alternative, phosphates and carbonates have been demonstrated to be efficient [121].

Several materials including organic ones containing sulfur (hair or cysteine), manganese compounds, zeolite, or iron oxide [70] can also be applied. Nowadays, one of the aims is to use waste-derived resources, that are cost-effective and environmentally-friendly, such as biochar [122,123]. Biochar is a carbonaceous material produced by pyrolysis, that is able to stabilize heavy metals and metalloids [124]. Islam et al. [71] used waste (eggshells and cockle shells) to immobilize Cd, Pb, and Zn in mine tailing soil.

These stabilizers can be sprayed in aqueous solutions over a site if they are water-soluble; alternatively, the chemical agents can be mixed with contaminated soil.

This process aims to immobilize heavy metals [82], but the used chemicals will remain in the soil, and their concentrations will have to be monitored after the remediation.

4.2.2. Nanoparticles

In the last few years, nanotechnologies have been widely applied in many fields, including soil remediation. The synthesis of nanoparticles (D < 100 nm) for heavy metal removal has demonstrated feasibility for cleaning soils. In general, nanoparticles can remove pollutants through different mechanisms: adsorption [125], redox reactions [126], precipitation [127], and co-precipitation [128], all enhanced by a large specific surface area.

Studies making use of different nanomaterials are available. The results evidenced that an excellent removal can be achieved with zero-valent iron nanoparticles (nZVI), where the iron support can have different origins: for example, bentonite [72,73], zeolite [74,75], biochar [76,77], vinegar residues [78], rhamnolipid [79], carboxymethylcellulose [80], and starch [81]. In general, this kind of nanoparticle has shown very good results for the removal of all heavy metals and metalloids.

Recently, attention has been paid to the use of nanoparticles based on a metal–organic framework. This kind of nanoparticle has found wide use in wastewater treatment [129]. However, preliminary tests have also demonstrated positive results for its application to polluted soil remediation [130]. Further studies are needed.

However, nanoparticle techniques are the most controversial, since, at present, the effects on soil properties are not well known, especially in a real long-term scale. Considering the high reactivity of nanoparticles, the main problems to be solved are the potential toxicity of the nanomaterials, the interaction of soil–nanoparticles, the impacts on biodiversity and different ecosystems present in the soil, and the actions to regenerate nanoparticles. This requires a deeper knowledge of the question, given the transfer of this technique to a larger scale.

4.2.3. Stabilization/Solidification

Solidification is a chemical technique where a binding agent, commonly cement, asphalt, fly ash, or clay, is added to a contaminated zone to form a solid block that prevents heavy metals/metalloids from leaching.

The two chemical techniques (stabilization and solidification) can be used together to achieve and maintain the desired physical properties of the soil and chemically stabilize the contaminants in a solid phase. Stabilization/solidification is less harmful to the environment and biota since the chemical reagents remain only in the treated area. The first step is stabilization to reduce the mobility of contaminants with the chemical agents, and then the solidifying agents are added to avoid pollutant diffusion to the surroundings in the future. For the stabilization of heavy metals, traditional additives include cement and silica fume. Liu et al. [82] used a resin (water-soluble thiourea-formaldehyde (WTF)) to adsorb and fix cadmium and chromium. The results showed that this resin is suitable for stabilization, is easier to use than other agents, and is not toxic to indigenous microorganisms.

4.2.4. Chemical Soil Washing

Chemical soil washing permits the elimination of heavy metals/metalloids from contaminated soils by extraction of the pollutants followed by a reaction to produce insoluble compounds. Leaching needs an extractant solution, which can be water, chelators, inorganic and organic acids, or surfactants, also containing the reactant that will permit the production of metal hydroxides, sulfides, carbonates, and phosphates. The derived solid particles can be separated via sedimentation or filtration at the end of the process. The description of the chemical soil washing method is reported, for example, by Zhang et al. [131], who underlined how this technique permits to reduce the most mobile metals. The drawback is the chance to destabilize some strongly bound fractions, compromising the effectiveness of the process itself.

Several agents have been studied. The most-used chelator is ethylenediaminetetraacetic acid (EDTA), which is excellent for the process since it has a strong extraction capacity, but it may cause secondary pollution [83]. EDTA is poorly biodegradable and persistent in soil, and is damaging to soil functions. For this reason, more environmentally friendly agents have been tested.

Feng et al. [83] used ethylenediamine tetra (methylene phosphonic acid) (EDTMP) and polyacrylic acid (PAA) for soil washing, and tried to optimize operative conditions and reduce ecological risks and toxicity. The same was done by Wang et al. [84] who studied four types of acids that are less toxic and more biodegradable than EDTA, namely iminodisuccinic acid (ISA), glutamate–N,N–diacetic acid (GLDA), glucomonocarbonic acid (GCA) and polyaspartic acid (PASP). They demonstrated that these acids are more biodegradable but less effective than EDTA. Zhai et al. [85] coupled soil washing with soil stabilization to improve results. They tested the addition of some reactants (lime, biochar, and carbon black) to reduce the bioavailability of residual metals, and these agents caused less damage to soil microbial communities.

Chemical soil washing is an efficient, rather fast, and widely used method. The main drawbacks are damage to soil properties and the creation of secondary pollution due to the presence of chemical agents.

4.2.5. Electrochemical Remediation

Electrochemical remediation promotes the migration of heavy metals and metalloids to oppositely charged electrodes under a direct-current electric field. Electrokinetic technology involves the transport of charged chemical species in fluid (electromigration), the motion of a fluid (electro-osmosis), the movement of charged particles (electrophoresis), and the chemical reactions associated with an electric current (electrolysis) [132]. Electrochemical remediation technologies have already been described by several authors, such as Reddy and Cameselle [133]. Sun et al. [134] estimated a model to simulate and describe heavy metal transport in soil under an electrical field.

Electrodes are generally immersed into wells containing an electrolytic solution and they are inserted into the area to be treated (Figure 4). An electric field gradient is generated so that metal ions migrate towards the oppositely charged electrodes. Then, the contaminants that accumulate at the electrodes are treated and eliminated with various physical–chemical approaches (electroplating, precipitation, pump-and-treat the water near the electrodes, or sorption with ion-exchange resins).

The electrokinetic method is used since it is efficacious, even in low permeability soils, and does not excessively change soil properties [86]. The combination of extraction with low-molecular-weight organic acids and electrochemical adsorption promotes the decrease of pollutant concentrations in soil [87–89]. Different acids can be used to extract heavy metals from the soil: sulfuric, ethylene diamine tetraacetic (EDTA), acetic, and citric acid. Cameselle and Pena [86] demonstrated that the use of citric acid efficiently removes cadmium, cobalt, chromium, copper, lead, and zinc, since it favors the acidification of soil, solubilization of metals, their transportation by electro-osmosis, and their electromigration towards the cathode. The efficiency of citric acid is also relevant in the removal of arsenic [90].

Soil acidification is not environmentally acceptable, and this must be assessed before the choice of technique that will be adopted is made. A low pH has two severe drawbacks:

- In these conditions, usually, the metals are in an ionic form; this is to say they can be mobilized from soil.
- The vegetal regeneration of soil could be limited and made more difficult.

Electrochemical remediation is rather efficient, especially in saturated clay soils, but it is rather complex to carry out.

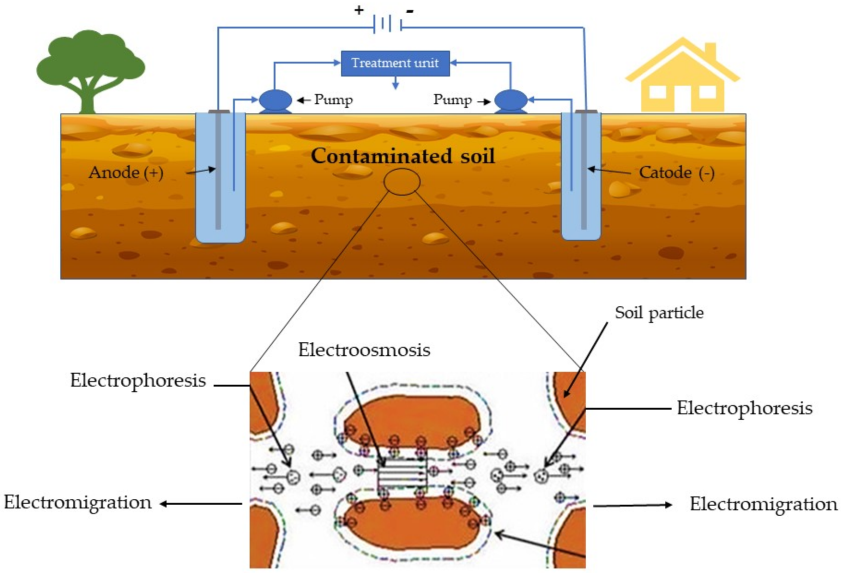

Figure 4. Electrochemical remediation scheme.

4.3. Biological Processes

Biological processes permit the removal of heavy metals and metalloids by exploiting microorganisms and plants. Biological agents respond to contamination through their defense mechanisms, such as enzyme secretion and cellular morphological changes. Typical biological techniques are bioaccumulation, bioleaching, biosorption, phytostabilization, and phytoextraction (as showed in Figure 5). Heavy metals and metalloids are not degraded by microorganisms or plants, but they are accumulated, stabilized, or bonded in less toxic volatile compounds. Specific microbial strains can encourage the degradation of pollutants and also improve soil characteristics, such as fertility [93].

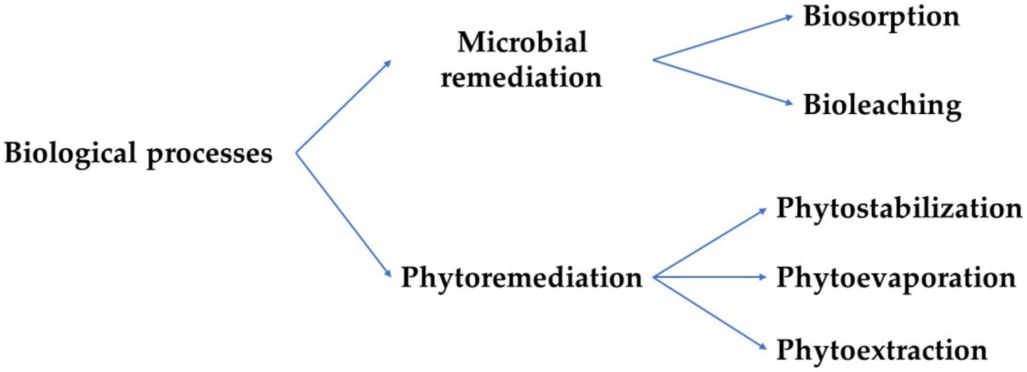

Figure 5. Biological processes to remove heavy metals and metalloids.

4.3.1. Microbial Bioremediation

The removal of heavy metals and metalloids can be actuated by fostering the growth and development of specific microorganisms in contaminated soil, namely through bioaugmentation and/or biostimulation processes. Heavy metals/metalloids can be oxidized, reduced, immobilized, and metabolized by microorganisms. Different from organic pollutants, heavy metals/metalloids are not degraded by microorganisms, but simply accumulate and are adsorbed at the binding sites present in the cellular structure, for example into microbial tissue.

The main microbial processes are biosorption and bioleaching, and are described in the study by Zabochnicka-Świątek and Krzywonos [135].

Biosorption

In the biosorption process, the heavy metals are immobilized onto the cellular structure of microorganisms. This is possible through the extracellular binding created between the cell surface (anions) and metal ions (cations). Extracellular materials have active functional groups that promote the binding mechanisms. The biosorption mechanism is complex and may include physical adsorption, ion exchange, complex formation, reduction, and precipitation. The efficiency of biosorption is influenced by several factors: metal ion properties, process conditions, density of sorption centers, and types of immobilization agents, as shown in the study by Velkova et al. [136].

Typical bioadsorbents are bacteria [91–94], fungi [95–98], and algae [99]:

- Bacteria: heavy metal ions can be bound and accumulated on polysaccharide slime layers of bacteria through functional groups, such as carboxyl, amino, phosphate, or sulfate groups.
- Fungi: are used to adsorb the heavy metals and metalloids through ion exchange and coordination in the chitin–chitosan complex, glucuronic acid, phosphate, and polysaccharides present in their cells.
- Algae: the absorption of heavy metals/metalloids occurs since algae form peptides as a defense mechanism. The functional groups (carboxyl, amino, sulfhydryl, and sulfonate) are among the constituents of the algal cell wall, and ion exchange promotes the adsorption of metal ions.

Bioleaching

The bioleaching process reduces mobility and stabilizes pollutants using the capacity of microorganisms to produces secretions, such as low molecular weight organic acids, that can dissolve heavy metals and soil particles containing heavy metal ores. In this way, heavy metals are directly solubilized by the metabolism of microorganisms or indirectly by their metabolites [101]. The agents that promote the leaching are biosurfactants, namely polysaccharides, lipids, and lipopeptides, produced by microorganisms, with a high surface activity that permits the formation of chelating metals and binding of metal ions [100]. This method has been extensively studied since it is an environmentally-friendly and inexpensive technique. For example, Yang et al. [100] showed the capability of a biosurfactant produced by a microbial strain isolated from cafeteria sewer sludge.

In general, all microbial biodegradation is low cost and eco-friendly. However, there are some limits:

- several microorganisms cannot bind toxic metals into harmless metabolites;
- the process is slower than others;
- it is efficient if the environmental conditions are suitable for microbial metabolism.

4.3.2. Phytoremediation

Phytoremediation is a bioremediation technique that exploits the capacity of plants to intercept, take up, accumulate, adsorb, or stabilize contaminants. The phytoremediation process aims to sequester contaminants via the roots of plants to lesser toxic elements or absorb them to the roots or shoots [102]. Some plants, called hyperaccumulators, can tolerate and accumulate more than 1000 $mg \cdot kg^{-1}$ of dry matter of copper, cadmium, chromium, lead, nickel, cobalt, or up to 10,000 $mg \cdot kg^{-1}$ of dry matter; this is to say, 1% by weight on a dry basis, of zinc or manganese [137].

The process is slow, and, for this reason, if a plant has large roots and/or shoots, large quantities of pollutants can be accumulated.

Several trees, as well as agricultural and herbaceous crops, are used, such as willow (*Salix* spp.) [103–105], poplar (*Populus* spp.) [102–104], wheat (*Triticumaestivum* L.) [106], sweet and grain sorghum (*Sorghum bicolor*) [107,108], and smilo grass (*Piptatherum miliaceum*) [109]. The phytoremediation process can be assisted by natural chelators, which promote the bioavailability and adsorption of heavy metals, such as copper [138].

Depending on the type of pollutants, plants, and removal mechanism, the phytoremediation techniques can be divided into phytostabilization, phytoevaporation, and phytoextraction.

Phytostabilization

In phytostabilization, plants prevent the mobility and the bioaccumulation of heavy metals and metalloids. The mechanism entails the complexation of metal ions with the roots, or with the cell walls, binding with molecules present in the roots, such as phytochelatins and metallothioneins, and finally sequestering them to root vacuoles [139]. Saran et al. [111] studied *Helianthus petiolaris* to treat soil contaminated with cadmium and lead, and showed that this plant does not interact with the activity of microorganisms already present in the root zone, and is efficient if the soil Cd concentration is lower than 50 $mg \cdot kg^{-1}$ and the Pb concentration is lower than 1000 $mg \cdot kg^{-1}$.

Phytoevaporation

In phytoevaporation, heavy metals and metalloids are bound to volatile organic compounds which are then released into the atmosphere through the transpiration process of the plants. Sakakibara et al. [117] studied the phytovolatilization of arsenic from soil using *Pteris vittata* plant. This plant is capable of metabolizing arsenic into volatile forms (arsenite and arsenate), reducing the arsenic concentration in soil. In nature, few plants are able to carry out phytoevaporation. For this reason, genetically modified plants are used, such as transgenic tobacco plants, that are able to remove mercury from contaminated soils [116]. This technique is not exempt from drawbacks. The main problem is that the volatile substances emitted into the atmosphere can be still toxic, and their emission constitutes secondary pollution around the plants themselves.

Phytoextraction

Phytoextraction is an absorption process of heavy metals and metalloids from soil through the plant roots. Then, the pollutants are transported and accumulated in the aboveground biomass, such as shoots. Bioaccumulation in shoots is advantageous for harvest. Mahmood-ul-Hassan et al. [112] studied different non-eatable floriculture plants, i.e., antirrhinum, pansy, calendula, and marigold, in soil contaminated by cadmium, chromium, nickel, and lead. They added a bacterial inoculum and EDTA, finding that both promoted the growth of biomass and the accumulation of contaminants in the roots, and this limited the transfer of contaminants to the shoots.

Phytoremediation allows to have a cheap and ecologically sustainable approach, but it is slow and depends on plant growth, seasonality, and environmental conditions. For these reasons, phytoremediation is often combined with other removal techniques. Combination is useful for improving removal efficiency, for example, using:

- phytoremediation + bioaugmentation;
- phytoremediation + EDTA amended soil [112];
- electrokinetic remediation + phytoremediation [113].

Agnello et al. [114] compared biological processes such as natural attenuation, bioaugmentation, and phytoremediation. They found that bioaugmentation-assisted phytoremediation optimizes the synergy effect of plants and microorganisms, improving the removal of heavy metals and metalloids [115].

5. Case Studies and Estimation Costs

At a large scale, the choice of technique for the removal of heavy metals and metalloids must consider several factors: removal efficiency, cost, treatment duration, pollutant concentration, and soil properties. In the literature, there are few case studies and field applications of various techniques for heavy metal remediation. Some examples are summarized in Table 5.

Table 5. Case studies for heavy metals/metalloids.

Technique	Metals/Metalloids	Size	Location	Year	Ref.
Soil replacement	Hg, Cd, Ni, Cu, Cr, Pb, Zn, As, Sb, Ba, Be, Mo, Se	-	Serbia	2014	[140]
Electrokinetic remediation	As, Cu, Pb	26.25 m^3	Janghang, South Korea	2013	[141]
Electrokinetic remediation	-	57 m^2	Paducah, Kentucky	1997	[142]
Chemical stabilization	Cd, Pb, Zn	10 m^2	Biscay, Spain	2012	[143]
Soil washing and phytoremediation	Cd, Zn, Pb, Cu	64 m^2 (8 plots of 8 m^2)	Shaoguan, China	2011	[144]
Phytoremediation	Cr, Zn, As, Cd, Pb	1600 m^2	Taranto, Italy	2013	[102]
Phytoremediation	As, Zn, Pb, Cd	1000 m^2	Porto Marghera, Italy	2008	[145]

Several companies are specialized in the stabilization/solidification technique at an industrial scale, but they do not usually publish financial information.

It is difficult to estimate actual costs due to a lack of recent and large-scale data. For example, by referencing 2010, the cost for an electrokinetic method that implements a 1 $V \cdot cm^{-1}$ voltage slope to eliminate copper is about 13–40 $USD \cdot m^{-3}$ of soil [89].

Chen and Li [146] had estimated the costs for soil washing and phytoextraction (year 2000):

- for soil washing, the cost is in the range of 200 $USD \cdot m^{-3}$ (small sites) to 70 $USD \cdot m^{-3}$ (large sites);
- for phytoextraction, the cost can go from 35 $USD \cdot m^{-3}$ (small sites) to 10 $USD \cdot m^{-3}$ (large sites).

6. Conclusions

Around the world, many polluted sites have been and are currently being cleaned up by adopting one of the above-described techniques. However, as noted, little data on large-scale operations can be found in the literature. A desirable outcome is that the shortage of data on remediation at a real-scale is filled, and is supported with tighter cooperation between research and industry. This will be of help to drive future soil clean-up, which is sometimes urgent and cannot wait for experimental findings to be achieved using new techniques.

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