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MAESTRÍA DE INVESTIGACIÓN EN METALURGIA

REVISIÓN DEL ORIGEN DE LA CONTAMINACIÓN DE SUELOS CON CADMIO, SUS ESTRATEGIAS DE REMOCIÓN Y EL CASO DE CULTIVOS DE CACAO EN EL ECUADOR

TESIS PREVIA A LA OBTENCIÓN DEL TÍTULO DE MAGÍSTER EN METALURGIA

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AUSPICIO

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DEDICATORIA

Al amor infinito de una madre, que siempre muestra una palabra de aliento y no desmaya nunca en su afán de ver cada día mejores a sus hijos, ese que nunca se termina, que no se rinde y siempre espera; ese que es el motivo de crecimiento del ser humano.

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Review Paper

Revisión del origen de la contaminación de suelos con cadmio, sus estrategias de remoción y el caso de cultivos de cacao en el Ecuador *(Review of soil cadmium removal strategies: the case of cacao crops)*

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Resumen: Cadmium is an inorganic, non-elemental heavy metal widely distributed in nature that can affect the quality of agricultural products due to its bioaccumulation potential. In cocoa beans, the basic raw material in chocolate production, cadmium can occur due to uptake by the cocoa tree of this heavy metal. Several researchers have focused their attention on the concentration of cadmium in soils of cocoa crops since this value has a relation with the concentration of this heavy metal in the beans. Many soil treatments for the removal of cadmium from soils were tested over time. Techniques of physical, chemical and biological remediations of soils containing cadmium were tested and also some combinations of these remediation strategies were evaluated. All remediations that can be applied to soils can affect the content of micronutrients, and this is an important issue that must be addressed. Therefore, a revision of available literature concerning the occurrence of cadmium in soils of cocoa crops, remediation of soils containing cadmium and the implications of treatments for cadmium removal is presented. The revised information is discussed and trends, as well as perspectives for future research works, are proposed.

Abstract: Cadmium is an inorganic, non-elemental heavy metal widely distributed in nature that can affect the quality of agricultural products due to its bioaccumulation potential. In cocoa beans, the basic raw material in chocolate production, cadmium can occur due to uptake by the cocoa tree of this heavy metal. Several researchers have focused their attention on the concentration of cadmium in soils of cocoa crops since this value has a relation with the concentration of this heavy metal in the beans. Many soil treatments for the removal of cadmium from soils were tested over time. Techniques of physical, chemical and biological remediations of soils containing cadmium were tested and also some combinations of these remediation strategies were evaluated. All remediations that can be applied to soils can affect the content of micronutrients, and this is an important issue that must be addressed. Therefore, a revision of available literature concerning the occurrence of cadmium in soils of cocoa crops, remediation of soils containing cadmium and the implications of treatments for cadmium removal is presented. The revised information is discussed and trends, as well as perspectives for future research works, are proposed.

Keywords: Cadmium; cocoa; Ecuador; micronutrients; heavy metal; soil remediation techniques.

Introduction

The pollution of air, water and soil with heavy metals is an important environmental issue recognized worldwide. Besides natural sources, anthropogenic sources like mining, smelting, combustion of fossil fuels (including coal), disposal of municipal waste, sewage irrigation and agriculture activities (application of pesticides and fertilizers), a variety of industrial activities are the main responsible for the release of heavy metals to water, soil and eventually air [1,2]. There are 90 naturally occurring elements, 53 of them are considered heavy metals, including the metalloid arsenic [3]. However, heavy metals must be differentiated in terms of their toxicity; some of them, in low concentrations, are considered micronutrients and only when their concentration is above a threshold, they produce adverse effects in living organisms. On the other hand, there are heavy metals without such threshold and they are toxic even at very low concentrations [3]. To this last group of elements belong cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr) and mercury (Hg), and they are usually referred to in the literature as potentially toxic metals and metalloids (PTMs).

The PTMs are known for their bioaccumulation capacity in the food chain [4,5]. The exposition pathways to PTMs are the direct inhalation, ingestion (intentional and unintentional), dermal contact and drinking of contaminated water. Dermal contact is especially important for Hg and Pb [6].

Cadmium is an inorganic, non-elemental heavy metal widely distributed in nature that occurs in association with different mineral forms including sphalerite and smithsonite (Cd can be a substitute for Zn), pyrite (important sink for Cd), apatite (can replace Ca). Commonly, Cd is an impurity in phosphates and phosphoric rocks [7]. Cadmium is present in higher concentrations in sedimentary rocks than in igneous rocks [8]. Quezada-Hinojosa et al. [9] reported anomalous high Cd concentrations in limestone rocks and concluded that it's a natural source because it had no anthropogenic influence due to its remoteness from urban and industrial activity zones. Predominant rocks in the region can influence the composition of the heavy metals of soils; cadmium and other heavy metal can reach the soil environment through meteoric, biogenic and volcanic processes as well as due to effects of erosion, leaching and winds [10]. Cadmium is a ubiquitous pollutant and its occurrence has been reported in different soils in the world [11]. The occurrence of cadmium in soil, in most cases, can be attributed to a natural process affecting the parent rock and clearly human perturbance can enhance such processes [9].

The occurrence of cadmium in soils is a very important subject studied by researchers in many countries [7–9,12]. There are reports of cadmium-polluted soils in Asian countries like India, Thailand, Korea and China, with cadmium concentrations in soils are India, Thailand, Korea, and China, in the last one, over 16.76% of all cropland is polluted by heavy metals including cadmium [13–15]. In South America, there are many countries where cadmium is present in soils such as Peru [16], Ecuador [17,18], Brazil [19], Bolivia [20], Colombia [21], etc. High concentrations of cadmium were observed in soils in England [22], Spain [23] and Australia [24]. Table 1 shows data collected by Alloway [12] on the content of cadmium in soils in different regions of the world.

Table 1. The concentration of cadmium in topsoils in regions around the world

Region	Cadmium content **[mg kg^{-1}]**
Europe	0.145
Baltic states	0.13
Ireland	0.326
England and Wales	0.7
Netherlands	0.14
Denmark	0.16
USA	0.16
World average	1.1

Table 1 shows a remarkable high cadmium content observed for the world average and this is explained by the fact that in different sites where the cadmium concentration in soils is higher, soils studied were from agricultural and mining sites; for example, in some Zn and Pb mines the Cd concentration in soil reaches 360 mg kg^{-1}. Jamaica has phosphorite deposits considered as 'cadmiferous' with natural contamination that could reach Cd concentrations around 16540 mg kg^{-1} [12].

Cadmium present in the soil, from natural or anthropogenic origin, has a direct effect on crops since this heavy metal can be absorbed by plants, thus entering the food chain [25,26]. Taking into account the presence of cadmium in soils worldwide, all agricultural products contain cadmium and, therefore, all living beings are exposed to the uptake of this heavy metal at least in natural levels [27].

There are multiple reports on the occurrence of cadmium in crop products, for example, Uraguchi et al. [28] and Zou et al. [29] published reviews which collect multiple reports on the occurrence of cadmium in rice and toxicity issues related with this heavy metal. In most cases, the origin of cadmium present in soils is natural. Independently of the origin (natural or anthropogenic), cadmium affects plants because it is absorbed instead of micronutrients like zinc, thus having implications on the development of the plant [30]. Cadmium toxicity in plants is noticeable by its appearance since less biomass is produced and yield of crops has a notorious decrement [27,31].

As previously suggested, anthropogenic contamination has largely contributed to the increasing presence of Cd in the environment. As a pollutant, cadmium could be present in the soil, water, and air because its mobilization through the ecological compartments is relatively easy. Cadmium rarely occurs in the environment as a pure metal, it could be found in different forms as oxides, sulfates, or chlorides [32]. Cadmium occurs in nature associated with zinc base ores and also it could be an impurity in copper and lead ores; volcanic activity and weathering of parent rocks are other important sources [25].

Cadmium is produced in many countries in the world, it is produced as a secondary product from the metallurgical treatment of zinc or lead; it is present in sulfur form and after the process there are oxide formation [33].The most important producers are China, South Korea, Japan, Mexico, Canada and Russia [34]. Both the production of cadmium and its use are (direct and indirectly) responsible for pollution related to this heavy metal. As an example, in China, according to estimations, around 743.77 tonnes of cadmium were released into the environment the year 2009 [5]. Li et al. [35] reported data on heavy metal pollution in China with a special focus on Cd, As, Pb, Hg, Ni, Zn, Cu, Ag and certainly much of the concern is related to cadmium. Due to the pollution, some Brazilian soils have concentrations of cadmium as high as 20 mg kg^{-1} [36] while average concentrations of cadmium in soils worldwide are around 1 mg kg^{-1} [37].

Cadmium can be released into the environment due to activities of a variety of industries such as smelting, metal manufacturing and refining, pesticides, paintings, fertilizers and manures, wastewater irrigation, iron and steel plants [31,38–40]. The production of rechargeable batteries is the industrial activity requiring the highest amounts of cadmium, therefore, it can also be considered the highest source of this heavy metal to soils [5]. Fertilizers are also an important source of cadmium in the soil. Alloway [12] reported the cadmium concentration in fertilizers and manure, which are highly variable depending on the region they are produced. According to Alloway [12], in the world, the concentrations of cadmium in phosphatic, nitrogen and lime fertilizers, and manures are in the ranges 0.1-170, 0.05-8.5, 0.04-0.1 and 0.3-0.8 mg kg^{-1}, respectively.

As mentioned before, the combustion of fossil fuels results in the emission of heavy metals into the atmosphere. Several investigations reported that cadmium is present in coals in many countries around the world such as China (0.24-0.81 mg kg^{-1}), USA (0.47 mg kg^{-1}), and India (0.75 mg kg^{-1}) [41,42].

In general, pollution affects flora and fauna by interfering in natural processes and disturbing ecosystems. In addition, pollutants have adverse effects on human health, and heavy metals are a good example of that. Cadmium is considered a toxic and carcinogenic element [43]. This metal represents a high risk to human health due to its adverse effects [44]. Early in 1858, the case of people suffering gastrointestinal problems was reported. These health problems were attributed to cadmium carbonate powder which was used to polish [45]. The first toxicological studies of cadmium were carried out, in 1919. In 1957, after the World War II, the “itai-itai” disease (“ouch-ouch” disease in Japanese) was discovered in Japan by Dr. Hagino and linked to human exposure to cadmium by ingestion of rice contaminated with cadmium in Toyama prefecture. This disease affects bones causing fractures and severe pain [45,46]. In the human body, cadmium has a half-time life of about 30 years and causes renal and lung dysfunction, bones and muscular pain, and could increase the risk of cardiovascular disease, among other health issues [43,47].

Usually, dietary intake constitutes the most important intake pathway of cadmium. In many Asian countries in which rice is a key dietary ingredient (e.g., Japan, China, Thailand, Bangladesh and others), cadmium intake was associated to the consumption of this grain [48]. Depending on soil characteristics and other regional features, the concentration of cadmium in rice grains is variable. Reported average concentrations of cadmium in rice grains are between 0.33 and 0.69 mg kg^{-1} (China), 0.38 mg kg^{-1} (Japan) [49]. Wang et al. [50] reported the content of heavy metals such as copper, zinc, lead, cadmium, mercury and chromium in vegetables and locally produced fish in several districts of Tianjin, China and confirmed them as a dietary source of cadmium. However, there are other ways for the absorption of this heavy metal by the human body. For example, smokers can inhale cadmium released to the gas phase during the combustion of the tobacco leaves [47].

Cadmium compounds are very toxic and non-biodegradable, and their elimination from the body is difficult [51]. This ability of cadmium to remain (accumulate) in the body of human beings and other organisms, combined with its high toxicity, makes it a very concerning pollutant [32]. In this work, aspects concerning the occurrence of cadmium in soils of cocoa crops and the associated problems are considered. The principle of soil remediation techniques is briefly explained and works on the removal of cadmium from agricultural soils were collected and discussed. Moreover, based on the available information in the scientific literature, the effects of soil remediation techniques on soil quality are discussed and perspectives for future researches are formulated.

Section 1: Cadmium in soils of cocoa crops

Cadmium is dangerous for human health and could produce negative effects when it gets into the food chain [40]. This concern has motivated the study of the content of toxic elements (among them, cadmium) in foodstuff [52]. The accumulation of heavy metals by plants depends on the species and the plant tissue [53]. Furthermore, it is a well-known fact that heavy metals can accumulate more in some parts of the plant than in others and this results in complications when the accumulation is higher in the edible parts [54]. In this sense, currently, there is a lot of concern about the beans of the cocoa tree (*Theobroma cacao*), which accumulate cadmium even in higher concentrations than other parts of the plant [17]. Cocoa is a high-value commodity for many countries and an essential raw material of food industries as it is the main ingredient in chocolate [55]. Therefore, strict controls on the content of cadmium in cocoa beans are performed by importing countries. The European Union stablished a maximum cadmium level in cocoa beans of 0.8 mg kg-1 (allowed maximum levels of pollutants stablished by the European Union are often lower than those stablished by the Codex Alimentarius) [56].

Cocoa trees are cultivated in many regions of South America, Central America and the Caribbean, West Africa, Southeast Asia and Oceania [19]. In Africa, important cocoa producers are countries like Nigeria, Congo, Sierra Leone, Madagascar, Tanzania, Uganda, Ivory Coast, Ghana, and Cameroon, among others. In Central America and the Caribbean, the production is led by Trinidad and Tobago, Cuba, Dominican Republic, Grenada, Mexico and Honduras, while in Asia and Oceania is produced by Indonesia, Philippines, Malaysia and Papua New Guinea. In Latin America, cocoa is produced in the rainforest of Brazil, Peru, Ecuador, Colombia, Bolivia and Venezuela [21,57–64]. About 72% of the world’s total production comes from Africa, and Ivory Coast is the top producer (43% of the world’s total production) [65]. According to estimations, 4,784 million tonnes of cocoa will be produced in the year 2021 and Ecuador contributes 6% of this production [18,60].

Cocoa-based products are widely consumed in the whole world and cocoa from South America is used to produce premium quality chocolate. Therefore, concerns referred to the content of toxic trace elements in soils of cocoa crops are justified [19,66]. Bertoldi et al. [61] reported the concentration of 56 macro, micro and trace elements in samples of cocoa beans from 23 countries, and in several samples, the content of the toxic elements Cd, Pb and Hg were higher than the permissible limits. Since toxic heavy metals can be found in cocoa, studies on the composition of cocoa products were also carried out. In this sense, Yanus et al. [67] reported a study on the content of trace elements in cocoa solids and chocolate of different brands and countries demonstrating that children could be the population group with the highest exposition to heavy metals due to the high chocolate consumption. It has also been found that the cadmium content in chocolates shows variations depending on the type of chocolate (i.e., the content of cocoa), decreasing in the following order: dark chocolate, milk chocolate and white chocolate [55].

It is known that soil properties such as pH, organic matter content, electrical conductivity, the occurrence of microorganisms (type and variety), macro and micronutrient content, cation exchange capacity, texture and mineralogy, influence the bioavailability of cadmium (i.e., the proportion of the total amount of cadmium in soil that is available for incorporation into plants) and these properties could be manipulated to limit the cadmium uptake by plants [68]. There are many reports of studies focused on the quantification of cadmium (and other toxic metals) and the effects of their occurrence on cocoa crops. Lewis et al. [69] measured the concentration of 8 heavy metals (Cd, Cr, Zn, Pb, Mn, Ni, Cu, Fe) in 12 soils in Ecuador and tried to find patterns among the content of metals and their concentrations in leaves of cocoa trees. Nnuro et al. [57] reported the results of the quantification of lead, copper, cadmium, manganese, zinc and iron in cocoa beans from 5 selected cocoa growing areas in Ghana, and high contents of heavy metals in beans were attributed to their presence in soil, likely due to mining activities. Gramlich et al. [62] focused their attention on soils of different sites in Honduras and the influence of their characteristics on the cadmium uptake by cocoa leaves and beans. These authors, based on concentrations of cadmium in the parts of cocoa trees (leaves, pod husks and beans) and the surrounding soils, found that cadmium in soil determined by the diffusive gradients in thin films (DGT) method is a good predictor of the cadmium uptake by the plant.

Many works focusing on the occurrence of cadmium and other heavy metals can be found in scientific literature. Table 2 summarizes studies on cadmium (and other relevant heavy metals) content in soils of cocoa crops in Latin America. Different strategies were considered in order to assess the content of cadmium in soils; in some studies, soils were sampled with the consideration of the depth and in others, only the first centimeters of soil were considered. The concentration of cadmium in soils is variable among countries and regions, ranging between 0.16 to 2.85mg kg^{-1}. Remarkably high content of cadmium in soil was observed in Trinidad and Tobago (20.78 mg kg^{-1}) [70]. Moreover, the results of the studies presented in Table 3 suggest that the concentration of cadmium in soils decreases with depth. This is an important aspect that should be considered when techniques for cadmium removal are selected and, later, applied.

Table 2. Occurrence of cadmium and other heavy metals in soils of cocoa crops in Latin America

Country	**Region**	**Analyzed heavy metals**	**Total cadmium concentration (mg kg^{-1})**	**Analytical Technique[1]**	**Reference**
Ecuador	Guayas and El Oro	Cd	Average values Depth 0-5 cm: 1.54 Depth 5-15 cm: 1.39 Depth 15-30 cm: 0.77 Depth 30-50 cm: 0.85	ICP-OES	[17]
Trinidad and Tobago	Trinidad island	Cd	Depth 0-30 cm: Sample 1: 2.71 ± 1.47 Sample 2: 20.78 ± 1.12	FAAS	[70]
Trinidad and Tobago	Not specified	Cd	Depth 0-30 cm: 0.3 to 1.7	FAAS	[55]
Peru	Tumbes, Piura, Cajamarca, Amazonas, Huanuco, San Martin, Junin, Cuzco	Cd, Fe, Cu, Zn, Mn, Ni, Pb	Depth 0-20 cm: 0.00±0.00 to 0.53 ± 0.02 (variable contents of cadmium depending on the region)	AAS	[16]

Bolivia	Alto Beni	Cd	Average values Depth 0-10 cm: 0.12 to 0.18 Depth 10-25 cm: 0.08 to 0.1	AAS	[20]
Ecuador	Morona Santiago (4 samples), Orellana (8 samples), Sucumbíos (10 samples), Manabí (3 samples), Esmeraldas (6 samples)	Cd	Depth 0-5 cm: 4.15 ± 0.01 to 8 ± 0.04 Depth 5-20 cm: 4.22 ± 0.02 to 7.66 ± 0.02 Depth 20-60 cm: 4.37 ± 0.04 to 7.90 ± 0.01 Depth: 60-80 cm: 4.40 ± 0.00 to 7.53 ± 0.06 Depth 80-100 cm: 4.49 ± 0.02 to 5.10 ± 0.01	ICP-MS	[66]
Colombia	Arauca, Boyaca and Santander	Cd	Arauca: 0.81 – 1.25 Boyaca: 1.13 – 3.70 Santander: 2.41 – 3.29	ICP	[21]
Honduras	Santa Bárbara, Cortés, Atlántida, Yoro and Gracias a Dios	Cd	Average values Depth 0-10 cm: 0.25 ± 0.02 Depth 10-25 cm: 0.16 ± 0.01	AAS	[62]
Ecuador	Azuay, Bolívar, El Oro, Esmeraldas, Guayas, Los Ríos, Manabí, Napo and Santo Domingo	Cd Ni Pb	Average values Azuay: 0.6 Bolívar: 0.7 El Oro: 0.4 Esmeraldas: 1.25 Guayas: 1.7 Los Ríos: 0.9 Manabí: 0.5 Napo: 0.25 Santo Domingo: 0.4	FAAS GFAAS	[18]
Ecuador	Coastal and Amazonia regions	Cd, Zn	Average value: 0.44	ICP-MS	[71]
Peru	Huanuco	Cd	Depth 0-20 cm: 0.04 ± 0.00 to 1.42 ± 0.43	AAS	[72]
Trinidad and Tobago	Trinidad island	Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn	Average value: 0.3 to 2.5	ICP-OES	[69]

[1] ICP-OES: Inductively Coupled Plasma - Optical Emission Spectrometry; FAAS: Flame Atomic Absorption Spectrometry; AAS: Atomic Absorption Spectrometry; GFAAS: Graphite Furnace Atomic Absorption Spectrometry

Some countries in Latin America have cocoa as one of the most important commodities and the economy of farmers lies in the production of cocoa beans. This is the case of Ecuador, which is also a country internationally recognized for the production of the highly appreciated cocoa of the variety National (also known as "Arriba") [73]. An obvious threat for this important Ecuadorian commodity is the presence of cadmium in cocoa beans in concentrations higher than values established by regulators of importing countries. Therefore, a lot of attention was paid to the content of cadmium in Ecuadorian soils; Romero-Estévez et al. [18] studied the content of cadmium in soils of 9 provinces of

Ecuador. The knowledge of the origin of cadmium in soils is essential to manage soil treatment strategies as well as the prevention of pollution. Therefore, the water of rivers in the south of Ecuador was analyzed and high concentrations of heavy metals were observed [74]. The use for irrigation of water from these rivers, which may be polluted by mining activities, could be a source of cadmium to soils of cocoa crops. This a concerning potential source of pollution of soils. Data for Ecuador on the concentration of cadmium in soils, cocoa trees and cocoa beans indicates that, in many cases, levels of cadmium are higher than the permissible limits [17,59,66,71,75], being this the motivation to search strategies to deal with a problem having social implications, economic consequences and negative effects to human health.

Section 2: Treatments for the removal of cadmium in soils

The effects of cadmium on crops have been widely studied over the years. Several reviews have collected valuable data on this topic [2,30,76,77]. It is known that cadmium phytotoxicity causes a delay in plant growth, as well as an alteration in the concentration of nutrients in roots and leaves, and in high concentrations, it could cause the death of plants [27,78,79]. As occurs with other heavy metals, cadmium can easily be absorbed by plants and, therefore, products harvested from contaminated soils have high concentrations of the metal with the consequent negative effect on the safety of foodstuff [31,37].

A high concentration of heavy metals in cocoa beans and other agricultural products can be observed for soils containing higher concentrations of heavy metals. Specifically, for cocoa, Chavez et al. [17] found a correlation between the cadmium concentration in cacao bean and the extractable cadmium in soils. Other authors have found strong correlations of the cadmium concentration in the plant with the total cadmium concentration in soil [55]. These apparent discrepancies may be explained by taking into account the specific characteristics of the studied soils. In any case, a strategy to reduce the intake of cadmium by plants was the treatment of soils containing high concentrations of this heavy metal.

Soils containing heavy metals can be treated with many techniques (*in situ* and *ex situ*) [2,30,76,77]. Most of these techniques are expensive and cause the reduction of soil productivity because chemical and biological properties are altered [80].

Remediation techniques applied for the treatment of soils containing heavy metals can be grouped into three types: 1) Physical remediation, 2) chemical remediation, and 3) biological remediation (or bioremediation). A summary of reported works on techniques used to remove cadmium in the soil is presented in Table 3. The explanation of the principle and relevant scientific information on the treatments for cadmium removal from soils are presented in the following subsections.

Table 3. Remediation techniques applied for cadmium removal from soils.

Method	**Technique**	**Short description of the study**	**Reference(s)**
Chemical remediation	**Electrokinetics & soil washing**	The electrokinetic remediation was enhanced by washing the soil with purging solutions. Real contaminated soil from an abandoned military area containing 55.0 ± 5 mg kg^{-1} of Cd was used for the tests. The soil also contained Ni (34.4 ± 6.0 mg kg^{-1}), Pb (81.1 ± 10.0 mg kg^{-1}), Zn (1238 ± 140 mg kg^{-1}), Cu (406 ± 60 mg kg^{-1}) and Cr (39.3 ± 8.0 mg kg^{-1}). Acetic acid, hydrochloric acid and ethylenediaminetetraacetic acid (EDTA) were used for purging solutions.	**[81]**
		The electrokinetic remediation was enhanced by washing the soil with ammonium citrate (1 M), sodium citrate (1 M) and non-ionic surfactant Tween-20 (0.2 % v/v). Tests were made at different pH values: 2, 7 and 12. Spiked soil with Cd and Cu from agricultural fields was used. Concentrations of Cd and Cu in soil were 10044 and 15880 mg kg^{-1}, respectively.	[82,83]
		The electrokinetic remediation was enhanced by washing the soil with organic acids (EDTA and citric acid). Spiked soil from a farm in Spain with a concentration of Cd of 141 mg kg^{-1} was used in this study. The soil also contained Cr (1000 mg kg^{-1}), Co (185 mg kg^{-1}), Cu (1023 mg kg^{-1}), Pb (1000 mg kg^{-1}) and Zn (1001 mg kg^{-1}).	[84]
	Soil washing & adsorption	Cadmium was removed by a combined process involving soil washing and adsorption. Spiked soil from a local garden in Jordan, with a concentration of cadmium of 200 mg kg^{-1} was washed with aqueous solutions containing organic acids, mainly citric acid. To remove cadmium from the organic acid-bearing soil-washing water, the adsorbents magnetite (Mag), magnetic wood (MW) and citric acid-modified magnetic wood (CA-MW) were tested.	[85]
		A nano hydroxyapatite aqueous suspension containing fluvic acid was used to remove (elute) Cd of soil. Real soil from Shenyang (China), containing cadmium in a concentration of 0.19 mg kg^{-1} was spiked to reach the concentration of 16.94 ± 0.23 mg kg^{-1}.	[86]
	Soil washing & freeze-thaw	Use of the method of freeze-thaw chemical washing with ethylene diaminete traacetic acid (EDTA) as eluent to study the cadmium Cd and Pb remotion of contaminated clay soils. The content of Cd and Pb in soil samples of Henan (China) was 253.8 and 1821 mg kg^{-1} respectively.	[87]

	Soil washing	Polyaspartate synthesis using L-Aspartic acid for soil washing and extraction of Cd ions from 47 different samples of spiked soil from Saudi Arabia. These samples had a content of Cd between 100 and 500 mg kg^{-1}.	[88]
		Three washing agents, carboxyalkylthiosuccinic acid (CETSA), copolymer of maleic and acrylic acid (MA/AA) and ethylenediamine tetra acetic acid (EDTA), were used to remove heavy metals such as Cd, Pb and Zn from contaminated soil from Sichuan (China) with 18.82, 2809.8 and 1175.63 mg kg^{-1} respectively.	[89]
		Cd removal using four washing agents: soapnut, shikakai, rhamnolipids and EDTA in Cd-spiked soil from garden in Edinburgh. Cadmium concentration was 700 mg kg^{-1}.	[4]
		The use of recalcitrant chelating agent EDTA and the biodegradable chelating agents N,N-bis (carboxymethyl)-L-glutamate (GLDA), iminodisuccinate (IDS), S,S ethylenediamine-disuccinate (EDDS) for contaminated soil remediation. Real soil from Arnoldstein (Austria) was used. Cd, Zn and Pb concentrations were 4.5 ± 0.0, 448 ± 11 and 809 ± 18 mg kg^{-1} respectively.	[90]
		Application of rhamnolipid surfactant to evaluate heavy metals remotion in Brazilian soils from short and long-term contamination sites. The first sample was artificially contaminated and reached Cd concentration of 20 ± 0.8 mg kg^{-1}. Second sample was collected from a deactivated mining site with Cd concentration of 122 ± 3.5 mg kg^{-1}. First and second soils samples also contained As (182 ± 10 and 114 ± 0.8 mg kg^{-1} respectively) and Zn (983 ± 30 and 3339 ± 60 mg kg^{-1} respectively)	[36]
	Immobilization	Two different phosphates, potassium dihydrogen phosphate (PDP) and dipotassium hydrogen phosphate (DHP), were used to immobilize multiple heavy metals in contaminated soil from Hezhang (China) with 31.83 mg kg^{-1} of Cd, 1141.6 mg kg^{-1} of Pb and 2119.28 mg kg^{-1} of Zn.	[40]
		Use of biochar produced from wheat straw in five soil samples collected in five polluted rice paddies in China to prevent Cd-tainted rice grains. The Cd concentration levels for each paddie was: 21.84, 4.83, 0.5, 0.16 and 4.63 mg kg^{-1}.	[91]
		Biochar obtained from rice straw at 640 and 420 °C, leca, pumice, bentonite and zeolite were used as soil amendments to reduce the availability of Cd and, therefore, the uptake by maize (*Zea mays L.*). Spiked soil from Iran with a concentration of Cd of 150 mg kg^{-1} was used in this study.	[92]

		Biochar and lime were used as soil amendments for Cd immobilization in soil. Real soil from cocoa in Trinidad & Tobago crops were used in this study. The concentration of Cd in soil was 0.77 ± 0.25 mg kg^{-1}.	[64]
Bioremediation	Phytoremediation	The use of Korean ecotype of black nightshade plant (*Solanum nigrum*) for phytoremediation of Cd-spiked sands from Korea was reported. The concentrations of Cd used in this study were 0 (control), 10, 30, 50 and 80 mg kg^{-1}.	[93]
		Two types of Japanese rice cultivars (Nipponbare and Milyang 23), two of soybean (Enrei and Suzuyutaka), and one of maize (Gold Dent) were cultivated in Cd contaminated soils to evaluate and select the best cadmium hyperaccumulator. The three real soils from Japan used in this study were an Andosol and two Fluvisols (Fluvisol 1 and 2), with concentrations of Cd of 4.29, 2.68 and 0.83 mg kg-1, respectively.	[94]
		Six Chinese cabbage cultivars (Beijingxiaoza 56, Suancaiwang, Quansheng, Qiubo 60, Xianfengkuaicai, and Chunkang) were grown in three soils to evaluate their Cd phytoextraction ability. The three real Chinese soils used in this study were from the: Shenyang Station of Experimental Ecology (SSEE), the Shenfu Irrigation Area (SIA) and the Zhangshi Irrigation Area (ZIA), with concentrations of Cd of 0.15, 1.15 and 2.25 mg kg^{-1}, respectively.	[95]
	Microbial remediation	Evaluation of the behavior and effectiveness in Cd immobilization in soils of different cadmium tolerant bacteria strains. Soils were collected from 26 farms of Colombia. The concentrations of Cd in soils were between 0.81 and 3.7 mg kg^{-1}.	[21]
		Rhodobacter sphaeroides was used to transform available metal (Cd and Zn) fractions to less accessible metal forms to limit the uptake by plants. Spiked soils from China were used in this study. The concentrations of Cd in soils ranged between 0.12 ± 0.05 and 65.33 ± 1.63. Additionally, concentrations of Zn ranged between 69.89 ± 1.64 and 964.8 ± 12.45 mg kg^{-1}.	[96]
	Microbial remediation & phytoremediation	The phytoextraction of Cd was enhanced by inoculating the endophytic fungus *Microdochium bolleyi* in barley plants. Spiked sandy soils from Iran were used in the study. Four concentrations of cadmium were considered: 0, 10, 30 and 60 mg kg^{-1}.	[97]

	Microbial remediation & immobilization	The phytoextraction of cadmium was enhanced by inoculating 42 culturable endophytic fungal isolates to *Solanum nigrum*. Spiked soils were used in this study. Four concentrations of Cd were considered: 0, 15, 20, 25 mg kg^{-1}.	[98]
		Fermented cedar bark was used as an organic amendment in rice paddies. The use of this amendment allowed to retain of heavy metals (especially cadmium) in the soil and reducing the uptake of heavy metals in brown rice. Fermentation was achieved with white-rot fungus. Real Japanese soil used for rice cultivation, with a concentration of Cd of 2.2 ± 0.7 mg kg^{-1} was used in tests.	[13]
		The immobilization of Cd and Pb was enhanced by the mean of phosphate solubilizing bacteria. 16 bacterial strains and one consortium (*Enterobacter* spp., *Bacillus* spp., and *Lactococcus* spp.) were tested. Real soils from Guizhou Province (China) containing Cd and Pb in concentrations 5.86 and 435.36 mg kg^{-1}, respectively were used in this study.	[99]
	Vermiremediation	Enhancement of vetiver grass phytoremediation by the use of earthworms (*Eisenia fetida*) for removing Cd from spiked soils from Sichuan province (China) with four concentrations: 0, 5, 10 and 20 mg kg^{-1}.	[100]
		Evaluation of the influence of biochar and Bacillus megatherium on Cd removal from spiked soils using earthworms (*Eisenia fetida*). Uncontaminated soils from Shaanxi (China) were collected and spiked with a Cd solution until 2.5 mg kg^{-1}.	[80]
		Use of earthworm (*Eisenia fetida*) alone or combined with ethylenediaminetetraacetic acid (EDTA) or bean dregs for Cd removal from soils. Uncontaminated soils from Yangling (China) were collected and spiked with a Cd solution util 2.5 mg kg^{-1}.	[101]
Chemically enhanced bioremediation	Soil washing & phytoremediation	Cd uptake by corn crops enhanced by the addition of the biosurfactants rhamnolipid and saponin. For the experiments, real soil samples from Mae Sot district (Thailand) contained cadmium in a concentration of 12.64 mg kg^{-1} were spiked to reach a concentration of 36.80 mg kg^{-1}.	[102]
		Enhancement of ryegrass (*Lolium perenne* L.) soil phytoextraction of Cd and Zn with hydrochloric acid (HCl), ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA), several biodegradable natural low molecular mass organic acids (LMMOAs). Total Cd and Zn concentrations in real soil samples from Shaanxi (China) were 27.13 and 1690 mg kg^{-1}, respectively.	[103]

2.1. Physical remediation

Physical techniques of remediation include soil substitution, surface capping, landfilling, encapsulation [104,105]. The process of substitution consists of the mechanical removal of the polluted soil, its mobilization to a treatment facility or an appropriate landfill, and the replacement with clean soil. This strategy is not economically viable and time-consuming in most cases [104]. Surface capping consists of the application of a waterproof layer over the polluted area; this is not considered a real remediation process because pollutants are not removed. Surface capping aims to avoid the migration of pollutants to unpolluted soils due to environmental factors and the contact of pollutants with living beings (including humans). Surface capping, due to its characteristics, is an option only applicable for scenarios with highly polluted soils, therefore, the area is converted into non-productive land, and only can be used for other civil purposes (edifications). As mentioned before, once removed polluted soils for substitution purposes, the soil can be treated (see subsection 2.2) or simply landfilled. Landfilling consists of the indefinite disposition of soil in a facility designed to prevent the release of pollutants to the environment. It is expensive and the risks of pollutants leaching into soil and (ground)water cannot be ruled out [105,106]. Encapsulation consists of the construction of barrier layers with materials of low permeability to isolate polluted soils and prevent the contact of pollutants with unpolluted soils and groundwater [105,107].

Based on the characteristics of techniques of physical remediation, their application do not allow to recover soil for agricultural uses. These techniques are applied for highly polluted soils (usually resulting from anthropogenic activities like mining) to avoid further environmental damages and protect human health.

2.2. Chemical remediation

Chemical techniques of remediation include soil flushing and washing, immobilization (stabilization), electrokinetic methods, vitrify technology, chemical leaching and chemical fixation [101]. Soil washing is an important ex situ remediation technology; it is widely used and considered time-saving and an efficient technique [105,106].

Soil flushing (in situ) and washing (ex situ) are two methods using water or an appropriate aqueous solution to remove soil contaminants [2]. In order to achieve a higher extraction of heavy metals (in general) with lesser volumes of water, chelating agents and surfactants are added to water. Typically used chelating agents include ethylenediamine tetraacetate (EDTA) and its sodium salt form (Na-EDTA), [S,S]-isomer of ethylene diamine disuccinate (EDDS), N,N-bis(carboxymethyl)-Lglutamic acid (GLDA) [107]. Surfactants are usually applied to remediate contaminated soils, there are anionic, cationic and nonionic; rhamnolipids, polyethylene oxides, sodium dodecyl sulfate, dodecylamine hydrocloride are examples of many surfactants with different mechanisms depending on the soil characteristics and metals present [95,108]. Some of these substances (inorganic agents, surfactants, and chelators) are preferred due to their low costs, however, they could negatively impact on soil properties. This is the case of inorganic agents [95]. Other compounds, like ethylenediamine tetra acetic acid (EDTA), show high efficiencies in heavy metal removal but their limited biodegradability could produce secondary pollution [95]. Therefore, despite they are more expensive, biodegradable chelating agents and surfactants like water, saponin, organic acids, then inorganic agents, are preferred for both soil flushing and washing [2].

Concerning cadmium removal from soils by soil washing, a variety of reports can be found in the scientific literature and removal efficiency reaches 90% [33]. Gluhar et al. [109] published a report on a technology named “ReSoil”, which was applied for the removal of cadmium, lead and zinc from soils using recalcitrant chelating agent EDTA and the biodegradable chelating agents N,N-bis (carboxymethyl)-L-glutamate (GLDA), iminodisuccinate (IDS), S,S ethylenediamine-disuccinate (EDDS). They concluded that EDTA outperformed the biodegradable chelating agents considered in their study, however, they also warned about the limitations of the study: only a few biodegradable chelating agents were tested, and experiments were carried out with one type of soil. This remark is important since, as the authors sustained, the extractability of metals and the nature of the contamination of soils are variable for different scenarios. There are other reports of studies in which different aqueous solutions of chelating agents and surfactants were used, with a special focus on biodegradable washing agents. Xia et al. [95] studied the cadmium, lead and zinc removal from soil by aqueous solutions of carboxyalkylthiosuccinic acid (CETSA), a copolymer of maleic and acrylic acid (MA/AA) and EDTA. Real soil containing Cd, Pb and Zn with concentrations 18.82, 2809.8 and 1175.63 mg kg-1, respectively, were used in the experiments and the highest metal removals (83.5% for cadmium, 94.13% for lead and 80.37% for zinc) was achieved with CETSA with washing time of 90 min. Chibuzo et al. [4] proposed the cadmium removal using the biodegradable surfactants soapnut, shikakai and rhamnolipids and observed that the removal efficiencies of these surfactants were improved by the addition of EDTA, reaching cadmium removal efficiencies of 87.4%. An interesting washing agent extracted from Pseudomonas aeruginosa (rhamnolipid surfactant) was used for the removal of cadmium, arsenic and zinc from soils and showed an alternative source of materials used for remediation [30]. Another biodegradable chelating agent tested for cadmium removal was polyaspartate [96].

The efficiency in the removal of cadmium and other heavy metals from soils depends on the capability of washing solutions to dissolve them. Therefore, some authors have tested methods to enhance the transfer of heavy metal ions to the aqueous solution. Park et al. [105] used ultrasonic irradiation to enhance mechanical soil washing. These authors used a solution of hydrochloric acid (HCl) for soil washing and irradiated the soil-solution mixture with ultrasound (28 kHz) while ensuring an appropriate mechanical mixing. Soil and liquid (HCl solution) ratios for proves were this fusion of 1:2 and 1:3. It was found that this soil washing strategy increased the removal efficiency of soil washing as follows: from 39.4% to 66.8% for Cu, from 27.3% to 65.6% for Pb and from 42.2% to 65% for Zn (1:2 soil: liquid solution ratio); and from 47.2% to 76.2% for Cu, from 46.9% to 75.4% for Pb and from 46.3% to 72% for Zn (1:3 soil:liquid solution ratio). A repeated freeze-thaw of soil with the use of appropriate washing solutions was proposed by Rui et al. [93]. A (clay) soil containing in its structure an aqueous solution of EDTA was frozen and then thawed, and this process induced destruction of the structure of soil with a consequent better contact of the solution and soil particles. As the soil thawed, the aqueous solution was capable of dissolving heavy metals, cadmium among them. As suggested by Rui and coworkers, soils can be frozen due to seasonal drops in temperature and afterward soils also thaw, and this cycle could be used for purposes of remediation of soil.

Remediation by soil washing can also be combined with the adsorption of heavy metals on solid particles. This approach was tested by El-Sheikh and coworkers using magnetite, magnetic wood and citric acid-modified magnetic wood as adsorbents [92]. Also, in another study, nano hydroxyapatite aqueous suspension containing fulvic acid was used to remove (elute) Cd from soil [93]. In both cases, cadmium removal improvements were attributed to the adsorption of the heavy metal to these solids.

An effective way for reducing the toxic effects of heavy metals on biota and, eventually, in humans, is immobilization, which uses fixatives to decrease the leachability of heavy metals [108]. Yuan et al. [37,99] used phosphates for the immobilization of multiple heavy metals since this anion reacts with metallic cations to produce insoluble heavy metal phosphates. If heavy metals are in the form of an insoluble salt, their bioavailability is limited; Immobilization could be enhanced from 28.38% to 30.81%. In this sense, the addition of K_2HPO_4, and KH_2PO_4 (soluble salts) for the immobilization of cadmium, lead and zinc was studied [37]; this strategy showed a high efficiency in the immobilization of lead in contrast to cadmium that showed low efficiency and was highly dependent of phosphate addition (larger amounts of phosphate are required to obtain cadmium phosphate). According to Yuan and coworkers, it seemed that the mobility and availability of zinc in the long-term contaminated soils that were subject of study remained unchanged. Similarly, Zhang et al. [109] studied immobilization in the soil of lead, zinc and cadmium by the addition of three phosphates (K_3PO_4, K_2HPO_4, and KH_2PO_4) and considering the variation of pH. These authors found that the highest immobilization was achieved with K_3PO_4 under alkaline conditions, being lead the metal showing the highest immobilization (immobilization of cadmium was less than lead and zinc). Soils with an alkaline pH seem to facilitate the immobilization, as also observed by Ming et al. [110], who performed sorption tests of cadmium and zinc on soil at different pH values.

Another approach to immobilize heavy metals is the use of soil amendments. Amendments like manure, compost, biochar, clay minerals, phosphate compounds, among many others, are added to soil to reduce heavy metals bioavailability in soils through mechanisms such as precipitation, complexation, redox reactions, ion exchange, and electrostatic interaction [111]. For example, $Ca_3(PO_4)_2$ was used for the immobilization of Pb y Cd [99]. Similarly, the immobilization of cadmium and lead in agricultural soils in Florida (USA) by means of dolomite phosphate rock, humic acid activated dolomite phosphate rock and biochar was tested [112]. Biochar is an interesting material that can be obtained from bio-waste and carbon-rich solid residues. Bian et al. [98] used biochar obtained from wheat straw as a soil amendment to immobilize cadmium in soils of rice paddies. Biochar was also proposed for its application in soils of mining sites to reduce the bioavailability of cadmium, lead and zinc [113]. Shahkolaie et al. [92] compared different amendments, biochar (obtained from rice straw), leca, pumice, bentonite and zeolite, for the reduction of the availability of cadmium and the uptake by maize (*Zea mays L.*). In this case, it was found that zeolite was the most effective amendment. It must be pointed out that biochar can reduce available heavy metal in soil but, in some cases, have a limited effect on the prevention of the heavy metal uptake by plants [91,114]. There are other materials, of organic origin, that were also proposed as amendments; Mori et al. [13] used a fermented bark as an organic amendment to control the cadmium uptake in rice paddies.

The addition to the soil of some micronutrients could modify the cadmium uptake by plants. It was observed that the cadmium uptake by plants can be limited by the addition of certain micronutrientes. This is the case of zinc and copper; a study reported by Murtaza et al. [115] indicates that the soil application of zinc and copper, individually or combined, favored the biomass production of two legumes (chickpea and mungbean) and two cereals (wheat and maize). Moreover, these authors also found that the addition of zinc and copper also lead to the decrease of the concentration of cadmium in plant tissues.

Electrokinetic methods were considered to remediate heavy metals-polluted soils. It has been considered for in situ remediations. These methods require the installation of electrodes and metallic cations are mobilized through the soil due to an electric field generated by a direct current source [82,84,116]. In order to improve electrokinetic methods, they were combined with proper washing solutions. For this purpose, many works were published; typical washing solutions contained a variety of surfactants and chelating agents [88-91][116]. These methods reach ranges between 40 and 85% reduction of cadmium concentration and could also affect the concentration of micronutrients since these cations can be removed at the same time of toxic heavy metals [81].

A technique to immobilize pollutants, and avoid their migration, is soil vitrification. It consists of a thermal treatment that converts polluted soils into a stable and inert glassy product. Any toxic heavy metal contained in the soil is immobilized into the structure of this material and cannot be washed out. It is highly efficient in the destruction of organic compounds, thus reducing the volume of the material, and can be used for waste treatment [117,118]. The applicability of vitrification to soils is limited, however, this technique can efficiently be used to treat fly ash and hazardous substances resulting from municipal solid waste incinerators and similar processes [118,119].

2.3. Bioremediation

Bioremediation can be considered a group of techniques that use biological mechanisms inherent in living organisms (plants, some animals, and microorganisms) to remove, degrade and/or immobilize hazardous contaminants occurring in soil. Heavy metals cannot be degraded, therefore, living organisms act immobilizing and accumulating these pollutants. These techniques are eco-friendly but need long periods to ensure the adaptation of organisms being a major challenge due to the variability of ecosystems [108]. Bioremediation is classified in microbial remediation (bacteria, fungi, algae), animal remediation (earthworms) and phytoremediation (plants); the last one has captured more attention [5,120,121].

Bioremediation is used for both, solutions and soils. Several researchers have studied the use of bacteria in the process of remediation of heavy metal contaminated soils, with reports of Cd exchangeable phases reduction of 30.7% [96,122]. Other studies discuss the use of different techniques for mobilizing or immobilize heavy metals [123].

2.3.1. Microbial remediation

There are other strategies for cadmium removal involving the combination of microbial action and phytoremediation. Such strategies are described in subsection 2.3.2. This type of remediation uses tolerant microorganisms with the capability of modifying the oxidation state of metals and/or transform the metal to non-assimilable form Different processes are involved in this method of remediation [122].

Commonly, the use of tolerant microorganism for the remediation of soils contaminated with cadmium intend to immobilize the heavy metal in soil, thus making it less available for plants. This was achieved with certain bacteria strains, as reported by Bravo et al. [62]. These authors, working with Colombian soils destined to cocoa crops, found that Enterobacter sp. strain CdDB4 showed the highest Cd immobilization capacity. Similarly, Peng et al. [96] Rhodobacter sphaeroides was used to immobilize cadmium and zinc in soil and make them less accessible for uptake by plants. Aspects referred to kinetics and mechanisms of bioremediation with Rhodobacter sphaeroides were previously reported by Bai et al. [124]. These authors found that bioprecipitation as cadmium sulfide was the predominant process promoted by Rhodobacter sphaeroides and biosorption played a minor role.

There are other strategies for cadmium removal involving the combination of microbial action and phytoremediation. Such strategies are described in subsection 2.3.2.

2.3.2. Phytoremediation

Phytoremediation is a technique used to remove cadmium and other heavy metals from soils employing plants [5,125]. As its name suggests, phytoremediation uses plants as pollutant accumulators. To grow and develop, plants absorb a variety of nutrients and other (toxic) species that accumulate in leaves, stems, roots and/or fruits [126]. Phytoremediation is considered a low-cost and eco-friendly technique because the disturbance of surface soil is minimum. However, this technique may not apply to soils with severe contamination issues due to its low efficiency [103]. Phytoremediation includes phytostabilization, phytoextraction, phytofiltration or rhizofiltation (heavy metals extraction by roots of plants), phytodegradation, and phytovolatilization [125]. Phytostabilization is a process consisting in re-vegetation of remediated areas with metal tolerant plant species [125]. For the phytoextraction process, plants should tolerate and accumulate important amounts of heavy metals, have rapid growth and produce high amounts of biomass, as observed for garlic (*Allium sativum L.*) and its capability to absorb cadmium [127]. Phytofiltration (rhizofiltration) consists of the heavy metal uptake from aqueous solutions using aquatic plants. For this method, the perfect plant requires quick roots development and the ability to uptake heavy metals during extended periods [125,128]. Phytodegradation is a method used for degradation of organic pollutants such as solvents, petroleum, and aromatic compounds by the action of plants and their associated microorganisms, but are not available for heavy metal contaminated soils [129–131]. Phytovolatilization consists of metals uptake by roots and passes through plants and leaves reaching chemical conversion into less toxic and volatile compounds that are released to the atmosphere during the plant transpiration process [132–134].

Some plant species are excellent cadmium hyperaccumulators and are used for water and soil remediation [5]. Khan et al. [93] reported that at least 400 plant species are considered hyperaccumulators of different heavy metals. Concerning cadmium hyperaccumulator , the following plant species can be highlighted: *Arabidopsis Alleri* [135]. *Thlaspi caerulescens* [136], *Cardaminopsis helleri* [137], *Thlaspi caerulescens* [138] and *Solanum nigrum* [93,139]. There are reports on experiments using plants for the removal of cadmium of soils; the phytoextraction of cadmium of three Chinese soils employing cabbage cultivars (Beijingxiaoza 56, Suancaiwang, Quansheng, Qiubo 60, Xianfengkuaicai, and Chunkang) was successfully achieved [95]. Also, the accumulation of cadmium by two types of Japanese rice cultivars (Nipponbare and Milyang 23), two of soybean (Enrei and Suzuyutaka), and one of maize (Gold Dent) were tested, being the Milyang 23 rice the best plant for phytoextraction of cadmium from paddy soils, reaching an accumulation from 10 to 15% of total Cd [94]. The use of spinach (*Spinacia oleracea* L.) was proposed for phytoremediation purposes since this plant was able to uptake cadmium in greenhouse pot culture studies and no cadmium toxicity signs were observable [140].

Phytoremediation can also be applied in combination with selected microorganisms. Tiwari et al. [141] reported a study in which a consortium of bacteria (*Bacillus endophyticus, Paenibacillus macerans, and Bacillus pumilus*) present in the rhizosphere allowed munja (*Saccharum munja*), a type of grass growing in arid zones, to improve the plant uptake of heavy metals from soil. The mutualistic association of soil fungi and plants can help the plant to increase the tolerance to heavy metals [142]. If a plant can tolerate heavy metals, it can also be a good candidate for phytoremediation. In this sense, Shadmani et al. [97] reported that a fungal inoculation facilitated the absorption of cadmium by barley and, interestingly, cadmium was accumulated in roots (a non-edible part). Similarly, Khan et al. [98] achieved an improvement in the phytoextraction of cadmium from the soil by inoculating endophytic fungal isolates to black nightshaded (*Solanum nigrum*).

As mentioned in subsection 2.2, a chemical strategy to enhance the removal of metals by soil washing is the use of chelating agents such as EDTA (ethylenedinitrilotetraacetic acid), DTPA (diethylenetrinitrilopentaacetic acid), HEDTA (hydroxyethylenediaminetriacetic acid), CDTA (trans-1,2-cyclohexylenedinitrilotetraacetic acid), EGTA (ethylenebis tetraacetic acid). This chelating agents form complexes with metallic ions, that increase the concentration of metals in the aqueous solution and facilitates the mobility to upper parts of the plants [122,125]. Therefore, if the plant produces high amounts of biomass, as expected for heavy metal hyperaccumulators, more metal from soil can be absorbed by the plant. Based on this argumentation, some researchers decided to combine soil washing and phytoremediation [78,94]. Such a strategy could be interpreted (and classified) as chemically enhanced bioremediation. An interesting example is the work of Mekwichai et al. [78] in which cadmium was removed from soil by corn. These authors used two biosurfactants, rhamnolipid and saponin to assist the phytoremediation. They found that plants accumulated more cadmium when the biosurfactants were used.

Taking into account reports on the applicability of phytoremediation for the removal of cadmium from soils, some features can be noticed. Many cadmium hyperaccumulators are known and they can be used for the removal of cadmium from soils without adverse effects on the structure and healthy composition of the soil. Perhaps even the periodic use of these plants could be part of a strategy to maintain the productivity of soils, for example, by including them in crop rotation programs. Crop rotation is a well-known practice worldwide that has demonstrated important benefits in terms of reducing the use of pesticides and protecting soils [143]. Moreover, if diversity is included in such crop rotation programs, an increase in agricultural resilience to adverse growing conditions can be achieved in the long term [144]. However, independently of the phytoremediation strategy used to remove cadmium, an obvious question emerges: Can the resulting vegetable material used for any beneficial purpose? Reports on the application of plants for cadmium removal suggest that the possibility of using such vegetable material cannot be ruled out. Mekwichai et al. [78] found that cadmium can be removed from soils by corn and, as expected, cadmium occurs in corn kernels. However, under certain conditions of phytoremediation (in this case, saponin-assisted phytoextraction), concentrations of cadmium in corn kernels can be below the allowable limits for animal feedstock and, therefore, the use of this product may be a candidate for animal feed.

2.3.3. Animal remediation

Animal remediation uses animals such as earthworms (*Eisenia fetida, Perionix ceylanensis, Eudrilus eugeniae, Lampito mauritii, Allolobophora rosea*, and *Nicodrilus caliginosus, etc.*) for the removal of many toxic compounds in soils, among them, heavy metals, pesticides, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and crude oil [145]. The process using earthworms is called vermiremediation or vermicomposting, and is used to sanitize several industrial wastes [146]. It is an alternative and high sustainable technology due to its simplicity and economy [147]. Researchers made efforts to understand mechanisms and pathways promoted and taking place in earthworms that allow neutralizing toxic metals in vermicomposts obtained of cotton textile sludge [146], market wastes and rice straw [147], municipal solid wastes [148], palm oil mill effluents [149] and tea coal ash [150].

Vermicomposting involves the action of microorganisms and earthworms to biodegrade solid wastes; earthworms contribute to aeration, disaggregation of the material and providing conditions for a high microbial activity [149]. Curry and Schmidt [151] discussed aspects concerning earthworms, their food preferences, ingestion, assimilation and others. Earthworms can resist high concentrations of soil pollutants and can absorb heavy metals through the skin and by ingestion; they can process ingested materials with help of their diverse intestinal microflora [80,145,146,152]. This tolerance to toxic heavy metals can be explained considering the occurrence of metal-chelating substances (metallothioneins) in the organism of these animals [153]. Metallothioneins are the best-known example of metal-binding proteins [40]; they are a family of low-molecular-weight, metal-binding and cysteine-rich proteins (over 30%), and can be used as biomarkers of environmental contamination. Since metallothioneins have a high affinity for non-essential metals, which can be introduced into the earthworm body and no appreciable consequences in the normal functions of the organisms can be observed. Therefore, earthworms are important in the remediation process of contaminated soils [101,154]. Studies on metallothioneins response in earthworms living in soils with high contents of cadmium suggest that *Eisenia fetida* is a species with a high affinity to cadmium [155]; the content of metallothioneins in this earthworm increases when the concentration of cadmium in soil rises. Stürzenbaum et al. [156] studied with more detail metallothioneins occurring in *Lumbricus rubellus* and identified an specific cadmium-responsive metallothionein.

Earthworms were a subject of study for many years due to many reasons and probably the most important was the ecological role that these animals play in the soil. On this topic, the reviews published by Curry and Schmidt [151], and Sun et al. [157] can be highlighted. Also, mechanisms allowing the remediation of soils using earthworms were studied by many researchers [145]. Heavy metal concentrations can be reduced due to vermicompost by the mediated biodegradation of organic materials with the consequent increase in the level of the humic fraction that strongly immobilizes metals (formation of stable complexes) [158], and the bioaccumulation of the heavy metals in the earthworms through mechanisms involving metallothioneins [159]. The capability of earthworms to remove toxic heavy metals from solid industrial residues was demonstrated in different reports; Paul et al [146] demonstrated the use of *Eudrilus eugeniae* to treat a cotton textile sludge and removals between 50 and 70% were observed for lead, cadmium, chromium and zinc. On their side, Goswami et al. [150] studied the removal of heavy metals from a tea factory coal ash by vermicomposting using *Eisenia fetida*. Concerning the remediation of soils, Wu et al. [100] tested the use of *Eisenia fetida* for the removal of cadmium and reported a reduction of 17.6% in the concentration of the heavy metal in the soil after 28 days of treatment.

In order to improve the removal of heavy metals by using earthworms, treatments involving these animals were combined with other processes. In this sense, the removal of cadmium from soils with *Eisenia fetida* was enhanced by the addition EDTA and bean Liu et al [101] studied the enhancing of cadmium removal with *Eisenia fetida* earthworms adding EDTA and bean dregs reaching a cadmium removal of 36.53%. Xiao et al. [80] reported the use of earthworms and biochar for cadmium removal and the neutralization of available cadmium. They concluded that soils become more fertile after vermiremediation.

In all cases when earthworms were used for remediation purposes, clues and evidence on the improvement of soil fertility were obtained. Earthworms were not only able to remove and immobilize cadmium (and other toxic heavy metals), but also promote healthy conditions of the soils.

Section 3: Effects of cadmium removal strategies on soil micronutrient content

Macronutrients and micronutrients are elements with physiological function in plant metabolism [160]. Micronutrients are required by plants in lower amounts than macronutrients. Macronutrients such as calcium (Ca), potassium (K), magnesium (Mg), nitrogen (N) and phosphorous (P), and micronutrients such as sodium (Na), boron (B), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), selenium (Se) and zinc (Zn) are commonly present in soil destined to agricultural production. Nutrients are dissolved in water and then can be assimilated by plants. In this way, and depending on the specific physiological characteristics of plants, a variety of elements occur in fruits, greens, cereals and other edible agricultural products [63,161]. Some parts of the plants can also preferentially concentrate certain elements; these are processes widely used for nutritional purposes (utilization of selected parts of the plant for human and animal feed) [162]. The content of some nutrients in parts like leaves could be an indicator of the health of the plant as well as the content of the same nutrients in edible parts [163]. However, such correlations may be distorted by multiple factors, mostly related to the environment and development characteristics of plants [163]. In any case, special attention must be paid to micronutrients because these elements are usually in low concentrations in soils and bad agricultural practices, as well as soil treatments, could affect their availability.

Cocoa is produced in countries in the tropical zone (i.e., the region of Earth surrounding the Equator), where warm weather and high humidity provide conditions for the growth and development of cocoa trees [63,164]. Cocoa tree needs a high nutrient concentration in soils for growing well [63]. Low soil fertility is considered a major cause of the reduction of cocoa crop yield. Many cacao crop soils have become acidic and infertile due to long-term cultivation, nutrients leaching and lack of adequate fertilization [165,166]. The optimum pH range for cocoa growing is between 6.0 and 7.5 and some elements can exert a negative effect; in acid soils, aluminum is a highly limiting factor for plant development, thus considering cocoa an Al-sensitive crop [63,167]. Moreover, a high concentration of aluminum reduces the uptake of phosphorus, iron and zinc [166].

Among micronutrients, zinc is an important trace element for plants and animals. In crop soils, zinc deficiency is an important problem affecting the productivity of soils [168]. For example, in wheat, zinc deficiency causes shoot growth problems and a low final dry weight, i.e., low production [169]. On the other hand, the presence of zinc in the soil can modulate cadmium accumulation in plants since these two elements occur together in the environment and have similar chemical properties [12,110,168,170]. There are several interactions between metals present in the soil, and also with plants and microbiota. Therefore, soil treatments for the removal of one or more toxic heavy metals can affect the content of other metals acting as micronutrients. The deficiency of micronutrients can cause growth problems and decrease crop yields. For the case of cadmium removal, zinc is a micronutrient that can be removed from soil together with cadmium due to their chemical similarities [160].

Although there are many reports on soil remediation for the removal of cadmium, only a few studies critically addressed the implications of treatments on the concentration of soil nutrients or the fertility of soils. Techniques that use biological mechanisms for the removal of toxic heavy metals like cadmium, likely will not produce disturbances in the nutrient composition of soils [122].. Techniques based on microorganisms, certain plants and animals (earthworms) can gradually remove toxic heavy metals from the soil, however, these processes are slow enough to avoid any imbalance in soils. These techniques are considered environmentally friendly and can even be beneficial in ensuring the conservation of healthy soil. Some techniques of chemical remediation can be more aggressive to soils and affect their characteristics since they imply the addition to soil of some chemical compounds. For soil washing, the washing solution includes some chemical compounds to facilitate the transfer of toxic heavy metals from the soil to the aqueous solution. However, not only the target metals can be dissolved but also other soil components contributing to soil fertility. Therefore, the efficiency of cadmium (and other toxic heavy metals) removal was determined for different washing soil strategies and also aspects referred to affectation of the soil structure, biological activity and fertility were evaluated [171–175].

The use of chelating agents for the removal of heavy metals affects the soil enzyme activity and the germinability of seeds. Evidently, biodegradable and non-biodegradable chelating agents have different effects. Wang et al. [171] tested four biodegradable chelating agents for the removal of cadmium from soil and compared them with the well-known non-biodegradable chelating agent EDTA. Two of the biodegradable chelating agents, iminodisuccinic acid (ISA) and glutamate-N,N-diacetic acid (GLDA), showed similar reductions of the labile fraction of cadmium, lead and zinc compared to EDTA, however, both the enzyme activities and microbial biomass were improved in soils washed with the biodegradable chelating agents. Also, germination of seeds was higher in soils washed with the biodegradable agents, an aspect that was interpreted by the author as a decrease of phytotoxicity of treated soils compared with the treatment with EDTA. These results suggest that both biodegradable and non-biodegradable chelating agents can remove the target and non-target metals, however, aspects referred to the health and conservation of nutritional values of soils are better when the soil is washed with biodegradable chelating agents. Tests on the remediation of soils with EDTA were conducted by Jelusic et al. [175] and they observed that soil washing resulted in soils with less bioavailable micronutrients (plant biomass was reduced). These authors also observed manganese deficiency and that phytoaccessibility of micronutrients copper, iron and manganese in soil was notoriously affected. Other authors also observed adverse effects of EDTA treatments; Zupanc et al. [174] observed that yield of white clover on remediated soil was reduced compared to the untreated soil and the structure of soil was also modified resulting in changes in water retention, aggregate fractionation and stability. Some additives must be applied to the remediated soil to recover soil properties and then the yield, as these authors concluded. Other authors found that a mixture of chelating agents can reduce negative effects on soils, as reported by Guo et al. [172]. Another approach that was explored is the use of certain waste derivatives from industrial processes as washing solutions. Liu and Chen [173] proposed the use of dissolved organic matter solution originating from wine-processing waste sludge as washing solution for the removal of cadmium from soils and their results showed that 80% of cadmium can be removed with a moderate loss of fertility.

Also, there is a risk of losing nutrients when soil washing is combined with other techniques. Xiao et al. [103] applied a soil washing strategy combined with phytoremediation for the removal of cadmium and zinc and observed a decrease in soil nutrient contents; calcium was especially affected and the inhibition of plant (ryegrass) germination and growth was observed.

Other techniques of chemical remediation were also tested in terms of the affectation of the soil properties. Giannis et al. [81] found that leaching of macronutrients was minimum when salts of weak organic acids were used for enhancing electrokinetic remediation with soil washing. Other authors reported that the application of electrokinetic methods could even increase the bioavailability of soil nutrients [176].

The scarce information available on the effects of soil remediation on the nutrient content in the soil and fertility is usually limited to macronutrients and the response of plants to the treated soil. Future efforts in the field should be focused on the determination of changes in the concentration of micronutrients like zinc, manganese and others.

Section 4: Discussion

Cadmium is one of the most toxic heavy metals, therefore, its occurrence in foodstuff is subject to strict controls. Plants can bioaccumulate cadmium and transfer it to edible parts. This allows cadmium to make its way into the food chain and reach humans. The human exposition to cadmium leads to serious health conditions, and special concerns are related to the more susceptible age groups, among them, children. Some foodstuffs are consumed with preference by children, such as the case of chocolate. The most important raw material in the production of chocolate is the fermented cocoa beans, harvested from cocoa trees (Theobroma cacao), which is an important accumulator of cadmium. Moreover, cocoa beans accumulate cadmium in concentrations that can easily exceed allowable limits for human consumption. There are risks to human health as well as economic threats for producing countries, most of them with poor populations that live from agriculture.

Concerns on cadmium in cocoa beans have motivated research focused on different aspects of cocoa production, one of them is soil. If concentrations of cadmium in soils are high, even if this heavy metal does not have an anthropogenic origin, agricultural products will contain cadmium in concentrations that could easily exceed allowable limits. Therefore, important efforts have been made in the remediation of soils containing cadmium (and other heavy metals).

There are different types of remediation techniques applicable to soils containing cadmium in concentrations that can affect its use for agricultural purposes. Based on the descriptions previously presented, physical remediation cannot be considered as a feasible type of remediation to remove cadmium from soils dedicated to agriculture. The movement of enormous amounts of soil both during removal and substitution required for fields occupying, perhaps, tens of thousands of hectares, makes unrealistic the application of physical remediation of soils for agriculture. These strategies aim to contain polluted soil and prevent further pollution. Currently, there are cases of highly polluted soils as a result of many decades of mining activities. These soils cannot be used for agriculture; the implementation of processes for the removal of the pollutants may be too expensive. However, the nature of pollution and the influence of environmental factors could mobilize hazardous pollutants to unpolluted zones, thus affecting especially water and productive soils. In such cases are feasible the soil substitution, surface capping, landfilling and encapsulation. Employing these techniques is not possible for the recovery of soils for agricultural purposes.

Chemical remediation is a type of remediation that can be applied for the recovery of contaminated soils for agricultural uses. The treatments by most of these techniques, which include soil washing, electrokinetic methods and immobilization, do not necessarily imply the movement of materials to other locations and this is itself an important advantage. There are reported Cd removal efficiencies for chemical techniques such as soil washing (reaches up to 90%), immobilization (between 28.38 and 30.81%), electrokinetic methods (between 40 and 85%) [33,37,81]. Electrokinetic methods are expensive since the energy requirements are considerable, thus limiting their applicability for soils destined for agriculture. Washing the soils does not require only water, but also certain chemicals, usually chelating agents and surfactants that can negatively affect living organisms in the soil. A detail that may be underestimated when soil is washed to extract cadmium (and, perhaps, other heavy metals) is the biodegradability of the chelating agents and surfactants since a certain amount of these chemicals remains in the soil. The recalcitrant nature of these compounds is not necessarily the only inconvenience, but also the associate toxicity for microorganisms and animals, like earthworms, can affect the productivity of the treated soils. It must be considered that a "healthy" soil contains a very rich microbial flora and a variety of microscopic and macroscopic invertebrates, which also harbor a complex microbial community [166,167]. There is still limited data on the effects on soil biota of emerging pollutants (for example), however, some authors suggested that these compounds can represent a risk to the soil compartment [168]. If there is a risk due to emerging pollutants, i.e., compounds that can be found in concentrations in order of milligrams or nanograms per kilogram of soil, it would not be difficult to imagine the implications to soil biota of recalcitrant, toxic and even xenobiotic substances introduced to this compartment for heavy metal removal purposes. The loss of microbial and animal diversity in the soil would easily rebound on the fertility of the soil and, therefore, the productivity of crops. The degradation of productive soils, which currently is already a serious issue, can be accelerated with further consequences including even threats to food security. On the other hand, if the chelating agents and surfactants used in soil remediation are biodegradable, depending on their concentration in soil, naturally occurring bacteria and other organisms could eliminate them in a relatively short frame of time. Therefore, a minor impact on soil biota can be expected and, in this sense, natural self-purification processes could eliminate any substance introduced during the treatment.

It is also concerning the effects of solutions containing chelating agents, surfactants and other substances used to wash soil on the concentration of micronutrients. These substances could interact, in a non-selective way, with other metals essential for growth and development for plants (i.e., micronutrients). In such cases, soil washing leads to a negative affectation on soil quality and crops are negatively affected, as observed by Im et al. [177]. Electrokinetic methods and the use of amendments can have the same drawback of removing micronutrients and affecting the productivity of the treated soil. Although many reports on chemical remediation methods focused on the removal of cadmium and other toxic heavy metals, the unintended removal of mineral micronutrients (e.g., calcium, zinc, etc.) was not properly addressed. In this sense, bioremediation methods could overcome such drawbacks at the same time that any chemical compound, biodegradable or not, is added.

Bioremediation, which includes techniques of microbial remediation, phytoremediation and animal remediation, could be less "aggressive" to the soil. The fact that bioremediation techniques use living organisms for both immobilization and removal of cadmium (and other heavy metals) from soils is an important advantage that should not be underestimated. Bacteria can modify the chemical form of cadmium into an insoluble form, thus making it less available for plants and limiting its leaching potential. Certain fungi could promote the accumulation of cadmium in non-edible parts of the plant, like roots, and facilitate the progressive removal of the heavy metal from soil. Also, cadmium hyperaccumulator plants can resist relatively high concentrations of cadmium in soil and concentrate this heavy metal in their tissue. There are studies that report Cd remotion efficiencies for different techniques like phytoremediation (reaching a Cd accumulation of 15% of total Cd), animal remediation (reaching a Cd removal of 36.53%) [94,101]. All these biological strategies based on microorganisms, plants and even their combination, have no adverse effect on soil structure and mineral nutrients. In fact, the use of other plants different from commercial crops in agricultural soils could be useful as a strategy to protect productive soils and prevent their degradation. Crop rotation is a recommended agricultural practice consisting of intercalating with different plants the use of the soil. Plants used in crop rotation programs have different nutritional requirements and allow the soil to recovery certain nutrients. However, when it comes to remediation of soils containing cadmium, selected plants (cadmium hyperaccumulators) could be included in the program to achieve the progressive removal of the toxic heavy metal from soil. Potential benefits of such strategy should be studied in future works, however, benefits as the increase of diversity in crop soils can be anticipated. The combined use of surfactants and/or chelating agents and phytoremediation should be carefully evaluated since combinations of this type could induce the removal from soil not only of the target toxic heavy metal but also metals acting as micronutrients. In this sense, is highly recommended a study that compares the removal of micronutrients from the soil due to the application of washing soil and phytoremediation together, and phytoremediation alone. It is not only important the removal of toxic heavy metals like cadmium, but also the conservation of healthy soil conditions.

The remediation of soils of cocoa crops can be more challenging compared to soils of other crops. The cocoa tree is an evergreen tree (i.e., it remains green and functional through more than one growing season) that requires about five years to produce its first fruit or cacao pod. Most of the existent cocoa trees in producing countries are several decades old, therefore, trees cannot be removed to perform the remediation of the soil. This is a different scenario compared to maize or another annual crop in which the soil could be treated after the crop is harvested. Any remediation strategy to remove cadmium from soils of cocoa crops must be applied to maintain the trees on the field. Clearly, techniques of chemical remediation are very limited, in this case not only due to the impact that they could produce on the soil structure and micronutrient content but also due to the possibility of manipulating the soil (it cannot be removed from the place). The use of amendments could still be a possibility if the roots of the trees are not affected. Techniques of bioremediation seem to be the best option for cadmium removal from soils of cocoa crops; perhaps some plants can be grown between cocoa trees and maybe certain microorganisms could also be applied. These techniques and their variations should be the subject of study in the future to gradually lower the content of cadmium in cocoa beans from currently producing areas.

Section 5: Conclusion

Cocoa beans can accumulate cadmium in concentrations beyond limits established by regulators. The origin of such contamination was attributed to soils of cocoa crops, which contain variable concentrations of cadmium. Cadmium is a ubiquitous pollutant and the remediation of soils containing this toxic heavy metal was studied not only to ensure the safety of cocoa beans (and chocolate) but also other agricultural products.

Techniques of physical remediation for the removal of cadmium from soils do not apply to crop soils and their applicability is restricted to scenarios with soils containing high concentrations of heavy metals, which are usually related to pollution attributable to mining activities. Techniques of chemical remediation for the removal of cadmium from soil have characteristics that make feasible their application in crop soils. Soil washing has low selectivity; solutions of surfactants and chelating agents typically used in soil washing can remove toxic heavy metals as well as micronutrients, thus affecting the productivity of soils. Moreover, the addition of foreign substances into soils, especially if they have limited biodegradability, can affect microbial communities and animals present in healthy soil. Electrokinetic methods could also affect the content of micronutrients in the soil. Similar to the other techniques, the use of amendments to immobilize cadmium must be evaluated in terms of the effect they have on the availability of micronutrients.

Phytoremediation seems to be the best technique for the removal of cadmium from crop soils. This technique could easily be incorporated to crop rotation programs to gradually remove cadmium and other toxic heavy metals from soil. It can also be combined with the use of certain specialized microorganisms (bacteria or fungi) to facilitate de removal of heavy metals.

In the context of cocoa crops, due to the characteristics of the cocoa tree (an evergreen tree), remediation strategies for the removal of cadmium from soils must take into account that trees cannot be removed. Therefore, feasible techniques can be the use of amendments of soil and phytoremediation. Implications of these techniques on both the productivity of the crops and the content of cadmium in cocoa over the time should be quantified in future studies in this field. It is remarkable to know that biological methods have the best results but changing the soil properties, biological are the best in terms of keeping soil conditions but they are time-consuming; heavy metals removal from agricultural soils is important but, depending on the technique used, there are future implications like soil fertility decreasing. In future works, researchers could study soils micronutrients status after remediation techniques because of most of them will be used to new cultivars and purpose forms to mitigate problems in the future to enhance productivity and crop yields.

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