#### **REVIEW ARTICLE**



## From classic methodologies to application of nanomaterials for soil remediation: an integrated view of methods for decontamination of toxic metal(oid)s

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#### Abstract

Soil pollution with toxic elements is a recurrent issue due to environmental disasters, fossil fuel burning, urbanization, and industrialization, which have contributed to soil contamination over the years. Therefore, the remediation of toxic metals in soil is always an important topic since contaminated soil can affect the environment, agricultural safety, and human health. Many remediation of each methodology (including high energy input and generation of residues). This scenario has motivated this review, where we explore soil contamination with arsenic, lead, mercury, and chromium and summarize information about the methods employed to remediate each of these toxic elements such as phytoremediation. Considering all the discussed techniques, nowadays, different techniques can be combined together in order to improve the efficiency of remediation besides the new approach of the techniques and the use of one technique for remediating more than one contaminant.

Keywords Soil contamination · Mercury · Lead · Arsenic · Chromium · Soil remediation

## Introduction

The environment is constantly being exposed to different chemical elements from natural and anthropogenic sources. Due to industrialization and urbanization in many regions of the world, the release of toxic elements from anthropogenic sources continues to rise (Wu et al. 2016). When toxic elements such as arsenic (As), lead (Pb), chromium (Cr), and mercury (Hg) accumulate in sediments, they can enter the food chain as bottom sediments in aquatic ecosystems and subsequently threaten the aquatic flora and fauna directly or indirectly (Hsu et al. 2016).

Environment contamination with toxic elements is not restricted to the aquatic ecosystem: soil can also be contaminated and has, therefore, become an important issue of

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Lilian Rodrigues Rosa Souza lilianrosa@alumni.usp.br environmental protection worldwide. The most significant anthropogenic sources of toxic metals accumulated in soil include effluents from industrial activities, sewage from domestic and industrial sources, and vehicular emissions, as illustrated in Fig. 1 (Soodan et al. 2014; Su et al. 2014).

Water contamination can also culminate in soil contamination, especially when contaminated water is used in irrigation. Recently, a case of contamination with arsenic became a serious problem when contaminated water was employed to irrigate rice, which could cause hazardous effects on human health (Sohn 2014).

Although this issue has been explored by various authors (Adegbeye et al. 2020; Allevato et al. 2019; Asgari Lajayer et al. 2017; Chen et al. 2015, 2018; Motuzova et al. 2014; Nriagu and Pacyna 1988), and despite the development of numerous remediation methodologies (Bolade et al. 2020; Bolan et al. 2014; Fernández et al. 2005; Gavrilescu 2004; Liang et al. 2016; Mao et al. 2015; Qin et al. 2019; Salt et al. 1995), environmental contamination by toxic metals remains a recurrent problem.

Toxic metals are considered soil contaminants when (I) they persist in soil for a long time after their introduction,

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Fig. 1 Anthropogenic sources of soil contamination with toxic metal(oid)s (Soodan et al. 2014; Su et al. 2014)

(II) they have high concentration in discarded products compared with their concentration in the receiving environment, (III) they can be easily transferred from an environment to another where direct or indirect exposure can occur, (IV) they can be interconverted to different species and become more bioavailable or toxic, adversely affecting the ecosystem and the human health. Furthermore, the presence of toxic metals can inhibit organic compound biodegradation in soil (Wuana and Okieimen 2011).

Recently, Rio Doce, a river in Brazil, made the international headlines because of the mining tailing dam disaster that happened in November 2015: toxic metals including arsenic, copper, and mercury contaminated the river and resulted in the largest Brazilian environmental disaster (dos Reis et al. 2017; Escobar 2015). In 2014, a catastrophic branch of the Mount Polley mine, in Canada, released 25 million cubic meters of tailings into the West Basin of the Quesnel Lake, where metals and metalloids such as As, copper (Cu), francium (Fr), and manganese (Mn) were detected at concentrations above British Columbia's freshwater sediment quality guidelines (Petticrew et al. 2015). These disasters can have long-lasting harmful effects on the environment. A classic example is the disaster in the Aznalcollar pyrite mine in Sevilla, Spain. In 1998, the waste dumps broke, releasing  $9 \times 10^5$  m<sup>3</sup> of toxic tailings into the Agrio and Guadiamar rivers. Despite the investments made to remediate the affected area, residual soil pollution can still be detected nowadays (García-Carmona et al. 2017).

In view of these facts, new studies about the toxic effects of metals and new strategies for their remediation must be implemented, so that satisfactory results can be achieved by means of simple methodologies that use non-toxic reagents at low cost. This review was designed using mainly studies from the last 5 years, using three different sources of research (ScienceDirect, Scopus, and Google Scholar), and keywords related to "soil remediation" were employed in the research.

## **Remediation techniques**

Several remediation methodologies have been developed to solve or to minimize the impact of contamination. These technologies include physical, chemical, and biological methods and are summarized in Fig. 2 (Song et al. 2017).

Physical remediation uses physical technologies. Capping consists of placing a suitable isolating material over contaminated soil to isolate the contaminants. Soil replacement refers to replacing contaminated soil with non-contaminated soil (Khalid et al. 2016; Song et al. 2017).

Chemical remediation employs chemical reactions to remove contaminants and includes immobilization, soil washing, and encapsulation. Immobilization reduces contaminant mobility, bioaccessibility, leachability, and bioavailability through complexation, adsorption, and precipitation. Soil washing removes soil contaminants by extraction, whereas encapsulation involves mixing the contaminant with other materials, such as concrete, to immobilize the contaminant (Khalid et al. 2016).

Biological remediation uses microorganisms or plants to remove contaminants from soil. The most common bioremediation method is phytoremediation, which employs plants to remediate contaminated soil (Khalid et al. 2016).

In addition to their classification into physical, chemical, and biological methods, remediation methods can be divided into two main strategies: in situ remediation and ex situ



**Fig. 2** Some methodologies for soil remediation (Khalid et al. 2016; Song et al. 2017)

remediation. In situ remediation is carried out at the originally contaminated site without the need to move the soil or the sediment itself. Ex situ remediation is conducted by excavating and treating the contaminated soil in a place away from the original site (Song et al. 2017). Ex situ and in situ techniques have specific benefits and costs. In situ remediation techniques are favored over ex situ techniques because excavation is expensive and excavators are exposed to adverse health risks posed by the contaminants (Kuppusamy et al. 2016).

#### Lead

#### Sources of lead and soil contamination with lead

Lead (Pb) is a toxic metal that has been included in the United States Environmental Protection Agency (U.S. EPA) "probable carcinogen" list. The major sources of contamination with lead include solid waste incineration, mining operations, and the chemical, metallurgical, and petrochemical industries (Du et al. 2014; Pinto and Al-Abed 2017).

The earliest record of lead mining dates back to as far as 6500 BC in Turkey. During the Roman period, lead was employed in the building of aqueducts and as a pigment in paint. It was also used to sweeten wine and to preserve fruit by addition of lead(II) acetate (Dapul and Laraque 2014).

Compared with other toxic metals, lead is highly persistent in soil due to its low solubility. It has harmful effects on human health, which is the reason why it has been banned from gasoline formulation (Cristaldi et al. 2017). The accepted safe lead concentration in soil is 400  $\mu$ g g<sup>-1</sup> in residential areas (Dapul and Laraque 2014).

The contamination of Pb in Brazil is largely from urban waste; approximately 215 thousand tons of municipal solid waste are generated daily. About 40.9% of this waste goes directly to the inadequate landfill and open dumps, causing contamination of the soil (Costa et al. 2019).

#### Toxic effects of lead

Lead accounts for one of the oldest occupational intoxication cases, dating back to the Christian era. The toxic effects of inorganic lead include neurological disorders, hypertension, cognitive impairment, and IQ loss. For all these reasons, it has been established that there is no safe level for lead exposure in children (Gidlow n.d.; Wu et al. 2016). Furthermore, Pb, which is initially present in the blood, is stored in bone for years, so bone becomes a long-term chronic source of lead back into the bloodstream (Laidlaw et al. 2017). Lead also binds to calcium-activated proteins with higher affinity than calcium, hence interfering in various calcium-dependent cellular functions (Dapul and Laraque 2014).

Poisoning with inorganic lead can be treated by chelation therapy, which helps to eliminate the metal. Although chelators such as CaNa<sub>2</sub>EDTA and meso-2,3-dimercaptosuccinic acid (DMSA) exert protective effects against lead, CaNa<sub>2</sub>EDTA can cause renal toxicity especially during treatment with high doses, whereas DMSA may cause appetite loss and nausea (Zhai et al. 2015).

The use of lead in the petrochemical industries is decreasing; in fact, the only compound that is currently produced in this industry is tetra-ethyl lead. Nevertheless, lead naphthenates and stereates are still employed as stabilizers for plastics (Gidlow n.d.).

Tetra-ethyl lead and inorganic lead have distinct toxicological profiles. Tetra-ethyl lead produces acute toxic psychosis, but the early symptoms can be easily missed. However, continuing exposure reveals further symptoms of toxic psychosis, and even coma may occur. Unfortunately, there is no specific antidote for organic lead poisoning other than sedation and supportive treatment (Gidlow n.d.).

#### **Remediation of lead in soil**

Intense use of lead in fossil fuels, paints, and plumbing can pollute the soil. In view of this problem, numerous methodologies have been developed to remediate lead in soil, including soil washing, phytoremediation, use of phosphates to immobilize lead, and, more recently, the use of nanoparticles.

#### Soil immobilization

Soil immobilization consists of adding reagents or materials into the contaminated soil to reduce the mobility of toxic substances and their solubility, thereby preventing toxic metals from migrating to other environmental media (Fig. 3) (Derakhshan et al. 2018). This method is relatively



Fig. 3 Schematic representation of the immobilization method

inexpensive. Nonetheless, if soil properties change, pollutants can become available again, so constant monitoring is crucial (Derakhshan et al. 2018).

The immobilization of metals can be evaluated by sequential extraction, which is a procedure that evaluates the leachability of metal in different extractor solutions. In soil, the exchangeable metal form is usually the most mobile and toxic form. A decrease in the exchangeable phase reduces mobility (Tao et al. 2017).

In soil, many materials can immobilize lead. The sludge from drinking water treatment (DWTS) can be used to this end because it contains iron and aluminum oxides that can bind lead and decrease its mobility. Recently, Souza and colleagues reported that this DWTS can efficiently reduce lead mobility and bioaccessibility (Souza et al. 2018). After a period of 4 months, samples containing a contaminated soil/sludge ratio of 1:1 present less than 3% of lead concentration in exchangeable fractions, and lead bioaccessibility decreased by 28.8% (Souza et al. 2018).

Okkenhaug and co-workers employed a mixture of oxyhydroxide powder (CFH-12) (2%) and limestone (1%) to remediate lead in soil. They also tested zerovalent iron (2%). According to the authors, all the sorbents decrease lead in water and extractable phase significantly (89% and 99% respectively). In addition, remediation remains stable over a 4-year experimental period, which indicates that the method is highly efficient (Okkenhaug et al. 2016).

Natural polymers like lignin, carboxymethyl cellulose, and sodium alginate can effectively immobilize lead. According to Tao et al. (Tao et al. 2017), all these materials diminish lead leachability and bioaccessibility, but lignin provides the best results: it lowers lead concentration in the exchangeable fraction to less than 10%. Furthermore, lignin forms a threedimensional molecular structure bearing oxygen-containing functional groups that efficiently bind lead (Tao et al. 2017).

#### Remediation with phosphate

The addition of phosphate is another in situ technique for lead remediation. Lead phosphates are 44 orders of magnitude less soluble than other lead minerals such as  $PbSO_4$ , PbS,  $PbCO_3$ , and PbO, which is important for effective immobilization (Zeng et al. 2017). The suggested mechanisms for lead immobilization include lead retention by hydroxyapatite in ionic exchange with calcium and reaction of lead with hydroxyapatite in solution, to form stable pyromorphite-type minerals like  $[Pb_5(PO_4)_3X; X = F, Cl, Br, and OH]$  with Kps  $10^{-71.6}$ ,  $10^{-84.4}$ ,  $10^{-78.1}$ ,  $10^{-76.8}$ , respectively, as demonstrated by the following equations (Melamed et al. 2003; Zeng et al. 2017):

$$Ca_{10}(PO_4)_6(OH)_2 + 14 H^+ \rightarrow 10 Ca^{2+} + 6 H_2PO_4^-$$
  
+ 2 H<sub>2</sub>O (1)

$$10Pb^{2+} + 6 H_2PO_4^{-} + 2 H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2$$
(2)

The method can be more efficient in acid soil because lead solubilization allows it to react with phosphorus. Therefore, remediation can be divided into two stages: soil acidification and addition of phosphorus, followed by the addition of limestone to make the soil alkaline. However, these procedures can be expensive and problematic (Laidlaw et al. 2017).

According to Seshadri and colleagues, countless phosphorus compounds, soluble and insoluble, can stabilize lead. These authors measured lead bioaccessibility in soil amended with diammonium phosphate (DAP) and with reactive (Sechura, SPR) and unreactive natural phosphate rock (Christmas Island; CPR), so that they could study how effective lead immobilization was. They showed that reactive SPR and DAP reduce lead bioaccessibility by 67.1% and 78.9%, respectively (Seshadri et al. 2017).

Yuan and co-workers verified that the addition of iron hydroxyl phosphate (FeHP) in soil effectively immobilizes lead. The DTPA-extractable phase decreases with increasing FeHP concentration in soil: FeHP at 4 wt% provides 55% lead immobilization (Yuan et al. 2017).

Although effective immobilization results have been achieved, some aspects must be considered before using phosphates to immobilize lead, including the risk of eutrophication in water environment and the increase in arsenic, selenium, and antimony leachability due to competition of these oxoanions for the adsorption site in soil as also reported by Hafsteinsdóttir et al. (Hafsteinsdóttir et al. 2014; Zeng et al. 2017). These authors treated the soil of East Antarctica with triple superphosphate and phosphate rock and a buffer of magnesium carbonate and magnesium oxide and observed higher arsenic leachability. They also noted that the time required for lead leachability to reduce to values below the value of the untreated landfill was 1 month because the presence of chlorides at high concentration of (from the ocean) and organic matter slowed the process of lead fixation on phosphorus through formation of pyromorphite (Hafsteinsdóttir et al. 2014).

#### Phytoremediation

Phytoremediation has been employed to remediate lead in soil. Phytoextraction and phytostabilization are particularly relevant to lead-contaminated soil. Phytoextraction entails using plants to absorb and to translocate lead to tissues, which is accumulated in the biomass, and can be removed by harvesting, while phytostabilization uses plants to stabilize lead in situ, by complexation or precipitation, in order to reduce the risks posed by this contaminant to the environment and the human health (Laidlaw et al. 2017) as illustrated in Fig. 4.

For phytoextraction to be effective, some characteristics are necessary including fast plant growth and a combination of



Fig. 4 Illustration of the phytoremediation process

high lead accumulation and large biomass to ensure efficient lead removal. Even though some plants can hyperaccumulate lead, they have small biomass and grow slowly, while high biomass-yielding non-hyperaccumulating plants generally lack the ability to accumulate high lead levels (Gupta et al. 2013; Laidlaw et al. 2017).

The uptake mechanism of metals by plants depends on the metal bioavailability and involves the root interception of the metal ions, their entry in the roots and their translocation through mass flow and diffusion. The phytostabilization mechanism indicates that plants sequester the metals in the rhizosphere through metal complexes with organic compounds, adsorption on roots surfaces, and metal accumulation in root tissues (Jabeen et al. 2009; Sabir et al. 2014). The metallothioneins (MTs) are metal-binding proteins with low molecular weight which provide thiol groups for metal chelation, participating in the phytostabilization mechanism. Their production by the plants enhances the metal translocation and sequestration, since they may be transported into vacuoles for long-time sequestration (Jabeen et al. 2009). It is important to take into account that each plant has its own phytostabilization and phytoextraction mechanism: Sedum alfredii H stabilizes Pb by induction of glutathione biosynthesis that binds Pb in the roots and the phytoextraction of Pb occurs by induction and accumulation of phytochelatin that binds metals in aboveground parts (Sabir et al. 2014).

According to Yildirim and Sasmaz, *Phlomis* sp. is a good phytoremediator of lead. These authors described lead concentrations of 4180, 1424, and 1050 mg kg<sup>-1</sup> in contaminated soil and in plant roots and shoots, showing that this plant has a high root and shoot enrichment coefficients and can be applied as bioaccumulator (Yildirim and Sasmaz 2017).

The use of more than one plant for soil decontamination has also been explored (as shown in Table 1). Recently, Desjardins and colleagues studied the use of three different plants, grown in mono- and polyculture, for phytoremediation of trace metals. They reported that combinations of two (*F. arundinacea* and *M. sativa*) and three (*S. miyabeana*, *F. arundinacea*, and *M. sativa*) plants resulted in higher lead accumulation than the use of *M. sativa* monoculture:  $21.6 \pm 3.9$ ,  $20.6 \pm 4.7$ , and  $6.3 \pm 1.2$  mg Pb m<sup>-2</sup>, respectively (Desjardins et al. 2018).

Although some authors have examined the combination of phytoremediation and chelating agents (Attinti et al. 2017; Babaeian et al. 2016; Mani et al. 2015; Zaier et al. 2014) in an attempt to increase metal bioavailability and plant uptake, it is important to evaluate the potential toxicity of chelating agents to plants and soil microorganisms, as well as the degradation of such agents (Evangelou et al. 2007).

#### **Remediation using nanoparticles**

Metallic nanoparticles have been used to remediate lead. However, caution must be taken to avoid using a nanoparticle that might pollute the environment. In this context, iron nanoparticles are a suitable option (Laidlaw et al. 2017).

Remediation depends on the standard redox potential ( $E^0$ ) of the metal contaminant in relation to the standard redox potential of iron ( $E^0 = -0.44$  V). If  $E^0$  of the toxic metal is significantly lower than iron  $E^0$ , the pollutant will be adsorbed in iron. On the other hand, if  $E^0$  of the toxic metal is significantly higher than iron  $E^0$ , the toxic metal will undergo reduction and precipitate (Laidlaw et al. 2017). Lead ( $E^0 = -0.13$  V) is a metal that can be either adsorbed or reduced, and the iron nanoparticles can also be composed of oxides/ hydroxides that can co-precipitate with lead, diminishing lead solubility in soil (Laidlaw et al. 2017).

Lead can be distributed in a more stable fraction in the soil such as the organic, residual, and Fe-Mn fractions by using ZVIN-Starch (starch stabilized zerovalent iron nanoparticles) measuring 9.28 nm as described by Okuo and colleagues (Okuo et al. 2018). Treatment of contaminated soil with 1000 mg kg<sup>-1</sup> ZVIN-Starch decreases the lead mobility factor by 18.87%.

Gil-Díaz and co-workers studied the efficiency of zerovalent iron nanoparticles (ZVINs) for lead immobilization in acidic soil and observed that these nanoparticles reduce leachability by 98% (Gil-Díaz et al. 2014). Recently, Moazallahi et al. also reported on the efficiency of ZVINs for lead immobilization. Among the three different synthesized ZVINs, the most effective is  $ZVIN_{EDTA}$  (ZVINs stabilized by EDTA), which diminishes lead release by 86.4% (Moazallahi et al. 2017).

Various types of soil can be treated with iron nanoparticles. Emadi and colleagues reported that ZVINs measuring 50 nm decrease extractable lead with increasing ZVIN dose at contamination levels of 50 and 150 mg kg<sup>-1</sup>. Some kinds of soil (sandy, acidic, and calcareous soils) have been evaluated, to

Table 1Some plant species forlead phytoextraction andphytostabilization (Gupta et al.2013; Salazar and Pignata 2014;Zou et al. 2011)

Phytoextraction		Phytostabilization	
Plant Lead concentration (mg kg <sup>-1</sup> )		Plant	Lead concentration (mg kg <sup>-1</sup> )
Arabis paniculata	33,900 in roots	Athyrium wardii	15,542.1 in roots
Sedum alfredii	1182 in shoots	Bidens pilosa L.	100.6 in leaves
Pennisetum polystachion	24,705 in roots	Sorghum halepense	1406.8 in roots
Polygala umbonata	21,670 in shoots	Tagetes minuta L.	380.5 in leaves

show that acidic soil experiences the greatest reduction in the extractable lead (Emadi et al. 2016).

Hydroxyapatite (HAP) is another nanomaterial that is effective for remediation. Li et al. studied lead immobilization in soil by hydroxyapatite at the nano and micrometer scale (nHAP and mHAP, respectively). Although both these phosphate-based materials effectively immobilize lead, mHAP is even better than nHAP (Li et al. 2014).

Nanoadsorbents of TiO<sub>2</sub> have also been evaluated for remediation of lead in soil. Recently, Khalaf et al. synthesized three different mesoporous TiO<sub>2</sub> by using CTAB, SDS, and PEG as cationic, anionic, and non-ionic surfactant template, respectively, and obtained the materials designated Ti C, Ti S, and Ti P. The authors reported spontaneous lead adsorption on TiO<sub>2</sub> surfaces due to negative  $\Delta G^0_{ads}$  values; lead adsorption follows the order Ti S > Ti C > Ti P. The total adsorptive capacity of these materials in soil containing 100 mg L<sup>-1</sup> lead is 97.6, 99.1, and 95.3% for Ti C, Ti S, and Ti P, respectively (Khalaf et al. 2018).

## Arsenic

## Sources of arsenic and soil contamination with arsenic

Arsenic (As) is a crystalline metalloid, a natural element with intermediate features between metals and non-metals. It is the 20th most abundant element in the geosphere and is considered extremely toxic to the environment and human health. Arsenic minerals and compounds are usually soluble; however, arsenic mobility is limited because it has a strong tendency to adsorb onto clays, organic matter, and hydroxides (Singh et al. 2015; Tarvainen et al. 2013; Vithanage et al. 2017).

The primary source of arsenic in the environment is its release from arsenic-enriched minerals (including volcanic rocks, coal, and geothermal waters) due to geochemical factors. Anthropogenic actions that release arsenic include industrial processes, mining, coal combustion, wood preservation, fossil fuel processing, application of phosphate fertilizers and herbicides, and incineration of municipal and industrial wastes (Singh et al. 2015; Wang and Mulligan 2006).

According to the U.S. Environmental Protection Agency, the permissible limit of arsenic in soil is 24 mg kg<sup>-1</sup>. Table 2 summarizes soil contamination with arsenic in different countries (Singh et al. 2015).

## Toxic effects of arsenic and its different species

Arsenic speciation is an important topic to investigate why many species have different mobility in soil and distinct toxicity. Arsenic speciation depends on its source and on environmental conditions like moisture content, redox potential, and microorganisms (Fayiga and Saha 2016). Different arsenic species can be found in organic or inorganic compounds, and arsenic exists mainly in four oxidation states: (i) As(V), arsenate; (ii) As(III), arsenite; (iii) As<sup>0</sup>, arsenic; and (iv) As<sup>-3</sup>, arsine. As(III) compounds are more mobile than As(V) compounds, suggesting that As(III) migration in the soil is more favorable (Guemiza et al. 2017).

In general, inorganic arsenic species are more toxic than organic ones. As(III) is the most toxic arsenic species, and organic forms of As(III) have been reported to be more toxic than inorganic ones (Fayiga and Saha 2016; Singh et al. 2015).

Methanogenic bacteria convert inorganic arsenic to organic forms by reducing As(V) to As(III) and methylating both these species to give monomethylarsonic acid (CH<sub>3</sub>AsO(OH)<sub>2</sub> or MMA) and dimethylarsinic acid ((CH<sub>3</sub>)<sub>2</sub>AsOOH or DMA). This conversion can be represented by the following equation (Jaishankar et al. 2014):

Table 2Arsenic concentration in contaminated soil and sediments indifferent countries (Liao et al. 2016; Singh et al. 2015; Wang andMulligan 2006)

Country	Region	Concentration (mg kg <sup>-1</sup> )
USA	Tulare Lake	280
Canada	Goldenville, NS	230-1980
Brazil	Minas Gerais	200-860
Spain	Duero Cenozoic Basin	23
China	Hunan Province	555

Other organic arsenic species exist, including trimethylarsine oxide ((CH<sub>3</sub>)<sub>3</sub>AsO or TMAO), arsenobetaine ((CH<sub>3</sub>)<sub>3</sub>As+CH<sub>2</sub>COOH or AsB), arsenocholine (AsC), arsenosugars (AsS), and arsenolipids (Fayiga and Saha 2016; Singh et al. 2015).

The organic forms MMA and DMA have been widely used as pesticides and herbicides; DMA is also employed as a cotton defoliant. Therefore, in terms of toxicity, these arsenic forms can be ordered as follows: MMA(III) > As(III) >As(V) > DMA(V) > MMA(V) (Singh et al. 2015).

The toxic effects of arsenic are well documented: cancer, pigmentation changes, hyperkeratosis, neurological disorders, muscular weakness, and cardiovascular diseases such as hypertension and stroke. Moreover, long-term exposure to low arsenic doses can induce varying chronic health effects (McGrory et al. 2017; Mohan and Pittman 2007). Women are especially affected by arsenic during pregnancy—this element underlies spontaneous abortion, stillbirth, and preterm birth rates (Ahmad et al. 2001).

### **Remediation of arsenic in soil**

In view of the environmental and health problems caused by soil contamination with arsenic, there has been increasing concern about soil remediation, and various strategies and methods have been developed to remediate arsenic (Song et al. 2017). Table 3 shows numerous methodologies for the remediation of arsenic in the soil.

#### Phytoremediation of arsenic in soil

Phytoremediation, which is also known as phytoaccumulation, phytoabsorption, or phytosequestration, uses plants to extract pollutants like toxic metal(oid)s through the plant roots, causing the pollutants to translocate and to accumulate in aboveground biomass. This method is viewed as an ecologically responsible alternative for environmental remediation (Alkorta et al. 2004; Mahar et al. 2016).

Phytoremediation offers the following advantages: it can effectively extract toxic metal(oid)s non-intrusively, it is easy

to implement and to maintain, it reduces the amount of waste going to landfills, it is inexpensive, and it can be employed with other techniques to improve the remediation efficiency. Nevertheless, some disadvantages can be cited: it is limited by contaminant depth (roots), solubility, and availability; it requires a long time of exposure; it depends on the climate season, and contaminants can be transferred to the food chain (Alkorta et al. 2004).

To be applied in phytoremediation, a plant should be tolerant of high levels of the contaminant, have a rapid growth rate, and accumulate reasonable levels of the contaminant (Alkorta et al. 2004). Table 4 depicts the plants that are most frequently employed to remediate arsenic in the soil.

Recently, Kumar et al. reported that arsenic successfully accumulates in *Pongamia pinnata*: about 1129–3322 mg kg<sup>-1</sup> of dry weight in roots, with bioaccumulation and translocation factors > 1. Therefore, this plant can potentially remediate arsenic in soil (Kumar et al. 2017).

Genetic engineering has attracted attention because it can help to improve the levels of plant tolerance to contaminants and their accumulation in plants. Nahar and colleagues modified the tobacco (*Nicotiana tabacum*) genome with the *Arabidopsis thaliana* AtACR2 gene. They found that transgenic tobacco is more tolerant of arsenic than wild-type tobacco, which helps to promote the field of genetic engineering applied to soil remediation (Nahar et al. 2017).

Coupling phytoremediation with the addition of bacteria enhances remediation. Franchi and co-workers observed that phytoextraction assisted by indigenous PGP bacteria (PGPB) makes the phytoremediation of arsenic 85% more effective (Franchi et al. 2017).

Recently, Lei and colleagues used the plant *Pteris vittata* to remediate arsenic for 2 years. They reported 16.09% remediation efficiency calculated from arsenic uptake by *P. vittata* (Lei et al. 2018). However, this plant did not provide a level of remediation with efficiency as high as the efficiency reported for other plants discussed in this topic.

#### Soil washing

Soil washing uses washing solutions to extract pollutants from soil. The extraction process is controlled by dissolution of the metal(oid)-mineral bond, which is followed by dispersion of

 Table 3
 Methodologies for remediation of arsenic in soil

Methodology	Ex situ/in situ	Reference
Phytoremediation	In situ	Liang et al. (2016)
Soil washing	Ex situ	Wang et al. (2017b), Wei et al. (2016a)
Electrokinetic remediation	Both in situ and ex situ	Shin et al. (2017)
Remediation by nanoparticles	Both in situ and ex situ	Gil-Díaz et al. (2017), Mansouri et al. (2017), Mueller and Nowack (2010)

Table 4         Plants used for phytoremediation of arser	c in soil
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Plant	Reference	
Tobacco (Nicotiana tabacum)	Nahar et al. (2017)	
Chinese brake fern (Pteris vittata)	Danh et al. (2013)	
B. juncea	Franchi et al. (2017)	
Pongamia pinnata	Kumar et al. (2017)	
Pteris vittata	Lei et al. (2018)	

the contaminant in the washing solution (Fig. 5) (Ko et al. 2006).

In this methodology, selecting the washing solution(s) is the most important step: the extraction efficiency of a certain contaminant depends on the washing solution features, but the soil characteristics and the bond strength must also be considered (Jang et al. 2007). Particle size distribution in the soil can also be determinant in this method: in most cases, the contaminants will concentrate on the fine particle fraction. Thus, information about soil characteristics including soil particle fractions can significantly improve the efficiency of the method (Ko et al. 2006).

Several washing solutions for remediation of arsenic in soil have been studied, e.g., NaOH,  $H_3PO_4$ , EDTA, oxalate, and HCl. Arsenic solubility increases with increasing pH, so an alkaline washing solution is best to treat arsenic (Cao et al. 2016). Cao et al. reported that oxalate is able to remove 52% of arsenic from contaminated soil. Moreover, soil washing combined with zerovalent iron treatment gives arsenic removal as high as 94% after 120 min (Cao et al. 2016). Different washing solutions can be combined to increase the remediation efficiency.

Fig. 5 Schematic diagram of soil washing

The sequence of washing solutions phosphoric acid-oxalic acid-Na<sub>2</sub>EDTA (POE) removes 41.9% of arsenic as reported by Wei and co-workers (Wei et al. 2016a).

Soil washing extracts toxic metal(oid)s adsorbed onto soil and reduces the volume of contaminated soil. Furthermore, this method can be applied to large contaminated areas because it is efficient and fast (Jang et al. 2007). Nevertheless, this method can modify the soil properties related to soil quality, including soil texture, water holding capacity, organic matter content, and total nitrogen concentration (Im et al. 2015). For this reason, Wang and colleagues recently investigated how various washing solutions impact arsenic removal from soil. According to these authors, NaOH decreases the total phosphorus, organic carbon, and nitrogen content; H<sub>3</sub>PO<sub>4</sub> lowers Ca, Mg, Al, Fe, and Mn concentrations, but it increases total nitrogen and phosphorous contents; and EDTA decreases the total organic carbon, phosphorous, Ca, Mg, Al, Fe, and Mn contents. However, the soil treated with NaOH provides the best conditions for wheat to grow compared with the other washing solutions (Wang et al. 2017b).

Simultaneous application of oxalic acid and dithionite to extract arsenic from amorphous and crystalline iron oxides present in the soil is less effective. Lee et al. observed that the use of each solution alone is not efficient, either. During the application of oxalic acid after dithionite is added to soil, the amount of arsenic bound to amorphous iron oxides and dithionite produces reduced forms of sulfur, which reacts with the extracted arsenic to form an arsenic sulfide precipitate as residual fraction. In turn, simultaneous application of oxalic acid and dithionite removes 74% of arsenic bound to amorphous iron oxides and 65% of arsenic bound to crystalline iron oxides (Lee et al. 2018).



#### **Electrokinetic remediation**

Electrokinetic remediation (EKR) consists in applying an electrical field to the contaminated soil to remove toxic metal(oid)s. The main goal is to get the contaminants to migrate under the applied electric field via electroosmosis, electromigration, or electrophoresis (Shin et al. 2017; Virkutyte et al. 2002).

During electroosmosis, the soil moisture moves from the anode to the cathode of an electrolytic cell. During electromigration, ions are transported to the electrode of opposite charge. During electrophoresis, contaminants bound to mobile matter can be transported and eliminated under an electric field (Fig. 6) (Virkutyte et al. 2002).

The advantages of EKR include its potential applicability to several pollutants and its high efficiency and timeeffectiveness in medium with low permeability such as soil (Kim et al. 2005). Nonetheless, this method has drawbacks: (i)



Fig. 6 Electrokinetic remediation illustration. a Electroosmosis. b Electromigration. c Electrophoresis

it consumes a high amount of electricity, which raises remediation costs; (ii) the resulting OH<sup>-</sup> reacts with cations, to form sediments that decrease the diffusive flow because they clog the spacing between soil particles; (iii) the gas produced during electrolytic dissociation is attracted to the electrode surface, which slows remediation down because bubbles cover the cathode surface and increase resistance (Suzuki et al. 2013; Virkutyte et al. 2002).

Ryu and colleagues obtained positive results when they used the EKR method to remediate arsenic in soil. They observed that NaOH addition increased the removal of both As(III) and As(V), which was 25% in one of the samples (Ryu et al. 2017).

To boost EKR efficiency, different methods can be combined with EKR. Soil washing can be accomplished before EKR, as reported by Mao and co-workers. The latter authors employed a  $KH_2PO_4$  solution for the washing and, after this process, they conducted EKR and achieved arsenic removal efficiency of 52% in the cathode area (Mao et al. 2017). Phytoremediation can also be used with EKR to enhance remediation efficiency. Mao and colleagues observed that both these methodologies could be coupled to improve remediation. The latter authors reported that arsenic bioaccumulation in plants (Indian mustard, spinach, and cabbage) goes up, indicating that EKR is a good method to be coupled with phytoremediation (Mao et al. 2016).

#### **Remediation using nanoparticles**

Nowadays, there has been increasing interest in the use of nanoparticles (NPs) in environmental remediation. NPs have small size, high reactivity, and large surface area, which help to improve the adsorption of contaminants. For example, iron oxide NPs offer 10 times greater sorption capacity than microscale particles (Liang and Zhao 2014). The advantages of this method are its low cost, low energy demand, and applicability to in situ treatment. However, it is important to consider the effects of NPs on the environment (Wang et al. 2012b).

Many NPs have been studied for the adsorption (and consequently remediation) of arsenic (Goswami et al. 2012; Nabi et al. 2009; Zhang et al. 2010). Iron oxide NPs such as hematite and magnetite and zerovalent iron NPs are the most promising for this purpose (Liang and Zhao 2014; Zhang et al. 2010). The mechanism of interaction of As and iron nanoparticle compounds, such as FeS, is different depending on the oxidation of As. The As(V) interacts with FeS particles by forming an outer sphere complexation and chemical complexation, and the As(III) at pH > 6 interacts by surface sorption, on the other hand, in pH 5, the interaction occurs by the following equation (Gong et al. 2016):

 $3\text{FeS} + \text{H}_3\text{AsO}_3 + 3\text{H}^+ \Rightarrow 1/2 \text{ Fe}_3\text{S}_4 + \text{AsS} + 3/2 \text{ Fe}^{2+1}$ 

$$+ 3H_2O$$
 (4)

Some studies have employed zerovalent iron NPs (ZVI NPs) to remediate arsenic in soil [61,62]. Gil-Díaz and coworkers reported that arsenic in the exchangeable fraction decreases by 70% in the presence of 5% ZVI NPs (Gil-Díaz et al. 2017).

Magnetite NPs (magNPs) can also be used to decontaminate soil polluted with arsenic. Yang and colleagues observed that magNPs reduce arsenic concentration in the easily extractable phase due to adsorption of the contaminant onto the NPs (Yang et al. 2017). Liang et al. studied As(V) immobilization by magNPs and reported a 93% decrease in As(V) in the water-leachable phase, indicating that these NPs can stabilize arsenic in soil and reduce its mobility (Liang and Zhao 2014).

Recently, Li et al. synthesized ZVI NPs supported on zeolite (Z-NZV) to remediate arsenic in a real sample. They observed that arsenic adsorption depended on the soil pH: alkaline soil promoted co-precipitation of As(V) and iron hydroxide, thus enhancing arsenic immobilization. Nevertheless, in both types of soil, acid, and alkaline, the available arsenic concentration decreased: 30 mg kg<sup>-1</sup> Z-NZV in the soil samples lowered arsenic to 30% and 13% of the initial arsenic concentration in acid soil and in alkaline soil, respectively (Li et al. 2018).

Babaee and Mulligan employed Fe/Cu NPs to remediate arsenic in a chromated copper arsenate (CCA)-contaminated soil. The NP solution effectively reduced arsenic leachability: the water-soluble arsenic was transferred to the nanoparticle phase, and the water-leachable arsenic concentration decreased by 92% (Babaee and Mulligan 2018).

NPs of binary oxides can also be prepared to immobilize arsenic in soil, thereby working as an in situ technique. Fe-Mn binary oxide NPs efficiently immobilize arsenic: water-leachable arsenic decreases by 91–96%, and the toxicity characteristic of the leaching procedure (TCLP) reduces by 94–98% (An and Zhao 2012).

#### Mercury

## Sources of mercury and soil contamination with mercury

Mercury (Hg) and its compounds are potentially hazardous to all organisms. Trace levels of this element occur naturally in the environment through volcanic activities and geological weathering. However, anthropogenic action has increased mercury release into the environment by a factor of three to ten. The largest sources of mercury emission are fossil fuel burning, which releases elemental mercury, and artisanal and small-scale gold mining: these activities release more than 1000 tons of mercury each year (Esdaile and Chalker 2018; Odumo et al. 2014; Pogrzeba et al. 2016; Provencher et al. 2014). Mercury is emitted into the atmosphere primarily as Hg<sup>0</sup> and is removed from the atmosphere after its oxidation to Hg<sup>2+</sup>, which is then deposited in either aquatic or terrestrial environment, where it is more persistent than in any ecosystem (Lamborg et al. 2014; Xu et al. 2015).

Mercury emission from anthropogenic sources is approximately 2500 tons yearly. This emission is distributed into the air, water, and land at a 45:7:48 ratio (Odumo et al. 2014). In this scenario, regulatory agencies have estimated guideline mercury levels in soil to protect both the environment and human health. In the UK, the inorganic mercury guideline level depends on land use; the lowest value is 8  $\mu$ g g<sup>-1</sup>. In Canada, this value is 6.6  $\mu$ g g<sup>-1</sup>. In the Netherlands, the maximum permissible added content of mercury is 1.9  $\mu$ g g<sup>-1</sup> (Tipping et al. 2010).

#### Toxic effects of mercury and its different species

Mercury is recognized as a highly toxic metal that causes severe harmful effects to human health and the environment. Brain damage, central nervous system (CNS) malfunctioning, memory loss, cardiac disease, liver damage, blindness, and loss of sensation are among its toxic effects on human health. Additionally, mercury can affect pregnant women and their babies because this metal can pass through the placenta and lead to low birth weight, as well as delayed neurodevelopment, growth, and development (Ha et al. 2017; Mahbub et al. 2017).

The mercury species can exist both in the inorganic and organic form and their toxicity and bioavailability depend on the form. Inorganic mercury exists both as elemental mercury ( $Hg^0$ ) and divalent mercury ( $Hg^{2+}$ ). Exposure to  $Hg^0$  occurs mainly through dental amalgam, and workers at small-scale gold mining can also be exposed to this mercury species. The most soluble form of mercury is mercury chloride: it is more easily transported than other inorganic forms; moreover, it serves as a substrate for methylation.  $Hg^0$  and its amalgams are less toxic than inorganic mercury, the target organs include the brain and kidneys. High mercury ingestion results not only in brain and kidney damage but also in digestive tract disorder, which can culminate in death (Ha et al. 2017; Rice et al. 2014; Sysalová et al. 2017).

The most common form of organic mercury is methylmercury (MeHg), which is the major source of organic mercury in the environment. The main source of MeHg is seafood and fish (Ha et al. 2017; Rice et al. 2014). Compared with other mercury forms, MeHg has the highest bioavailability and can cause permanent injury to the CNS because it is easily absorbed by the digestive tract (approximately 95% absorption) (Ha et al. 2017; Rice et al. 2014).

#### **Remediation of mercury in soil**

During soil remediation, Hg cannot be degraded in the same way as organic contaminants. Therefore, different methodologies to remediate mercury in soil had to be developed, including soil washing, thermal treatment, phytoremediation, and use of nanoparticles (Xu et al. 2015).

#### Soil washing

The soil washing method can be applied to remediate mercury in soil. This method uses an extractant solution that decreases the mercury concentration in soil. This method depends on soil characteristics like particle size and organic matter (OM) content. In soil, OM at high levels tends to bind mercury, thereby interfering in mercury distribution in particle size fractions and in mercury mobilization, which limits the effectiveness of this method (Xu et al. 2015).

Although soil washing is inexpensive compared with thermal treatment, and even though a smaller volume of soil has to be further treated or disposed after soil washing, issues may arise when (i) mercury is strongly bound to soil particles owing to high levels of insoluble humic substances, (ii) mercury is present in all particle size fractions, (iii) differences in density or surface properties between mercury-bearing and clean particles are not significant (Xu et al. 2015).

Different extractants can be employed to remediate mercury, including EDTA, thiosulfate, and iodide ( $\Gamma$ ) solutions. Iodide increases the solubility of mercury in soil by forming a soluble complex, HgI<sub>4</sub><sup>2-</sup>, as shown by the following equation (Wang et al. 2012b):

$$\operatorname{soil} \times \operatorname{Hg}(\operatorname{OH})_{x} + 4\Gamma \rightarrow \operatorname{HgI}_{4}^{2-} + xOH^{-} + \operatorname{soil}$$
 (5)

EDTA and thiosulfate solutions can remove mercury with 30% efficiency. Nevertheless, better results can be achieved by using a mixture of HCl and KI, which can provide mercury removal efficiency as high as 77%. The only problem is that this mixture changes the soil properties (Wang et al. 2012b).

Sodium sulfite is also an extractant solution that promotes mercury desorption in soil (Lu et al. 2017; Qi et al. 2017). Recently, Qi and colleagues obtained 92.05% mercury desorption by using 0.7 mol  $L^{-1}$  sodium sulfite after 24 h (Qi et al. 2017).

The soil washing method can also employ supercritical fluids like  $CO_2$ . To this end, mercury must be strongly chelated with a ligand that is soluble in the supercritical fluid, and the resulting complex must be soluble in the medium (He et al. 2015).

#### Thermal treatment

Thermal treatment employs high temperatures to remove mercury from the soil through volatilization followed by condensation of mercury vapors into liquid elemental mercury (Fig. 7) (Xu et al. 2015).

Whereas this method provides acceptable levels of decontamination, it consumes high amounts of energy for temperatures above 600 °C to be reached, and the treated soil is not suitable for agricultural reuse (Ma et al. 2015).

Inorganic mercury is usually present as  $Hg^0$  or as Hg(II) compounds like HgS, HgO, and HgCO<sub>3</sub> in soil. When the thermal treatment temperature reaches 600–800 °C, these mercury compounds are converted into gaseous elemental mercury, which can be easily recovered (Wang et al. 2012b).

The temperature employed during thermal treatment depends on the phase to which mercury is linked and on mercury speciation. Temperatures ranging from 460 to 700 °C afford greater efficiency (Sierra et al. 2016; Xu et al. 2015).

Hung et al. reported high mercury removal when they used this method. Despite the high temperature of the thermal treatment, 700 °C, these authors obtained 97.8% of mercury removal from a soil simultaneously contaminated with mercury and pentachlorophenol (Hung et al. 2016).

Recent studies have been geared toward reducing energy costs by decreasing the treatment temperature and by using solar energy. Zhao and co-workers removed 70% of mercury by treating soil at 350 °C for 30 min in engineering-scale experiments (Zhao et al. 2018). Citric acid can also be used to reduce the treatment temperature. Ma et al. showed that citric acid reduces the energy input by 35% compared with the traditional thermal treatment method. More specifically, mercury concentration decreases from 134 to 1.1 mg/kg when a temperature of 400 °C is used for 60 min (Ma et al. 2015). Sierra and colleagues controlled thermal desorption by using a



Fig. 7 Schematic representation of the thermal treatment process

solar furnace, which is a sustainable alternative for this treatment. They reported a total mercury release of more than 80% at 280 °C, indicating that the technique is efficient (Sierra et al. 2016).

#### Phytoremediation

Phytoremediation can also help to remediate mercury in soil and involves phytostabilization, phytoextraction, and phytovolatilization. Phytostabilization immobilizes mercury in soil through mercury absorption and accumulation in roots, thereby preventing mercury migration by soil erosion. During phytoextraction, mercury is absorbed and translocated by roots into plant parts lying above the ground, which can then be harvested. Phytovolatilization relies on the high volatility of mercury, which is taken up by roots, transported through the xylem, and released from cellular tissues into the atmosphere. Efficient mercury absorption by plants depends on factors that affect the availability of the contaminants, e.g., soil pH, organic matter, microbial biomass, and competitive cations (Sarwar et al. 2017b; Xu et al. 2015).

Some plants listed in Table 5 can be applied in phytoremediation. Marrugo-Negrete's research group studied the plant *Jatropha curcas* and observed that mercury concentration behaves as follows: roots > leaves > stems. The highest cumulative mercury absorption occurs between the second and the third month of exposure. Although the mercury concentration absorbed by aerial parts is low, the researchers concluded that this plant can be used in phytoremediation because it can adapt to eroded soil and is easily found near mining areas affected by pollution (Marrugo-Negrete et al. 2015).

As recently reported by Franchi and colleagues, addition of bacteria to the phytoremediation process can increase the remediation efficiency. The authors verified that indigenous PGP bacteria (PGPB) boost the phytoaccumulation efficacy for both *B. juncea* and *L. albus*. In the former plant, mercury phytoaccumulation reaches 45% (Franchi et al. 2017).

Mobilizing agents such as EDTA and HCl can improve this methodology. Rodríguez et al. tested EDTA and HCl solutions and observed that EDTA reduces plant (*Lupinus albus*) growth. Although mercury absorption takes place, phytoextraction is not significantly higher compared with the control sample. In turn,

 Table 5
 Some plants that can be used in the phytoremediation of mercury (Mahar et al. 2016)

Plant species	Mercury accumulation (mg kg <sup>-1</sup>	
Achillea millefolium	18.275	
Armoracia lapathifolia	0.97	
Cicer arietinum	0.2	
Festuca rubra	3.17	
Helianthus tuberosus	1.89	

HCl improves root growth, and mercury uptake is 3.7 times higher compared with the control sample (Rodríguez et al. 2016).

### Remediation using nanoparticles

In recent years, immobilization of toxic metal(oid)s by NPs has become a promising alternative. Mercury tends to form strong bonds with sulfur because it behaves as a soft Lewis acid. Interestingly, HgS formation is considered one of the primary mercury sinks in the environment (Gong et al. 2012). Possible mercury reactions in sulfidic soil include (Gong et al. 2012):

$Fe-S-Hg^{2+} \rightarrow Fe(Hg)S + Fe^{2+}$	(6)
(mercury inclusion into FeS)	(0)

$$FeS + Hg^{2+} \rightarrow HgS + Fe^{2+}$$
(ion exchange reaction) (7)

$$\frac{\text{FeS} + \text{Hg}^{2+} \rightarrow \text{Fe}-\text{S}-\text{Hg}^{2+}}{(\text{mercury adsorption})}$$
(8)

The affinity between mercury and sulfur makes mercury immobilization in soil with FeS NPs a promising remediation methodology. For example, Gong et al. reported that FeS NPs decrease leachable mercury in soil by 90–93% (Gong et al. 2012).

Selenium (Se) belongs to the same group as sulfur in the Periodic Table and also has affinity for mercury. Therefore, SeNPs can be a promising material to remediate mercury in soil. SeNPs can efficiently immobilize mercury through formation of HgSe, which is a less toxic compound. About 45.8–57.1% and 39.1–48.6% of mercury can be converted into HgSe under anaerobic and aerobic conditions, respectively (Wang et al. 2017a).

Zerovalent iron NPs can also be employed to remediate soil contaminated with mercury. Gil-Díaz and colleagues investigated the use of zerovalent iron NPs for mercury immobilization in soil and observed that, at 10%, these NPs decrease the mercury exchangeable phase by 63–90% (Gil-Díaz et al. 2017).

Wang and colleagues recently explored the use of SeNPs stabilized by extracellular polymeric substances (EPS) from *Citrobacter freundii* Y9 and observed that SeNP EPS at low doses promote high Hg<sup>0</sup> immobilization (over 88.8%) (Wang et al. 2018).

## Chromium

# Sources of chromium and soil contamination with chromium

Chromium (Cr) is the 21st most abundant metal in the Earth's crust. It is extremely toxic to the environment and the human health. It occurs naturally in weathering rocks and volcanic

gases and is adsorbed by minerals present in soil particles, such as manganese (Mn), aluminum (Al), and iron (Fe, as ferrochromite ( $Fe_2Cr_2O_4$ )). Natural sources emit an estimated 43 thousand tons of chromium per year worldwide. Anthropogenic actions, like the production of pigments in textile industries and the tanning of leather in tanneries, also contribute to the release of this element into the environment (Hsu et al. 2015; Nriagu and Pacyna 1988; Shahid et al. 2017).

According to the State Environmental Protection Administration (SEPA) in China, the permissible limit of chromium in soil is 250 mg kg<sup>-1</sup> (Khan et al. 2008). Table 6 depicts the contamination of soil with this element in different countries.

In Brazilian agriculture, the soil is disturbed by toxic metals such as Cr due to coal mines (Rodriguez-Iruretagoiena et al. 2015) and also from agricultural supplies such as fertilizers (Turra et al. 2010). It is also important to notice that since Brazil is among the five largest producers of leather, processing about 42 million cattle hides per year, the impact of this activity may be the release of Cr in the soil due to the inappropriate disposal (Araújo et al. 2014).

#### Toxic effects of chromium and its different species

Chromium speciation is an important topic because its species display distinct toxicity and soil mobility. The most common and stable chromium species in the environment is Cr(III), which forms a complex with organic matter present in soil and aquatic environments. Cr(III) can also occur in the form of chromic oxide (Cr<sub>2</sub>O<sub>3</sub>), hydroxide (Cr(OH)<sub>3</sub>), or sulfate  $(Cr_2(SO_4)_3.12 H_2O)$ , which have low solubility at pH < 5.5. Indeed, the soil pH governs Cr(III) adsorption and desorption. Because Cr(III) compounds are highly stable in soil, they have lower mobility in plant roots. In addition, this species is less toxic than hexavalent Cr(VI), which is considered the most harmful form. Cr(VI) comes associated with chromate ( $CrO_4^2$  $\overline{}$ ) or dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) ions, which are toxic to living organisms and promote carcinogenesis, mutagenesis, and teratogenesis. Furthermore, Cr(VI) is soluble in water; that is, it is more bioavailable, and consequently has greater mobility in

Table 6Maximum allowed levels of total chromium in agricultural soil(CETESB 2016; Ding et al. 2014)

Concentration (mg $kg^{-1}$ )
150
100-200
100
64
100
150 (intervention value)

soils and plants (Prado et al. 2016; Shahid et al. 2017; Sinha et al. 2018).

#### **Remediation of chromium in soil**

Due to the harmful effects of Cr to the environment and health, different methods of Cr remediation were studied. The remediation methods described in this section are in situ, which minimize the soil disturbance and cost as described in the "Remediation techniques" section. However, conditions such as climate, soil permeability, depth of contamination, and deep leaching of chemicals must be carefully examined (Liu et al. 2018).

#### Phytoremediation

Phytoremediation has been employed to remediate chromium in soil. In a study by Shahandeh and Hossner, thirty-six plant species of plants were investigated for Cr phytoremediation, although some species showed to be tolerant to Cr, they reported the difficulty of plants to be tolerant to Cr (VI) toxicity (Shahandeh and Hossner 2006). However, other studies reported some plants that can be tolerant to Cr (VI) and employed for soil phytoremediation as shown in Table 7.

Diwan et al. investigated the phytoremediation of Cr by different species of Indian mustard. Among the studied genotype, Pusa Jai Kisan is a hyperaccumulator of Cr with a maximum amount of 1680  $\mu$ g Cr g<sup>-1</sup> (for the dry weight) besides to be tolerant to the oxidative stress caused by Cr (Diwan et al. 2008).

Panikum (*Panicum antidotale*), Napier grass (*Pennisetum purpureum*), squash (*Cucurbita pepo*), cotton (*Gossypium hirsutum*), and sunflower (*Helianthus annuus*) were evaluated as Cr phytoremediator by Lotfy and Mostafa. The range of Cr removal by these plants was 29.9 to 36.5% and the sunflower roots showed the highest Cr accumulation about 58% (Lotfy and Mostafa 2014).

Recently, oregano was studied for Cr phytoremediation by Levizou and co-workers (Levizou et al. 2019). They reported

Tab	le 7	Some plant	s employed	for Cr p	hytoremediation
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Plant	Total chromium accumulated (mg $kg^{-1}$ )	Reference
Origanum vulgare	4300	Levizou et al. (2019)
Cynodon dactylon	152.1	Sampanpanish et al. (2006)
Pluchea indica	151.8	Sampanpanish et al. (2006)
Cichorium spinosum	330	Antoniadis et al. (2017)
Vigna mungo	$74.22\pm2.04$	Saravanan et al. (2019)
Leersia hexandra	2978	Zhang et al. (2007)

a bioaccumulation of Cr(VI) of 4300 mg kg<sup>-1</sup> for the dry biomass in both roots and aerial part in a soil containing a range of 150–200 mg kg<sup>-1</sup> of Cr (Levizou et al. 2019).

Although some plants can be used as bioaccumulator, Cr can cause stress and decrease the effectiveness of the remediation. In view of this fact, microbial-mediated remediation can improve this process by decreasing the metal stress in the plant and also by altering soil pH, release of chelators, thus improving the phytoremediation process. The inoculation of *P. aeruginosa* in soil enhanced the Cr accumulation in maize shoots by a factor of 4.3 by the increase production of siderophores (Pinto et al. 2018).

#### Bioremediation

Bioremediation remediates soil through microorganisms, which are stimulated to degrade contaminants to acceptable levels in soil and effluents (Liu et al. 2018).

The microbial mechanisms of chromium detoxification include absorption and oxidation. Absorption is known as bioaccumulation or biosorption; oxidation is called biorreduction and entails reduction of Cr(VI) to Cr(III), which is less toxic, immobile, and insoluble. Biosorption is an inexpensive, fast, and reversible physicochemical process involving the metallic species (sorbate) and the biological material (biosorbent); the surface/ volume ratio is high. However, metals accumulate through various mechanisms, such as transport, formation of extracellular complexes, and precipitation (Fernández et al. 2018).

Microorganisms can remove Cr(VI) through biosorption processes because the microbial cell wall contains functional groups like carboxylate, hydroxyl, amino, and phosphate, which can bind to the ions of potentially toxic metals (Fernández et al. 2018).

Ksheminska et al. reported that Cr(VI) compounds enter the microorganism cells through the anion channel via nonselective diffusion and are sensitive to the oxidative state. Cell membranes are impermeable to Cr(III), supposedly because they form little soluble complexes (Ksheminska et al. 2006).

#### **Electrokinetic remediation**

Electrokinetic remediation is an effective and environmentally friendly technique to remove toxic metals, like Cr, from contaminated soil.

As discussed in the "Toxic effects of chromium and its different species" topic, the toxicity of the Cr(III) and Cr(VI) are different, thus the reduction of Cr(VI) to Cr(III) is also important in order to decrease it toxicity. Wei et al. added NaHSO<sub>3</sub> to the soil before EKR and reduced 90.3% of Cr(VI) to Cr(III). The method of EKR with approaching anodes (Aas) was effective in Cr removal with 64.4% of efficiency for the total Cr concentration (Wei et al. 2016b).

The soil acidification can improve of EKR efficiency of Cr removal. Meng and co-workers reported that after addition of citric acid (0.9 mol  $L^{-1}$ ) in soil the Cr(VI) and total Cr removal rates were 77.66% and 26.97% respectively, while in soil without addition of citric acid, the removal rates were 6.23% and 19.01% for total Cr and Cr(VI), respectively, after a period of 5 days (Meng et al. 2018). Although in the study of Meng et al. the change in pH of soil after addition to 8.43 after addition of citric acid), it is important to mention that changes in pH can affect the microbiota and nutrient uptake of the plants.

The pulsed electrokinetic remediation (PEKR) is an improvement of the EKR method by pulsing the electric field in the electrokinetic remediation with reduction of energy consumption. Mu'azu et al. reported an achievement of 89.64% in Cr remediation in bentonite soil by using PEKR (Dalhat et al. 2016).

The concern about methods that follow the principles of green chemistry is getting attention and due to this, to reduce the energy input is important in the EKR method. In view of this challenge, recently, Zhou and colleagues investigated the efficiency of solar energy with exchange electrode-EKR (EE-EKR) for Cr remediation. After the remediation, the residual concentration was 10% and 58% for Cr(VI) and total Cr, respectively (Zhou et al. 2018).

#### Remediation using nanoparticles

Nanoparticles are used as adsorbent material due to their high specific surface area (availability of active sites), high reactivity, and high reduction capacity. According to Cao et al. (2006), 1 g of iron nanoparticles can reduce 69.3–72.7 mg of Cr(VI) in chromium ore. Singh et al. (2012) revealed that the efficiency of the remediation of Cr(VI) in soil is 99% after 40 days of contact with 5 g L<sup>-1</sup> iron nanoparticles (Cao et al. 2016; Singh et al. 2012).

Wang et al. synthesized iron sulfide nanoparticles (FeS NPs) stabilized with carboxymethyl cellulose (CMC) for Cr(VI) remediation. The FeS NPs decreased the Cr(VI) concentration from 4.58 mg  $L^{-1}$  to 46.8–80.7 µg  $L^{-1}$  (Wang et al. 2019).

Recently, nanomagnetic  $MnFe_2O_4$  were employed for Cr immobilization in soil. Eyvazi and co-workers reported the decrease of leachability of Cr(VI) in soil from 70.95 to 4.22% using 2 g L<sup>-1</sup> of nanomagnetic MnFe<sub>2</sub>O<sub>4</sub> during 192-h remediation time. Besides the high efficiency of Cr(VI) immobilization, they observed a high decrease in bioaccessibility of Cr(VI) in soil with a reduction from 86.76 to 4.42% (Eyvazi et al. 2019).

Carbon nanotubes comprise layers of coiled graphene that form a cylinder. They exhibit excellent thermal, electrical, and mechanical properties and are also employed for Cr remediation (Alim et al. 2018). Upon adsorption onto the surface of multi-walled carbon nanotubes, Cr(VI) can be reduced to Cr(III), and part of the latter species can be released into solution along the adsorption process, in acidic medium (Anastopoulos et al. 2017).

Carboxylated and hydroxylated multi-walled carbon nanotubes (MWCNT-COOH and MWCNT-OH) were studied for Cr(VI) adsorption by Zhang et al. and they reported that the Cr adsorption of MWCNT-COOH and MWCNT-OH could reach 8.09 and 7.85 mg g<sup>-1</sup>. They also observed the influence of pH which its decrease enhances the Cr(VI) adsorption in both carbon nanotubes (Zhang et al. 2018).

#### Remediation using biochar

Biochar is another kind of material with a potential to be employed in soil remediation, which is the carbon-rich final product of the thermal degradation of organic biomass in the absence of oxygen (Lahori et al. 2017).

The mechanisms involved in the immobilization of pollutants by biochar include (i) electrostatic attraction: due to the high electronegativity of biochar, the electrostatic attraction of positively charged ions is facilitated; (ii) ion exchange: the high CEC of the biochar release cations which exchange the metal ions from soil; (iii) complexation: the surface functional groups from biochar, such as –OH, –COOH, –C=O–, and C=N, can immobilize the toxic metals by complexation; and (iv) precipitation: some mineral elements in the biochar may precipitate with metals, such as inorganic P which can precipitate Pb forming  $Pb_{10}(PO_4)_6(OH)_2$  (He et al. 2019).

The efficiency of biochar-supported zerovalent iron nanoparticles (nZVI@BC) for Cr(VI) remediation was studied by Su and co-workers. The immobilization efficiency of nZVI@BC reached 100% by 8 g nZVI@BC per kg of soil for 15 days of remediation. They also reported that the exchangeable soil phase was almost completely converted to Fe-Mn oxides and organic matter, which are stable phases from the soil (Su et al. 2016).

Xu et al. reported that biochar acts as a redox process of soil active components. They evaluated the effects of Fe mineral and lactate, and observed that mineral iron decreases the Cr (VI) reduction rate by biochar due to surface oxidation and Febiochar complex coverage, attributed to Fe electron transfer (II) and by biochar (Xu et al. 2019).

Liu et al. demonstrated that the application of biochar in the remediation of Cr in soil is directly related to pH since the decrease of soil pH increases the availability of acid-soluble Cr. The application of biochar reduced the Cr availability rate by 55% (Liu et al. 2020).

## Determination of toxic metals in soil

Toxic metal contamination in soil can be determined by a wide range of techniques and atomic absorption spectroscopy (AAS) (Souza et al. 2019), high-resolution continuum source atomic absorption spectrometry (HR CS AAS) (Souza et al. 2018), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometer (ICP-MS) (Ran et al. 2016) are the most employed. However, different techniques can also be used for this purpose as detailed below.

Zhang and researchers synthesized a magnetic porous carbon adsorbent using a nitrogen-doped humic acid lignin coated for Cr (VI) adsorption and reduction. Analysis on AAS revealed that the adsorbent has a high adsorption capacity of 130.5 mg  $g^{-1}$  for Cr (VI), with partial reduction of toxic Cr (VI) to non-toxic Cr (III) (Zhang et al. 2020).

Zhao et al. quantitatively evaluated soil Pb by femtosecondnanosecond double-pulse laser-induced rupture spectroscopy (DP-LIBS) analysis. The researchers demonstrate this technique is an efficient spectroscopic tool for analysis of Pb in soil, obtaining values of relative standard deviation (RSD), mean square cross-validation error (RMSECV), and detection limit (LOD) of 99.42%, 2.99%, 0.42% by weight and 8.13 mg/kg, respectively. They also observed that a lower density of aerosol particles from soil is produced by the filament ablation target; thus, the Pb determination was strongly dependent on the delay time between pulses (Zhao et al. 2019).

Cheng and co-workers investigated the accumulation of mercury in soil from atmospheric deposition in temperate steppe of Inner Mongolia, China. They determined the Hg by Zeeman atomic absorption spectroscopy (ZAAS) and achieved a detection limit of 0.5 mg kg<sup>-1</sup>. The average Hg content found in the topsoil and subsoil was  $14.9 \pm 10.4 \ \mu g \ kg^{-1}$  and  $8.9 \pm 5.8 \ \mu g \ kg^{-1}$ , respectively (Cheng et al. 2019).

## Concomitant soil decontamination of Pb, Hg, As, and Cr

In areas with high industrial/mining activity, different toxic metals can contaminate the soil, and in order to remediate these areas, it is important to take in account an efficient methodology for all the contaminants, since it is unlikely that only one of these elements will occur separately. As discussed in all previously section of this review, different methodologies have been applied for soil decontamination. Among these techniques, some can be applied for remediate multiple contaminants at the same time as showed in Table 8.

The phytoremediation is a technique that can remediate more than one toxic element, as reported by Mattina and coworkers. According to their study, tomato (*Lycopersicon esculentum*) showed a bioconcentration factor (BCF) of 0.18 and 0.01 for Pb and As, respectively, besides to be able to remediate organic compounds (chlordane) presenting a BCF value of 0.05 (Mattina et al. 2003). Although it is possible to remediate concomitantly different pollutants by

Contaminant	Reference
As and Pb	Gong et al. (2018), Kim et al. (2014)
Hg and Cr, As and Cr	Moharem et al. (2019), Galdames et al. (2017)
Pb and Cr	Gong et al. (2018)
	Contaminant As and Pb Hg and Cr, As and Cr Pb and Cr

 Table 8
 Methodologies employed for remediation of multiple contaminants

phytoremediation, higher efficiency can be achieved using different techniques together. Mao et al. coupled the phytoremediation with electrokinetic remediation for Pb and As remediation. The acidification in the anode soil increased the water-soluble and exchangeable Pb and As, which consequently enhanced the solubility of these metals and increased their bioaccumulation in *Brassica juncea*, which were accumulated more in plant roots than in shoots (Mao et al. 2016).

Ferric and aluminum water treatment residues can be employed as immobilizers for remediation of multiple toxic metal(oid)s in soil according to the study by Wang and coworkers. Pb and As were transformed in more stable forms in the soil besides the decrease of As bioaccessibility by 25% (Wang et al. 2012a).

Nanoparticles also can remediate more than one metal in soil. Water treatment residual nanoparticles (nWTR) presented high efficiency in reducing the accessible forms of Hg and Cr in calcareous soil due to the formation of stable Hg and Cr species such as Hg(OH)<sub>2</sub> amor, CrSO<sub>4</sub>. xH<sub>2</sub>O, and Cr(OH)<sub>2</sub>. Furthermore, the concentration of Hg and Pb increased in residual phase of the soil (from 69.27% and 52.62% to 93.89% and 90.05%, respectively) which is the more stable fraction of the soil (Moharem et al. 2019).

## Future perspectives and challenges

A wide range of techniques can be employed to remediate soil, including the use of nanoparticles, phytoremediation, and electrokinetic remediation as mentioned in this review. However, new approaches within each of these technologies must also be explored in order to overcome the issues of each existing methodology.

Electrokinetic remediation requires considerable water and electrical energy, which can be a disadvantage. However, bioelectrokinetic remediation (Bio-EK) is a new strategy that is more environmentally friendly and which has potentially higher efficiency (Surya et al. 2018). The use of microorganisms can induce geochemical transformations of metals by oxidation or reduction (bioleaching) and facilitates precipitation for remediation (He et al. 2018). The bioleaching mechanism depends on the microorganism, but primarily, the process is driven by Fe- and S-oxidizing in aerobic conditions (Lee et al. 2011). The mechanism for *Thiobacillus ferrooxidans* is categorized by contact by electrostatic attachment and non-contact, with the production of extracellular substances and the formation of biofilm on the metal sulfide surface (Huang et al. 2017).

One example is a study by He et al., who reported that bio-EK enhances the efficiency of remediation of chromium in the soil to 90.67% in the presence of the bacterium Microbacterium sp. Y2 compared with the traditional EKR (80.26% of efficiency) (He et al. 2018).

Traditional phytoremediation methodologies are less economical for application on a large scale because hyperaccumulators grow slowly. Transgenic plants obtained through genetic engineering produce higher biomass, accumulate more metal, and adapt more easily to different climatic



Future perspectives of techniques for soil remediation

Fig. 8 The new approaches of the techniques for soil remediation

Methods	Advantages	Disadvantages
Soil washing	High efficiency, remove permanently the contaminant from the soil, rapid method	High cost, loss of the nutrients from the soil, soil structure deterioration
Soil immobilization	Simply and fast, cost effective	Long-term monitoring is needed, cannot remove heavy metals from soil
Thermal treatment	Effective extraction and recovery of Mercury, simply	High cost, damage for the soil structure
Electrokinetic remediation	Short repair time, high efficiency	Limited treatment depth, the soil heterogeneity can decrease the efficiency
Phytoremediation	Non-invasive, cost effective	Limited treatment depth, long repairing cycle

Table 9 Advantages and disadvantages of the methods of soil decontamination (Gong et al. 2018)

conditions, which make them effective for large-scale decontamination (Sarwar et al. 2017a). Considering that the efficiency of remediation in a plant is limited by the steps of the phytoremediation, the transgenic plants is improved in the following approaches: (i) the metal transporter proteins, which regulates the metal uptake; (ii) the translocation and storage of metal(iod)s in vacuoles; (iii) the production of detoxifying substances such as metallothioneins and phytochelatins in order to increase the plant tolerance to the pollutants; (iv) metabolic transformations of the metals in a non-toxic and volatile form. For this purpose, genes from other plant species and bacteria can also be introduced in order to improve the efficiency (Kaur et al. 2019).

Immobilization of NPs such as ZVIN onto supports is an innovative solution to overcome issues such as aggregation and formation of bulky corrosion products. Materials like carbons, resins, zeolites, and chitosan are easy to operate. Polyelectrolytes can be an alternative for soil deliverable ZVIN, which can be used for in situ remediation (Litter 2018).

Another promisor material for remediation is the biochar (BC), as discussed in the "Remediation using biochar" section. This material has a porous structure and large surface with micropores that can adsorb the pollutants present in soil (Lahori et al. 2017) (Fig. 8).

## Conclusion

Undoubtedly, the environmental contamination, especially the soil contamination, is one of the great concerns nowadays and different remediation strategies have been developed to solve this issue.

Although many methods are available for soil remediation, as discussed in this review, it is important to take into account the disadvantages and specific use of them (Table 9). However, in order to overcome these disadvantages, these methodologies can be combined to increase the efficiency such as phytoremediation with electrokinetic remediation (Mao et al. 2016), soil washing and immobilization (Zhai et al. 2018), and the use of nanomaterials with phytoremediation (Zhu et al. 2019).

In conclusion, choosing the best method for soil decontamination depends on the contaminant, the treatment depth, the cost involved, and also the soil characteristics which, consequently, is not a simple choice. Furthermore, designing new methodologies and improving on the existing soil remediation methods (by reducing cost and boosting efficiency) are crucial to deal with a recurrent topic and to avoid contamination of food and the environment, as well as health hazards.

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