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Review

Remediation of Arsenic and Cadmium Co-Contaminated Soil: A Review

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Abstract: The concurrent presence of arsenic (As) and cadmium (Cd) contamination in soil is widespread and severe, highlighting the need for remediation. However, remediating As and Cd co-contaminated soils is more complex than remediating soils contaminated with a single heavy metal due to the opposite properties of As and Cd in soil. Thus, the different forms of As and Cd in co-contaminated soils and their transformation rules have been systematically reviewed in this paper. Simultaneously, hyperaccumulators and immobilization amendments used in the remediation of As–Cd co-contaminated soil were reviewed. Moreover, the mechanisms of phytoremediation and chemical immobilization techniques in the treatment of As and Cd co-contaminated soil and the remediation effects were expounded in detail. To promote the development of ecological civilization, this paper proposes further remediation strategies and guidance for the remediation of As–Cd co-contaminated soil.

Keywords: arsenic; cadmium; co-contamination; hyperaccumulator; immobilization

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1. Introduction

Regular mining activities have led to notable heavy metal pollution [1,2]. These heavy metal substances are easily combined with other minerals and are sensitive to deposition in the atmosphere, and thus exhibit characteristics of co-contamination [1,2]. For example, arsenic (As) and cadmium (Cd), two sulfur-loving elements, often coexist in sulfide minerals, causing co-contamination problems [3–5]. The sulfide minerals' high toxicity, propensity for accumulation, and slow degradation pose significant threats to the ecological environment [6]. Numerous studies have reported the presence of As and Cd co-contamination in paddy fields [1]. China is one of the largest industrial producers, which makes its emission of As and Cd relatively high [7]. The agricultural practices in China have also aggravated the problem of arsenic and cadmium pollution, such as the use of fertilizers and pesticides containing As and Cd [5,8]. Long-term intake of rice contaminated by these elements will cause serious damage to various organs [7,8]. For instance, arsenic poisoning can lead to various cancers, including skin and lung cancers [3], while cadmium toxicity can induce pathological changes in multiple organs, including the kidneys, bones, and lungs [9]. The literature indicates that As and Cd are considered resistant to degradation under natural conditions [10]. They persist in the environment, undergoing migration and transformation, and may potentially exacerbate pollution [10]. Therefore, the remediation of soil co-contaminated with As and Cd is urgently needed.

The key to the remediation of soils contaminated by As and Cd lies in reducing their concentrations in soil to mitigate the risk of uptake by crops, especially in agricultural fields [11,12]. Remediation of As and Cd co-contaminated soil is more complex than single metal remediation due to the intricate interactions and transformation mechanisms inherent in such soil [13]. The distinct forms and chemical properties of As and Cd in soil can vary widely [14,15]. Changes in soil pH or Eh can lead to contrasting transformation trends for As and Cd, thereby significantly impacting the effectiveness of collaborative remediation efforts [16]. In recent years, phytoremediation and chemical immobilization techniques have been widely utilized in the treatment of soil contaminated by As and Cd [17]. These methods offer numerous advantages, including economic feasibility, simplicity, environmental friendliness, and practicality, while causing minimal soil disruption [18]. Therefore, the two technologies mentioned above contribute to the remediation of As- or Cd-contaminated soil. Among these, phytoremediation involves utilizing plants' abilities to absorb, transport, accumulate, or degrade pollutants to reduce pollutant concentrations in soil [19]. Chemical immobilization involves the application of amendments to contaminated soil, altering the chemical forms or states of As and Cd [20–23]. However, achieving collaborative remediation of both As and Cd through these methods remains challenging [24]. Few plant species can hyperaccumulate both As and Cd, and suitable amendments for simultaneously immobilizing these two elements are limited by various factors [25–27].

The purpose of this paper is to review the current status of research on phytoremediation and chemical immobilization techniques for the management of As and Cd co-contaminated soils. We elaborate on the forms of existence and the mechanisms of transformation of As and Cd in co-contaminated soil. We also summarize the efficiency and main mechanisms of hyperaccumulators and immobilization amendments in remediating As and Cd co-contaminated soil. Finally, we provide some constructive guidance for greener, more economical, and more efficient remediation of As and Cd contamination, aiming to promote the development of ecological civilization.

2. Forms and Transformation Mechanisms of As and Cd in Soil

According to the risk control standard for soil contamination of agricultural land (China, GB15618-2018) [28], the risk screening values of As and Cd in paddy soil are 30 and 0.4 mg/kg, respectively, while in the other types of soil, they are 40 and 0.3 mg/kg, respectively. Figure 1 illustrates the extent of As and Cd co-contamination in soils across various regions, and this As and Cd co-contamination is usually found in rice-growing areas [29–35]. In several regions, such as Huize County in Yunnan Province, China, and Jhang, Pakistan, there have been notable instances of arsenic or cadmium pollution surpassing acceptable limits [29,33]. Similarly, in locations like Gejiu City, Chenzhou City, and Shaoguan City in China, Saitama in Japan, and Gyeonggi Province in South Korea, both arsenic and cadmium have exceeded permissible levels to a significant degree [32–35]. In particular, in the city of Gejiu, As contamination exceeded the limit by a factor of 7.55 and Cd exceeded it by a factor of 11.3, resulting in As and Cd exceeding the standards in rice by 100% and 55%, respectively [30]. In Chenzhou City, As exceeded the pollution limit by 5.35 times, and cadmium exceeded it by 10.7 times [31]. Co-contamination with As and Cd is widespread and therefore the remediation of As and Cd co-contaminated soil is urgently needed. However, the forms and transformation mechanisms of As and Cd in the soil are different. Hence, understanding the forms and the transformation mechanisms of As and Cd in the soil is a prerequisite for further comprehending remediation techniques for As and Cd co-contamination.

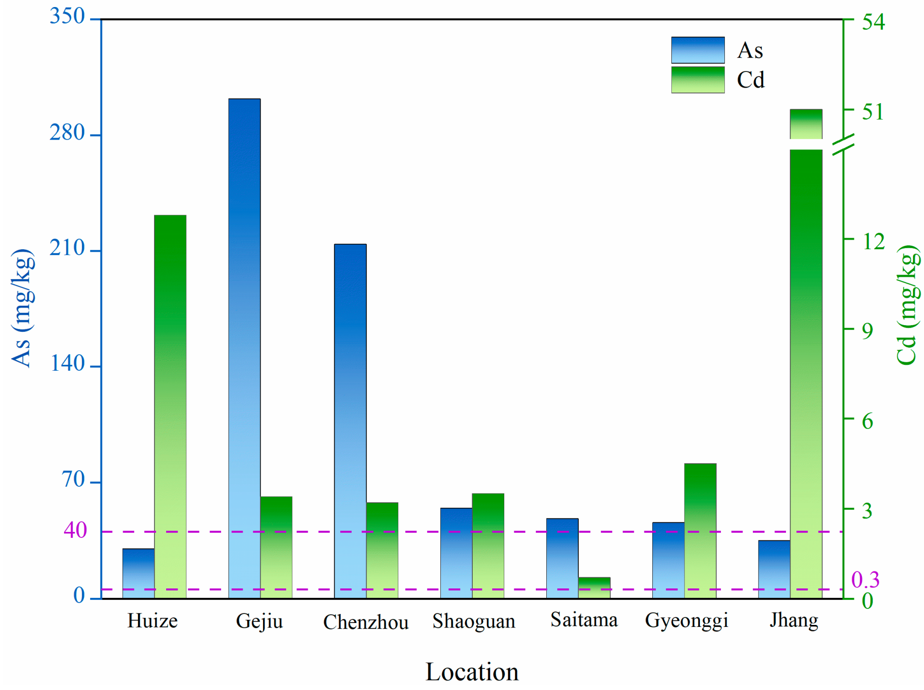

Figure 1. As and Cd co-contamination of soil in different regions. The dotted lines represent the respective contamination risk values of As and Cd in agricultural soils with pH values ranging from 5.5 to 6.5 according to the risk control standard for soil contamination of agricultural land (China, GB15618-2018). The regions are as follows: Huize, Huize County, Yunnan Province, China [29]; Gejiu, Gejiu City, Yunnan Province, China [30]; Chenzhou, Chenzhou City, Hunan Province, China [31]; Shaoguan, Shaoguan City, Guangdong Province, China [34]; Saitama, Saitama, Japan [35]; Gyeonggi, Gyeonggi Province, South Korea [32]; Jhang, Jhang, Pakistan [33].

2.1. Different Forms of As and Cd in Soil

In soils contaminated with both As and Cd, these elements are commonly found in several forms, including the ionic state, redox state, adsorption state, complexation, and precipitation [36,37]. The ionic state of As is usually As^{5+} or As^{3+}, and the ionic state of Cd is Cd^{2+} [38]. The redox state of As and Cd mainly includes arsenite, arsenate, and cadmium oxide, which will change with the redox conditions [39]. The adsorption state of As and Cd is mainly through interaction with the adsorption sites of minerals in the ionic form, and thus through adsorption on soil particles, especially on the surfaces of minerals such as iron oxide and alumina [40]. Bolan et al. [15] showed that soil adsorption of As was mainly specific, whereas adsorption of Cd was mainly electrostatic. Under appropriate conditions, As and Cd in the adsorbed state on the surface of soil particles can be re-released back into the soil solution [12]. In addition, arsenic and cadmium can form complexes with both organic and inorganic matter present in the soil, giving rise to organic arsenic complexes, organic cadmium complexes, sulfate complexes, ammonia complexes, and more [37]. Arsenic and cadmium tend to form different precipitates with other ions in the soil [41]. For example, in oxygen-deficient conditions, arsenic can react with calcium ions to produce calcium phosphate precipitates; with iron ions to yield iron–arsenic precipitates; and with aluminum ions to generate aluminum–arsenic precipitates [39]. Cadmium can associate with carbonate ions to form insoluble cadmium carbonate precipitates or with sulfate ions to produce cadmium sulfate precipitates [12]. However, the chemical forms and transformations of As and Cd depend on the physicochemical properties of the soil, the environmental conditions, and the properties of the elements themselves [14,42]. Therefore, the states in which As and Cd exist in the soil are determined by the environmental conditions of the soil.

2.2. Transformation Rules of As and Cd in Different pH–Eh Soil

The transformation rules of As and Cd in soil vary depending on the pH and Eh levels of the soil. [15,16,43]. For example, when soil pH rises, the increased negative charge leads to Cd cation precipitation, reducing Cd bioavailability [12]. Conversely, arsenic predominantly exists in the form of anions in soil, and the pH increase enhances electrostatic repulsion between soil particles and arsenate ions, consequently increasing the mobility and bioavailability of As [43]. Moreover, soil redox conditions also significantly impact the bioavailability of As and Cd [12]. For instance, Cd^{2+} tends to precipitate in the form of Cd sulfide under reducing conditions; thereby, Cd becomes immobilized [12]. The reduction of Eh also leads to the reduction of As (V) to As (III), which disrupts the lattice structure of As and Fe–Mn oxides, resulting in the re-release of As previously adsorbed on the oxides into the soil solution, thereby increasing the mobility of As and improving its bioavailability [11,12]. The different transformation rules of As and Cd under varying pH–Eh conditions increase co-remediation challenges (Figure 2) [44,45]. Some studies have shown that adjusting paddy soil conditions, such as pH and Eh, can influence As and Cd transformation through the soil and rice uptake [7,46]. However, the simultaneous reduction of As and Cd concentrations through pH and Eh manipulation alone remains a significant challenge. Therefore, understanding the distinct transformation rules of As and Cd is essential for developing effective remediation strategies for co-contaminated soils.

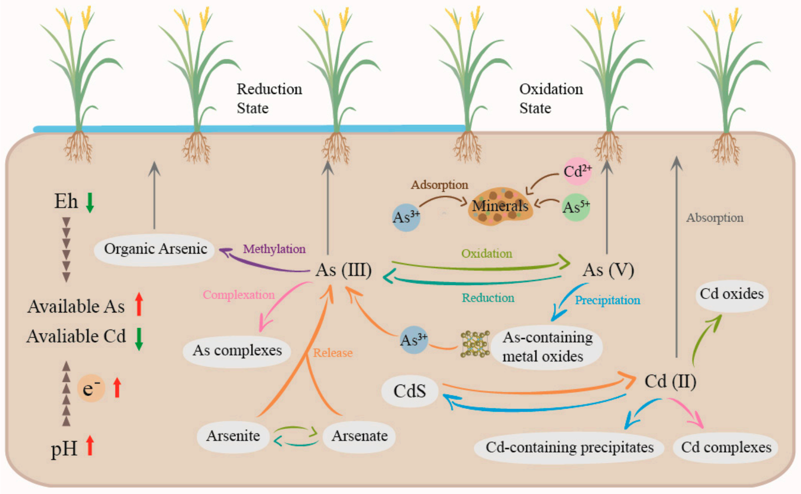

Figure 2. Changes in bioavailability of As and Cd under different environmental conditions.

3. Phytoremediation Techniques for As and Cd Co-Contaminated Soils

Planting specific plants at contaminated sites to reduce contaminants in the soil through the actions of specific plants towards contaminants (phytoextraction, phytostabilization, phytovolatilization, and inter-root filtration) is the main principle of phytoremediation [19]. Previous studies have attempted to find plants with strong tolerance to and hyperaccumulation of heavy metals [47]. To date, a large number of studies have focused on hyperaccumulators capable of accumulating As or Cd alone [24]. However, few plants have been reported to be able to hyperaccumulate both As and Cd. Therefore, exploring more plants with the ability to hyperaccumulate As and Cd is the key to realizing the remediation of As and Cd co-contaminated soils.

3.1. Arsenic and Cadmium Hyperaccumulators

Through searching, we found four As and Cd hyperaccumulators, which are *Xanthium strumarium L.*, *Helianthus annuus* L., *Brassica juncea* L., and *Pteris vittata* L., as shown in Table 1 [24,48,49].

X. strumarium, belonging to the family Asteraceae, is an annual herbaceous plant with significant biomass. Research indicates that *X. strumarium* is efficient in removing soil co-contaminated with As and Cd [50]. It exhibited a biological enrichment factor and biological transfer factor for Cd greater than 1, accumulating a Cd content of 1.84 mg/kg. Zhang et al. (2022) [48] conducted field trials and determined that the mature plant's total dry weight ranged between 440 g and 470 g. The results showed that the accumulation of As and Cd in a *X. strumarium* plant could reach 0.85 mg/kg and 0.83 mg/kg, respectively, with As primarily concentrated in the roots and Cd accumulating mainly in the roots and stems [48]. While the accumulation levels of As and Cd in *X. strumarium* may not be exceptionally high, its biomass surpasses that of other hyperaccumulators [50]. Furthermore, there are also studies showing that the addition of chelating agents and organic acids can enhance the plant's ability to accumulate As and Cd [48]. However, long-term usage of chelating agents and organic acids may impact the forms of As and Cd in the soil, potentially causing the capability of *X. strumarium* to accumulate As and Cd to decrease over time. Therefore, the use of chelating agents and organic acids requires reasonable control of their dosage.

H. annuus, belonging to the family Asteraceae, is an annual herbaceous plant with substantial above-ground biomass. Research conducted [51] during a field trial in the Chenzhou mining area confirmed that *H. annuus* exhibited a significantly greater capacity for extracting As compared to maize and rapeseed. Under the rapeseed and *H. annuus* planting model, the extraction of heavy metals As and Cd reached 250 g and 659 g per hectare per year, respectively [51]. Luo et al. (2016) [52] found that *H. annuus* used to produce oil has significant enrichment properties for heavy metals such as As and Cd. The results of a study conducted by Han (2020) [53] on the remediation of an agricultural field co-polluted with As and Cd showed that the average total dry weight of mature *H. annuus* was about 130 g per plant. The total accumulation of As and Cd in *H. annuus* was 1.11 mg/kg and 1.59 mg/kg, respectively, with the maximum Cd extraction reaching 2.31 mg/kg [53]. Research revealed that the addition of chelating agents could lead to an accumulation of Cd exceeding 100 mg/kg in the above-ground parts of *H. annuus* [54]. In comparison to other hyperaccumulators, *H. annuus* exhibits a significant advantage in terms of biomass and heavy metal extraction [51].

B. juncea, a member of the Brassicaceae family, is a fast-growing annual herbaceous plant with the capacity to accumulate heavy metals such as As, Cd, Cu, Zn, and Pb [55]. Research by Yang et al. [56] demonstrated that *B. juncea* possesses a strong ability to accumulate As, with the capability to accumulate and translocate As exceeding 576 mg/kg from both soil and aquatic systems. Additionally, *B. juncea* is recognized as a Cd hyperaccumulator. Experimental findings indicated that the above-ground parts of *B. juncea* could accumulate Cd in the range of 0.31 to 2.43 mg/kg, while the below-ground parts could accumulate Cd in the range of 0.44 to 2.94 mg/kg [57]. *B. juncea* employs induced antioxidant defense systems and enhances the activity of antioxidant enzymes to mitigate the stress imposed by heavy metals like As and Cd [58]. *B. juncea* can not only co-enrich As and Cd, but it also has significantly higher biomass and growth rates than singular hyperaccumulators for As or Cd [59]. These advantages contribute to the effective removal of As and Cd in co-contaminated soil through the use of *B. juncea*.

P. vittata, a member of the Pteridaceae family, is a perennial herbaceous plant with robust adaptability. In 2001, Ma et al. (2001) [60] reported its extraordinary As hyperaccumulation capabilities in the United States. Chen et al. (2002) [24] also identified it as a hyperaccumulator of As, capable of accumulating up to 8406 mg/kg of As, with enrichment factors reaching 71 for below-ground parts and 80 for above-ground parts. In comparison to typical plants, multiple phosphate transport proteins within *P. vittata* exhibit enhanced abilities for transporting arsenate. Research indicates that *P. vittata* not only demonstrates strong As accumulation capabilities, but also exhibits considerable tolerance to Cd [49]. It can endure high concentrations of soil Cd (reaching up to 301 mg/kg) and accumulate Cd contents as high as 186 mg/kg in its fronds. Thus, *P. vittata* is effective in remediating soil co-contaminated with As and Cd [61].

Table 1. Enrichment capacity of plants for As and Cd.

Plant Name	Family	Genus	Life Form	Plant Biomass	Accumulation	References
X. strumarium	Asteraceae	Artemisia	Annual	470 g	As: 0.85 mg/kg Cd: 1.84 mg/kg	[48]
H. annuus	Asteraceae	Carthamus	Annual	130 g	As: 1.11 mg/kg Cd: 2.31 mg/kg	[53]
B. juncea	Brassicaceae	Raphanus	Annual	35.4 g	As: 576 mg/kg Cd: 5.37 mg/kg	[56,57]
P. vittata	Pteridaceae	Pteris	Perennial	7.25 g	As: 8406 mg/kg Cd: 186 mg/kg	[24,49]

3.2. Enhancement Measures for Phytoremediation

However, the efficiency of phytoremediation of co-contaminated soils is still limited by factors such as different growth cycles and biomass. The synergistic use of multiple remediation methods to treat the soil is a more effective approach. The key factors in phytoremediation are plant biomass and the ability to accumulate heavy metals, which can be enhanced through the integration of chemical, physical, and microbial methods [62]. Research has shown that in soils co-contaminated with As and Cd, the rational application of chelating agents and organic acids can significantly improve the absorption efficiency of plants like *X. strumarium*. and *H. annuus* for As and Cd [48]. The combined use of multiple chelating agents has been found to be more effective than using a single chelating agent [63]. Research [64] demonstrated that intercropping three plant species (Chinese brake fern, mulberry tree, and Paulownia tree) increased the absorption of As and Cd by the Chinese brake fern, leading to a significant increase in biomass.

In addition, the rhizosphere bacterial community plays an important role in the remediation of As and Cd co-contaminated soil. Researchers primarily investigate several aspects, including the diversity and functions of rhizosphere bacterial communities, bacteria-mediated soil environmental regulation, plant–bacteria symbiotic relationships, and the involvement of rhizosphere bacteria in biogeochemical processes [65,66]. Certain microorganisms, such as Shewanella, possess tolerance to heavy metals like As and Cd, and their cell walls can adsorb significant amounts of these metals. Inoculating kidney beans with Shewanella has demonstrated potential for remediating As and Cd. The results indicated that the translocation of heavy metals from roots to shoots decreased by 10% to 50%, while plant biomass increased by 10% to 40% [62]. In another study, Li et al. (2020) [67] inoculated intestinal bacteria into water pepper (*Polygonum hydropiper* L.) and pale smartweed (*Polygonum lapathifolium* L.), which grew in soils co-contaminated with As and Cd. This approach enhanced the plants' antioxidant enzyme activity, alleviating As and Cd stress and thus improving their remediation efficiency. Therefore, regulating the composition of the rhizosphere bacterial community reasonably can enhance the effectiveness of the phytoremediation technique.

4. Chemical Immobilization Remediation for As and Cd Co-Contamination

Chemical immobilization technology involves adding chemical amendments to contaminated soil to transform mobile pollutants into precipitates or strongly adsorbed states, thereby reducing their bioavailability in the soil [20]. Some amendments have a strong immobilizing effect on As and Cd, such as 10% iron hydroxyapatite and iron sulfate, which can reduce As by 69% and 64.0%, respectively, and Cd by 44% and 98.4%, respectively [68]. However, for the remediation of As and Cd co-contaminated soil, the mechanism of simultaneous immobilization is intricate. Factors such as soil environment, type and dosage of immobilization amendments, and their stability significantly influence the immobilization effects, and may potentially activate another heavy metal [69]. Utilizing a single immobilization amendment is challenging when attempting to achieve simultaneous immobilization and inhibition of multiple heavy metals. Therefore, investigating the mechanism of immobilization is essential for the remediation of As and Cd co-contaminated soils.

4.1. Mechanisms of Soil Remediation through Immobilization Amendments

Different types of amendments can remediate soil heavy metals to varying degrees. Exploring their mechanisms can significantly enhance remediation efficiency. However, the mechanisms of remediation using different types of immobilization amendments vary (Table 2). Immobilization amendments can achieve the remediation of soils co-contaminated with As and Cd through the adjustment of soil pH, adjustment of soil CEC, physical–chemical adsorption, chemical precipitation, complexation and chelation interactions, and site competition [25–27].

This study has shown that the adjustment of soil pH is one of the mechanisms by which As and Cd are immobilized [70,71]. Soil pH significantly impacts the speciation of heavy metals such as As and Cd. By using alkaline immobilization amendments, the soil pH can be increased, increasing the negative electric charge on the soil surface [70,71]. The increase in negative electric charge enhances Cd^{2+} adsorption to soil particles and promotes Cd precipitation [72].

Adjustment of soil CEC is also one of the mechanisms by which As and Cd are immobilized. Certain immobilization amendments can enhance Cd adsorption by increasing soil colloidal cation exchange CEC [72–74]. Examples include organic fertilizers, phosphorus-based materials, and lime. Cations such as Ca^{2+} and Mg^{2+} in biochar can be exchanged with Cd^{2+} from soil particles to form surface or inner layer complexes [73]. Some studies have shown that zeolite can produce strong ion exchange and adsorption effects on Cd^{2+} through Si-O tetrahedral and Al-O octahedral structures [74]. It might be attributed to zeolite containing a large number of ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+} that can undergo an exchange reaction with H^+ and Al^{3+} in soil particles, thereby adjusting soil CEC and enhancing the adsorption of Cd^{2+} [75]. Adjustment soil CEC alone is generally used to immobilize Cd, while for the remediation of As and Cd co-contamination, other mechanisms must be employed.

Physical–chemical adsorption is a way to immobilize As and Cd in co-contaminated soil. Many immobilization amendments exhibit strong adsorption capacities, stable structures, and large surface areas [25–27]. These amendments, including silicate calcium substances, biomass char, clay minerals, and novel materials, can immobilize As and Cd in soils through physical–chemical adsorption mechanisms [70,71]. The co-sorption of As and Cd by this type of amendment requires suitable soil environmental conditions and a long immobilization time. In the future, researching more effective adsorption amendments is key to managing As and Cd co-contaminated soil.

Chemical precipitation immobilizes As and Cd in the soil. Some immobilization amendments can chemically precipitate with free As and Cd in the soil to form hydroxides, carbonate precipitates, metal oxides, etc. [76]. Secondary minerals can co-precipitate with As in the soil, reducing its bioavailability [77]. Under higher pH conditions, Cd is often immobilized through precipitation [78]. These studies suggest that soil environmental conditions are important for the generation of arsenic–cadmium precipitates.

Arsenic and cadmium are also immobilized in the soil through complexation and chelation. Free As and Cd can complex and chelate with organic matter and humic substances in the soil [79]. Aromatic functional groups in biochar engage in cation-π interactions, forming complexes with Cd’s d orbitals [80]. High-molecular-weight humic acids can also complex with As, consequently lowering the bioavailability of As [81].

Table 2. Remediation effect of immobilization amendments for As and Cd co-contamination.

Classification	Immobilization Amendments	Immobilization Mechanism	Application	Immobilization Rates	Experiment	References
Phosphates	Phosphates, hydroxyapatite, phosphate rock powder, phosphogypsum, and phosphate fertilizers	By forming insoluble phosphate precipitates and surface adsorption of heavy metals.	hydroxyapatite with iron	As: 69%; Cd: 44%	Pot experiment	[82–86]
			Complexation of ferric sulfate and dihydrocalcium phosphate (7.2:1)	As: 69%; Cd: 41%	Pot experiment	[17]
Metals and Their Oxides	Zero-valent iron, goethite, hematite, magnetite, acicular goethite, ferrous sulfate, and red mud	Adsorption and co-precipitation effects.	Ferrous sulfate	As: 64%; Cd: 98%	Pot experiment	[68,73,87]
			Zero-valent iron (Fe content 98%)	As: 54%; Cd: 22%	Field experiment	[88]
			Steel slag (Fe content 20%)	As: 33%; Cd: 56%	Field experiment	[89]
			Red mud (Fe content 21%)	As: 47%; Cd: 90%	Pot experiment	[90]
Clay Minerals	Zeolite, bentonite, loess, kaolinite, diatomaceous earth, montmorillonite, etc.	Adsorption, ion exchange, and coordination reactions.	Loess	As: 18%; Cd: 41%	Field experiment	[25–27,91]
			Limestone, zeolite, and ferrous sulfate (8:4:2)	As: 55%; Cd: 51%	Pot experiment	[92]
			Limestone, zeolite, and titanium dioxide (8:4:2)	As: 44%; Cd: 74%	Pot experiment	[92]
Limestone	Quicklime, hydrated lime	Increasing soil pH, altering soil CEC, and changing redox potential.	Limestone	As: 5–60%; Cd: 5–60%	Field experiment	[93–95]
Organic Fertilizers	Composting using animal manure, biomass solids, etc.	Adsorption, redox reactions, organic complexation reactions.	Fly ash mixed composting of sludge	As: 72%; Cd: 72%	Column experiment	[96–98]
Biochar	Biochar	Raising pH, adsorption, complexation, precipitation, and ion exchange.	Hydroxyapatite, zeolite, and biochar (2:1:2)	As: 55%; Cd: 33%	Pot experiment	[70,71,99]
			Co-application of steel slag and biomass charcoal (4:1)	As: 20%; Cd: 42%	Field experiment	[100]
			Modified biochar, acid-modified zeolite, and acid-modified vermiculite (27:23:50)	As: 99%; Cd: 81%	Pot experiment	[101]

Some scholars have suggested that the immobilization of As and Cd may also be due to site competition [84–86]. Due to the similarity of their ionic structures, phosphate and silicate ions can compete for active adsorption sites with arsenate or arsenite ions [82], and Fe^{2+} and Zn^{2+} can compete for divalent cation adsorption sites with Cd^{2+} [84–86]. However, this mechanism is applied to relatively few materials.

However, an immobilization amendment may contain multiple mechanisms, Chen et al. [102] successfully prepared a novel coal gangue-based magnetic porous material (MPCG) that reduced effective As and Cd by 17.94–29.81% and 14.22–30.41%, respectively, and the remediation mechanism of As by MPCG included adsorption, oxidation, ion exchange, complexation, and precipitation. Furthermore, MPCG's ability to promote the remediation of As–Cd co-contaminated soil is also achieved by manipulating the abundance of functional genes of relevant microorganisms. MPCG enhances sulfate reduction by boosting the expression of dsrA genes in the soil, leading to the production of sulfide. This sulfide then reacts with arsenic and cadmium, facilitating their precipitation and removal from the soil (Figure 3a). A novel calcium-based magnetic biochar (Ca-MBC) is mainly used for the simultaneous remediation of As and Cd through the elevation of pH and CEC, the formation of bidentate chelates and ternary surface complexes on the surface of iron oxides, and strong adsorption, as shown in Figure 3b [103]. By now, researchers are constantly working on new materials to keep As and Cd immobilized in the soil at the same time.

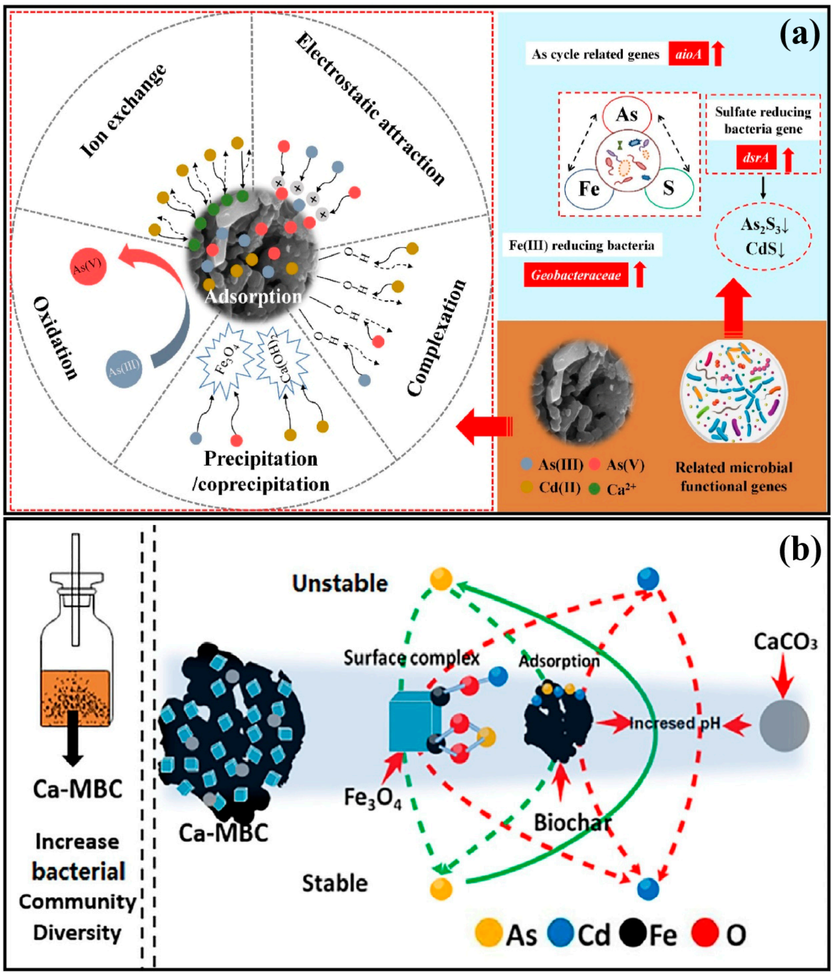

Figure 3. Mechanisms of a novel coal gangue-based magnetic porous material (MPCG) and a calcium-based magnetic biochar (Ca-MBC) for co-remediation of As and Cd. (**a**) Schematic illustration of potential mechanisms for remediation of As–Cd co-contaminated soil by coal gangue-based magnetic porous material [102]. (**b**) Schematic illustration of mechanisms for remediation of As–Cd co-contaminated soil by a novel calcium-based magnetic biochar [103]. Figure 3 from the article [102,103].

4.2. *Arsenic and Cadmium Co-Immobilization Amendments*

Due to the different chemical mechanisms of As and Cd in soil, the use of a single immobilization amendment is often ineffective in immobilizing both As and Cd, resulting in limited remediation of As–Cd co-contaminated soil [15,43]. Hence, researchers typically modify or combine immobilization amendments based on the degree and characteristics of As–Cd co-contamination in the soil to achieve improved remediation results [92,101]. Table 2 summarizes commonly used immobilization amendments and their remediation effects on As–Cd co-contaminated soils. Wu et al. (2015) [17] combined ferric sulfate and calcium dihydrogen phosphate in a ratio of 7.2:1, achieving 69% and 41% removal rates for available As and Cd, respectively, after 7 days of immobilization. The combination of limestone, zeolite, and titanium dioxide reduced exchangeable As and Cd content in soil by up to 43.8% and 73.7%, respectively, and lowered As and Cd content in rough rice by 34.1% and 64.7%, respectively [92]. The combination of steel slag and biochar reduced As and Cd content in rice grown on co-contaminated soil by 20.0% and 41.9%, respectively [100]. Xiong et al. (2019) [101] found that modified biochar combined with acid-modified zeolite and acid-modified vermiculite decreased As and Cd content by 99.8% and 80.8%, respectively. Fly ash mixed with composted sludge also exhibited significant immobilization effects, reducing the leaching rates of As and Cd by 72.0% and 72.2%, respectively [98]. While synergistic immobilization amendments for As and Cd have been identified, their stability, durability, and appropriate application rates are crucial factors that influence the remediation outcomes. Proper application is necessary to avoid secondary pollution, and the exploration of more effective, environmentally friendly, and sustainable novel immobilization amendments is essential.

5. Conclusions and Outlook

In summary, there exist complex interactions and opposite transformation rules between the As and Cd elements in co-contaminated soils. Soil environmental factors, such as changes in pH and Eh, influence the transformation processes of these two elements, thereby affecting their bioavailability. Neither phytoremediation nor immobilization techniques can remediate As and Cd co-contaminated soils well. In order to better manage As and Cd co-contaminated soils, the following outlook is proposed in this paper:

Further exploration of novel As–Cd hyperaccumulators and their integration with other technologies to better improve remediation efficiency should be explored. Despite the environmental, green, and economic advantages of phytoremediation technology, there are still challenges in treating As and Cd co-contaminated soils. Currently, the number of hyperaccumulators capable of simultaneously accumulating both As and Cd heavy metals is limited, and most of them are confined to the pot experiment stage, and not yet widely applied in practical remediation projects. Therefore, to address co-contamination, it is imperative to explore more novel hyperaccumulators, as well as to research how to combine other techniques—such as the addition of chelating agents and intercropping with multiple plants—to enhance the remediation efficiency of hyperaccumulators.

Combining phytoremediation and immobilization techniques may be a novel and effective remediation approach due to the diametrically opposite transformation rules of As and Cd in soil. Currently, only a few immobilization amendments can simultaneously immobilize As and Cd. Most immobilization amendments that immobilize one heavy metal may activate the other, making it difficult to achieve synergistic remediation of As and Cd, and immobilization merely immobilizes the heavy metals in the soil without completely removing them. Therefore, using a single phytoremediation technique or chemical immobilization technique is challenging for the simultaneous remediation of As and Cd co-contaminated soils. Given the complex interactions and contrasting transformation rules between As and Cd, a comprehensive system of multiple remediation techniques should be adopted based on their environmental behavior characteristics and the extent of As and Cd co-contamination. For instance, raising soil pH or lowering Eh can reduce the mobility of Cd cations, thereby decreasing the bioavailability of Cd. Conversely, increasing soil pH or lowering Eh can activate As, enhancing its mobility and bioavailability. Due to the opposite transformation rules of As and Cd, a directional remediation approach (immobilization + phytoremediation) can be chosen. For example, arsenic is immobilized in the soil through the application of immobilization amendments, but the amendments either have no immobilizing effect on Cd or have an activating effect on Cd, and then the Cd is taken up and transported by planted cadmium hyperaccumulators. This approach leads to opposite transformation directions of As and Cd in the soil, as shown in Figure 4. This can effectively reduce the content of bioavailable As and Cd in the soil, enhance the remediation efficiency, and provide new environmentally friendly guidance for the remediation of As and Cd co-contaminated soils through the integrated use of multiple strategies.

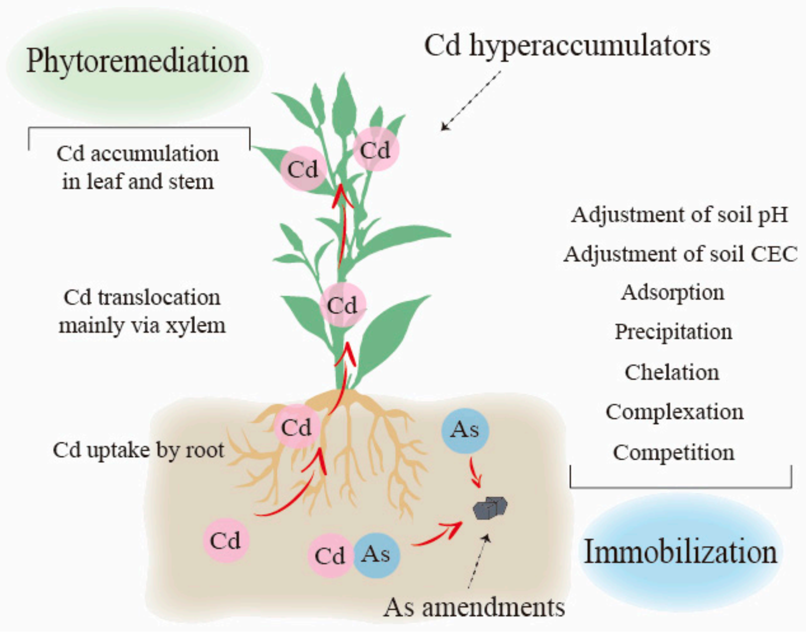

Figure 4. Remediation of As–Cd co-contaminated soil through phytoremediation and immobilization.

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