Heavy Metal Contaminated Soil Imitation Biological Treatment Overview

Chang Pan¹, Jun Chen², Ke Wu³*, Zhongkai Zhou¹ and Tingting Cheng¹

¹Department of Biological and Environmental Engineering, Hefei University, Hefei 230601, P. R. China.
²Anhui Key Laboratory of Sewage Purification and Ecological Rehabilitation Materials, Hefei 230601, P. R. China.
³Collaborative Innovation Center for Environmental Pollution Control and Ecological Restoration of Anhui Province, Hefei University, Hefei 230601, P. R. China.
*Corresponding author

Abstract. In this paper, the treatment methods of heavy metal pollution in soils were analyzed, the existence and transformation of heavy metals in soil were explored, and the mechanism of heavy metal absorption by plants was studied. It was concluded that the main form of plants absorb heavy metals in the soil is exchangeable. The main mechanism was that the plant cell wall can form complex with heavy metals, so that heavy metals fixed on the cell wall, and through the selective absorption of plasma membrane into the plant body. In addition, the adsorption mechanism of the adsorbed material was analyzed. According to the results of some researchers, it was found that the mechanism of adsorption of heavy metals was similar to that of plants. According to this, using adsorbent material as the main material, Imitate the principle of plant absorption of heavy metals in the soil to removing heavy metals in the soil at one-time and can be separated from the soil after adsorption to achieve permanent removal of heavy metals in the soil was feasibility.

Keywords: Soil heavy metals; Adsorbent materials; Imitation biology; Heavy metal pollution.

1. Present Situation and Harm of Heavy Metal Pollution in Soils

Soil is an indispensable part of the biosphere, but with the development of human activities in recent years, especially the development of mining and industry has led to a large number of exogenous heavy metals into the soil, so that the soil by different degrees and different types of heavy metal pollution, resulting in changes in soil physical and chemical properties and reduced biological suitability, affecting the growth of plants and animals. Heavy metals can also be gathered through the food chain in the human body caused by a variety of diseases, and even cancer. Previous reports indicate that the accumulation of heavy metals in vegetables and rice is not an isolated phenomenon, and vegetables are one of the most susceptible to heavy metal contamination, and human vitamins are mainly derived from vegetables [1]. The history of heavy metal pollution incidents frequent, 1931 Japan Toyama bone disease incident sensation of the world. China's heavy metal pollution is also very serious, China currently has at least 300 million mu of land (accounting for the country's arable land area of 1/6) to varying degrees by heavy metal pollution [2]. Urban areas have not been spared, such as Lianyungang area of soil heavy metal content was significantly higher than other coastal cities in China [3]. Soil mainly polluted heavy metals include Cr, Cd, Pb, Hg, As, Cu, Zn and Ni. The pollution of heavy metals in many soil pollutants is attracting more and more attention at home and abroad because of its strong concealment, long residual time, high toxicity, difficult to degrade, difficult to repair and easy to enter the human body through the food chain.
2. Main Control Measures and Advantages and Disadvantages of Heavy Metal Pollution in Soil at Home and Abroad

After years of research and practice, scholars at home and abroad have summed up several soil remediation techniques and got very good results, and the domestic and foreign technology is not very different. Foreign technologies include the use of major absorbers, chelating agents and biology-based technologies [4], and current research focuses on phytoremediation and natural transfer and attenuation [5]. China’s main technical and research hotspots mainly include barrier landfill, curing / stabilization, phytoremediation, soil cleaning, thermal analysis and electric repair, etc. The electric repair is still in the laboratory research stage [6]. In general, soil remediation techniques include physical repair techniques, chemical repair techniques, bioremediation techniques, and joint repair techniques.

Physical repair technology has a soil extraction method, isolation embedding method, heat recovery method and so on, which is characterized by the use of physical methods to dilute, transfer, fixed heavy metal pollutants to the standard level, the physical repair method has quick, does not destroy the soil chemical properties and other characteristics, but not suitable for large-scale soil pollution treatment, nor suitable for serious areas of pollution. Chemical repair technology refers to the addition of chemical substances, which directly or indirectly change the form of heavy metals and their bioavailability to inhibit or reduce plant absorption of heavy metals. Mainly including chemical improver method, chemical leaching method [7]. Chemical modifier method that is added to the soil chemical deactivators such as phosphate, lime, etc., so that heavy metals to form insoluble precipitation or into a harmless complex to improve the soil. Chemical leaching method refers to the removal of heavy metals by dissolving heavy metals from the soil by adding dissolving agent to the soil, and then recovering the eluent. The chemical method is applicable to a wide range, but the removal rate is greatly influenced by the selected reagents, and chemical agents may cause secondary contamination of the soil. Bioremediation is the use of biological life metabolic activities, transfer, fix heavy metals and thus reduce the amount of heavy metals in the soil. Biology has a strong enrichment effect on heavy metals, for a certain heavy metal has a strong adsorption capacity, but for other heavy metal adsorption capacity is not strong. For example, castor can selectively absorb copper in the soil[8], kale can selectively absorb the soil of chromium [9]. Therefore, bioremediation technology is not suitable for a variety of heavy metal pollution repair, and due to the impact of biological growth cycle, repair efficiency is very low. Joint repair technology refers to the application of a variety of means to reduce the soil heavy metal content of the technology, such as chemical - plant joint repair technology, electric - chemical repair technology. This method combines the advantages of traditional repair methods, with high efficiency, flexibility, wide range of applications, and so on, at present in the laboratory inquiry stage. The main repair techniques are shown in Table 1.
Table 1. Summary of technical methods for remediation of heavy metals in major soils

| Category          | Main means                        | Main measures                                      | Principle                                                                 | Advantage                                      | Disadvantages                                      |
|-------------------|-----------------------------------|----------------------------------------------------|---------------------------------------------------------------------------|-----------------------------------------------|---------------------------------------------------|
| **Chemical treatment** |                                   |                                                    |                                                                           |                                               |                                                   |
| Chemical modifier method | Add limestone, phosphate, organic matter, iron and so on | Precipitation, adsorption, oxidation and reduction of a series of chemical anti | Easy to operate, quick, limited small | Causing secondary pollution, did not really remove heavy metals |
| **Chemical leaching method** | Add organic acids, surfactants and so on | Transfer heavy metal to liquid phase and collect | Quick, limited small | Pollution of groundwater, destruction of soil structure, resulting in nutrient loss |
| **Land transfer method** | Remove contaminated soil and replace it with new soil | Transfer contaminated soil to soil of lower metal content | Quick, easy to operate | Large amount of work, not suitable for large area processing |
| **Isolation method** | Construction of the wall around the contaminated soil | Isolate contaminated soil | Effective, suitable for serious areas of pollution | Large amount of work, not suitable for large area, decentralized treatment |
| **Deep plowing** | The contaminated soil will be buried in the soil | Reduce the contact rate of heavy metals and organisms in the soil | Effective, suitable for large areas of pollution disposal | Did not really eliminate the hidden dangers, the amount of work |
| **Phytoremediation** | Planting hyperaccumulators | The use of plants to absorb and enrich heavy metals | Economy, easy to operate | Long cycle, selective absorption of heavy metals |
| **Biological treatment** | Animal repair method | Stocking animals such as earthworms, nematodes and so on | The use of animals for heavy metal absorption and transformation | Low cost, enhance fertility | Not suitable for polluting areas |
| **Microbiological repair method** | Inoculation with microorganisms with degradative effect | Microbial absorption of heavy metals, redox and so on | Low cost, limited small, good effect | Not suitable for polluting areas |

In general, although the current soil heavy metal pollution control methods are varied, but in addition to plant remediation method can permanently remove heavy metals in the soil, other methods can only reduce the toxicity of heavy metals in the soil and cannot achieve the purpose of permanent removal, these Potential heavy metals under certain conditions will reactivate the environment. Some methods such as leaching method can achieve the purpose of permanent removal, but its high cost and not suitable for large area of local governance, narrow range of applications, should not be promoted. Therefore, it is the primary task to deal with the heavy metal pollution of the soil by finding a cost-effective method for dealing with heavy metal pollution in the soil.

3. Morphology and Mutual Transformation of Heavy Metals in Soils

The distribution of heavy metals in the soil is affected by many factors, including the physical and chemical properties of the soil, such as pH value, organic matter content, soil particle size [10], and other factors such as rainfall, Zheng Shunan [11] found in laboratory simulated rainfall that within a period of 2000 mL of rainfall and leaching, the release of heavy metals was rapid during this period. In addition, there are biological and human factors, many organisms can secrete organic acids and other substances to promote the transformation of heavy metals in the soil, such as oat and other cereal crops root acidic substances can dissolve carbonate heavy metals, so that bio-absorption of heavy metal components increased [12]. Human activities are the main factors in the heavy metal elements in the soil.
The soil heavy metal form is mainly divided into exchangeable state, carbonate state, iron and manganese oxidation state, organic state and residual state [13]. Exchangeable state is mainly adsorbed on the surface of the soil, although the proportion of exchangeable heavy metals in the soil is not large, it is most likely to be bio-absorbed. Carbonate is the main form of heavy metal precipitation and deposition, and can be converted into exchangeable state under acidic conditions. Iron and manganese oxidation state is a heavy metal with a strong binding force adsorbed in the soil of iron and manganese oxide, this state of stability is not strong, easy to dissociate to form other forms. Organic state is mainly composed of heavy metals and organic complexes, organic state heavy metals are some easily soluble and some insoluble, plants can only absorb soluble organic binding state [14]. Residual state heavy metals are the main part of the heavy metals in the soil. It can be used as the soil background value of the heavy metal elements. The heavy metals in the residual state are very stable and the bioavailability is not significant. In general, the form of heavy metals in the soil can be converted to each other in a variety of environments, and ultimately to achieve dynamic balance, the main conversion path as shown in Figure 1.

![Figure 1](image)

**Figure 1.** Main ways and mechanism of heavy metal transfer to exchangeable state in various forms of soil

The distribution of heavy metals in the soil is also regular, such as exogenous mainly in the soil 0-5cm surface, Fe and a variety of other heavy metals are related; heavy metals are obvious to the soil fine particle enrichment characteristics [16]. The water-soluble state can be directly absorbed, the exchangeable state is most easily absorbed, and the carbonate state is also easier to re-release into the water phase, for the iron and manganese oxidation state, when the oxidation-reduction potential changes will be released, the organic sulfide state is not easy to be absorbed; residue state is not effective for biology [17]. Although the content of heavy metals in different soils is different, but in general the residue state heavy metal in the soil is the main form, followed by iron and manganese oxidation state and carbonate state, these three forms account for about 70% of heavy metals in the soil [14]. Heavy metals in the soil can transform each other between forms, is a dynamic process.

4. **Mechanism of Bioavailability of Heavy Metals in Soil**

The use of plants to repair soil heavy metal pollution is currently the cleanest method. At present, more than 700 species of hyper accumulators have been found, and are widely distributed in about 50 families, and are mainly concentrated in Cruciferin [18]. A great deal of research has been done on its mechanism both at home and abroad. Plants are exchange material with the soil through the roots, through the cell wall adsorption, the selective absorption of plasma membrane and chelate also other ways to achieve the absorption of heavy metals, transport and toxicity degradation [19]. At the same time, the plant roots change the pH of the soil through the secretion of organic acids, such as oxalic acid, citric acid, fatty acids and interactions with microbial communities, to continuously dissolve the heavy metals in the carbonate and iron-manganese oxidation states, make it become exchangeable state, activation of the heavy metals in the soil, thereby promoting the absorption of heavy metals and
the leaching of heavy metals into groundwater [20]. The plant cell wall is rich in pectin, hemicellulose, cellulose and lignin macromolecules and contains coordination groups such as hydroxyl, carboxyl, aldehyde, amino or phosphate groups. They can bind to heavy metal ions in the cell wall precipitation down [8]. For example, 70% ~ 90% of the Cd absorbed from the roots of the super-rich plant is accumulated on the apical cell wall [21]. In addition, plants can also secrete some special oxidoreductase to change the valence of heavy metals, reduce its toxicity. Many studies have shown that plant adsorption to heavy metals is consistent with the Langmuir model and the quasi-second-order kinetics [32,33], suggesting that the absorption of heavy metal ions in plant roots does not only have surface complexation interactions such as ion exchange.

Therefore, the main mechanism of plant absorption of heavy metals is that plants can interact with the rhizosphere microorganisms to activate heavy metals in the soil, and then form a complex through the plant cell wall with heavy metals, so that the heavy metal immobilized on the cell wall, and through the selective absorption of plasma membrane into the plant body, by forming chelates in plants, or migrating into vacuoles and other intracellular organs detoxification, or excreted [8]. The ability of plants to absorb heavy metals is not only related to the form of heavy metals, but also to soil water content, moisture, organic matter, soil size, pH, temperature and so on [22]. The main process of plant to absorb heavy metals in soil is shown in Fig2.

![Figure 2](image)

**Figure 2.** Schematic diagram of heavy metal absorption in plants

Therefore, according to the mechanism of plant absorption of heavy metals, it is possible to find substances rich in various active groups to adsorb heavy metals in the soil to achieve the purpose of thorough treatment. Existing studies shown that the use of plant residues can be treated to achieve this effect. This not only for the management of heavy metal pollution to provide new means but also to achieve the purpose of waste treatment waste.

5. **Available Materials**

The mesoporous material refers to a porous material having a pore size of 2 to 50 nm. Mesoporous materials have important properties in terms of selective adsorption and separation of the surface due to their special pore structure and quantum effect [23]. Liu Xinliang [24] In the study of the adsorption of sugarcane pulp on the adsorption of materials, after the sugar cane pulp modified and then the adsorption solution of copper and lead experiments found that the modified fiber NH$_2$ and OH or ether C-O-C is involved in the adsorption of heavy metal ions. The phenolic hydroxyl groups and amine groups in the modified lignin also contribute to the adsorption of heavy metal ions. This is consistent
with the above mentioned principle of plant absorption of heavy metals, indicating that it is feasible to use artificial materials to treat heavy metal pollution according to the principle of plant roots absorbing heavy metal ions. Xu Sheng [25] in Ramie anesthesia adsorption of heavy metals in the study found that a large number of adsorption on the surface of the nuclide distribution of amino, carboxyl, hydroxyl, ether, ester and other functional groups, the main mechanism of the process of adsorption of heavy metal ions on the nugget is complexation. Further illustrates the possibility of guessing this article.

Liang Yuan [26] found that the use of biochar can make Pb, Zn and Cd complex contaminated soil TCLP extraction of heavy metals decreased significantly. She proposed bio-carbon absorption of heavy metals in the soil on the one hand affected by the soil hydrodynamic dispersion, soil saturated water content, hydraulic leaching rate, soil and sewage contact time, sewage heavy metals blocking capacity; on the other hand, biochar can interact with heavy metal, sedimentation, ion exchange and so on, so as to improve the adsorption capacity and adsorption rate of Cd and Zn in soil. Xia Jingjing in the modified biochar Ni\(^{2+}\) and Cu\(^{2+}\) adsorption study found that biochar absorption of heavy metals in line with the Langmuir model and quasi-second-order kinetics too [34]. Zhang Yue [35] found that the high-temperature ammonia-treated biochar on the heavy metal element lead absorption capacity is very strong, lead removal rate of 99% or more, the absorption process is also consistent with Langmuir model and quasi-second-order kinetics. So, bio-carbon can also be used as an ideal soil heavy metal pollution repair material.

In general, mesoporous adsorbent materials and biochar can not only be used to adsorb heavy metals in aqueous solutions, but also in soils. Unlike aqueous solutions, their adsorption capacity is affected by soil moisture, pH, and other major factors. But in essence, the mesoporous material absorbs heavy metal ions in the aqueous phase.

Other materials such as ion exchange resins are also potentially available materials. The ion exchange resin is a kind of organic polymer with a network, there are many active groups on the skeleton of the network structure, and there are dissociable ions in the active group. The ion exchange reaction takes place on the active group. Ion exchange resin can be reused, recovery and recycling treatment costs are low, ion exchange resin production process is also relatively simple [27]. At present, ion exchange resin has been widely used in the field of water treatment, and occupies a very important position [28]. However, ion exchange resin is low in strength, low temperature, low adsorption rate and other shortcomings, to be further improved [29]. In addition, nano-materials can also be used for soil heavy metal pollution control, nano-materials with high specific surface area, high reactivity and strong adsorption characteristics, has been used for a large number of water pollution control; such as Fe\(_3\)O\(_4\), SiO\(_2\) and other substances with magnetic of the porous nanomaterials can greatly improve the adsorption capacity of Cd and Pb by modification [30]. At the same time, the application of nanomaterials in soil environmental pollution control has been paid more and more attention. Chen jiehua[31] found that nano-hydroxyapatite can reduce the amount of heavy metals in the soil desorption. So, combined with the advantages of a variety of materials can also be treated in the soil of heavy metal pollution ideas.

6. Conclusion

Through the above analysis we can conclusion that the use of plant residues through the technical treatment to imitate the plant absorb of heavy metals in the soil is low cost, wide range of sources, good adsorption effect, does not destroy the soil physical and chemical environment, can be completely controlled and so on. It is feasible to select the appropriate adsorbent material and combine certain methods (such as the use of microorganisms to change the soil pH) while adsorbing various heavy metals in the soil, thus permanently removing heavy metals in the soil and achieving the purpose of controlling heavy metal pollution in soil. But it should be noted that, most of the current research is still limited to water environment, due to the water environment and the soil environment are very different, the actual operating conditions also need a lot of experimental exploration. In addition, how to increase the contact area between the adsorbent and the soil, how to separate the adsorbent material from soil, how to improve adsorption capacity effectively and how to operate under different types of soil and climatic conditions should be studied.
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