Study on the repair of heavy metal contaminated soil

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Abstract. Soil heavy metal pollution was serious in our country and the soil quality was not optimistic. The heavy metal pollution in the soil was concealment, accumulation, non-degradability, uneven distribution and regionality, which was difficult to treatment. Based on the sources of heavy metals in the soil, the characteristics of heavy metal pollution and potential hazards, this paper briefly analyzed the physical methods to repair heavy metal pollution in soil. Then it summarized the related researches on the direction of soil heavy metal pollution remediation by chemical method, biological method and joint repair method in recent years, and on this basis, the future research direction of soil heavy metal repair was prospected.

1. Sources and hazards of heavy metals in soil

1.1. Sources of heavy metals in soil

Heavy metals can enter the soil in a variety of ways, causing pollution. (1) Mineral resources development. The development of various mines will cause serious heavy metals in the mining area and surrounding soil. The contents of cadmium, lead, zinc and copper in farmland soil near a lead-zinc mine in western Fujian Province exceeded the soil background value of Fujian Province. The heavily polluted farmland is as high as 97.44%. Among them, cadmium is the most polluted, and lead and zinc are the second. The changes of cadmium, lead, copper and zinc contents in different fields reached 21.5, 10.6, 5.8 and 10.8 times, respectively, indicating that the distribution of heavy metals in soil is highly complex [1]. (2) Industrial production. Wastewater, waste gas and waste residue produced by industrial production often contain a large amount of heavy metals, which enter the soil through dust reduction and soil erosion, resulting in heavy metal pollution in the soil. (3) Use of pesticides and fertilizers. Pesticides and various fertilizers contain more or less heavy metals. When pesticides and fertilizers are applied, heavy metals are also introduced into the soil. As time goes by, heavy metals in the soil gradually accumulate. (4) Automobile exhaust. Automobile exhaust contains heavy metals such as copper, chromium and lead, which are enriched by sedimentation in the soil beside the road [2, 3].
1.2. Hazards of heavy metal pollution in soil

Soil heavy metal pollution is different from other water pollution and air pollution, and it is more difficult to control. Features include: (1) concealment. Heavy metal pollution in the soil cannot be recognized by the human senses, can only be found through detection and analysis; (2) cumulative. The migration rate of heavy metals in the soil is very slow, resulting in an increase in the content of heavy metals in the soil; (3) non-degradability. Unlike organic pollutants in the soil, heavy metals in the soil cannot be effectively degraded, but can only be converted from one state to another through treatment; (4) distribution inhomogeneity. Due to poor soil fluidity, heavy metals diffuse and migrate in the soil, so the distribution of heavy metals in the soil is uneven, and the spatial difference of heavy metals in the soil is large; (5) Regionality. Heavy metal pollution occurs mostly in the mining, smelting, chemical and electroplating industries. The concentrations and types of heavy metals in different regions are significantly different. [4, 5].

At present, China's heavy metal-contaminated arable land has reached 20 million hectares, and the annual grain output has been reduced by more than 10 million tons. The grain contaminated by heavy metals has exceeded 12 million tons, resulting in economic losses of more than 20 billion yuan [6]. Moreover, when the heavy metals in the soil are excessive, the activities of SOD and CAT enzymes in the plants are inhibited, resulting in disorder of plant metabolism and decreased sensory quality [3].

Heavy metals in the soil easily enter the food chain and are enriched in the human body through the food chain. When heavy metals enter the human body, they can cause disorder of the human body. For example, heavy metal lead can cause damage to the human nervous system, hematopoietic system, and digestive system; mercury poisoning can cause symptoms such as dizziness, fatigue, and mental disorders; cadmium can cause chondral, generalized pain, and even cancer [7]. Therefore, it is extremely urgent to take effective measures to improve the soil contaminated by heavy metals.

2. Heavy metal contaminated soil repair method

According to the principle of the repair method, the repair methods of heavy metal contaminated soil are mainly divided into: physical method repair, chemical method repair and biological method repair.

2.1. Physical method repair

The physical restoration method mainly includes the guest soil, soil replacement and deep tillage method, thermal analysis method and electroanalytical method.

2.1.1. Guest soil, soil replacement and deep tillage. The method of soil, soil replacement and deep tillage is the most commonly used method in engineering management. The principle of this method is to replace the soil contaminated with heavy metals on the surface with clean soil or into the deep layer, which is easy to operate. However, this method has a large amount of engineering and high investment, and is suitable for small-scale heavy metal contaminated soil treatment, and the heavy metals in the soil are still present in the soil, and the purpose of completely removing heavy metals in the soil is not achieved, and secondary pollution is likely to occur.

2.1.2. Thermal analysis. The thermal analysis method uses microwave, steam or infrared radiation to heat the contaminated soil, and the volatile heavy metals in the soil are heated and then volatilized to achieve the purpose of repair. For example, electroanalytical methods can effectively repair soil contaminated with mercury. However, the repair effect of difficult-to-volatile heavy metals is poor, so the thermal analysis method also has certain limitations.

2.1.3. Electric repair. The electric repair is to add electrodes to the soil contaminated by heavy metals. Under the action of the electric field, the heavy metals in the soil move in a certain direction and then be concentrated. This method can repair soil contaminated with heavy metals in situ, and is efficient and energy efficient.
2.2. Chemical repair
Chemical methods for repairing heavy metal contaminated soils can be divided into chemical passivation and chemical leaching.

2.2.1. Chemical passivation. Chemical passivation is to reduce the migration ability of heavy metals by adding a curing agent to the soil contaminated with heavy metals, causing heavy metal ions to precipitate or complex with the curing agent to passivate the heavy metals. Common curing agents include biochar, clay minerals, silicates, and carbonates.

Biochar is a product of pyrolysis of biomass below 900°C under anaerobic or anaerobic atmosphere. It is widely used in soil heavy metal repair due to its large specific surface area and high organic matter content [8]. The use of biochar to repair heavy metal contaminated soil can also reduce waste biomass emissions and avoid environmental pollution. After adding corn stalk biochar in lead-contaminated soil near Xiangnan mining area, soil pH can be increased by 0.50~0.67, organic matter content is increased by 6.9%~25.1%, soil exchangeability is increased by 24.7%~41.3%, lead in soil Toxicity leaching decreased by 4.4% to 25.9% [9]. Chen Hongwei et al. [10] investigated the repair of mercury-contaminated cinnamon soil by corn straw biochar. After the application of biochar, the pH of the soil is significantly increased, effectively reducing the water-soluble mercury content. The bioavailability of heavy metal mercury decreased by 0.583 μg·kg⁻¹ per 1% biochar. Moreover, it effectively inhibits the migration of mercury to plants and reduces the heavy metal content in plants. The application of phosphorus-modified cow dung biochar promotes the conversion of heavy metals in the soil from a free state to an oxidizable state as well as a residual state. When phosphorus-modified biochar was added to the soil contaminated by lead and cadmium, the oxidizable and residual lead increased by 19.4% and 16.9%, respectively, and the oxidizable and residual cadmium increased by 17.4% and 9.9%, respectively. In addition, phosphorus-modified biochar can effectively increase the effective phosphorus content in soil and the amount of soil cation exchange [11].

After adding calcium dihydrogen phosphate, sodium silicate and calcium carbonate to the soil contaminated by lead and copper, the lead content in the soil decreased by 98.98%, 94.23% and 90.91%, respectively, and the copper content decreased by 20.40% and 86.24%, respectively. 93.51% [12]. After adding 2% ferric sulfate or ferrous sulfate to the contaminated soil, the stable efficiency distribution of strontium in the soil reached 59% and 43.7% [13].

2.2.2. Chemical leaching. Chemical leaching mainly uses chemical solvents to clean heavy metal contaminated soil, and dissolution, sequestration and precipitation reactions between heavy metals and chemical reagents, thereby transferring heavy metals in the soil to chemical solvents to achieve the purpose of repairing heavy metal contaminated soil. Common eluents mainly include water, acid, alkali and other inorganic eluents, chelating agents and surfactants. Heavy metals can react with inorganic acids to extract heavy metals from the soil; chelating agents can convert insoluble heavy metals in the soil into stable water-soluble chelate by chelation, thereby resolving heavy metals from soil particles. Surfactants mainly enhance the solubility of organic ligands in water by changing the physicochemical properties of soil, and promote the transfer of heavy metals from solid phase to liquid phase [14]. The carboxyl group and the amide group in the polyacrylamide can form a complex with a heavy metal ion through a coordination bond or a hydrogen bond, thereby functioning to repair heavy metal contamination. In addition, polyacrylamide can also interact with clay minerals in the soil to enhance the adsorption of heavy metals [15]. Different heavy metals have different physicochemical properties, and the corresponding elution reagents may be different. Therefore, often an eluent is only suitable for the repair of a single heavy metal, but does not achieve the purpose of simultaneously repairing a variety of heavy metal contaminated soil.

2.3. Biological method repair
Bioremediation methods for heavy metal contaminated soils include phytoremediation, animal remediation, and microbial remediation.
2.3.1. Phytoremediation. The phytoremediation method refers to the use of plants to absorb and fix heavy metals in the soil, thereby purifying the soil.

The use of phytoremediation for soil contaminated by heavy metals has a number of advantages, including: (1) low cost and economical practicality; (2) phytoremediation of heavy metals contaminating soil while maintaining the surrounding water and soil environment. (3) It can increase the content of soil organic matter and improve soil quality. However, phytoremediation also shows defects such as limited heavy metal enrichment, slow plant growth and long repair cycles.

Comparison of the absorption and enrichment of cadmium in soil by comparing 35 herbaceous plants, Li Ximing et al. [16] found that the ability of legumes and warm season grass to absorb cadmium was higher than that of cold season grass. The cadmium content of the aboveground part of Baimaigen is the highest. The accumulation of cadmium in annual ryegrass is high, and it belongs to hyper accumulators. The root, stem and leaf and rapeseed of rapeseed have different enrichment ability for heavy metals, and stems and leaves have the strongest enrichment ability for lead and cadmium [17]. Therefore, the thorny vegetables belong to super-enriched plants, and the thorns have higher biomass, which is beneficial to improve the repair efficiency of soils that can be used for heavy metal pollution.

In addition, the application of urea can promote the growth of thorns, further increase the extraction rate of cadmium, and show better soil remediation effect [18]. Li Xiaotong et al. [19] studied in detail the restoration of different soils contaminated by different heavy metal cadmium concentrations in rapeseed, spinach, sage, and leeks. When the cadmium concentration is high, the growth of leafy vegetables is inhibited. At lower concentrations, the cadmium enrichment coefficient of amaranth grown in Jiangxi red soil was as high as 1.165. Therefore, in the soil remediation of heavy metal pollution, different soil types and different plants have different enrichment conditions for heavy metals. It is necessary to adapt to local conditions and select suitable restoration plants to achieve better repair effects.

2.3.2. Animal Repair Method. As the most invertebrate in the terrestrial ecosystem, earthworm has shown great potential for repairing heavy metal pollution in soil [20]. Helium is rich in heavy metals in the soil. It mainly concentrates heavy metals through passive diffusion and feeding. Heavy metals in the soil can enter the body from the soil solution through the corpus callosum, or can be swallowed into the body by cockroaches [21]. Fu Liaoyang et al. [22] studied the effects of different repair time and different heavy metal concentrations on the repairing effect of earthworm repairing heavy metal contaminated soil. It was found that as the repair time prolonged, the maximum enrichment of various heavy metals appeared differently. At the second week, the enrichment of copper and lead was maximized. At the fourth week, the enrichment of zinc reached its maximum. The enrichment of heavy metals increases with increasing concentrations of heavy metals within the range of enthalpy. However, different heavy metals have different effects on the enzymes in the cockroaches, and have different effects on the physiological and biochemical functions of cockroaches. The order of absorption of different heavy metals is different. The order of absorption of heavy metals is zinc, copper, lead and mercury.

2.3.3. Microbial Remediation. Microbial cells generally contain anion groups such as -NH₂, -SH, and PO₄³⁻, and heavy metal ions can be combined with these groups by ion exchange, complexation, etc., thereby achieving the purpose of adsorbing heavy metals in the soil. Under the action of microorganisms, heavy metals can undergo redox, which changes the mobility of heavy metals. For example, Cr⁶⁺ in soil can be reduced to Cr³⁺ by microorganisms, and Cr³⁺ has poor mobility in soil, thus playing the role of fixing heavy metals. In addition, the inorganic salts produced by microbial metabolism can react with heavy metals to produce precipitates, which promote the conversion of heavy metals from the Free State to the residual state [23].
2.4. Joint repair method

2.4.1. Chemical leaching-chemical passivation combined repair. Li Ming et al. [24] first compared the effect of EDTA-2Na, hydrochloric acid and citric acid leaching to repair cadmium in soil. It was found that EDTA-2Na had the best leaching effect and the cadmium content in soil decreased by 51%. Then, after using corn stover bio-carbon treatment, the cadmium content in the soil was further reduced from 8.31 mg·kg⁻¹ to 0.42 mg·kg⁻¹. Li et al. [25] first used iron chloride to wash soil contaminated with heavy metals, which could remove cadmium, lead, zinc and copper from 62.9%, 52.1%, 30.0% and 16.7%, respectively. Curing with lime can further reduce cadmium, copper, lead and zinc in the soil by 36.5%, 73.6%, 70.9% and 53.4%, respectively.

2.4.2. Animal-chemical passivation combined repair. In lead-contaminated soils, strontium is able to reduce lead levels. The addition of biochar after the introduction of plutonium will further reduce the lead content in the soil. It shows that the combined action of strontium and biochar has stronger ability to repair heavy metals [26].

3. Conclusions and prospects

The use of physical, chemical and biological methods can effectively repair heavy metal pollution in the soil, each of which has advantages and disadvantages. But so far, in practical engineering applications, it is widely used because of the simple operation of physical methods. Other chemical methods and biological methods have not been widely applied due to technical limitations or cost reasons. With the breakthrough of various technologies, they will gradually be applied to the actual soil heavy metal pollution.

In future research, further research can be conducted from the following directions. (1) Develop super-accumulated plants resistant to cold, high temperature or drought, and improve the biomass of plants through various means to further improve the soil heavy metal repair ability. (2) Develop a corresponding repair method for a certain or a certain class of heavy metal contaminated soil, and gradually enlarge the experiment to form a feasible technical system. (3) Bio-char is derived from waste biomass, and variable waste is a treasure. It can repair heavy metal pollution and increase soil biomass content in soil heavy metal repair applications. Biochar can be selected or modified for biochar according to soil conditions. For example, for heavy metal pollution in acidic soils, biochar with high alkalinity can be selected. (4) Hyper accumulators tend to have a long growth cycle, so it is necessary to screen out the super-accumulated plants with short growth cycle to effectively shorten the repair time of heavy metals and improve the repair efficiency. (5) The joint repair method tends to have better repair efficiency, and it is necessary to further study the joint repair methods of plant-microorganism, plant-biochar/clay mineral, and plant-animal.

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