Research Progress of Remedial Materials for Heavy Metal Contaminated Soil

Weiwei Chen^{1, 2, 3, 4, 5, *}, Zhaoxin Zhang^{1, 2, 3, 4, 5}

¹Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an 710021, China

²Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an 710075, China

³Key Laboratory of Degraded and Unused Land Consolidation Engineering, Ministry of Natural Resources, Xi'an 710075, China

⁴Shaanxi Engineering Research Center of Land Consolidation, Xi'an 710075, China ⁵Land Engineering Technology Innovation Center, Ministry of Natural Resources, Xi'an 710075, China

*chenweiwei736@126.com

Abstract

The farmland soil is combined pollution by multi-heavy metals in China, which seriously threatens the food security and the human health. This paper makes a review of the characteristics of the heavy metal contaminated farmland soil and the types and characteristics of common remedial materials. In addition, this paper analyzed and forecasted the problems that need to be solved in the future for remedial materials for heavy metal contaminated soil. Common remediation materials include biochar, clay minerals, organic matter, phosphates, metal oxides and composite remediation materials, etc. The remediation materials can effectively reduce the mobilization and bioavailability of heavy metals. This paper summarized the types and characteristics of remedial materials for heavy metal contaminated soil, so as to provide theoretical basis for remediation materials and prevention and control strategy for the heavy metal pollution.

Keywords

Heavy Metal; Remedial Materials; Farmland Soil.

1. Introduction

The situation of the heavy metal contaminated farmland soil in China is serious and complex, that has been a serious threat to ecological environment, food security, human health and sustainable agricultural development. The total exceeding standard rate of soil pollutants was 16.1%, including cultivated soil points exceedance rate of 19.4 % [1]. Moreover, the content of heavy metals in soil in southern China was significantly higher than that in northern China [2]. The farmland soil is combined pollution by multi-heavy metals. The main soil pollutants include Cd, Cr, Pb, Cu, Hg, As and some organic pollutants. According to the degree of soil pollutants, the order is Cd, As, Hg, Pb and Cr. Heavy metals are easy to accumulate, difficult to volatilize and toxic, which can long-term harm to farmland soil and human health. Therefore, the remediation and treatment of farmland soil that polluted by heavy metals currently have become one of the hotspots in the research of farmland pollution. At present, remedial materials for heavy metal contaminated soil are various and their characteristics are different. So, it is particularly important to summarize the research progress of the remediation materials. This paper

summarizes the relevant researches at home and abroad in recent years, to provide the reference for the soil remediation and realize the sustainable and safe utilization of farmland soil.

2. Characteristics of Farmland Soil Polluted by Heavy Metals

There are various sources and large pollution area of heavy metals in farmland. And, the depth of pollutants is shallow, that most pollutants are within 30cm of the surface of the soil. Those lead to a long restoration period. The main sources of pollution are industrial emissions and agricultural production, for example, Cd mainly coming from industrial emission sources, Hg mainly from pesticide application and waste mixed sources [3]. These result in the combined pollution of heavy metals in farmland soil. Moreover, Cd, Hg, Pb and as are the considerable widespread heavy metals in the environment. Some special sites such as mining areas, chemical factories and some surrounding farmland soils are mainly affected by mining, chemical emissions and other activities. Heavy metals are mainly minerals from mining areas or chemical plants. For example, the contents of Mn and Zn pollution in farmland around Mn mine areas are more than others. There are interactions between multiple metal elements or compounds in soil and between heavy metals and soil interface, which are generally manifested as additive effect, antagonistic effect and synergistic effect, that make the restoration of contaminated farmland more challenging. In addition, given the large area of contaminated farmland and the high cost, in-situ repaired technology should be given priority to farmland with low pollution level. At the same time, there are heavy metals in some remedial materials that should be considered. And secondary pollution should be prevented in the application process to ensure the sustainability of agriculture. Therefore, it is necessary to develop vigorously the green environment-friendly materials to deal with complex pollution situations.

3. Types and Characteristics of Remedial Materials

3.1. Biochar

Biochar is a kind of carbon-containing porous material produced by anaerobic pyrolysis of biomass. The complexation of surface functional groups and the precipitation of inorganic salts in biochar play a main role in the adsorption and fixation of heavy metals in soil. And the remediation effect can be improved by modification measures. As a new amendment, straw biochar can effectively alleviate or repair heavy metal contaminated farmland soil. Studies showed that straw returning helps to alleviate soil acidification, and increase soil organic matters and cation exchange capacity, which can improve the adsorption of heavy metals and reduce the enrichment of heavy metals by crops [4]. Previous studies reported that biochar produced from different raw materials has a good effect on the adsorption of heavy metal cations such as Cd (II). The adsorption capacity of biochar to anions such as arsenate and arsenite is limited by the surface negative charge, and the ability to repair As is weak [5]. In order to realize the simultaneous fixation of various pollutants by biochar-based remediation materials, most biochar materials will be applied in combination with other materials or modified.

3.2. Clay Minerals

Clay minerals mainly include sepiolite, bentonite, kaolin, zeolite, attapulgite, diatomite, palygorskite and so on. The specific surface area of mineral structure is relatively large, and the structural layer is charged. Clay minerals reduce the concentration and activity of heavy metal ions in soil solution through adsorption, coprecipitation, coordination and ion exchange [6]. However, natural clay minerals have some defects in application, such as low load capacity, poor selectivity to metal ions, etc. Therefore, those are generally modified by heating, acid

treatment, organic modification, polymer insertion and other modification measures before used to improve their performance.

3.3. Organic Matter

Organic matter refers to organic fertilizer, solid residues produced in the process of treating domestic waste, etc. Organic matter mainly contains humus. Organic substances mainly contain humus, which usually have many important complex functional groups and chelating groups, such as carboxyl, hydroxyl, carbonyl and amino groups. The complex functional groups can provide electrons to form metal-organic complexes with metal ions, and the chelating groups can provide more than two electronic ligands to form chelates with metal ions. Therefore, the solubility of complexes and chelates determines the mobility of heavy metals. When the solubility is large, the mobility is enhanced, otherwise is weakened [6]. Studies have shown that the solubility of complexes formed by humus and metals is affected by the ratio of humic acid, fulvic acid in humus to heavy metals. Generally, when the ratio of fulvic acid to heavy metals is greater than 2, it is conducive to the formation of water-soluble complexes. And when it is less than 2, it is easy to form insoluble complexes. And the complexes formed by humic acid and metals are usually insoluble [7].

3.4. Phosphates

Phosphate-containing substances include soluble phosphate compounds and phosphate minerals. Soluble phosphates include phosphate and phosphoric acid. Natural apatite and synthetic apatite, hydroxyapatite and other phosphate minerals are commonly used in heavy metal pollution remediation, which have been widely studied. The combined application of phosphate and iron-containing materials can passivate Cd and as simultaneously. Besides, phosphate can also be used as fertilizer to provide nutrients for plant growth, but it is easy to lose phosphate and cause secondary pollution [8]. Some scholars have researched and developed a stable phosphate nanoparticles (carboxymethyl cellulose stabilized iron phosphate and calcium phosphate). This material not only has strong adsorption capacity, but also the released nanoparticles will not diffuse rapidly like soluble phosphate, thus achieving better in-situ passivation repair effect [9].

3.5. Metal Oxides

Metal oxides can be used to remediate the heavy metal contaminated soil through adsorption and co-precipitation mechanisms. But this is not an optimal option for agricultural sustainability. Agricultural sustainability is an important consideration in the remediation of contaminated farmland soil. And it is also the main factor different from the remediation of industrial contaminated sites.

3.6. Heavy Metal Remediation Composite

The interaction between elements in heavy metal contaminated farmland is complex. The activity of different heavy metals is prone to change in the soil environment with different redox potential and pH, which makes it difficult to use a remedial material to reduce the activity of all heavy metals in the contaminated soil. Hence, many studies have focused on the research and development of heavy metal remediation composite. Inorganic + inorganic composites are mostly used in the mixture of calcium-silicon + phosphate, and clay minerals + phosphate. Inorganic + organic composites are mostly used in calcium-silicon + biochar + clay minerals, calcium-silicon + organic materials + phosphates, etc. This kind of material not only has good repair effect on heavy metals, but also can play the advantages of inorganic materials to improve soil acidity and organic materials to improve fertility of poor soil. Zou et al. [10] found that the composite limestone + zeolite + phosphate rock powder + organic material increased soil pH and reduced the available contents of Cd, Pb, Zn and Cu in contaminated soil with pot

and field experiments. Moreover, the composite promoted the growth of plants and greatly reduced the content of heavy metals in crops. The combination of organic + organic materials such as biochar and organic materials makes the composite material contain a large number of functional groups, which can adsorb, ion exchange and complex with heavy metals in contaminated soil to passivate heavy metals [6].

4. Conclusion and Perspectives

The farmland soil is combined pollution by multi-heavy metals in China. Although a variety of remedial materials have been researched and developed in the prevention and control of farmland pollution in recent years, there are still many shortcomings.

- (1) At present, the evaluation of the effect of remedial materials is mostly carried out through pot experiments, which is difficult to reflect the complexity of the field. However, the remedial materials that tested in the field are still necessary to evaluate their long-term performance and stability, and taking into account the yield and quality to explore the optimum application amount, to maximize the economic and ecological benefits.
- (2) Some remedial materials contain an amount of heavy metals. Hence, secondary pollution should be prevented in the application process to ensure the sustainability of agriculture. And it is necessary to develop vigorously the green environment-friendly materials to deal with complex pollution situations.
- (3) The research and development of heavy metal remediation composite can effectively solve the problem of the farmland soil combined pollution by multi-heavy metals. We should strengthen the evaluation of the remediation effect of the composite, and continuously monitor the heavy metal status of farmland soil after remediation. Meanwhile, we should know the stability and timeliness of the composite should and promote the application and promotion of composite repair materials.
- (4) When repairing heavy metal contaminated farmland soil, it is necessary to prevent the use of remedial materials that damage soil fertility, affect the growth of crops, and ensure the sustainability of agriculture, including soil fertility improvement, agricultural product safety, and agricultural product yield increase.

Acknowledgments

We are grateful for the reviews and support that this manuscript received from the reviewers and editor.

This research was funded by the Shaanxi Provincial Land Engineering Construction Group Internal Research Project (DJNY2022-30).

References

- [1] Yu T, Jiang T, Liu X et al. Research progress in current status of soil heavy metal pollution and analysis technology[J]. Geology in China, 2021, 48(2): 460-476.
- [2] Chen W, Li Q, Wang Z et al. Spatial Distribution Characteristics and Pollution Evaluation of Heavy Metals in Arable Land Soil of China. [J]. Environmental Science, 2020, 41(06):2822-2833.
- [3] Li Z, Xiao M, Ren D et al. Heavy metal source analysis of the farmland soil of Zhijiang and Dangyang [J/OL]. Acta Scientiae Circumstantiae:1-9.
- [4] Wu G, Kang H, Zhang X, et al. A critical review on the bio-removal of hazardous heavy metals from contaminated soils: Issues, progress, eco-environmental concerns and opportunities. Journal of Hazardous Materials, 2010, 174(1/3):1-8.
- [5] Li Y, Shang J, Huang Y et al. Research Progress on Passivation Materials for Cadmium-Arsenic Co-Contamination in Soil[J]. Acta Pedologica Sinica, 2021, 58(4):837-850.

- [6] Wu X, Cao R, Mi C et al. Research progress of in-situ passivated remedial materials for heavy metal contaminated soil[J]. Journal of Agricultural Resources and Environment, 2019, 36(3):253-263.
- [7] Gao T, Yu G, Yang L et al. Impact of dissolved organic matter in landfill leachate on migration of heavy metals in soils[J]. Chinese Journal of Environmental Engineering, 2011, 5(5): 1176-1180.
- [8] Liu R Q, Zhao D Y. In situ immobilization of Cu (II) in soils using a new class of iron phosphate nanoparticles[J]. Chemosphere, 2007, 68(10): 1867-1876.
- [9] Liu R Q, Zhao D Y. Synthesis and characterization of a new class of stabilized apatite nanoparticles and applying the particles to in situ Pb immobilization in a fire-range soil[J]. Chemosphere, 2013, 91(5): 594-601.
- [10] Zou Fuzhen. Mixed Amendments for Immobilization of Cd, Pb, Cu and Zn in an Acidic Multi-metal Contaminated Soil[D]. South China Agricultural University, 2016.