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Study on Passivation and Remediation of Heavy Metal Contaminated Soil

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Abstract: *Land is the basis of human foothold. However, with the rapid development of human society, soil is no longer clean, and soil remediation is imminent. Passivating heavy metals in soil with passivating agent is an economic, rapid and reasonable treatment measure at present. This paper summarizes the basic mechanism, research progress and limiting factors of organic/inorganic materials' passivation of heavy metals in soil in order to provide theoretical support for the research and development of soil passivators.*

Keywords: *Heavy metal contaminated soil, Organic materials, Inorganic materials, Passivation*

1. Preface

Soil is one of the basic elements of the ecosystem, one of the most important natural resources of the country, and also the material basis for human survival and the main component of the ecological environment. However, with the rapid development of industrial and agricultural production, the rapid progress of human society, the discharge of "three wastes" in industrial production, the massive use of chemical fertilizers and pesticides in agricultural production, atmospheric sedimentation and other ways, a large number of heavy metals enter the farmland soil, Heavy metal pollution has the characteristics of long-term, concealment, accumulation, etc. [1], which not only poses a serious threat to the quality of cultivated land and agricultural products, but also can enter the human body through the food chain and endanger human health [2-4]. According to the survey, due to mining, metal smelting, industrial emissions and other reasons, China's cultivated land polluted by heavy metals such as arsenic, cadmium, mercury, zinc, copper, etc. covers an area of about 10 million ha, and the annual grain output polluted by heavy metals is about 10 million tons, causing huge economic losses and food safety hazards [5]. The first national soil pollution survey in 2014 showed that 16.1% of the country's land was polluted, and the rate of exceeding the standard of arable land, forest land and grassland soil sites was 19.4%, 10.0% and 10.4% respectively.

Soil pollution has the characteristics of regional distribution. The soil heavy metal pollution in China has regional characteristics, and the pollution situation in different regions is also different. The pollution of heavy metals in the soil in the central part is relatively prominent, while the eastern and western regions are relatively light, because there are a large number of metal mines and coal mines distributed in the eastern region. The pollutants are mainly inorganic elements, and there is also the phenomenon that the soil points exceed the standard, especially cadmium, followed by mercury and nickel. The governance is difficult. Under natural conditions, heavy metal pollutants in soil are difficult to be degraded. If they reach a certain level, they cannot restore the original natural state. In addition, the heavy metal pollutants in the soil can be adsorbed by the colloids in the soil after long-term accumulation. Because the chemical activity of heavy metals is relatively strong, they are easy to react with other substances, leading to changes in the pH value of the soil.

At present, there are many remediation methods for heavy metal pollution, including physical remediation, chemical remediation, biological remediation, and joint remediation; According to the repair site, it can be divided into in-situ repair and ectopic repair. Generally, heavy metal pollution in soil often involves a large area, and the treatment capacity of ex situ remediation technology is relatively small and the cost is often too high. In situ remediation technology is the trend of heavy metal remediation technology in the future. In situ remediation technology, soil leaching can effectively remove heavy metals, but the risk of secondary pollution is high; Phytoremediation technology is safe,

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economical and effective, but its effect is long; In situ passivation technology changes the chemical form and occurrence state of heavy metals in the soil by adding one or more passivation repair agents to the contaminated soil, regulating the physical and chemical properties of the soil and a series of reactions such as adsorption, precipitation, ion exchange, humification, oxidation and reduction [7-8], realizing the passivation/ stabilization of heavy metals in the soil and reducing their mobility and biological effectiveness in the soil, In order to prevent the migration and accumulation of heavy metals from the soil through the roots of plants to the above ground of crops, so as to achieve the purpose of controlling contaminated soil, it is a good choice for the remediation of moderately and slightly polluted soil at present [9-11].

Therefore, this paper analyzes the research progress of heavy metal passivation and remediation from the perspective of organic/inorganic and composite materials as passivators, aiming to provide scientific theoretical support for the development of heavy metal remediation agents in soil.

2. Inorganic materials passivate heavy metals

Inorganic materials mainly refer to inorganic substances, such as phosphate, clay minerals, silicon rich substances, lime and other materials. They can absorb heavy metals or change the pH value of the environment, and reduce the activity of heavy metals by using their huge specific surface area, high cohesion, strong adsorption and alkalinity. Inorganic materials are the most widely used passivating materials at present. They not only have good passivation effect, but also have low cost. They have good application prospects [12].

The main passivation mechanisms of inorganic materials are precipitation and physical adsorption. If gypsum and dolomite are applied to acidic soil, heavy metals such as Cd, Cu and Pb will precipitate on the surface of these materials to form complexes, reducing migration and bioavailability. The adsorption mechanism is mainly due to the large pores and high specific surface area of inorganic passivation materials, which directly adsorb and fix heavy metals. Studies have shown that bentonite, kaolinite, sepiolite, palygorskite and other clay minerals have a good passivation effect on metals in soil [13-15].

Zeng Hui et al. selected 5 kinds of mineral materials, including zeolite, diatomite, sepiolite, bentonite and limestone, and added them to 50g test soil at a concentration of 6g/kg respectively. Each passivator has a passivating effect on heavy metals in soil, and 1∶2 diatomite+limestone has a good passivation effect on Pb, Cd and Zn in soil [16]. Covelo et al. conducted adsorption and desorption tests on 11 acidic soils for 6 heavy metals, and found that they were fixed by clay minerals, such as kaolinite, boehmite and vermiculite 9^{+} [17].

In addition, activated carbon is also a good passivation and adsorption material. Biochar refers to a kind of stable, fine textured, carbon rich porous solid material produced by pyrolysis of biomass raw materials (wood, crop straw, urban living biological waste, etc.) under oxygen limited or anaerobic conditions at a high temperature (<700 ℃). Biochar immobilizes heavy metal ions by surface adsorption, complexation of surface oxygen-containing functional groups, and formation of carbonate and phosphate precipitation. Pyrolysis conditions and raw material types are the main factors affecting the adsorption capacity of activated carbon.

3. Organic materials passivate heavy metals in soil

Organic substances mainly form insoluble heavy metals and organic compounds through complexation to reduce the activity of heavy metals and prevent the pollution and diffusion of heavy metals. Common organic materials include municipal sludge, organic compost, biosolids, animal manure, etc. Organic materials are not only good soil fertility improvers, but also can be used as soil heavy metal adsorption and complexing agents, and are widely used in the remediation of soil heavy metal pollution.

Organic materials generally contain high humic organics, which can reduce the bioavailability of heavy metals in soil mainly by increasing the cation exchange capacity of soil and the adsorption capacity of ions, and forming insoluble metal organic complexes. The passivation mechanisms of organic materials mainly include chemical adsorption, ion exchange, organic complexation and redox.

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For example, red mud can form stable complexes by adsorbing heavy metals into the lattice of iron aluminum minerals. Generally speaking, organic substances have many organic functional groups, which can form complexes with heavy metals.

Zhang Yali and others effectively reduced the Cd content in soil through pig manure and other organic materials [18]. Brown et al. used compost, sludge, etc. to repair heavy metal contaminated mining areas, significantly reduce zinc content, and grow vegetables that meet safety standards [19]. Farrell et al. put forward that municipal solid waste and green waste compost can effectively improve soil pH, promote plant growth, and reduce the absorption and accumulation of As, Cu, Pb and Zn by plants when they are applied to acid soil polluted by heavy metals; However, the study also pointed out that the metal ions fixed by organic matter may be released again, and the long-term stability of the metal ions needs to be further solved. In addition, a large number of studies have pointed out that organic matter can promote the reduction of high valence Cr (VI) to weak toxicity Cr (III) after it is added to the soil, which deserves attention.

4. Passivation limitations

Although passivation materials can reduce the migration and activity of heavy metals, they cannot transfer heavy metals from soil. The Chinese official soil environmental quality standard (GB 15618-1995) takes the total concentration of heavy metals in soil as the assessment standard, but the total concentration of heavy metals in soil cannot fully explain the chemical behavior of heavy metals and potential environmental risks. The environmental risk and biological toxicity of heavy metals are not only related to the total amount, but also depend on their existing form and distribution in the soil. The existing forms of heavy metals are affected by many factors such as soil pH, Eh, CEC, organic matter content, clay mineral composition, etc. With the change of soil environment, the passivated heavy metals may be desorbed to an effective state, thus causing harm to soil animals and plants again. This requires regular detection of heavy metals in soil, prediction of the possibility of heavy metal transformation in advance, and reuse of passivators. Some clay minerals contain some heavy metals, so passivation materials should be strictly selected to prevent secondary pollution of soil. In addition, clay passivation materials have high clay content, and excessive application will change soil properties and cause soil hardening. Therefore, the amount of passivating materials should be strictly controlled. Although passivation materials are very limited, in-situ passivation repair is still a good repair method under the circumstances of large non-point source pollution of soil, high cost and great difficulty in off-site treatment.

5. Evaluation of repair effect

In situ chemical passivation of heavy metals aims to change the occurrence form of heavy metals, reduce their activity and bioavailability, but does not change their total amount. However, at present, the assessment of soil pollution remediation efficiency in China is mainly based on reducing the total amount of pollution, and this assessment system is not suitable for heavy metal in-situ passivation technology. However, the chemical extraction methods, extractants, extraction methods, and limited concentration standards based on the speciation analysis of heavy metals have not formed unified and authoritative standards, which need to be systematically studied and formulated. In addition, biological assessment methods (plant physiology, nutrition, animal and microbial biological activity, etc.) need to be paid attention to. In the evaluation system, both laboratory analysis methods and field monitoring and evaluation methods should be used to comprehensively consider economic and environmental benefits.

At present, the bioavailability of metal elements is mainly monitored through living organisms. Monitoring the growth of plants and the absorption and accumulation of metal elements is the most direct method for repair evaluation. However, previous studies have mostly used pot experiments or short-term field experiments to verify, and long-term positioning monitoring tests need to be further developed. In soil animal monitoring, earthworm is the most studied. In recent years, it is believed that microorganisms are more sensitive to heavy metal stress than plants and animals. Soil microbial activities, such as soil enzyme activity, soil microbial community structure and other indicators, have attracted more and more attention in the monitoring of soil heavy metal pollution.

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6. Conclusion

The research shows that the passivation materials can effectively inactivate heavy metals in soil, prevent the migration of heavy metals and harm soil animals and plants. There are many organic and inorganic passivating materials, and passivation and remediation are widely used for in-situ remediation of heavy metals in soil. In situ passivation remediation technology is an economical and efficient non-point source pollution treatment technology, which meets the needs of sustainable agricultural development in China. The key of in-situ passivation repair lies in the selection of passivating agents. At present, most studies on the treatment of heavy metal contaminated soil by passivation are aimed at single passivation materials, and the combination use of passivation materials is rarely considered. Moreover, most of the research objects are heavy metal contaminated soil made by manual preparation, and few are contaminated original soil and actual field application studies. Therefore, it is suggested to increase the research on composite passivation materials and modified passivation materials in future research, and carry out field tests to provide more better passivation materials for the remediation of heavy metal passivation in soil.

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