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Advances in research on repairing heavy metal pollution in soil by clay minerals

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Abstract: To reveal the repair potential and effect of clay minerals on heavy metal contaminated soil, this paper summarizes the application of common clay minerals such as kaolinite, montmorillonite and zeolite in the repair of heavy metals, and repairs heavy metals with clay minerals and biochar, lime and chelating agents. Correlation analysis illustrates the potential and mechanism of clay minerals for heavy metals. For one thing, clay minerals have a large specific surface area and a negative charge on the surface, which greatly increases their adsorption properties for heavy metals. for another, clay minerals have high nutrient elements and rich organic matter, Which increase soil fertility and trace elements, as well as crop yield. Clay minerals have been widely used in soil heavy metal pollution repair, but most of them still stay at the laboratory level. In the future, more attention should be paid to the application of clay minerals in practical engineering.

1. Introduction

At present, the deterioration of farmland soil environment in China is very serious. According to the 2014 National Soil Pollution Status Survey Bulletin, the over-standard rate of soil inorganic pollution accounts for 82.8%, and inorganic contaminated soil is mainly dominated by heavy metal pollution. The survey shows that the soil pollution exceeding the standard rate of cultivated land accounted for 19.4%, this pollution caused the degradation of farmland soil environment, and the quality of agricultural products was seriously threatened. Studies have shown that the grain yield caused by heavy metal pollution is reduced by about $1x10^7$t, and in addition to this, about $1.2x10^7$t of heavy metals in grain exceeds the standard. However, China's heavy metal pollution repair work is in its infancy, and the repair rate is less than 3% [1]. Therefore, heavy metal pollution control technology has become the primary problem for environmental workers.

The clay composition of soil minerals dominates. The clay minerals are mainly hydrated silicate minerals such as Mg and Al. The basic structure is mainly silicon tetrahedron and aluminoxy octahedron. Common clay mineral structural monomers are two types of structures: 1:1 and 2:1. The common 1:1 clay mineral is a layer of tetrahedron and a layer of octahedron. The clay minerals are mainly kaolin and halloysite. The 2:1 clay mineral is two layers of tetrahedron and one layer of octahedron. Clay-like minerals are mainly bentonite, vermiculite and illite. The repair of clay minerals is mainly to use physicochemical action to change the occurrence of heavy metals in the soil, reduce the concentration of heavy metal ions and its toxicity, so as to achieve the role of purifying the soil. This paper collects the latest research progress on clay minerals at home and abroad, mainly reviews the adsorption mechanism and influencing factors of heavy metals from clay minerals and modified clay minerals, in order to provide reference for the future research of clay minerals to repair heavy metal contaminated soil.

2. The potential of clay minerals to repair heavy metal contaminated soil

Heavy metals are difficult to be removed from the soil after entering the soil. They change soil fertility and affect crop yield by changing the structure of the microbial community and the physical and chemical properties of the soil. In addition, heavy metals in the soil can enter the human body through the food chain, endangering human health.

In previous studies, biochar, lime, and chelating agents were used extensively to contaminate soil with heavy metals to mitigate hazards. Lime repairing heavy metals mainly changes the pH of the soil, causing heavy metals to precipitate as oxides, reducing their bioavailability. However, when the pH of the soil is acidified, the heavy metal fixed by the lime will be re-released to the soil. At the same time, the lime will slowly weaken after a long time of dissolution or leaching, especially in acidic soil [2]. A class of solid materials with higher carbon content obtained by thermal conversion (<700 ° C) of biomass feedstock under anaerobic or anoxic conditions is called biochar [3], which has a unique pore structure and a large The specific surface area is therefore widely used in the repair of contaminated soil [4]. Su Fangli [5] and other studies found that the adsorption of Pb^{2+} in rice hulls was negatively correlated with pH, especially at pH 6-8; Qiao Dongmei et al [6] found in the study of the effect of pH on the adsorption characteristics of heavy metals Pb^{2+} When the pH is <7, the soil is sensitive to Pb^{2+} adsorption. The biochar system is huge, and the biochar prepared from different materials has different pH. In addition, biomass can enrich the heavy metals As, Cd, Pb and PAHs during pyrolysis of biochar, which increases the heavy metals in the soil environment [7]. The study found that [8] cow dung, sludge biochar Cd content was 0.28, 1.30mg / kg, Zn content was 17 ~ 500mg / kg; Kloss et al [9] found that straw, poplar, spruce in 400 ~ 525 The biochar produced by °C pyrolysis for 5~10h contained different concentrations of PAHs, and the PAHs content of straw produced at 525 °C reached 33.7mg/kg, far exceeding the EPA for biological solid waste used for land treatment. The specified safety limit (6 mg/kg) [10]. The combination of chelating agent and heavy metal ions in the soil can change the existence of heavy metals, transforming the heavy metals in the soil from insoluble to soluble, and the activation of heavy metals in the soil is greatly increased, which creates favorable conditions for leaching or plant absorption. . Therefore, chelating agents have received widespread attention in recent years in heavy metal repair applications. However, the degradation performance of the chelating agent in the environment is poor. For example, some forms of EDTA have high water solubility, so migration to surface water or groundwater leads to an increase in EDTA content. Moreover, the persistence of chelating agents in the soil environment causes the dissolution of heavy metals in the soil and its sediments, increasing the mobility of heavy metals in soils and sediments. The migration of these heavy metals increases the transport of heavy metals to groundwater or surface water. Risk [11].

The special crystal structure of clay minerals also gives it special properties. Clay minerals have a large specific surface area and a negative charge on their surface. This negative charge adsorbs positively charged heavy metal ions through adsorption and complexation, thereby passivating heavy metal contaminants in the soil. In addition, clay minerals are rich in organic matter and high nutrients, which can increase soil fertility, increase trace elements and increase crop yield. Studies by Bradl et al. [12] have shown that the proportion of clay minerals in the soil is closely related to soil self-purification. The adsorption and fixation of heavy metals by clay minerals is closely related to the organic matter rich in clay minerals, because the charge on the surface of organic matter is negative, thus increasing the negative charge of clay minerals, and the exchange of negatively charged clay minerals with heavy metal cations, thereby reducing heavy metals. content. Many studies have also shown that the adsorption of heavy metals in soil by clay minerals is positively correlated with the pH of the soil, that is, the ability of clay minerals to adsorb heavy metals in soils increases with increasing pH [13]. Moreover, the clay has been modified to increase its specific surface area, the adsorption performance is greatly increased, and the ion exchange capacity is also significantly improved [14-16].

As a new heavy metal repairing material, clay minerals have attracted more and more attention from environmental scholars.

3. Repair effect of clay minerals on heavy metal contaminated soil

Different clay mineral materials have different effects on the repair of heavy metals. Shi Huisheng et al [17] showed that bentonite was added to the soil contaminated by lead and zinc. After adsorption for 1 h, the adsorption capacity of bentonite for Pb^{2+} was 99.55 mg/g, for Zn^{2+}. The adsorption capacity is 99.37 mg/g; the study by Mahabadi et al. [18] shows that the adsorption of cadmium by natural zeolite is stable, and the leaching amount of cadmium in different texture soils such as clay, loam and sand is different. The reduction of the cadmium in soil is best when the amount of zeolite added is 15%. Nissen et al. [19] studied zeolites for sludge containing heavy metals such as Zn, Cu and Fe. Studies have shown that 0.5% and 0.1% zeolites effectively reduce dissolved Zn in 90 days; Kumpiene et al. [20] used montmorillonite Repairing heavy metal A contaminated soil, studies have shown that 10% of montmorillonite can reduce the amount of As in the soil by 50%. Hao Xiuzhen et al [21] studied the effect of montmorillonite on Zn by pot experiment. The study showed that the addition of montmorillonite can significantly reduce the available Zn content in tailings sand; Tu Naimei et al. [22] used different amendments for Pb and Cd. In polluted rice fields, studies have shown that the application of appropriate amount of sepiolite and kaolin can reduce the content of Pb and Cd in soil and brown rice, and can improve the growth and development of rice; Lin Dasong et al [23] added 4% of sepiolite to the soil. The content of water-soluble Cd and Zn decreased by 57.3% and 41.4%, respectively; Tan Keyan et al [24] found that the effective content of Cu, Zn and Cd in soil decreased by 31.5 by adding appropriate amount of attapulgite to heavy metal contaminated soil. %, 26.1% and 34.9%, while the absorption of Cu, Zn and Cd in vegetables decreased correspondingly; Jiang Weiwu et al [25] found that the removal of Hg^{2+} by zeolite was 32mg/g, and the removal rate of Hg was as high as 99%; Lu Gaoming et al [26] found that after adding bentonite in farmland soil, the exchangeable content of Cd and Pb decreased by 7.75% and 0.48%, respectively.

4. Repair mechanism of clay minerals on heavy metal contaminated soil

The adsorption of heavy metal ions by clay minerals is mainly manifested in three aspects: ion exchange, coprecipitation and complex reaction.

4.1. Ion exchange

Ion exchange is the exchange of ions adsorbed in the interbedded layer of clay minerals with heavy metal ions in solution. Due to the homomorphic displacement of clay minerals, the clay minerals carry a certain amount of negative charge and form a permanent negative charge. According to the principle of cation and anion electrical neutrality in the compound, there will be an equal amount of heavy metal cations and clay mineral surface and The anions between the layers are exchanged to achieve an electrical neutral balance. Heavy metal elements in contaminated soil are adsorbed and held by clay minerals. It reduces its ability to pollute the soil and its toxicity to plants, thus achieving the purpose of repairing heavy metal contaminated soil.

4.2. Total precipitation

The coprecipitation mechanism refers to the fact that clay minerals produce anions by self-dissolution and co-precipitation with heavy metal elements, thereby repairing heavy metals in the soil. Coprecipitation is mainly due to the formation of heavy metal hydroxides and carbonate-bound heavy metals in the soil, thereby changing the morphology of heavy metals in the soil. The apatite minerals in nature are widely distributed, and their complex composition affects their stability. Early studies have shown that apatite can remove Pb (%), Cd (37-99%), and Zn (27-99%) in soil to varying degrees, probably because the addition of apatite increases the pH of the soil. The heavy metal forms precipitates of $Pb_3(CO_3)_2(OH)_2$, $Pb(PO_4)_3(CO_3)_3$, $Cd(OH)_2$, ZnO and the like in the alkaline soil solution.

4.3. Coordination reaction
Infrared spectroscopy analysis shows that in the solid phase and liquid phase systems, the surface of the clay mineral is negatively charged, which is mainly due to the presence of a large amount of SiO_4^{4-} and AlO_4^{5-} groups in the silicate, which makes the water on the surface of the silicate particles. The formation of a hydrated oxide cap layer facilitates the progress of the compounding reaction. The ions with silanol groups (Si-OH) on the surface of clay minerals react with heavy metals Cu, Cd, Pb, Zn, Ni, etc. to achieve the effect of passivating heavy metal ions.
The complex reaction between silicate and heavy metal ions is as follows:

$$SiOH + M^{2+} = SiOH^{+} + H^{+}$$

$$SiOH + MOH^{+} = SiOMOH + H^{+}$$

$$SiOH + M^{2+} = SiOM^{+} + H^{+}$$

5. prospect
Clay minerals are inexpensive and environmentally friendly materials and have been widely used for soil heavy metal pollution restoration. However, clay clay minerals still have some problems in practical repair applications. Clay minerals mainly achieve the purpose of repairing heavy metal contaminated soil through the mechanism of adsorption and coprecipitation, but it is difficult to separate the clay minerals from the soil after repair. In addition, whether the heavy metal ions adsorbed by clay minerals will change with the change of soil environment Release to the soil also needs further exploration. Most of the current research on clay minerals remains at the laboratory level, and the realization of its large-scale industrial application has become an urgent problem to be solved.

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