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Effects of Different Passivating Agents on Cd Pollution in Alkaline Farmland Soil

Yujie Li[1, *]

[1] School of Resources and Environment, Henan Polytechnic University, Henan Jiaozuo 454003, China
[*] Corresponding Author

Abstract: In this study, cadmium-polluted farmland in the southern suburbs of Jiaozuo, Henan Province was selected as the research object. Under the field conditions, two passivating agents such as aluminosilicate and calcium-aluminum hydrotalcite were added respectively, and the cadmium form content was analyzed by BCR extraction method. The passivating effect of different passivating agents on soil cadmium in alkaline farmland in northern China was studied under the application rate of 200 and 400kg/mu. The results showed that silicoaluminate and calcium-aluminum hydrotalcite reduced soil pH value in different degrees, but had little effect on soil pH value. The two passivating agents can convert the soluble Cd of weak acid to the residual Cd, and the transformation effect is more significant with the increase of the applied amount. The passivation effect is ranked as calcium aluminum hydrotalcite > silicaluminate, among which 400 kg/mu of calcium aluminum hydrotalcite has the most obvious passivation effect, and the effective content of Cd is reduced by 70.5% compared with group CK. In general, after the application of two passivators and different amounts, the soluble Cd content of weak acid in soil decreased significantly, the reducible Cd content decreased slightly, the oxidizable Cd content increased slightly, and the residual Cd content increased significantly.

Keywords: Heavy metal; Farmland soil; Passivator; Heavy metal state.

1. Introduction

In recent years, with the continuous acceleration of industrialization and urbanization, heavy metal pollution in some farmland soils in China has become increasingly serious. Among many heavy metal pollution, Cd has attracted much attention due to its characteristics such as difficult degradation, persistence and strong toxicity[1]. According to the statistics of the Ministry of Environmental Protection, the total excess rate of heavy metals in China's soil is 16.1%, of which the heavy metal Cd exceeds the standard most seriously, and the point level exceeds the standard rate of 7.0%[2]. Cd in soil can accumulate in human beings and animals and plants through the food chain, causing immeasurable harm to human health, soil environment and ecological safety. Therefore, it is urgent to repair soil Cd pollution[3, 4]. There are many technologies for remediation of soil heavy metal pollution at home and abroad, including physical remediation, chemical remediation, biological remediation and combined remediation[5, 6]. In particular, the in-situ passivation technology in chemical remediation reduces the activity and biological availability of heavy metals in soil by applying passivation materials to contaminated soil. This technology has good effect, strong stability, simple operation and moderate cost, and can be used for large-scale soil pollution remediation[7, 8]. The types and mechanisms of passivating agents are different. It is very important to select the appropriate type of passivating agents and apply the optimal dose to the treatment and remediation of soil heavy metal pollution. Commonly used passivating agents are clay minerals, natural or synthetic minerals, silicaluminate and other inorganic materials.

At present, in-situ passivation remediation of soil heavy metal pollution is mainly concentrated in acidic soil in the south, and most studies on passivation remediation of alkaline soil in the north are pot experiments. There are few studies on remediation of Cd pollution in alkaline soil in the north under field conditions. Therefore, the selection of passivation materials suitable for remediation of soil pollution in alkaline farmland under field conditions has important theoretical and practical value for realizing the safe utilization of farmland in northern China. In this study, the farmland soil in the southern suburb of Jiaozuo, Henan Province, where cadmium has been found to have exceeded the standard, was studied and analyzed in terms of the passivation effects of different doses of aluminosilicate and calcium-aluminum hydrotalcite on soil cadmium pollution under the typical northern alkaline wheat planting system, and the passivation effects of different passivation agents on cadmium morphology and bioavailability were discussed. It provides theoretical support for in-situ passivation remediation and treatment of alkaline cadmium contaminated soil in northern China.

2. Materials and Methods

2.1. Overview of the study area

From 2022 to 2023, the experimental field is located in a farmland in the southern suburb of Jiaozuo City, Henan Province (35° 5'n, 113° 10'e), which belongs to the warm temperate continental monsoon climate, with obvious four seasons change. The annual average temperature is 15.2℃, the relative humidity is about 63%, and the average precipitation is 572.3 mm.The cultivated land area is about 192,700 hectares, accounting for 48.17% of the total land area of the city.Most of the cultivated land is distributed in the central and southern plain area, the soil types of farmland are mainly tidal soil and yellow brown soil, and the soil texture is mainly clay and light sandy soil.Soil basic properties: pH value 8.03, total Cd 3.15mg/kg.

2.2. Test material

The passivating agents selected in the test were CY brand

and CL brand. CY brand passivating agent was purchased from Shanxi Yimida Environmental Protection Material Co., LTD. The main component was silicaluminate.CL brand passivating agent purchased from Jiangsu Longchang Chemical Co., LTD., the main component is calcium aluminum hydrotalcite.

2.3. Experimental design and field management

The experiment was randomly divided into 5 plots, each with a length of 80 meters and a width of 7 meters. Each experimental plot was treated as follows: CK group was the blank control (no passivating agent added), CY1 (200kg/ mu of silicaluminate added), CY2 (400kg/ mu of silicaluminate added), CL1 (200kg/ mu of calcium-aluminum hydrotalcite added), CL2 (400kg/ mu of calcium-aluminum hydrotalcite added).Before sowing, apply passivating agent after turning the cultivated land with a large machine, and then use a small tillage machine to tillage repeatedly to ensure that the passivating agent is fully in contact with the farmland soil. The control group was subject to the same field management as the experimental field, including fertilization, irrigation and drainage, and weeding. All management measures had to be consistent and completed on the same day.

2.4. Sample collection and processing

In each test field, 0~20cm surface farmland soil was evenly collected from east to west, surface humus and stones were removed, and about 1kg of soil was evenly mixed and put into a ziplock bag and brought back to the laboratory.The collected samples were air-dried, ground, and finally passed through 60 mesh and 100 mesh nylon screens, labeled, classified and stored for later use.

2.5. Sample determination

Soil pH was determined by electrode method according to soil-water ratio of 1:2.5. The soil Cd morphology was determined by ICP-OES, and the soil sample after 100 mesh sieve was weighed to 1.0000g by BCR four-step extraction method. The detailed operation steps are shown in Table 1.

Table 1. Extraction of heavy metals from soil by BCR

State	Extractant	Equilibrium condition
Weak acid soluble state	HOAc	Oscillate 180 rpm for 16 h, centrifuge 4000rpm for 10min at 25℃
Reducible state	$NH_2OH \cdot HCl$(pH=1.5)	Oscillate 180 rpm for 16 h, centrifuge 4000rpm for 10min at 25℃
Oxidizable state	H_2O_2、NH_4OAc(pH=2)	After digestion at 25℃ for 1h, digestion in a water bath at 85℃, oscillation at 180 rpm for 16 h, centrifugation at 25℃ and 4000rpm for 10min
Residual state	HCl-HNO_3-HF-$HClO_4$	Four-acid electrothermal plate digestion method

3. Results and Analysis

3.1. Effect of passivating agent on soil pH Characteristics of heavy metal content in farmland soils along rivers in Jiaozuo area

Soil pH is an important factor controlling the absorption and transfer of heavy metals, and the change of soil pH will affect the bioavailability of heavy metals in soil. Generally, the smaller the pH, the greater the bioavailability of heavy metals, and the more conducive to Cd accumulation[9]. As shown in Figure 1, there was no significant difference between the two passivating agents applied in different doses compared to the control group.After adding CY passivation agent, soil pH value decreased with the increase of applied amount, decreased by 0.06 and 0.14, respectively, and there was no significant difference between the two applied amounts.After adding CL passivator, soil pH value decreased by 0.01 and 0.06, respectively, with the increase of the application amount, and there was no significant difference between the two treatments.The different composition properties of CY group passivating agents caused different differences in soil physicochemical properties[10, 11]. CY and CL passivators may reduce the bioavailability of heavy metals in soil by reducing soil pH, thus reducing their ecotoxicity. After passivating agent is applied, the pH value of farmland soil can meet the standard limit of soil environmental quality, and will not affect the quality of farmland soil.

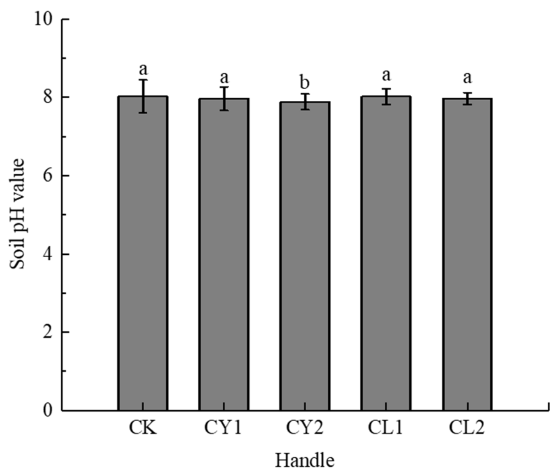

Figure 1. Effect of passivating agent on soil pH value

3.2. Analysis of Cd morphological content in farmland soil in the study area

In this study, the improved BCR extraction method was used to analyze the morphology of soil samples, and the four forms were exchangeable state, reducible state, oxidizable state and residual state. Figure 2 shows the percentage of soil Cd forms in different passivation treatments. The average content of Cd forms in farmland soil (CK) without passivating agent was exchangeable 1.18mg/kg, oxidizable 0.96mg/kg, reducible 0.82mg/kg and residual 0.19mg/kg, respectively. The exchangeable form was the main form of Cd, and the form content accounted for 37.46% of the total. Unpassivated soil not only has higher total Cd content, but also has higher available state content than other passivated soil, higher biological availability, and greater harm to soil environment.

It can be seen from FIG. 2 that CY and CL passivating agents both have certain passivating effects on Cd element in farmland soil in the study area. With the increase of passivating agent application, the sum of Cd exchangeable state content and Cd reducible state content decrease more, while the oxidizable state content of Cd has no obvious rule, while the residual state content of CD increases more significantly, indicating that the passivating effect is better.

4. Discuss

4.1. Effects of different passivating agents on pH of Cd contaminated soil under field conditions

Soil pH values control the chemical behaviors of heavy metals in soil, such as precipitation, dissolution and adsorption, and are important factors affecting the bioavailability and toxicity of soil heavy metals[12]. Generally speaking, in acidic soil, adding alkaline passivation materials to increase soil pH value can reduce the soil available state content and achieve the effect of soil pollution control and remediation, but in alkaline soil, only adjusting soil pH value obviously cannot achieve the remediation effect, and chemical reactions with heavy metals need to be added.Or surface adsorption and ion exchange to achieve the purpose of reducing the effective content of heavy metals, so as to achieve a better passivation effect, therefore, it is recommended to use a neutral pH passivation agent to repair alkaline farmland soil, which may be one of the differences between acidic soil and alkaline soil Cd pollution control and remediation.

Silicaluminate is a kind of natural and modified mineral material with abundant pores, large specific surface area, strong adsorption and purification capacity for heavy metal ions, and is the main component of zeolite, which is often used to repair heavy metal contaminated soil[13, 14]. In this study, the application of silicoaluminate passivator in alkaline farmland soil reduced soil pH value to a certain extent, and decreased significantly with the increase of the amount of passivator applied. There is an adjustment process in the soil medium, which can buffer the change of soil pH value caused by external materials. After the application of silicoaluminate passivator in this study, there is no significant difference in soil pH value. It is consistent with the results of Wang Hongpeng's study[15].

Calcium-aluminum hydrotalcite is a layered bimetallic hydroxide, in which metal cations such as calcium and aluminum ions are located in the main layer plate, and anions are distributed between the layers, which are composed of positively charged layers and interlayer anions[16]. In this study, the main component of CL passivator was calcium-aluminum hydrotalcite, and the soil pH value after application decreased slightly but had no significant difference compared with the control group, which may be related to the composition ratio of the passivator itself, or because the adsorption of calcium-aluminum hydrotalcite on Cd was not closely related to pH, which was consistent with the research conclusion of Zhang Yida[17].

4.2. Effects of different passivating agents on soil Cd morphology under field conditions

When the soil environment changes, all forms will transform each other to form a new equilibrium. In this study, the exchangeable and reducible contents of Cd in the soil that has not been passivated account for about 63.49% of the total amount, indicating that the biological availability of heavy metals in farmland soil in the study area is high and the ecological toxicity is strong.The different dosages of the two passivators promoted the conversion of Cd from exchangeable and reducible states to stable oxidizable and residual states, but the conversion degree of Cd was different with different kinds and dosages.

Silicaluminate is a kind of natural and modified mineral material with abundant pores, large specific surface area and strong adsorption and purification capacity for heavy metal ions. It is often used to repair heavy metal polluted soil. Surface adsorption and cation exchange adsorption with cadmium ions mainly depend on their own characteristics to reduce the activity of Cd[18]. In this study, the effective state content of Cd after CY passivation was reduced compared with that of the control group, but higher than that of CG passivation treatment. This is because under alkaline conditions, the adsorption sites of exchangeable state Cd and metal cations are limited and the process is reversible, and the absorbed Cd ions may be exchanged by neutral salts. If the passivator is mixed with other materials, its adsorption advantage may be better exerted to achieve remarkable results[18, 19].

Calcium-aluminum hydrotalcite is a layered bimetallic hydroxide, in which metal cations such as calcium and aluminum ions are located in the main layer plate, and anions are distributed between layers. It is a compound formed by the accumulation of positively charged layers and interlayer anions. The heavy metal cations are removed mainly through the adsorption of surface hydroxyl groups with metal cations, the complexation of special functional groups with metal cations, and the isomorphic displacement[20]. In this study, after the application of CL passivator, the contents of exchangeable state and reducible state of Cd in soil decreased, while the contents of oxidizable state and residual state of Cd increased. Because the interlayer anion of calcium-aluminum hydrotalcite is nitrate, and the ion radius of calcium and nitrate ions is large, the interlayer channel of calcium-aluminum hydrotalcite is high. It is more conducive for exchangeable Cd to enter the layered structure of calcium-aluminum hydrotalcite and replace calcium ions so as to be fixed in the lattice of calcium-aluminum hydrotalcite. On the other hand, the alkaline environment increases the negative charge on the surface of soil colloid, and the stability of adsorbed Cd is enhanced, and the concentration of hydrogen ions in soil decreases, which weakens the competition between Cd and cadmium ions. The combination of Cd and oxide is promoted to increase the content of Cd oxidizable states[21].

5. Conclusion

(1) Compared with the control group, silicoaluminate and calcium-aluminum hydrotalcite can reduce soil pH value, but not significantly, and the pH value of farmland soil after the application of passivating agent can meet the soil environmental quality standard limits, and will not affect the quality of farmland soil.

(2) Under the field test, both of the two passivators reduced the available Cd content in the soil in the study area, and Cd transformed from the soluble state of weak acid to the oxidizable state and residue state. The passivating effect on soil Cd became better with the increase of the dosage, and the

effect of CL passivating agent was due to CY passivating agent.

(3) Field conditions should consider the actual application and cost, and the gradient of passivation agent applied should be set less. In the later stage, considering whether the passivation agent has a negative impact on the soil, a reasonable gradient of passivation agent applied should be set to screen the best applied amount.

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