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Effects of Phosphate and Silicate Combined Application on Cadmium Form Changes in Heavy Metal Contaminated Soil

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Abstract: Pollution by heavy metal cadmium (Cd) in soil is still serious and control measures are constantly updated. In this paper, one indoor culture method was applied to investigate the effect of phosphate and thermo-activated nano silicate combined application on soil cadmium (Cd) speciation transformation. A total of 7 treatments were designed, which were: simulated cadmium-contaminated soil without phosphate and silicate recorded as the reference (CK) treatment; mixtures of 0.5%, 1.0%, and 2.0% soil heavy dose of potassium dihydrogen phosphate and 700 °C thermo-activated nano serpentine (potassium dihydrogen phosphate: thermo-activated nano serpentine ratio = 1:2) added to simulated cadmium-contaminated soil, denoted as nPS_{700}-0.5, nPS_{700}-1.0, and nPS_{700}-2.0, respectively; and 0.5%, 1.0%, and 2.0% soil heavy dose of potassium dihydrogen phosphate and 700 °C thermo-activated nano zeolite mixture (potassium dihydrogen phosphate: thermo-activated nano zeolite ratio = 1:2) added to simulated cadmium-contaminated soil, denoted as nPF_{700}-0.5, nPF_{700}-1.0, and nPF_{700}-2.0, respectively. The results showed that the combined application of potassium dihydrogen phosphate with thermo-activated nano serpentine or potassium dihydrogen phosphate with thermo-activated nano zeolite reduced the soil exchangeable Cd content to varying degrees and increased levels of carbonate-bound, Fe-Mn oxide-bound, organic-bound, and residual Cd forms to different degrees. In combined application of phosphate and thermo-activated nano silicate, the higher the dosage level, the greater the reduction of exchangeable Cd content and the better the effect on Cd-contaminated soil remediation: nPS_{700}-2.0 > nPS_{700}-1.0 > nPS_{700}-0.5, nPF_{700}-2.0 > nPF_{700}-1.0 > nPF_{700}-0.5 (N, P, S, and F represent nano, KH_2PO_4, serpentine, and zeolite, respectively, and 700 represents the activation temperature). At the same dosage level, the combined application of potassium dihydrogen phosphate and thermo-activated nano serpentine was more effective than that of potassium dihydrogen phosphate and thermo-activated nano zeolite in repairing Cd-contaminated soil (nPS_{700}-2.0 > nPF_{700}-2.0, nPS_{700}-1.0 > nPF_{700}-1.0, nPS_{700}-0.5 > nPF_{700}-0.5), which indicated that the combination of phosphate and thermo-activated nano silicate can passivate heavy metal cadmium (Cd) to a certain extent and promote the transformation of bioavailable Cd into an unusable state. The reason why potassium dihydrogen phosphate, zeolite, and serpentine can absorb heavy metal cadmium after entering the soil is because the silicate mineral itself can directly absorb cadmium. Second, after nano treatment and thermal activation, the specific surface areas and pores of the minerals increase, which enhances the adsorption performance. Third, because the pH value of the mineral itself is high, the pH value of the soil environment will rise, thereby transforming $H_2PO_4^-$ into PO_4^{3-}, which is conducive to the adsorption of Cd^{2+}.

Keywords: potassium dihydrogen phosphate; serpentine; zeolite; nanomaterials; the Cd forms

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1. Introduction

In June 2020, the Ministry of Ecology and Environment, the National Bureau of Statistics, and the Ministry of Agriculture and Rural Affairs jointly issued the "Second National Pollution Source Census Bulletin", reporting that the lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), and arsenic (As) emissions in Chinese national water pollution in 2017 were 182.54 t, a large part of which entered the soil, causing heavy metal pollution. Among them, soil Cd pollution is one of the most intractable environmental problems in the world [1,2] because approximately 2.0% of Cd entering the environment enters the atmosphere, 4.0% enters the water, and up to 94.0% enters the soil [3]. Once Cd enters the soil, it is not easily decomposed and transformed, but it easily accumulates and has hidden, long-term, and irreversible effects. Heavy metal Cd causes different hazards to animals, plants, and humans, such as damage to plant roots, effects on animal reproduction, and damage to human renal tubules [4]. It has become a hot spot of environmental pollution research at home and abroad [5–8].

Nanomaterials and nanotechnologies are the most promising materials and technologies in the 21st century. Nanomaterials have the advantages of small particle size, large specific surface area, fast adsorption rate, strong reactivity, and have strong adsorption capacity for heavy metals [9–11], which makes up for the deficiency of traditional adsorbents. Generally speaking, the adsorption capacity of natural silicate minerals for heavy metals is limited [12]. Nano treatment can significantly improve the adsorption effect of heavy metals.

In-situ passivation chemical remediation technology is one of the most widely used methods to treat heavy metal pollution. Common remediation substances include phosphate (potassium dihydrogen phosphate, apatite, phosphate powder, etc.) and silicate minerals (serpentine, zeolite, etc.). Phosphate stabilizes heavy metals and is effective in the remediation of heavy metal-contaminated soil [13–20]. Zeolite is an aluminosilicate mineral with a shelf-like structure that has been applied in the research field of heavy metal adsorption due to its large specific surface area, cation exchange capacity, and strong adsorption performance [21–28]. Serpentine has a high specific surface area, good pore structure, strong surface activity, and belongs to layered magnesium silicate minerals [29,30], which have been used in the study of heavy metal adsorption in water and soil [31–35].

The effects of single and mixed applications of phosphate and natural zeolite on the transformation of Cd forms in soil have been investigated in the laboratory. Research groups have studied the effects of natural and thermo-activated serpentine on the occurrence of cadmium forms in soil. Previous test results showed that the mixed application of phosphate and silicate had better adsorption effects on cadmium than the single application, and silicate had a better treatment effect on cadmium than phosphate [35,36]. The current study was designed after reviewing the literature and research performed by laboratory and research groups. The aim of the study was to determine the effects of silicate nano treatment and thermal activation combined with phosphate on the transformation of heavy metal cadmium forms in order to prevent and control heavy metal Cd pollution as well as provide more selectivity.

2. Materials and Methods

2.1. Experimental Materials

Tested soils: The soil samples were collected from 0–20 cm of uncontaminated farmland at the Scientific Research Base of Shenyang Agricultural University, Shenyang, Liaoning Province. The soil type was brown soil. The soil samples were collected, naturally air dried, mixed, ground, screened using a 2 mm sieve, and stored in a Ziplock bag for further use. The basic physical and chemical properties of the tested soils were pH 5.71, organic matter 26.93 $g \cdot kg^{-1}$, alkali-hydrolyzed nitrogen 50.02 $mg \cdot kg^{-1}$, available phosphorus 71.27 $mg \cdot kg^{-1}$, available potassium 183.59 $mg \cdot k^{-1}$, total phosphorus 0.63 $g \cdot kg^{-1}$, and total cadmium 0.18 $mg \cdot kg^{-1}$, which determined to according to the methods of ref. [37].

Simulation of Cd-contaminated soil: 50.0 g of the experimental soil was accurately weighed into a clean jar, and $CdCl_2 \cdot 2.5H_2O$ (AR) was added to the test soil in the form of a solution, so that the exogenous Cd content in the soil reached 10 $mg \cdot kg^{-1}$ [38–40]. After the soil was fully mixed with the $CdCl_2 \cdot 2.5H_2O$ solution, it was cultivated at room temperature (25 ± 2 °C) for one week, while the soil water content was maintained by weighing to 70% of the field water-holding capacity. Then, the treated soil was dried, ground, stored, and set aside.

The natural nano serpentine and nano zeolite tested were both collected from Liaoning Province. They were pulverized into 600 nm powder by high-energy nano impact grinding (highly dispersed, uniform particle size, basically controllable size), placed in a Ziplock bag, and stored in a desiccator for later use.

The composition and content of the tested soil, zeolite, and serpentine are shown in Table 1.

Table 1. The main components and content of the tested soil, zeolite and serpentine (wt. %).

Composition	SiO_2	Al_2O_3	MgO	K_2O	CaO	Na_2O	Fe_2O_3	P_2O_5	Other
Content in soil (wt. %)	72.23	10.33	9.83	2.55	2.23	1.66	0.17	0.23	0.16
Content in zeolite (wt. %)	76.32	12.49	3.78	3.24	2.30	1.29	0.58	0	0
Content in serpentine (wt. %)	57.24	0.11	37.97	0	3.20	0.18	1.30	0	0

Thermo-activated nano serpentine: The 600 nm natural nano serpentine powder was put into a crucible and calcined in a muffle furnace at 700 °C for 2 h at constant temperature. After cooling to room temperature, the nano serpentine powder was removed, put in a Ziplock bag, and stored in a desiccator. The thermo-activated nano serpentine obtained was abbreviated as nS_T (N, nano treatment; S, serpentine; T, activation temperature), namely nS_{700}, which stands for 700 °C thermo-activated nano serpentine.

Thermo-activated nano zeolite: The 600 nm natural nano zeolite powder was put into a crucible and calcined in a muffle furnace at 700 °C for 2 h at constant temperature. After cooling to room temperature, the nano zeolite powder was removed, put in a Ziplock bag, and stored in a desiccator. The thermo-activated nano zeolite obtained was abbreviated as nF_T (N, nano treatment; S, zeolite; T, activation temperature), namely nF_{700}, which stands for 700 °C thermo-activated nano zeolite.

Phosphate for testing: KH_2PO_4 (analytical reagent), denoted as P.

The combination of potassium dihydrogen phosphate and thermo-activated nano serpentine was recorded as nPS_{700}, and the combination of potassium dihydrogen phosphate and thermo-activated nano zeolite was recorded as nPF_{700}.

2.2. Experimental Design

In this experiment, the indoor culture method was adopted and a total of 7 treatments were designed. The ratio of phosphate and silicate in the different treatments is shown in Table 2. The treatment sets (each with 3 replicates) were: simulated cadmium-contaminated soil without phosphate and silicate as the reference (CK) treatment; mixtures of 0.5%, 1.0%, and 2.0% soil heavy dose of potassium dihydrogen phosphate and 700 °C thermo-activated nano serpentine (potassium dihydrogen phosphate: thermo-activated nano serpentine ratio = 1:2) added to simulated cadmium-contaminated soil, denoted as nPS_{700}-0.5, nPS_{700}-1.0, and nPS_{700}-2.0, respectively; and 0.5%, 1.0%, and 2.0% soil heavy dose of potassium dihydrogen phosphate and 700 °C thermo-activated nano zeolite mixture (potassium dihydrogen phosphate: thermo-activated nano zeolite ratio = 1:2) added to simulated cadmium-contaminated soil, denoted as nPF_{700}-0.5, nPF_{700}-1.0, and nPF_{700}-2.0, respectively. The mixtures were mixed well and then 50.0 g of each of the above-mentioned soils with different treatments was accurately weighed and put into jars. The jars were placed in a thermotank and cultivated at 25 ± 2 °C, and the soil water content was maintained at 70% of the field water-holding capacity by adding deionized water every other day, according to the weighing method. At the 0th, 7th, 14th, 28th, and 56th days of culture, appropriate

amounts of naturally air-dried and ground soil samples were weighed, and the levels of five forms of soil Cd were determined using the Tessier five-step continuous extraction method.

Table 2. Scheme of the ratios of potassium dihydrogen phosphate combined with thermo-activated nano serpentine and thermo-activated nano zeolite.

Sample	Potassium Dihydrogen Phosphate Dosage (%)	700 °C Nano Serpentine Dosage (%)	700 °C Nano Zeolite Dosage (%)
CK	0	0	0
nPS_{700}-0.5	0.17	0.33	
nPS_{700}-1.0	0.33	0.67	
nPS_{700}-2.0	0.67	1.33	
nPF_{700}-0.5	0.17		0.33
nPF_{700}-1.0	0.33		0.67
nPF_{700}-2.0	0.67		1.33

2.3. Measurement Indicators and Methods

Analysis of the different morphological contents of cadmium in soil was carried out using the Tessier continuous extraction method [41]. The detailed operations are shown in Table 3. The content of cadmium in the soil was measured by atomic absorption spectrophotometry (AAS).

Table 3. Tessier continuous extraction method.

Cd Form Name	Extractants and Extraction Conditions
Exchangeable state	8 mL 1 mol·L^{-1} $MgCl_2$ solution (pH adjusted to 7.0 with 0.1 mol·L^{-1} HCl) and continuously shaken horizontally at 25 °C for 1 h
Carbonate-bound state	8 mL 1 mol·L^{-1} NaOAc solution (pH adjusted to 5.0 with HOAc) and continuously shaken horizontally at 25 °C for 5 h
Iron-manganese oxide-bound state	20 mL 0.04 mol·L^{-1} NH_2OH·HCl HOAc (25%, *v*/*v*) solution, stirred continuously in a water bath at 96 ± 3 °C for 6 h
Organic-bound state	(1) 3 mL 0.02 mol·L^{-1} HNO_3 solution, then added 5 mL 30% H_2O_2 (pH adjusted to 2.0 with 2 mol·L^{-1} HNO_3), heated in a water bath at 85 ± 2 °C for 2 h and stirred constantly (2) 3 mL 30% H_2O_2 (pH adjusted to 2.0 with 2 mol·L^{-1} HNO_3) in a water bath at 85 ± 2 °C for 3 h and stirred intermittently (3) 5 mL HNO_3 (20%, *v*/*v*) solution containing 3.2 mol·L^{-1} NH_4OAc, continuously vibrated horizontally for 0.5 h at 25 °C
Residue state	HCl + HNO_3 + HF + $HClO_4$

2.4. Data Processing and Analysis

Microsoft Excel 2003 and origin 8.0 software were used to analyze and graph the data, and both the data significance tests and correlation analysis were performed using SPSS version 17.0 statistical software ($p < 0.05$).

3. Results and Analysis

The biotoxicity of heavy metals in soil is not only related to their total amount, but also depends mainly on the form in which they are present and the proportion of each form [42–46]. The Tessier five-step sequential extraction method for the determination of heavy metal Cd forms used in this experiment yields five forms, namely exchangeable (EXE), carbonate-bound (CAB), organic-bound (OM), iron-manganese oxide-bound (FMO), and residual (RES) Cd.

3.1. Effect of Phosphate and Thermo-Activated Nano Silicate Combined Application on the Exchangeable Cd Content in Soil

The change in EXE Cd content in soil with different dosages of potassium dihydrogen phosphate combined with 700 °C thermo-activated nano serpentine and 700 °C thermo-activated nano zeolite is shown in Figure 1. As can be seen from the figure, with increasing culture time under the same treatment, the soil EXE Cd content decreased slightly. Although the degree of decrease was not very obvious, the effect was more significant than the CK treatment. Compared with 0 d, after 56 d, the EXE Cd content of soil treated with CK decreased by 0.37, and the EXE Cd content of soil treated with nPS_{700}_0.5, nPS_{700}-1.0, and nPS_{700}-2.0 respectively decreased by 1.26, 1.55, and 1.91 units, and the EXE Cd content of soil treated with nPF_{700}-0.5, nPF_{700}-1.0, and nPF_{700}-2.0 decreased by 1.13, 1.38, and 1.70 units, in turn. For the same dose level and different culture times, the EXE Cd content of soil decreased significantly when treated with potassium dihydrogen phosphate combined with 700 °C thermo-activated nano serpentine compared with potassium dihydrogen phosphate combined with 700 °C thermo-activated nano zeolite; the nPS_{700}-2.0 and nPF_{700}-2.0 treatments decreased the EXE Cd content significantly and the nPS_{700}-2.0 treatment decreased the EXE Cd content the most. For the same culture time, compared with CK, the EXE Cd content decreased with different treatments. At 0 d of culture, compared with CK, the EXE Cd content of soil treated with nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively decreased by 1.92, 1.77, 2.21, 2.06, 2.60, and 2.40 $mg \cdot kg^{-1}$. When cultured for 56 d, compared with CK, the EXE Cd content of soil treated with nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively decreased by 2.81, 2.53, and 3.39, 3.07, 4.14, and 3.73 $mg \cdot kg^{-1}$. For the same culture time and dose level, potassium dihydrogen phosphate combined with 700 °C thermo-activated nano serpentine significantly reduced the EXE Cd content in soil compared to potassium dihydrogen phosphate combined with 700 °C thermo-activated nano zeolite; the nPS_{700}-2.0 and nPF_{700}-2.0 treatments significantly reduced the EXE Cd content, and the former was better than the latter. For the same treatment, the higher the dosage, the greater the reduction of EXE Cd content.

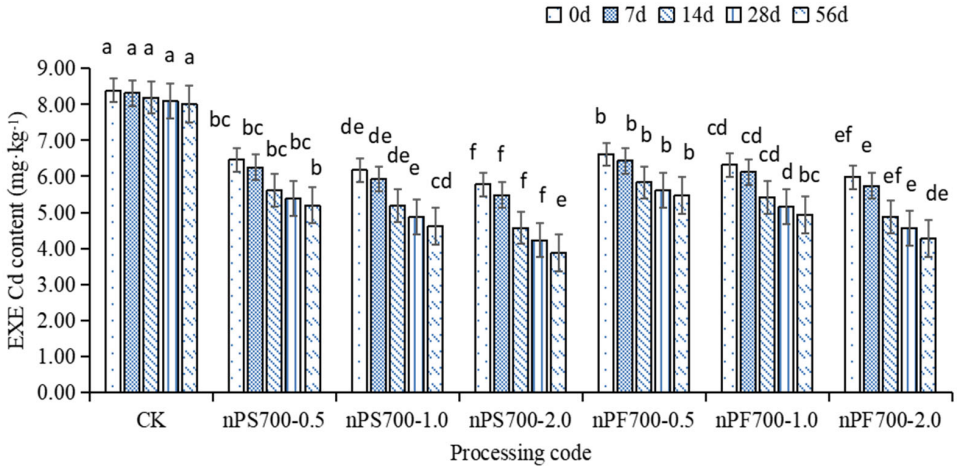

Figure 1. Effect of phosphate and thermo-activated nano silicate combined application on the exchangeable Cd content in soil. Different lower-case letters indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

According to the significance analysis of the influence of different treatments on the EXE Cd content, as shown in Figure 1, it could be seen that the combined application of phosphate and thermo-activated nano silicate could significantly reduce the EXE Cd content, and both showed significant differences compared to the CK treatment. For the same culture time and phosphate and thermo-activated nano silicate combined application, there were significant differences in the effects of different application dosages. The nPS_{700}-

2.0 and nPF_{700}-2.0 treatments had better effects, with the nPS_{700}-2.0 treatment having the best effect. For the combined application of the same kind of phosphate and thermo-activated nano silicate, increasing culture time had no significant effect on the EXE Cd content in soil.

3.2. Effect of Phosphate and Thermo-Activated Nano Silicate Combined Application on the Carbonate-Bound Cd Content in Soil

The changes in CAB Cd content of soil treated with potassium dihydrogen phosphate at different dose levels combined with nano serpentine thermally activated at 700 °C and nano zeolite thermally activated at 700 °C are shown in Figure 2. It can be seen from the figure that, for the same cultivation time, compared with the CK treatment, the CAB Cd content increased with different treatments. At 0 d of culture, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments respectively increased the CAB Cd content by 0.29, 0.29, 0.42, 0.39, 0.54, and 0.51 $mg \cdot kg^{-1}$. When cultured for 14 d, compared with the CK treatment, the CAB Cd content of soil treated with nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 increased by 0.35, 0.34, 0.52, 0.48, 0.66, 0.61 $mg \cdot kg^{-1}$, respectively. At 56 d of culture, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments increased the CAB Cd content by 0.40, 0.39, 0.59, 0.55, 0.74, and 0.68 $mg \cdot kg^{-1}$, in turn. For the same treatment, the CAB Cd content in soil increased slightly with increasing culture time. Cultured for 28 d compared with 0 d, the CAB Cd content of soils treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively increased by 0.04, 0.14, 0.13, 0.19, 0.18, 0.21, and 0.19 units. When cultured for 56 d compared with 0 d, the CAB Cd content of soil treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively increased by 0.06, 0.17, 0.16, 0.23, 0.22, 0.26, and 0.23 units. For the same treatment, the higher the application dose, the greater the increase in CAB Cd content. For the same dose level, potassium dihydrogen phosphate combined with nano serpentine thermally activated at 700 °C had a better effect on Cd-contaminated soil than potassium dihydrogen phosphate combined with nano zeolite thermally activated at 700 °C. The combined application of phosphate and thermo-activated nano silicate could increase the CAB Cd content in the soil. One reason for these results is that Cd^{2+} will react with OH^- to form $Cd(OH)_2$, and $Cd(OH)_2$ can absorb CO_2 to form $CdCO_3$ precipitates. Second, Cd^{2+} reacts directly with CO_3^{2-} in soil to form $CdCO_3$ precipitates.

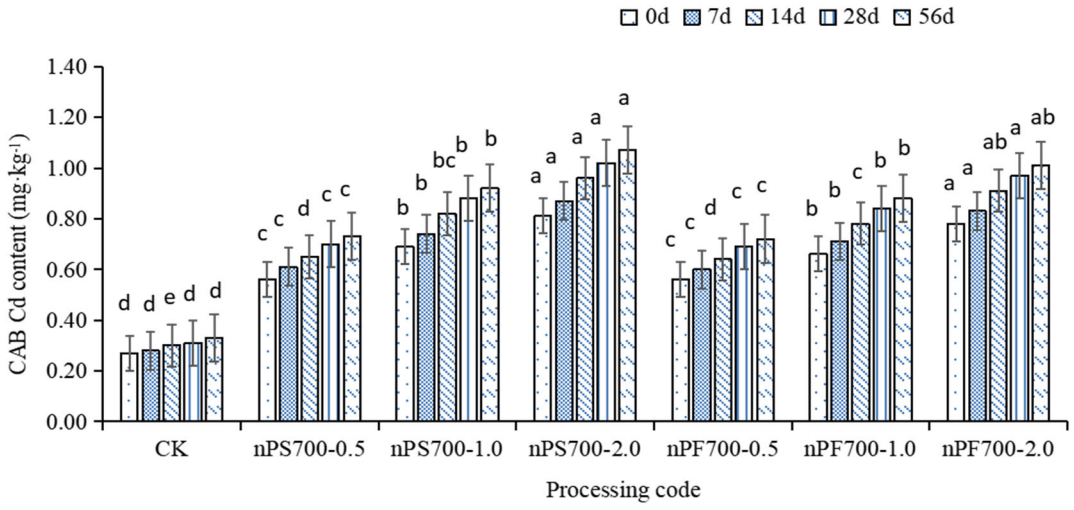

Figure 2. Effect of phosphate and thermo-activated nano silicate combined application on the carbonate-bound Cd content in soil. Different lower-case letters indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

It can be seen from Figure 2 that the combined application of phosphate and thermo-activated nano silicate could significantly increase the CAB Cd content, and the difference was significant compared with the CK treatment. On the whole, the treatment effect of phosphate combined with thermo-activated nano serpentine was better than that of phosphate combined with thermo-activated nano zeolite, but the difference was small.

3.3. Effect of Phosphate and Thermo-Activated Nano Silicate Combined Application on Organic-Bound Cd Content in Soil

Figure 3 shows the change in OM Cd content in soil when treated with potassium dihydrogen phosphate at different dose levels combined with nano serpentine thermally activated at 700 °C and nano zeolite thermally activated at 700 °C. As can be seen from the figure, the OM Cd content in soil increased slightly with increasing culture time under the same treatment. Cultured for 28 d compared with 0 d, the OM Cd content of soil treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively increased by 14.81%, 25.00%, 23.21%, 27.54%, 27.27%, 25.93%, and 24.36%. Cultured for 56 d compared with 0 d, the OM Cd content of soil treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPS_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively increased by 22.22%, 30.36%, 28.57%, 33.33%, 33.33%, 32.10%, and 29.49%; the nPS_{700}-2.0 treatment increased the soil OM Cd content the most. For the same culture time, compared with CK, the OM Cd content of the soil increased with different treatments. At 0 d of culture, compared with CK, the OM Cd content of the soil treated with nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 was respectively increased by 107.41%, 107.41%, 155.56%, 144.44%, 200.00%, and 188.89%. When cultured for 56 d, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments increased the soil OM Cd content by 121.21%, 118.18%, 178.79%, 166.67%, 224.24%, and 206.06%, in turn. In conclusion, different dosage levels of potassium dihydrogen phosphate combined with 700 °C thermo-activated nano serpentine or 700 °C thermo-activated nano zeolite could increase the soil OM Cd content; the higher the dose, the higher the OM Cd content. Among them, the nPS_{700}-2.0 and nPF_{700}-2.0 treatments increased the OM Cd content the most obviously, and the former treatment was better than the latter. The key to the increase in the OM Cd content was that the solubility of organic matter in soil increases with increasing pH value and the complexing ability also increases.

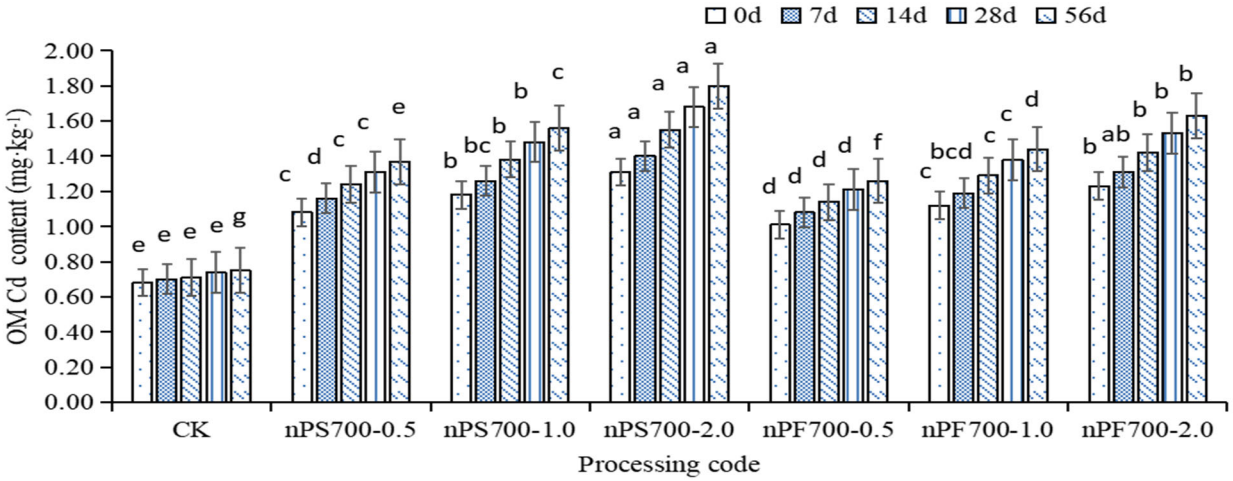

Figure 3. Effect of phosphate and thermo-activated nano silicate combined application on organic-bound Cd content in soil. Different lower-case letters indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

According to the significant analysis results of the effects of the combined application of phosphate and thermo-activated nano silicate on the OM Cd content in soil, as shown

in Figure 3, all treatments could significantly increase the OM Cd content in each culture period compared with the CK treatment. For the same application dose, the effect of phosphate combined with thermo-activated nano serpentine was more obvious than that of phosphate combined with thermo-activated nano zeolite.

3.4. Effect of Phosphate and Thermo-Activated Nano Silicate Combined Application on Iron-Manganese Oxide-Bound Cd Content in Soil

The changes in FMO Cd content in soil with different dose levels of potassium dihydrogen phosphate combined with thermo-activated nano serpentine and thermo-activated nano zeolite are shown in Figure 4. It can be seen from the figure that for the same incubation time, the combined application of potassium dihydrogen phosphate with 700 °C thermo-activated nano serpentine or 700 °C thermo-activated nano zeolite could increase the soil FMO Cd content compared with CK treatment. At 0 d of culture, compared with CK, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments respectively increased the soil FMO Cd content by 0.16, 0.15, 0.20, 0.18, 0.24, and 0.23 units. When cultured for 28 d, compared with the CK treatment, the soil FMO Cd content increased with the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments by 0.20, 0.17, 0.27, 0.23, 0.32, and 0.29 units, respectively. After 56 d of culture, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments respectively increased the soil FMO Cd content by 0.21, 0.17, 0.29, 0.24, 0.35, and 0.31 units. For the same treatment, the FMO Cd content increased slightly with increasing culture time. When cultured for 56 d, compared with 0 d, the FMO Cd content of soil treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 increased by 0.09, 0.14, 0.11, 0.18, 0.15, 0.20, and 0.17 $mg \cdot kg^{-1}$, in turn. For the same dose level, potassium dihydrogen phosphate combined with nano serpentine thermally activated at 700 °C increased the FMO Cd content more than potassium dihydrogen phosphate combined with nano zeolite thermally activated at 700 °C; the higher the dose level, the higher the soil FMO Cd content. The nPS_{700}-2.0 and nPF_{700}-2.0 treatments significantly increased the FMO Cd content, with the nPS_{700}-2.0 treatment causing the most significant increase.

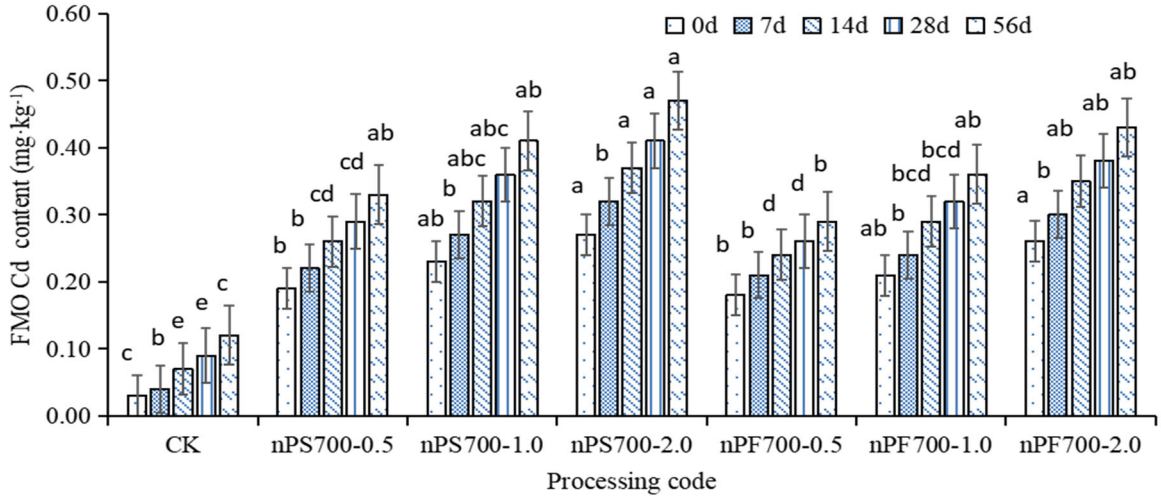

Figure 4. Effect of phosphate and thermo-activated nano silicate combined application on iron-manganese oxide-bound Cd content in soil. Different lower-case letters indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

From the significance analysis of the effects of different treatments on the FMO Cd content, as shown in Figure 4, it could be seen that the combined application of phosphate and thermo-activated nano silicate could significantly increase the FMO Cd content, and there were significant differences compared with the CK treatment. For the same kind of

phosphate and thermo-activated nano silicate treatment, increasing dosage had a significant effect on the change in FMO Cd content. With increasing culture time, there was no significant difference in the influence of different treatments on the FMO Cd content.

3.5. Effect of Phosphate and Thermo-Activated Nano Silicate Combined Application on Residual Cd Content in Soil

Figure 5 shows the changes in soil RES Cd content when potassium dihydrogen phosphate at different dose levels was combined with nano serpentine and nano zeolite thermally activated at 700 °C. In general, the RES Cd content was significantly increased after combined application of potassium dihydrogen phosphate and thermo-activated nano serpentine or with potassium dihydrogen phosphate and thermo-activated nano zeolite compared to CK treatment in Cd-contaminated soil. It can be seen from the figure that for the same treatment, with increasing culture time, the soil RES Cd content increased. When cultured for 56 d, compared with 0 d, the RES Cd content in soil treated with CK, nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 respectively increased 23.44%, 38.60%, 37.20%, 43.93%, 40.83%, 52.46%, and 51.43%. For the same culture time, different treatments could increase the RES Cd content compared with the CK treatment. At 0 d of culture, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments respectively increased the soil RES Cd content by 1.07, 1.00, 1.09, 1.05, 1.19, and 1.11 units. At 56 d of culture, compared with the CK treatment, the nPS_{700}-0.5, nPF_{700}-0.5, nPS_{700}-1.0, nPF_{700}-1.0, nPS_{700}-2.0, and nPF_{700}-2.0 treatments increased the soil RES Cd content by 1.58, 1.46, 1.70, 1.59, 2.00, and 1.86 $mg \cdot kg^{-1}$, respectively. In conclusion, for the same dose level, potassium dihydrogen phosphate combined with 700 °C thermo-activated nano serpentine had a better effect on Cd-contaminated soil than potassium dihydrogen phosphate combined with 700 °C thermo-activated nano zeolite. The soil RES Cd content increased most significantly with the nPS_{700}-2.0 and nPF_{700}-2.0 treatments, and the former increased the soil RES Cd content more significantly than the latter. For the same treatment, the higher the dose level, the higher the RES Cd content.

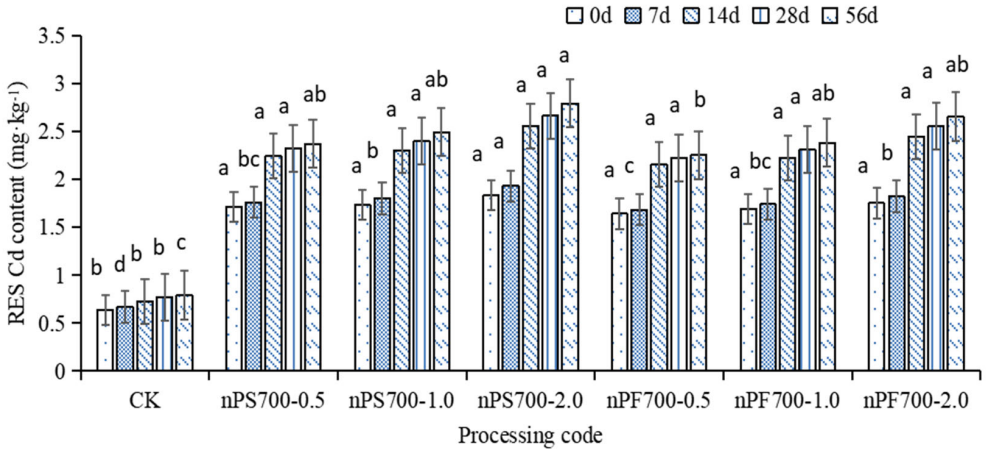

Figure 5. Effect of phosphate and thermo-activated nano silicate combined application on residual Cd content in soil. Different lower-case letters indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

Figure 5 shows the significance analysis of the different effects of phosphate and thermo-activated nano silicate combined application on the RES Cd content of soil with different culture times. It can be seen from the figure that all treatments significantly increased the RES Cd content compared with the CK treatment, with significant differences. For the same culture time, the treatment effect of phosphate combined with thermo-activated nano serpentine was better than that of phosphate combined with thermo-activated nano zeolite,

but the difference was not obvious. With increasing application dose of phosphate and thermo-activated nano silicate, the significant difference became more and more significant.

3.6. Effects of Phosphate and Thermo-Activated Nano Silicate Combined Applicationon the Proportions of Cd Forms in Soil

Figure 6 shows the changes in the proportions of soil Cd speciation after culturing for 56 d with phosphate and thermo-activated nano silicate. As can be seen from the figure, the effects of the combined application of phosphate and thermo-activated nano silicate on the forms of heavy metal Cd in soil were mainly as follows: the EXE Cd content gradually decreased and the CAB, OM, FMO, and RES Cd contents gradually increased. After 56 d of culture, the main form of Cd in CK-treated soil was EXE, accounting for 80.10%, followed by RES (7.90%), OM (7.50%), CAB (3.30%), and FMO (1.20%). Compared with the CK treatment, the soil EXE Cd content decreased by 35.08~51.69% with nPS_{700}-0.5~2.0 treatment, and the nPF_{700}-0.5~2.0 treatment decreased the soil EXE Cd content by 31.59~46.57%. This indicated that the higher the dosage level, the more the EXE Cd content decreased, with the nPS_{700}-2.0 treatment causing the most obvious decrease. The soil RES Cd content increased by 200.0~253.16% with the nPS_{700}-0.5~2.0 treatments and 184.81~235.44% with the nPF_{700}-0.5~2.0 treatments. The results showed that the combination of potassium dihydrogen phosphate and thermo-activated nano serpentine or potassium dihydrogen phosphate and thermo-activated nano zeolite could increase the RES Cd content, with the former significantly increasing the RES Cd content compared to the latter. To sum up, the combined application of potassium dihydrogen phosphate and thermo-activated nano serpentine or the combined application of potassium dihydrogen phosphate and thermo-activated nano zeolite could remediate Cd-contaminated soils. With increasing dose level, the stabilizing effect on heavy metal Cd also increased; the stabilization effects of the nPS_{700}-2.0 and nPF_{700}-2.0 treatments were the most obvious, with the nPS_{700}-2.0 treatment having a better stabilizing effect than the nPF_{700}-2.0 treatment. For the same dose level, the combination of potassium dihydrogen phosphate and thermo-activated nano serpentine had a better effect than potassium dihydrogen phosphate and thermo-activated nano zeolite on stabilizing heavy metal Cd.

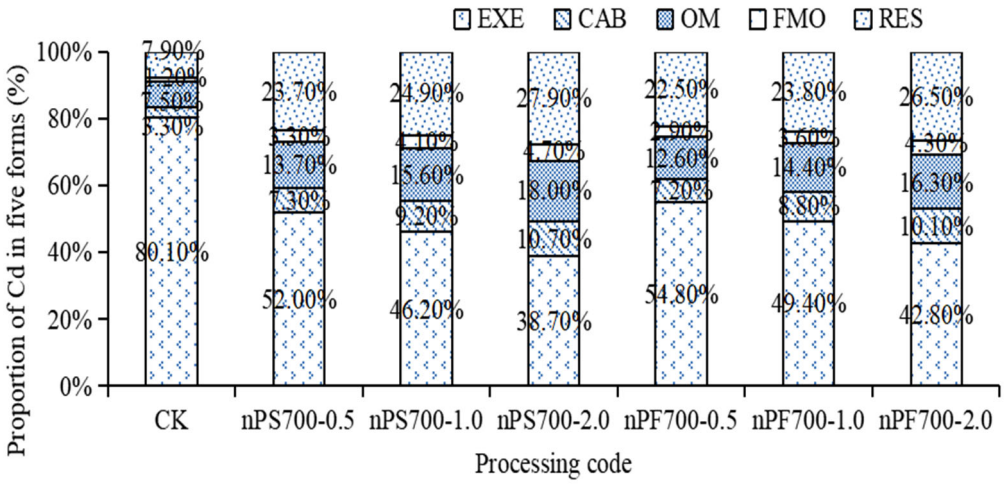

Figure 6. Effects of phosphate and thermo-activated nano silicate combined application on the proportion of Cd in soil after 56 d of culture.

3.7. Comparative Analysis between This Study and Other Studies

Wang et al. [35] explored the effects of different doses (1%, 3%, and 5% of soil weight) of thermo-activated serpentine on the occurrence of cadmium in soil contaminated by exogenous Cd, indicating that the proportion of exchangeable Cd in the soil decreased by 24.26~39.34% and the content of residual Cd increased by 10.61~12.66%.

Cao et al. [40] fixed Cd in simulated contaminated soil with thermo-activated serpentine. Under the same treatment conditions, compared with the CK treatment, adding S700 (serpentine activated at 700 °C) reduced the exchangeable Cd content by 23.76~36.49% and increased the carbonate-bound, iron-manganese oxide-bound, organic matter-bound, and residual Cd by 6.03~8.03%, 6.05~8.35%, 0.49~0.54%, and 11.17~19.58%, respectively.

Li et al. [47] added zeolite to simulated Cd-contaminated soil, which significantly reduced the exchangeable Cd content in soil by 26.50% compared with the control. The carbonate-bound and residual Cd contents increased and the organic-bound Cd content was slightly lower than with the control CK treatment.

Compared with other research results, this experimental study showed that treatment with phosphates and thermo-activated nano silicates has great potential for the immobilization of Cd in soil.

4. Discussion of the Mechanism Underlying the Ability of Phosphate and Thermo-Activated Nano Silicate Combined Application to Repair Cd Pollution

Potassium dihydrogen phosphate is a strong base and weak acid salt, and its effect after entering the soil is mainly reflected in the following aspects: firstly, it mainly exists in the form of $H_2PO_4^-$ after entering the soil solution, and OH^- can be resolved from the soil colloid through ion exchange, thereby resulting in an increase in soil pH [48], precipitation with Cd^{2+}, and removal of heavy metal Cd. Secondly, KH_2PO_4 in the soil exists in the form of ions, and the particle size of the ion is smaller than the pore size of zeolite (or serpentine). When the zeolite (or serpentine) is in contact with KH_2PO_4 solution, some ions will enter the zeolite (or serpentine) aperture and be adsorbed by the zeolite (or serpentine). Thirdly, when zeolite (or serpentine) is applied to soil, due to the high pH of the mineral itself, the soil environmental pH will increase, $H_2PO_4^-$ will be converted into PO_4^{3-}. PO_4^{3-} is the bridge between the soil surface and Cd^{2+}, producing the S-L-Mn^+ adsorption mode (S, L, and Mn^+ represent the soil surface, PO_4^{3-}, and metal ions, respectively) [49]. After PO_4^{3-} is adsorbed on the soil surface, the amount of negative charge on the surface increases, which is conducive to the non-obligate adsorption of positively charged Cd^{2+}, and the increased net surface charge also promotes continuous adsorption of Cd^{2+} by the soil via electrostatic adsorption [50].

Zeolite is a kind of shelf-like aluminosilicate mineral, which increases the cation exchange capacity of soil and enhances the adsorption capacity of heavy metal ions after being applied to the soil [51]. Ca^{2+}, Mg^{2+}, and Fe^{3+} in zeolite react with phosphate to form precipitates, and ligand exchange occurs between hydroxyl groups in Si-OH on the zeolite surface and phosphate radicals, leading to a large amount of OH^- entering the soil solution [52], which competes with PO_4^{3-} on the adsorption site. Compared with OH^- and PO_4^{3-}, Al^{3+} is more likely to precipitate with OH^-, when the amount of Al^{3+} is excessive, excess Al^{3+} will form precipitates with PO_4^{3-}. The solubility product constant of $Al(OH)_3$ is 1.3×10^{-33}, which is smaller than that of $AlPO_4$ (6.3×10^{-19}), so $Al(OH)_3$ more easily generates precipitates than $AlPO_4$. Compared with OH- and PO_4^{3-}, Cd^{2+} is more likely to form precipitates with PO_4^{3-}. When the amount of Cd^{2+} is excessive, excessive Cd^{2+} will form precipitates with OH^-. The solubility product constant of $Cd_3(PO_4)_2$ is 2.53×10^{-33}, which is much smaller than that of $Cd(OH)_2$ (5.27×10^{-15}), so $Cd_3(PO_4)_2$ more easily generates precipitates than $Cd(OH)_2$. In the same way, it can be seen that $Al(OH)_3$ more easily precipitates than $Cd(OH)_2$, and $Cd_3(PO_4)_2$ is more likely to form precipitates than $AlPO_4$. In summary, the sequence of precipitation formation is $Al(OH)_3$, $Cd_3(PO_4)_2$, $AlPO_4$, and $Cd(OH)_2$.

Serpentine is a kind of layered magnesium silicate mineral, which has a significant adsorption effect on various heavy metal ions. The adsorption of heavy metals by serpentine mainly depends on OH^- and the unsaturated Si-O-Si bonds of serpentine. The oxygen in the Si-O-Si bond exposed by nano treatment of serpentine combines with Cd^{2+} to stabilize heavy metal Cd. The OH^- in the serpentine magnesia octahedron is easier to dissociate than Mg^{2+}, making the surface of serpentine positively charged [53,54]. Mg^{2+} reacts with

phosphate to form complexes or MgO reacts with CO_2 to form $MgCO_3$ [55,56]. With continuous dissociation, OH^- levels in the solution increase, which produces competitive adsorption with PO_4^{3-} and CO_3^{2-}. Comparing OH^-, PO_4^{3-}, and CO_3^{2-}, Mg^{2+} is more likely to form soluble complexes or precipitates with PO_4^{3-}. When the amount of Mg^{2+} is excessive, the excessive Mg^{2+} will form precipitated $Mg(OH)_2$ with OH^-, and then form $MgCO_3$ with CO_3^{2-}. The solubility product constant of $Mg_3(PO_4)_2$ is 1.04×10^{-24}, which is less than that of $Mg(OH)_2$ (1.8×10^{-11}) and $MgCO_3$ (6.82×10^{-6}), so the order of the formation of precipitation is $Mg_3(PO_4)_2$, $Mg(OH)_2$, and $MgCO_3$. Comparing OH^-, PO_4^{3-}, and CO_3^{2-}, Cd^{2+} is more likely to form precipitates with PO_4^{3-}. When the amount of Cd^{2+} is excessive, excessive Cd^{2+} will form precipitated $Cd(OH)_2$ with OH^-, and then form $CdCO_3$ with CO_3^{2-}. The solubility product constant of $Cd_3(PO_4)_2$ is 2.53×10^{-33}, which is much smaller than that of $Cd(OH)_2$ (5.27×10^{-15}) and $CdCO_3$ (1.0×10^{-12}), so the sequence of the formation of precipitation is $Cd_3(PO_4)_2$, $Cd(OH)_2$, and $CdCO_3$. Similarly, it can be seen that $Cd_3(PO_4)_2$ more easily form precipitates than $Mg_3(PO_4)_2$, $Cd(OH)_2$ is more likely to form precipitates than $Mg(OH)_2$, and $CdCO_3$ is more likely to form precipitates than $MgCO_3$. In other words, the sequence of precipitation formation is $Cd_3(PO_4)_2$, $Mg_3(PO_4)_2$, $Cd(OH)_2$, $Mg(OH)_2$, $CdCO_3$, and $MgCO_3$.

In conclusion, potassium dihydrogen phosphate, zeolite, and serpentine can stabilize heavy metal cadmium to varying degrees, thereby adsorbing and precipitating it in the environment. The application of phosphate and silicate can stabilize heavy metal cadmium, but the application amount should also be appropriate since excessive application will cause a series of problems, such as economic burden and soil compaction. The next focus of this research will be on moving from the laboratory simulation to the field in order to explore the effects and problems generated in actual production and find the best method to control heavy metal cadmium pollution.

5. Conclusions

This paper conducted indoor tests of remediation of simulated Cd-contaminated soil through the combined application of phosphate and thermo-activated nano silicate, analyzing the effects of the combined application of phosphate and thermo-activated nano serpentine and the combined application of phosphate and thermo-activated nano zeolite on the five forms of Cd. The following conclusions can be drawn:

1. The effect of phosphate and thermo-activated nano silicate combined application on the form of heavy metal Cd in soil is mainly as follows: the content of exchangeable Cd was reduced and converted into carbonate bound form, Fe-Mn oxide bound form, organic bound form and the residual form Cd content, indicated that the combined application of phosphate and thermo-activated nano silicate can stabilize heavy metals and reduce the bioavailability of heavy metal Cd.
2. When phosphate and thermo-activated nano silicate were applied together, the heavy metal Cd content in soil changed from a biologically available state to a biologically unusable state with increasing culture time and application dose level. For the same incubation time, the order of the effect of potassium dihydrogen phosphate and thermo-activated nano serpentine on remediation of Cd-contaminated soil was: nPS_{700}-2.0 > nPS_{700}-1.0 > nPS_{700}-0.5. The order of the effect of the combined application of potassium dihydrogen phosphate and thermo-activated nano zeolite on the remediation of Cd-contaminated soil was: nPF_{700}-2.0 > nPF_{700}-1.0 > nPF_{700}-0.5. At the same dose level, compared with the combined application of potassium dihydrogen phosphate and thermo-activated nano zeolite, the combined application of potassium dihydrogen phosphate and thermo-activated nano serpentine was more effective in the remediation of Cd-contaminated soil (nPS_{700}-2.0 > nPF_{700}-2.0, nPS_{700}-1.0 > nPF_{700}-1.0, nPS_{700}-0.5 > nPF_{700}-0.5), and the nPS_{700}-2.0 treatment was more effective than the nPF_{700}-2.0 treatment in the remediation of Cd-contaminated soil.
3. The effects of potassium dihydrogen phosphate, zeolite, and serpentine after entering the soil are mainly reflected in the following aspects: first, potassium dihydrogen

phosphate mainly exists in the form of $H_2PO_4^-$ after entering the soil solution. OH^- can be exchanged and resolved from the soil colloid, and the hydroxyl groups in Si-OH on the zeolite surface can be exchanged with PO_4^{3-}, which makes OH^- enter the soil solution. After nano treatment of serpentine, the combination of oxygen in the Si-O-Si bond with Cd^{2+} can stabilize heavy metal Cd, while OH^- in the serpentine magnesia octahedron is easier to dissociate than Mg^{2+}. Second, KH_2PO_4 in the soil exists in the form of ions, and the particle size of the ions is smaller than the pore size of the silicate minerals, so some ions will enter the pores of the silicate minerals and be adsorbed by the silicate minerals. Third, after silicate minerals are applied to the soil, due to the high pH of the minerals themselves, the pH of the soil environment will increase and $H_2PO_4^-$ will be converted into PO_4^{3-}. PO_4^{3-} is the bridge between the soil surface and Cd^{2+}. As the soil surface adsorbs PO_4^{3-}, the negative charge on the surface increases, which is conducive to the non-specific adsorption of Cd^{2+}. Additionally, the increased net surface charge promotes the continuous adsorption of Cd^{2+} by the soil via electrostatic adsorption. To sum up, the combined application of potassium dihydrogen phosphate and thermo-activated nano serpentine and the combined application of potassium hydrogen phosphate and thermo-activated nano zeolite can repair cadmium pollution.

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