

Article

Effect of Thermal Activation Temperature of Nanoscale Phosphate and Silicate on the Morphological Transformation Characteristics of Cd in Heavy Metal Contaminated Soils

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Abstract: Purpose. The problem of heavy metal Cd pollution in the soil is still very serious. The widely used treatment measure is in situ passivation chemical remediation technology. Some studies have shown that the single application of phosphate or silicate can control soil cadmium pollution, but few studies have been conducted on the effect of the thermal activation temperature of nano phosphate and silicate-combined application on the transformation of Cd form in the soil. Materials and methods. Cadmium-contaminated soil was indoor-simulated, after which the 2.0% soil-weight dose of potassium dihydrogen phosphate was mixed with thermal activation nano serpentine or nano zeolite (potassium dihydrogen phosphate: thermal activation nano serpentine or nano zeolite = 1:2) at different temperatures (0, 350, 550, 700, 850 °C) and compared with the simulated cadmium-contaminated soil without adding a mixture of phosphate and silicate; cadmium content in soil was determined by Tessier five-step continuous extraction method after incubating for 0, 7, 14, 28, and 56 d in jars in the constant-temperature box. Results and discussion. Thermal activation temperature of nano phosphate and silicate could reduce the amount of exchangeable Cd content in the soil to a different degree; the content of Cd in carbonate-bound form, Fe–Mn–oxide-bound form, organically-bound form, and residual form increased. The order of effect of nanoscale potassium dihydrogen phosphate and serpentine or zeolite thermal activation temperature on remediation of Cd contaminated soil is nPS_{700-2.0} > nPS_{550-2.0} > nPS_{850-2.0} > nPS_{350-2.0} > nPS_{0-2.0}, nPF_{700-2.0} > nPF_{550-2.0} > nPF_{850-2.0} > nPF_{350-2.0} > nPF_{0-2.0} (n, P, S, and F represent nanometer, KH₂PO₄, serpentine, and zeolite, respectively; 0, 350, 550, 700, and 850 represent different activation temperatures T); 700 °C treatments performed better than other thermal activation temperature treatments, and nPS_{700-2.0} was better than nPF_{700-2.0}. Conclusion. Thermal activation temperature of nano phosphate and silicate-combined application can stabilize heavy metal Cd to some extent and promote the transition of Cd from a bioavailable state to a biounavailable state. The results showed that the combined application of thermal activation temperature of nano phosphate and silicate has a certain potential to control soil cadmium pollution.

Keywords: potassium dihydrogen phosphate; serpentine; zeolite; thermal activation temperature; nanomaterials; Cd form



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1. Introduction

Agricultural soil condition in China is generally stable, but heavy metal, among which Cd is one of the primary pollutants, showed in <2019 Report on the State of the Ecology and Environment in China> issued by the Ministry of Ecology and Environment, together with more than 10 departments including the National Development and Reform Commission and the Ministry of Natural Resources in May 2020 [1]. Heavy metal cadmium pollution

has been a serious environmental and agricultural issue. Therefore, immobilization of Cd(II) in the soil is crucial [2].

In situ passivation chemical remediation technology has the characteristics of simple operation and economic efficiency and is suitable for remediation of heavy metal contaminated soil in a large area; it is considered to be an effective treatment method for Cd contaminated soil in accordance with China's national conditions [3–8]. Commonly used remediation materials mainly include phosphate [9–21] (potassium dihydrogen phosphate, apatite, and phosphate powder, etc.) and silicate minerals (zeolite [22–37], serpentine [38–40], etc.). The adsorption of heavy metals by natural silicate minerals is limited. It is found that high-temperature thermal activation treatment can be used to increase its adsorption capacity and adsorption ability; otherwise, nano treatment can be carried out to increase its specific surface area and accelerate the suction rate. Nanomaterials and nanotechnologies are the most promising materials and technologies in the 21st century. Therefore, this study adopted thermal activation treatment of nano silicate mineral materials to treat soil contaminated by heavy metal Cd.

It was found that phosphate could precipitate with heavy metals under certain conditions [3,7,13], silicate minerals could adsorb heavy metals [22,29,38], and silicate minerals could also adsorb phosphate [41–43]. So far, potassium dihydrogen phosphate, serpentine, and zeolite applied alone could react with heavy metals and stabilize heavy metal Cd. However, there are few reports on the application of potassium dihydrogen phosphate with serpentine and zeolite on Cd-contaminated soil. Therefore, this study investigated the effects of potassium dihydrogen phosphate combined with thermal-activated nano serpentine and thermal-activated nano zeolite on Cd morphological transformation characteristics of contaminated soil in order to provide a theoretical basis for phosphate and silicate minerals to reduce heavy metal migration and bioavailability and to repair and utilize heavy metal Cd-contaminated soils.

2. Materials and Methods

2.1. Experimental Materials

Experimental soils. The soil samples were collected from the 0–20 cm soil layer of uncontaminated farmland in Shenyang Agricultural University Scientific Research Base (123°56' E, 41°82' N, 43 m above sea level), Shenyang City, Liaoning Province, and the soil type was brown soil. After the soil samples were collected, they were naturally air-dried, mixed, ground, sieved through 2 mm, and stored in zip-lock bags for future use. The basic physical and chemical characteristics of tested soil, which were analyzed according to the method of the literature [44], are listed in Table 1. The composition and content of the tested soil, zeolite, and serpentine are shown in Table 2.

Table 1. Physical and chemical properties of the tested soil.

Soil Type	pH	Organic Matter (g·kg ⁻¹)	Alkali- Hydrolyzable Nitrogen (mg·kg ⁻¹)	Available Phosphorus (mg·kg ⁻¹)	Available Potassium (mg·kg ⁻¹)	Total Phosphorus (g·kg ⁻¹)	Total Cadmium (mg·kg ⁻¹)
brown soil	5.71	26.93	50.02	71.27	183.59	0.63	0.18

Table 2. The main components and content of the tested soil, zeolite, and serpentine.

Composition	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	CaO	Na ₂ O	Fe ₂ O ₃	P ₂ O 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

Cd-contaminated soil. Accurately weighed 50.0 g of the test soil into a clean jar and added $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (AR) to the test soil in the form of a solution, so that the exogenous Cd content in the soil reached $10 \text{ mg} \cdot \text{kg}^{-1}$. After the soil was fully mixed with the $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ solution, it was cultivated at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$) for one week, while the soil water content was maintained by weighing method to 70% of the field water-holding capacity, and then the treated soil was dried, ground, stored, and set aside.

Natural nano serpentine and zeolite for testing. The natural nano serpentine and zeolite for testing were collected from Liaoning, crushed into 600 nm powder by high-energy nano impact grinding, put into self-sealing bags, stored in a dryer, and set aside. The main composition and content of the natural nano serpentine and zeolite are shown in Table 2.

Thermal-activated nano serpentine. The 600 nm natural nano serpentine powder was put into a crucible and calcined in a muffle furnace at 0, 350, 550, 700, and 850 $^\circ\text{C}$ for 2 h at a constant temperature. After the serpentine had cooled to room temperature, the serpentine was taken out, put in zip-lock bags, and stored in a desiccator. The resulting thermal-activated nano serpentine was briefly recorded as nS_T , n represented nano treated, S represented serpentine, and T represented the activation temperature, that was nS_0 , nS_{350} , nS_{550} , nS_{700} , nS_{850} , representing 0, 350, 550, 700, and 850 $^\circ\text{C}$ thermal-activated nano serpentine, respectively.

In the same way, thermal-activated nano zeolite was produced. The resulting heat-activated nano zeolite was simply noted as nF_T , n represented nano treated, F represented zeolite, and T represented the activation temperature, which was nF_0 , nF_{350} , nF_{550} , nF_{700} , nF_{850} , representing 0, 350, 550, 700, and 850 $^\circ\text{C}$ thermal-activated nano zeolite, respectively.

Phosphate for the test. KH_2PO_4 (Analytical Reagent) is denoted as P.

2.2. Experimental Designs

In this experiment, a total of 11 treatments were designed by the indoor culture method, and the ratio of phosphate to silicate in different treatments is shown in Table 3. Three replicates were set for each treatment, namely: simulated Cd-contaminated soil without added phosphate and silicate was recorded as the reference (CK) treatment; the Cd-contaminated soil with the addition of 2.0% soil weight dose of potassium dihydrogen phosphate mixture with different thermal-activated nano serpentine (potassium dihydrogen phosphate: different nano serpentine = 1:2) was recorded as $\text{nPS}_T\text{-2.0}$, where T (0, 350, 550, 700, 850) was the thermal activation temperature of serpentine. Similarly, the Cd-contaminated soil with the mixture of potassium dihydrogen phosphate and different thermal-activated nano zeolites (Potassium dihydrogen phosphate: different nano zeolite = 1:2) blended at 2.0% soil weight was recorded as $\text{nPF}_T\text{-2.0}$, where T (0, 350, 550, 700, 850) was the thermal activation temperature of zeolite. We made sure all mixtures were mixed well and then accurately weighed 50.0 g of each of the above-mentioned soils with different treatments and put them into jars. The jars were placed in a thermotank and cultivated at $25 \pm 2 \text{ }^\circ\text{C}$, and the soil water content was maintained at 70.0% of the field water-holding capacity by using deionized water every other day according to the weighing method. At the 0, 7, 14, 28, and 56 days of cultivating, an appropriate amount of naturally air-dried and ground soil samples were weighed, and the content of five forms of soil Cd was determined by Tessier five-step continuous extraction method.

Table 3. Scheme of the ratio of potassium dihydrogen phosphate combined with thermos-activated nano serpentine and thermo-activated nano zeolite (treatment dosage, %).

Sample	KH_2PO_4 (%)	Serpentine					Zeolite				
		0 $^\circ\text{C}$ (%)	350 $^\circ\text{C}$ (%)	550 $^\circ\text{C}$ (%)	700 $^\circ\text{C}$ (%)	850 $^\circ\text{C}$ (%)	0 $^\circ\text{C}$ (%)	350 $^\circ\text{C}$ (%)	550 $^\circ\text{C}$ (%)	700 $^\circ\text{C}$ (%)	850 $^\circ\text{C}$ (%)
CK	0	0	0	0	0	0	0	0	0	0	0
$\text{nPS}_T\text{-2.0}$	0.67	1.33	1.33	1.33	1.33	1.33					
$\text{nPF}_T\text{-2.0}$	0.67						1.33	1.33	1.33	1.33	1.33

2.3. Measurement Indicators and Methods

The analysis of different morphological contents of Cd in soil was carried out using the Tessier continuous extraction method [45]. The Cd content in the soil was measured by atomic absorption spectrophotometer (AAS).

2.4. Data Processing and Analysis

Microsoft Excel 2003 and Origin 8.0 software were used to analyze and graph data. Both the data significance test and the correlation analysis were performed by SPSS 17.0 statistical software ($p < 0.05$).

3. Results and Analysis

The biotoxicity of heavy metals in soils 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 [46–50]. The Tessier five-step sequential extraction method for the determination of heavy metal Cd forms used in this experiment consists of five forms, namely exchangeable (EXE), carbonate-bound (CAB), organically-bound (OM), iron–manganese–oxide-bound (FMO), and residue (RES).

3.1. Effect of Thermal Activation Temperature of Nanoscale Phosphate and Silicate on the Exchangeable Cd Content of Soils

The changes in the soil EXE Cd content of potassium dihydrogen phosphate at a 2.0% dose level and nano serpentine at different thermal activation temperatures are shown in Figure 1. As can be seen from the graph, both potassium dihydrogen phosphate and nano serpentine at different thermal activation temperatures reduced the EXE Cd content compared to CK. Compared to CK, soil EXE Cd content was reduced by 1.18, 1.42, 2.34, 2.60, and 2.10 units at 0 d incubation for nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 treatments, respectively; at 56 d incubation for nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 treatments reduced soil EXE Cd content by 1.55, 1.93, 3.33, 4.14 and 2.89 units, respectively; the same treatment, different incubation periods, slightly reduced soil EXE Cd content. From 0–56 d of incubation, the EXE Cd content was reduced by 0.37 mg·kg⁻¹ in the CK treatment and by 0.74, 0.88, 1.36, 1.91, and 1.16 mg·kg⁻¹ in the nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 treatments, respectively.

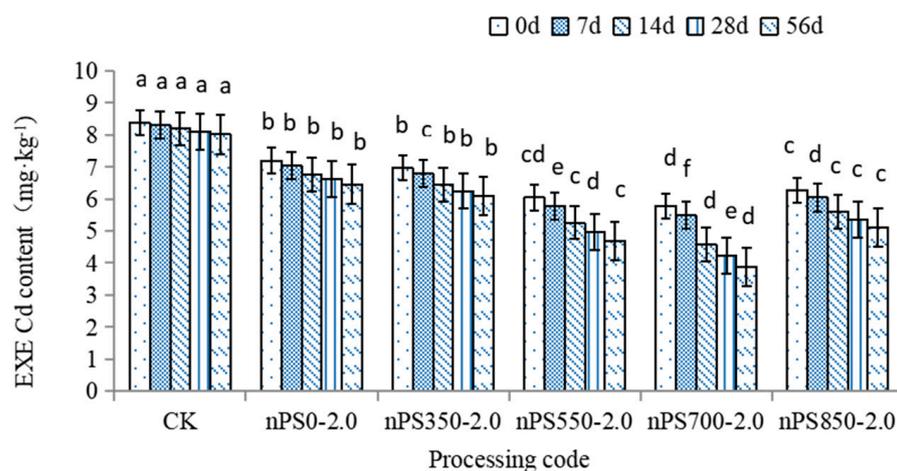


Figure 1. Effect of thermal activation temperature of nanoscale potassium dihydrogen phosphate and serpentine on the exchangeable Cd content of soils. Different lower-case letters marked in Figure 1 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

The changes in the soil EXE Cd content of potassium dihydrogen phosphate at a 2.0% dose level and nano zeolite at different thermal activation temperatures are shown in Figure 2. As can be seen from the graph, the application of potassium dihydrogen phosphate with nano zeolites at different thermal activation temperatures reduced the EXE

Cd content compared to CK. Compared to CK, the soil EXE Cd content was reduced by 1.13, 1.29, 2.10, 2.40, and 1.88 units at 0 d incubation for nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, respectively, and nPF₈₅₀-2.0 treatments; at 56 d incubation for nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 treatments reduced soil EXE Cd content by 1.39, 1.71, 2.93, 3.73 and 2.52 units, respectively, under the same treatment, different incubation periods, and slightly reduced soil EXE Cd content. From 0–56 d of incubation, the EXE Cd content was reduced by 0.37 mg·kg⁻¹ in the CK treatment and by 0.63, 0.79, 1.20, 1.70, and 1.01 mg·kg⁻¹ in the nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 treatments, respectively.

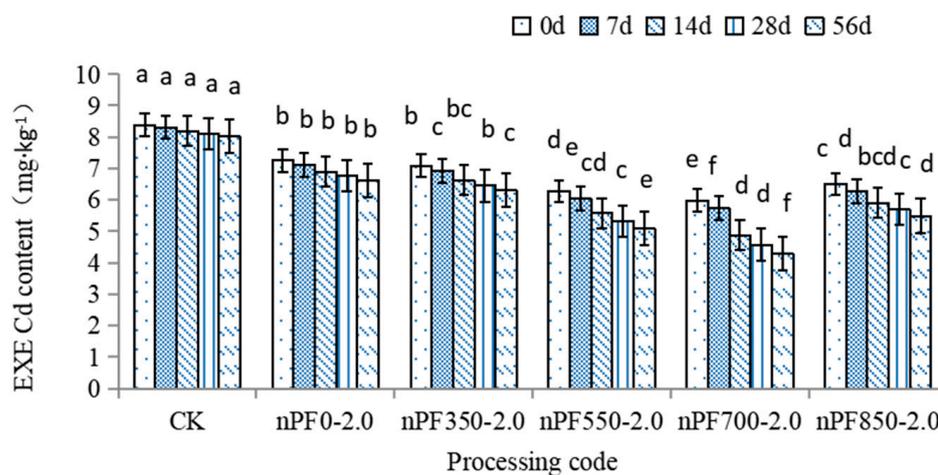


Figure 2. Effect of thermal activation temperature of nanoscale potassium dihydrogen phosphate and zeolite on the exchangeable Cd content of soils. Different lower-case letters marked in Figure 2 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

Potassium dihydrogen phosphate, together with nano serpentine and nano zeolite at different thermal activation temperatures, reduced soil EXE Cd to varying degrees. nPS₇₀₀-2.0 and nPF₇₀₀-2.0 treatments reduced EXE Cd to a greater extent than other thermal activation temperature treatments, and nPS₇₀₀-2.0 was more effective than nPF₇₀₀-2.0 in reducing EXE Cd. It is possible that serpentine can reduce EXE Cd content after thermal activation nano treatment because thermal activation breaks the O–Si–O bond and generates free oxygen, which, in turn, increases the active adsorption sites and effectively raises the soil pH. As the thermal activation temperature increases, the specific surface area of serpentine increases accordingly, enhancing the adsorption capacity of Cd, but it is not the case that the higher the thermal activation temperature is, the better it is. If the temperature is too high, it will cause the pore structure of the serpentine crystal to collapse and reduce the adsorption capacity of Cd.

3.2. Effect of Thermal Activation Temperature of Nanoscale Phosphate and Silicate on the Carbonate-Bound Cd Content of Soils

The changes in the soil CAB Cd content of potassium dihydrogen phosphate at a 2.0% dose level and nano zeolite at different thermal activation temperatures are shown in Figure 3. As can be seen from the graph, the CAB Cd content was slightly increased for the same treatment and for different incubation periods. Compared to 0 d of incubation, at 7 d, 14 d, 28 d, and 56 d of incubation, the content of soil CAB Cd in CK treatment increased by 0.01, 0.03, 0.04, and 0.06 mg·kg⁻¹; in nPS₀-2.0 treatment it increased by 0.05, 0.11, 0.14, and 0.17 mg·kg⁻¹, and in nPS₃₅₀-2.0 treatment it increased by 0.05, 0.11, 0.15, and 0.18 mg·kg⁻¹, respectively. The content of soil CAB Cd in nPS₅₅₀-2.0 treatment increased by 0.05, 0.12, 0.17, and 0.21 mg·kg⁻¹, respectively. The content of soil CAB Cd in nPS₇₀₀-2.0 treatment increased by 0.06, 0.15, 0.21, and 0.26 mg·kg⁻¹, respectively, and the content of soil CAB Cd in nPS₈₅₀-2.0 treatment increased by 0.05, 0.12, 0.17, and 0.21 mg·kg⁻¹, respectively, among

which the content of soil CAB Cd in nPS₇₀₀-2.0 treatment increased the most. Compared to CK, the CAB Cd content increased to different degrees in different thermal activation temperature treatments during the same incubation period. Compared to CK, the soil CAB Cd content of nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 treatments increased by 58.75%, 59.76%, 65.98%, 69.16%, and 64.52%, respectively, at 56 d of incubation.

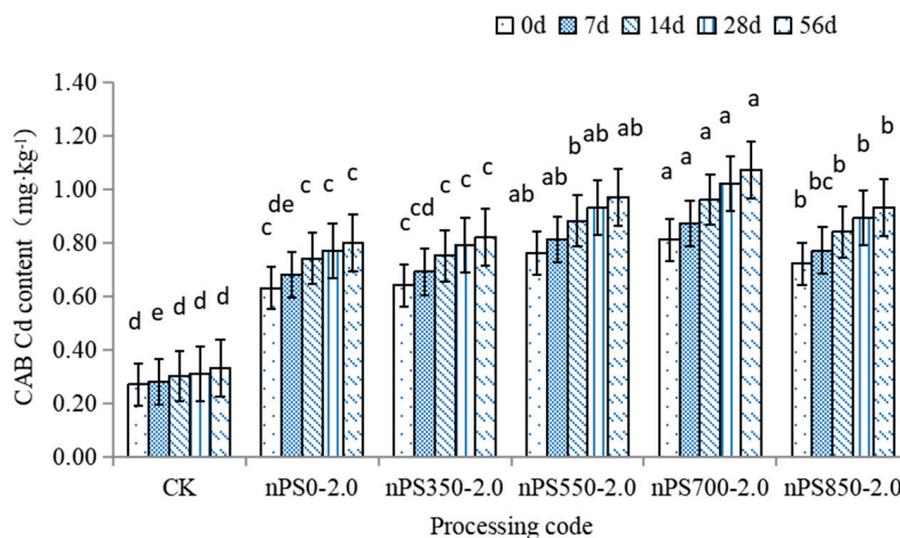


Figure 3. Effect of thermal activation temperature of nanoscale potassium phosphate and serpentine on the carbonate-bound Cd content of soils. Different lower-case letters marked in Figure 3 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

The changes in the soil CAB Cd content of potassium dihydrogen phosphate at a 2.0% dose level and nano zeolite at different thermal activation temperatures are shown in Figure 4. As can be seen from the graph, the CAB Cd content was slightly increased for the same treatment and for different incubation periods. Compared to 0 d of incubation, at 7 d, 14 d, 28 d, and 56 d of incubation, the content of soil CAB Cd in CK treatment increased by 0.01, 0.03, 0.04, and 0.06 $\text{mg}\cdot\text{kg}^{-1}$, respectively; in nPS₀-2.0 treatment it increased by 0.04, 0.09, 0.11, and 0.15 $\text{mg}\cdot\text{kg}^{-1}$, respectively, and in nPS₃₅₀-2.0 treatment it increased by 0.05, 0.10, 0.13, and 0.17 $\text{mg}\cdot\text{kg}^{-1}$, respectively. The content of soil CAB Cd in nPS₅₅₀-2.0 treatment increased by 0.05, 0.12, 0.17, and 0.21 $\text{mg}\cdot\text{kg}^{-1}$, respectively; the content of soil CAB Cd in nPS₇₀₀-2.0 treatment increased by 0.05, 0.13, 0.19, and 0.23 $\text{mg}\cdot\text{kg}^{-1}$, respectively, and the content of soil CAB Cd in nPS₈₅₀-2.0 treatment increased by 0.05, 0.11, 0.15, and 0.19 $\text{mg}\cdot\text{kg}^{-1}$, respectively, among which the content of soil CAB Cd in nPS₇₀₀-2.0 treatment increased the most. Compared with CK, the CAB Cd content increased to different degrees in different thermal activation temperature treatments during the same incubation period. At 56 d of incubation, the soil CAB Cd content increased by 57.69%, 57.69%, 64.13%, 67.33%, and 61.63% in the nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 treatments, respectively.

Potassium dihydrogen phosphate, together with nano serpentine and nano zeolite at different thermal activation temperatures, increased soil CAB Cd to varying degrees, and the former increased the CAB Cd content more than the latter. nPS₇₀₀-2.0 and nPF₇₀₀-2.0 treatments increased the CAB Cd content more than the other thermal activation temperature treatments, and nPS₇₀₀-2.0 increased the CAB Cd content more significantly than the nPF₇₀₀-2.0 treatment. The key to the elevated CAB Cd content of potassium dihydrogen phosphate in combination with thermally activated nano serpentine and thermally activated nano zeolite is in the presence of OH⁻, with which Cd²⁺ reacts to form Cd(OH)₂, which readily absorbs CO₂ and becomes a CdCO₃ precipitate; Cd²⁺ also reacts directly with CO₃²⁻ in the soil to form a CdCO₃ precipitate, resulting in an elevated CAB Cd content.

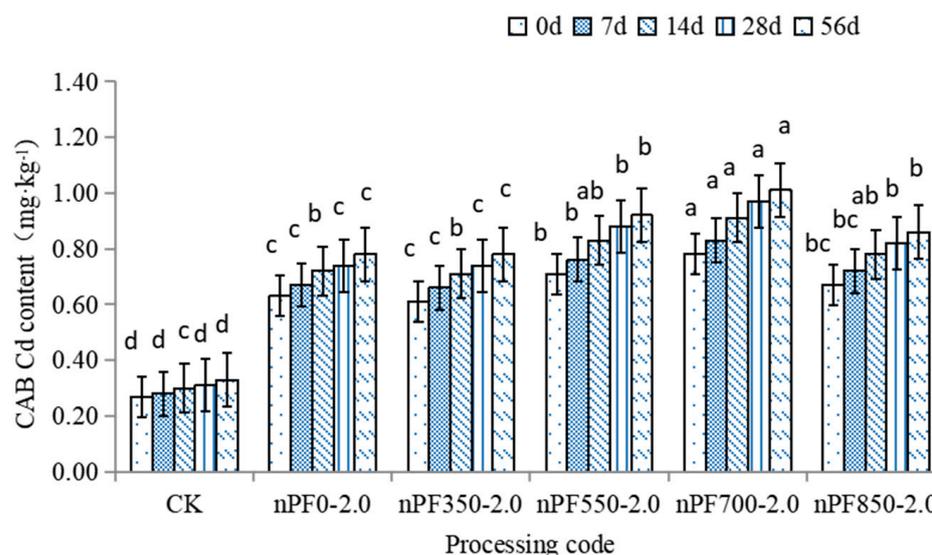


Figure 4. Effect of thermal activation temperature of nanoscale potassium dihydrogen phosphate and zeolite on the carbonate-bound Cd content of soils. Different lower-case letters marked in Figure 4 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

3.3. Effect of Thermal Activation Temperature of Nanoscale Phosphate and Silicate on the Organically-Bound Cd Content of Soils

The effects of a 2.0% dose level of potassium dihydrogen phosphate and nano serpentine at different thermal activation temperatures on the Cd content of soil organic matter are shown in Figure 5. It can be seen from the figure, with the increase in culture time, the content of Cd in soil organic matter increased slightly in CK treatment, Cd content in soil organic matter treated with potassium dihydrogen phosphate and nano serpentine with different thermal activation temperatures increased gradually, and both of them increased significantly compared with CK treatment. When cultured for 0 days, the Cd content of soil organic matter in nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 was 0.43 units, 0.48 units, 0.61 units, 0.63 units, 0.59 units higher than that in CK treatment. After 14 days of incubation, the Cd content of soil organic matter treated by nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 increased by 0.51, 0.58, 0.78, 0.84, and 0.73 units compared with CK treatment. When cultured for 56 days, the Cd content of soil organic matter treated with nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 increased by 0.53, 0.62, 0.93, 1.05, and 0.83 units compared with that treated with CK. Compared with the 0-day culture, the content of Cd in soil organic matter treated with CK, nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 increased by 0.03, 0.11, 0.13, 0.20, 0.24, and 0.17 units at 14-day culture, respectively. When cultured for 56 days, the contents of OM and Cd in soil treated with CK, nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 increased by 0.07, 0.17, 0.21, 0.39, 0.49, and 0.31 units, respectively.

The changes of Cd content in soil organic matter by a 2.0% dose level of potassium dihydrogen phosphate and nano zeolite at different thermal activation temperatures are shown in Figure 6. It can be seen from the figure that with the increase in culture time, the content of Cd in soil organic matter increased slightly in CK treatment. The Cd content of soil organic matter in the treatment of potassium dihydrogen phosphate combined with nano zeolite at different thermal activation temperatures increased gradually, which was significantly higher than that in CK treatment. When cultured for 0 days, the contents of Cd in soil organic matter treated with nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 were 0.41, 0.44, 0.54, 0.55, and 0.52 units higher than those treated with CK. When cultured for 14 days, the contents of Cd in soil organic matter treated with nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 were 0.48, 0.53, 0.67, 0.71, and 0.64 units higher than those treated with CK. When cultured for 56 days, the contents of Cd in soil

organic matter treated with nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 were 0.50, 0.57, 0.81, 0.88, and 0.72 units higher than those treated with CK. Compared with 0 days, at 14 d, the Cd content of soil organic matter treated with CK, nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 increased by 0.03, 0.10, 0.12, 0.16, 0.19, and 0.15 units, respectively. At 56 d, the content of Cd in soil organic matter treated with CK, nPF₀-2.0, nPF₃₅₀-2.0, nPF₅₅₀-2.0, nPF₇₀₀-2.0, and nPF₈₅₀-2.0 increased by 0.07, 0.16, 0.20, 0.34, 0.40, and 0.27 units, respectively.

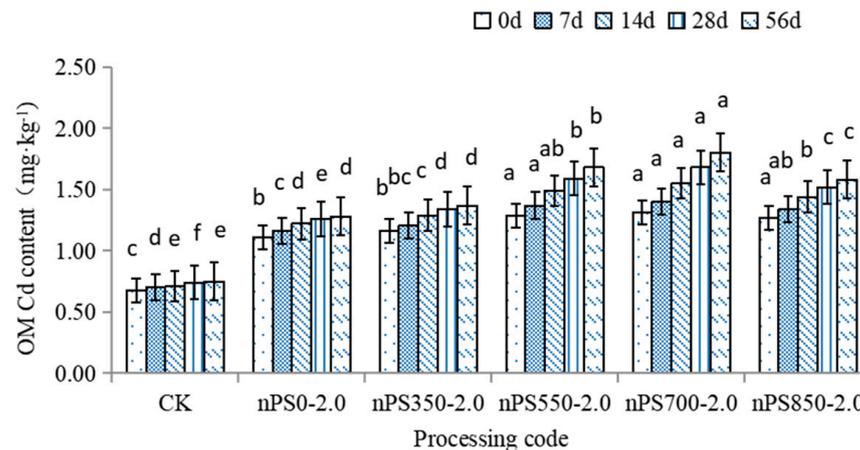


Figure 5. Effect of thermal activation temperature of nanoscale potassium phosphate and serpentine on the organically-bound Cd content of soils. Different lower-case letters marked in Figure 5 indicate a significant difference across different treatments ($n = 3, p < 0.05$).

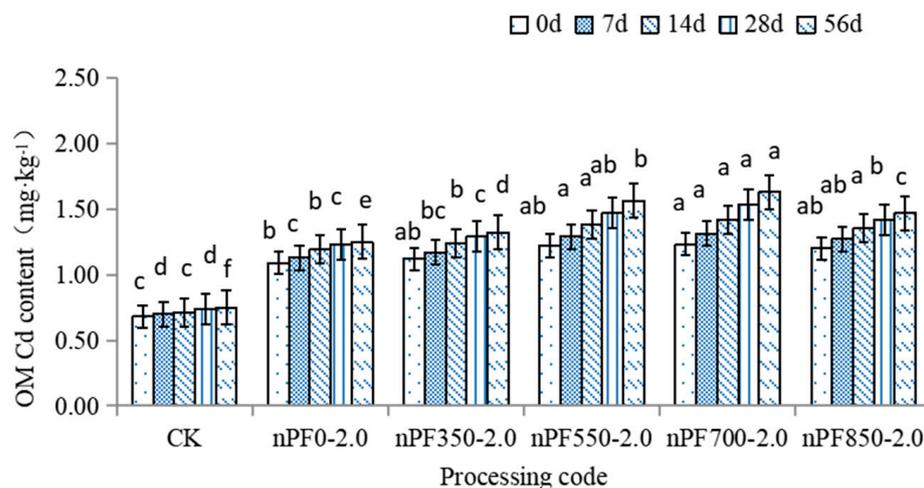


Figure 6. Effect of thermal activation temperature of nanoscale potassium dihydrogen phosphate and zeolite on organically-bound Cd content of soils. Different lower-case letters marked in Figure 6 indicate a significant difference across different treatments ($n = 3, p < 0.05$).

The changing trend of Cd content in soil organic matter treated with potassium dihydrogen phosphate and nano serpentine at different thermal activation temperatures and potassium dihydrogen phosphate combined with nano zeolite at different thermal activation temperatures is basically the same. The former can increase the content of Cd in organic matter more than the latter, but the increased range of Cd content in organic matter is small, which may be due to the limited contribution of silicate minerals. The small increase in content is due to the increase in the solubility of organic matter in soil with the increase in pH value. When the complexation ability increases, Cd is complexed to slightly increase organic matter Cd.

3.4. The Thermal Activation Temperature of Nano Phosphate and Nano Silicate Influence on Iron–Manganese–Oxide-Bound Cadmium in Soil

The effects of a 2.0% dose level of potassium dihydrogen phosphate and nano serpentine at different thermal activation temperatures on soil FMO Cd content are shown in Figure 7. It can be seen from the figure that in the same culture period, the combination of potassium dihydrogen phosphate and nano serpentine with different thermal activation temperatures can increase the content of FMO Cd, but the increase degree is different. With the increase in culture time, the increase in FMO Cd was also different. Compared with CK treatment, the soil FMO Cd content of nPS₀-2.0 treatment increased by 0.11 mg·kg⁻¹, nPS₃₅₀-2.0 treatment increased by 0.14 mg·kg⁻¹, nPS₅₅₀-2.0 treatment increased by 0.22 mg·kg⁻¹, nPS₇₀₀-2.0 treatment increased by 0.24 mg·kg⁻¹, and nPS₈₅₀-2.0 treatment increased by 0.21 mg·kg⁻¹. After 56 d of incubation, the content of FMO Cd in soil treated with nPS₀-2.0 increased by 0.17 mg·kg⁻¹, nPS₃₅₀-2.0 increased by 0.21 mg·kg⁻¹, nPS₅₅₀-2.0 increased by 0.31 mg·kg⁻¹, nPS₇₀₀-2.0 increased by 0.35 mg·kg⁻¹, and nPS₈₅₀-2.0 increased by 0.30 mg·kg⁻¹. After incubation for 0, 7, 14, 28, and 56 d, the soil FMO Cd content of nPS₀-2.0 treatment was 0.14, 0.16, 0.21, 0.24, and 0.29 mg·kg⁻¹, and that of nPS₇₀₀-2.0 treatment was 0.27, 0.32, 0.37, 0.41, and 0.47 mg·kg⁻¹. In the same treatment, the FMO Cd content increased slightly with the increase in incubation time.

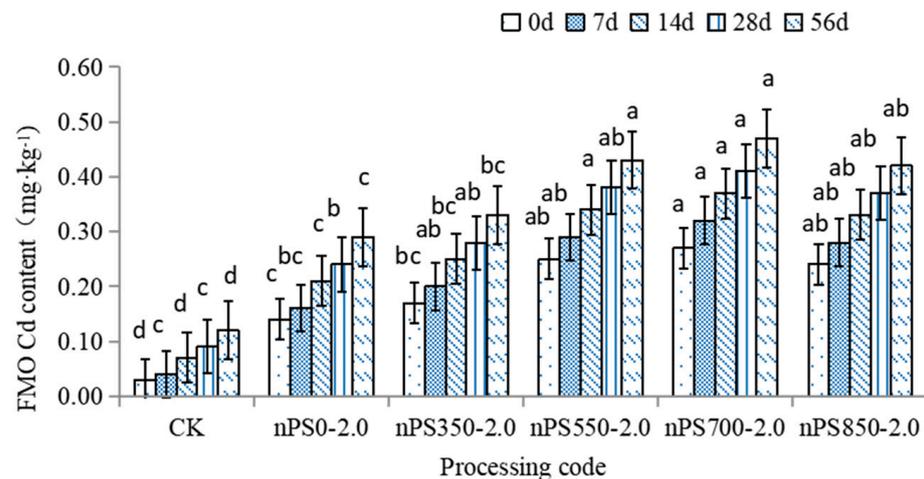


Figure 7. Effect of thermal activation temperature of nanoscale potassium phosphate and serpentine on the iron–manganese–oxide-bound Cd content of soils. Different lower-case letters marked in Figure 7 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

The changes in soil FMO Cd content by a 2.0% dose level of potassium dihydrogen phosphate and nano zeolite at different thermal activation temperatures are shown in Figure 8. It can be seen from the figure that in the same incubation period, the combination of potassium dihydrogen phosphate and nano zeolite with different thermal activation temperatures can increase the content of FMO Cd, but the increase degree is different. With the increase in culture time, the increase in FMO Cd was also different. Compared with CK treatment, the content of soil FMO Cd increased by 0.08 mg·kg⁻¹ in nPF₀-2.0 treatment, 0.11 mg·kg⁻¹ in nPF₃₅₀-2.0 treatment, 0.17 mg·kg⁻¹ in nPF₅₅₀-2.0 treatment, 0.23 mg·kg⁻¹ in nPF₇₀₀-2.0 treatment, and 0.16 mg·kg⁻¹ in nPF₈₅₀-2.0 treatment. After 56 days of incubation, the content of soil FMO Cd in nPF₀-2.0 treatment increased by 0.12 mg·kg⁻¹, nPF₃₅₀-2.0 treatment increased by 0.16 mg·kg⁻¹, nPF₅₅₀-2.0 treatment increased by 0.24 mg·kg⁻¹, nPF₇₀₀-2.0 treatment increased by 0.31 mg·kg⁻¹, and nPF₈₅₀-2.0 treatment increased by 0.23 mg·kg⁻¹. After incubation for 0, 7, 14, 28, and 56 days, the soil FMO Cd content of nPF₀-2.0 treatment was 0.11, 0.13, 0.17, 0.20, and 0.24 mg·kg⁻¹, and that of nPF₇₀₀-2.0 treatment was 0.26, 0.30, 0.35, 0.38, and 0.43 mg·kg⁻¹. In the same treatment, the FMO Cd content increased slightly with the increase in incubation time.

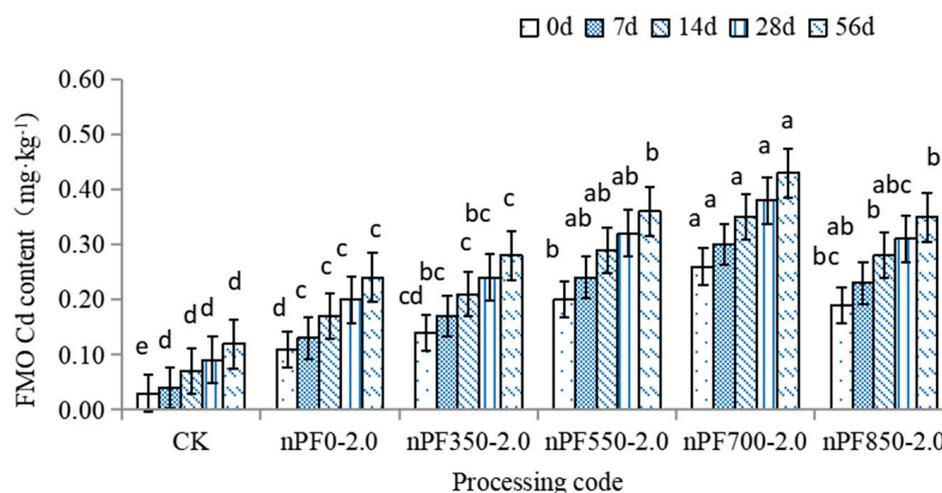


Figure 8. Effect of thermal activation temperature of nanoscale potassium phosphate and zeolite on the iron–manganese–oxide-bound Cd content of soils. Different lower-case letters marked in Figure 8 indicate a significant difference across different treatments ($n = 3$, $p < 0.05$).

Potassium dihydrogen phosphate combined with nano serpentine and nano zeolite at different thermal activation temperatures can increase the content of FMO Cd in soil, and the increase degree of the former is greater than that of the latter. The nPS₇₀₀-2.0 and nPF₇₀₀-2.0 treatments increased FMO Cd more than other thermal activation temperature treatments, and the nPS₇₀₀-2.0 treatment increased FMO Cd content more significantly than the nPF₇₀₀-2.0 treatment.

3.5. The Thermal Activation Temperature of Nano Phosphate and Nano Silicate Influence on Residue Cadmium in Soil

The changes in soil RES Cd content between potassium dihydrogen phosphate at the 2.0% dose level and nano serpentine at different thermal activation temperatures are shown in Figure 9. As can be seen from the figure, the content of RES Cd was slightly increased in the same treatment and at different incubation periods. Compared with the culture 0 d, the content of soil RES Cd in the CK treatment increased by 0.03, 0.09, 0.13, and 0.15 mg·kg⁻¹ at 7 d, 14 d, 28 d, and 56 d, respectively; the content of RES Cd in the soil treated with nPS₀-2.0 was increased by 0.04, 0.16, 0.20 and 0.25 mg·kg⁻¹; the content of RES Cd in the soil treated with nPS₃₅₀-2.0 was increased by 0.04, 0.20, 0.27, and 0.33 mg·kg⁻¹; the content of soil RES Cd treated with nPS₅₅₀-2.0 was increased by 0.09, 0.37, 0.47, and 0.58 mg·kg⁻¹; the content of RES Cd in soil treated with nPS₇₀₀-2.0 increased by 0.10, 0.72, 0.83, and 0.96 mg·kg⁻¹; the content of soil RES Cd in the nPS₈₅₀-2.0 treatment increased by 0.08, 0.29, 0.37, and 0.46 mg·kg⁻¹, respectively, and the content of RES Cd in the soil treated with nPS₇₀₀-2.0 was the most significant. Compared with CK, the content of RES Cd was increased to varying degrees during the same incubation period and under different heat activation temperatures. Compared with CK, the content of soil RES Cd treated with nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 was increased by 48.10%, 77.22%, 183.54%, 253.16%, and 146.84% at 56 d.

The changes in soil RES Cd content between potassium dihydrogen phosphate at a 2.0% dose level and nano zeolite at different thermal activation temperatures are shown in Figure 10. As can be seen from the figure, the content of RES Cd was slightly increased in the same treatment and at different incubation periods. Compared with the culture of 0 d, the content of soil RES Cd in the CK treatment increased by 0.03, 0.09, 0.13, and 0.15 mg·kg⁻¹ at 7 d, 14 d, 28 d, and 56 d, respectively; the content of RES Cd in the soil treated with nPS₀-2.0 was increased by 0.04, 0.11, 0.15, and 0.19 mg·kg⁻¹; the content of RES Cd in the soil treated with nPS₃₅₀-2.0 was increased by 0.04, 0.18, 0.24, and 0.28 mg·kg⁻¹; the content of soil RES Cd treated with nPS₅₅₀-2.0 was increased by 0.08, 0.33, 0.41, and 0.49 mg·kg⁻¹; the content of RES Cd in soil treated with nPS₇₀₀-2.0 increased by 0.07, 0.69,

0.80, and 0.90 $\text{mg}\cdot\text{kg}^{-1}$; the content of soil RES Cd in the nPS₈₅₀-2.0 treatment increased by 0.07, 0.25, 0.32, and 0.39 $\text{mg}\cdot\text{kg}^{-1}$, respectively, of which the content of soil RES Cd treated with nPS₇₀₀-2.0 was the most significantly increased. Compared with CK, the content of RES Cd was increased to varying degrees during the same incubation period and under different heat activation temperatures. Compared with CK, the content of soil RES Cd treated with nPS₀-2.0, nPS₃₅₀-2.0, nPS₅₅₀-2.0, nPS₇₀₀-2.0, and nPS₈₅₀-2.0 was increased by 40.51%, 67.09%, 163.29%, 235.44%, and 131.65% at 56 d.

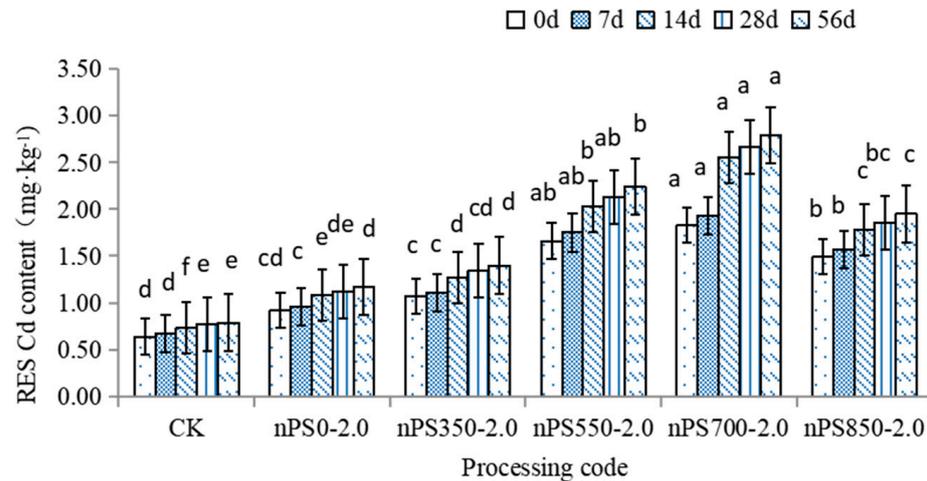


Figure 9. Effect of thermal activation temperature of nanoscale potassium phosphate and serpentine on residue Cd content of soils. Different lower-case letters marked in Figure 9 indicate a significant difference across different treatments ($n = 3, p < 0.05$).

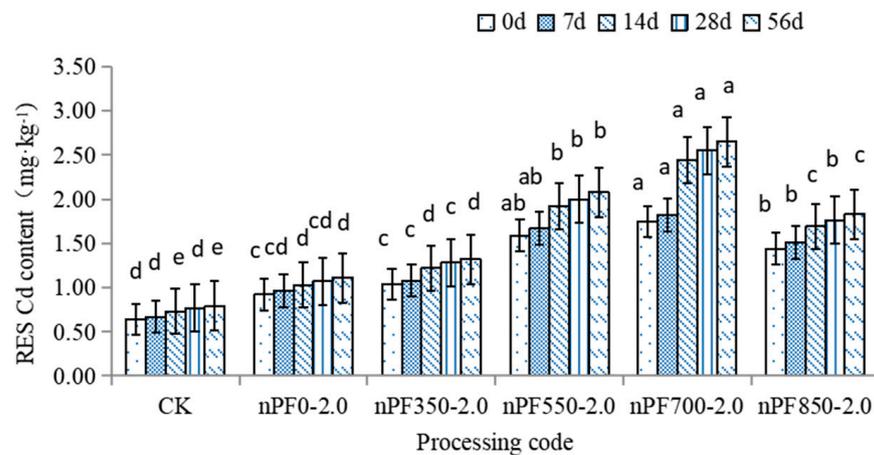


Figure 10. Effect of thermal activation temperature of nanoscale potassium phosphate and zeolite on residue Cd content of soils. Different lower-case letters marked in Figure 10 indicate a significant difference across different treatments ($n = 3, p < 0.05$).

3.6. The Mechanism of Nano Phosphate and Thermal Activation Temperature Silicate Combined to Restore Cd Pollution

Potassium dihydrogen phosphate is the salt of strong alkali weak acid. After entering the soil, part of it forms a precipitate with Cd^{2+} to remove heavy metals Cd; the other part exists in the form of ions whose particle size is smaller than the pore size of the silicate minerals and is adsorbed.

Zeolite is a rack-shaped aluminosilicate mineral which can be applied to the soil to form soil aggregates and organic and inorganic complexes with soil particles, which increases the amount of soil cation exchange and has a strong adsorption capacity for heavy metal ions [51]. Ca^{2+} , Mg^{2+} , and Fe^{3+} cations in zeolite can form precipitates with

phosphate. In addition, ligand exchange can also occur between hydroxyl and phosphate in the surface Si-OH, so that OH⁻ can enter the soil solution [52]. As OH⁻ increases, H₂PO₄⁻ converts to PO₄³⁻, and OH⁻ competes with PO₄³⁻ for adsorption points. When OH⁻, PO₄³⁻, and Al³⁺ coexist with Cd²⁺, the smaller the solubility product, the more likely it is to precipitate. In other words, the first to generate is the Al(OH)₃ precipitation, followed by Cd₃(PO₄)₂, AlPO₄, and Cd(OH)₂.

Natural zeolite has a low adsorption effect on phosphates and heavy metal Cd, so high-temperature heat activation is required to improve the adsorption effect. On the one hand, heat activation can remove water molecules, carbonates, organic matter, and other impurities from zeolite holes and channels to a certain extent, which increases the inner surface area of zeolite. At the same time, the zeolite crystal cavity has a strong coulomb field and polarity inside, which improves the adsorption capacity of zeolite. On the other hand, because natural zeolite has a certain degree of heat resistance, the water in the natural zeolite is removed after high-temperature roasting, but the shape of its crystal frame structure can remain unchanged, and the empty skeleton structure will increase the amount of adsorption. Typically, zeolite is roasted at temperatures above 350 °C, and when the heat treatment temperature is below 400 °C, the structure of the zeolite is not damaged [53]. When the temperature rises to 550 °C, the pore volume can be increased, and the specific surface area and the kinematic activity of the cation can be increased. When the temperature reaches 700 °C, the structure is destroyed, and the original pores of zeolite collapse, thereby reducing the adsorption performance of zeolite. After the calcination temperature reaches 800 °C, the original structure of zeolite is more damaged, the pore structure is retained to a lesser extent, and the adsorption performance and ion exchange performance are almost lost, so the zeolite thermal activation temperature should not be higher than 700 °C.

Serpentine belongs to the TO type layered magnesium silicate mineral, and the structural unit layer consists of silicon–oxygen tetrahedron and magnesia octahedron. Natural serpentine heat activation can improve the effect of removing heavy metals [54]. Generally, adsorption water and interlayer water are removed before 500 °C, and the dihydroxy lification rate is slower. After the heat activation temperature reaches 500 °C, the main loss stage of structural water, the hydroxyl group begins to lose a large amount, and a new phase of magnesium olivine appears, but the structure of the layer is still maintained. When the temperature reaches 700 °C, the layered structure of serpentine is completely destroyed, and the serpentine is completely dehydroxy, the crystallinity of magnesium olivine is increased, and a new phase of refractory pyroxene appears. When the temperature reaches about 850 °C, the content of magnesium olivine decreases slightly, and the phase of crystalline refractory pyroxene increases. Since heating to 700 °C is more conducive to residual OH⁻ dissolution, Mg²⁺ is less bound and will dissolve a large amount into the environment to compete with Cd²⁺. Mg²⁺ and Cd²⁺ can absorb CO₂ to form MgCO₃ or CdCO₃, where MgCO₃ can increase the environmental pH value by hydrolysis. If the heat activation temperature continues to increase and the serpentine is fully phased, its ability to adsorb heavy metal ions will decrease significantly, so the heat activation temperature of the serpentine is determined to be 700 °C.

At present, the adsorption of a variety of heavy metal ions by serpentine is achieved by the hydroxyl and unsaturated Si–O–Si bonds of serpentine. The oxygen exposed by the nano treatment grinding broken Si–O–Si bond can bind to Cd²⁺ and make it solidified; OH⁻ in serpentine magnesium oxygen octahedron in the soil aqueous solution is easier to dissociate than Mg²⁺, and the surface exposes the remaining Mg, resulting in a higher surface positive electricity [55,56]. Mg²⁺ combines with phosphate to form soluble complexes, or MgO reacts with CO₂ to form MgCO₃ [57–59]. With the continuous dissociation, the OH⁻ in the solution continues to increase, the attraction to PO₄³⁻ and CO₃²⁻ decreases, and the end surface group deprotonation strengthens, resulting in a decrease in the surface matching position. At the same time, OH⁻, PO₄³⁻, and CO₃²⁻ produce competitive adsorption. Under the same conditions, the smaller the solubility product, the easier it is to form

a precipitate. Therefore, when OH^- , PO_4^{3-} , CO_3^{2-} , and Mg^{2+} coexist with Cd^{2+} , the first to generate is the $\text{Cd}_3(\text{PO}_4)_2$ precipitation, followed by $\text{Mg}_3(\text{PO}_4)_2$, $\text{Cd}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, CdCO_3 , and MgCO_3 .

In summary, the thermal activation temperature of nanoscale potassium dihydrogen phosphate and serpentine is better than that of nanoscale potassium dihydrogen phosphate and zeolite thermal activation temperature for the removal of heavy metals Cd.

3.7. Comparative Analysis of the Research Results of This Study and Others

Xie et al. [60] found that, compared with the control, applying a high dosage of zeolite reduced the exchangeable Cd in soil by 25.99% and increased the residual form by 10.57%. Boostani et al. [61] found that with the increase in the zeolite application level, exchangeable form, carbonate-bound form, Fe–Mn–oxide-bound form, organically-bound form Cd decreased significantly, while residual form Cd increased.

Wang et al. [38] showed that compared with the control, the addition of natural serpentine and thermally activated serpentine at 700 °C could both reduce the content of exchangeable Cd in soil by 17.42% and 33.11%, respectively. Cao et al. [40] added S700 (700 °C serpentine activation) to improve the immobilization performance of Cd. The exchangeable Cd decreased by 23.76~36.49%, and the residual form Cd increased by 11.17~19.58%.

Wang et al. [27] found that the reduction rates of exchangeable Cd content after the application of different amendments were as follows: potassium dihydrogen phosphate treatment (5.2%), zeolite treatment (33.1%), zeolite combined with potassium dihydrogen phosphate treatment (48.5%), but the contents of the carbonate-bound form, Fe–Mn–oxide-bound form, organically-bound form, and residual form Cd increased gradually.

Compared with other research results, this experimental study shows that the thermal activation treatment of nano phosphates and silicates has a relatively obvious effect on the remediation of heavy metal Cd-contaminated soil, which is worthy of further promotion.

4. Conclusions

A laboratory experiment on remediation of simulated Cd contaminated soil by nanoscale phosphate and thermal-activated silicate was carried out; the effects of the thermal activation temperature of nanoscale potassium dihydrogen phosphate and serpentine, and nanoscale potassium dihydrogen phosphate and zeolite on the five forms of Cd were studied, and the following conclusions could be drawn.

The effects of thermal activation temperature of nanoscale phosphate and silicate on the morphology of heavy metal Cd in the soil are mainly shown as follows: the content of exchangeable Cd decreased gradually, while the content of the carbonate-bound form, Fe–Mn–oxide-bound form, the organically-bound form, and residual form increased gradually; with the increase in incubation time and thermal activation temperature, the degree of transition from the bioavailable state to the bioavailable state of soil heavy metals increased; at the same incubation time, the order of effect of nanoscale potassium dihydrogen phosphate and serpentine thermal activation temperature on remediation of Cd contaminated soil was $\text{nPS}_{700-2.0} > \text{nPS}_{550-2.0} > \text{nPS}_{850-2.0} > \text{nPS}_{350-2.0} > \text{nPS}_0-2.0$; the order of effect of nanoscale potassium dihydrogen phosphate and zeolite thermal activation temperature on remediation of Cd contaminated soil is $\text{nPF}_{700-2.0} > \text{nPF}_{550-2.0} > \text{nPF}_{850-2.0} > \text{nPF}_{350-2.0} > \text{nPF}_0-2.0$; the effect of thermal activation temperature of phosphate and silicate on the morphology transformation of Cd exhibits better than that of CK; the $\text{nPS}_{700-2.0}$ is better than the $\text{nPF}_{700-2.0}$ processing.

The adsorption effect of natural serpentine and zeolite on phosphate and Cd is low; thermal activation treatment can remove water molecules, organic matter, and other impurities in the pores and channels to some extent, increase the internal surface area, and improve the adsorption capacity. Thermal activation temperature of nano phosphate and silicate combined application can stabilize heavy metal Cd to some extent and promote the

transition of Cd from a bioavailable state to a biounavailable state. The results showed that the combined application of thermal activation temperature of nano phosphate and silicate has a certain potential to control soil cadmium pollution.

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