

## Article

# Effect of Potassium Dihydrogen Phosphate Combined with Thermally Activated Nano Serpentine and Thermally Activated Nano Zeolite on Cadmium in Soil

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**Abstract:** The combined application of potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) and thermally activated nano serpentine and KH<sub>2</sub>PO<sub>4</sub> and thermally activated nano zeolite could immobilize cadmium (Cd) in contaminated soils by increasing soil pH value. The results showed that adding nPS<sub>700</sub>-2.0 (KH<sub>2</sub>PO<sub>4</sub> and thermally activated nano serpentine activated at 700 °C, 2% addition) exhibited better performance under the same treatment condition; it reduced DTPA-Cd by 57.8% and exchangeable Cd by 48.76%. Adding nPF<sub>700</sub> (KH<sub>2</sub>PO<sub>4</sub> and thermally activated nano zeolite activated at 700 °C) reduced DTPA-Cd by 35.49–44.17% and exchangeable Cd by 35.89–42.57%, respectively. The increase of active adsorption points and the surface area of thermally activated nano serpentine reduced the bioavailability of Cd in soil, indicating that the combined application of phosphate and thermally activated nano serpentine has great potential for the immobilization of Cd in soil.

**Keywords:** phosphate; thermal activation; nano material; cadmium pollution; serpentine

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## 1. Introduction

Cadmium (Cd) is recognized as the first among 12 dangerous chemical substances of global significance by the United Nations Program [1]. It can cause damage to red blood cells and lead to anemia [2], and it can cause periodontal disease or induce local bone, cartilage [3], liver, and kidney destruction [4], etc. Cd was also declared as the first carcinogen by the International Agency for Research on cancer [5]. When it circulates into the environment, about 2% of Cd enters the atmosphere, 4% enters water, and 94% enters soil [6]. In the United States, 63% of a total of 1200 soil samples were investigated that were contaminated by heavy metals, in which 8% were contaminated by Cd, according to the National Priority List (NPL) [7]. In Japan, about 0.47 million hm<sup>2</sup> of farmland was polluted by Cd, accounting for 82% of the total area of farmland polluted by heavy metals [8]. In China, cultivated land polluted by heavy metals was 2.67 million hm<sup>2</sup> in 1980 and 6.7 million hm<sup>2</sup> in 1988, and it actually reached 20 million hm<sup>2</sup> in 2012 [9], accounting for 1/5 of the national farmland area [10,11]. Cd pollution in soil is a global thorny problem. It is difficult to be degraded, transformed, and enriched with the characteristics of crypticity, being long-lasting, and being irreversible [12–15], and it influences human health via the food chain. The topic of how to reduce Cd pollution has become a hot spot in recent years.

At present, there are generally two categories of remediation in soil heavy metal pollution: One is ectopic remediation technology, which directly removes heavy metals from the soil but has a high cost, is time- and labor-consuming, and damages original soil structure. The second is situ remediation technology, which can reduce mobility and bioavailability

by changing the form of heavy metals from the activated state to a stable state. It has the advantages of small investment, quick effect, complete treatment, and preservation of original soil structure [16,17]. Phosphate, clay minerals, red mud, lime, biochar, chitosan, arbuscular mycorrhizal fungi, etc., of heavy metals are all found as common remediation substances [18–21]. Among them, clay minerals, as one component of soil, can immobilize the heavy metals effectively by coprecipitation, coordination, and adsorption with specific surface and crystal layers, and they do not destroy the soil structure [22]. Zeolite [23–25] and serpentine [26,27] have been investigated more efficiently to be used for immobilization remediation in heavy metal-contaminated soils with outstanding resource advantages. Thermal-activated serpentine obtained by heating natural serpentine exhibited good adsorption performance to Cd [28]. A previous study reported that phosphate can precipitate with heavy metals under certain conditions [29], and high-temperature thermal activation treatment can be used to increase its adsorption capacity. As we all know, nanomaterial technology is one of the most promising technologies of the 21st century, and it can be used to increase the specific surface area of materials and accelerate the suction rate of heavy metals. Although the use of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), serpentine, and zeolite alone could stabilize heavy metal Cd in different degrees, there is rarely reports about phosphate combined with zeolite and serpentine. Therefore, an efficient and environmentally friendly technology is still urgently needed.

In this study, (1) we created two methods for reducing soil-available Cd:  $\text{KH}_2\text{PO}_4$  combined with thermal-activated nano-serpentine, and  $\text{KH}_2\text{PO}_4$  combined with thermal-activated nano-zeolite. (2) The best thermal activation temperature of the two methods was explored, respectively, by simulated incubation. (3) We analyzed DTPA Cd content, the exchange of Cd and pH in the soil, and the combined application of  $\text{KH}_2\text{PO}_4$  with thermally activated nano serpentine and thermally activated nano zeolite. We also provided a theoretical and application basis for Cd removal from soil.

## 2. Materials and Methods

### 2.1. Experimental Soils and Material

Uncontaminated soil was collected at a depth of 0–20 cm from the Test Base of Shenyang Agricultural University in Shenyang, Liaoning Province ( $123^\circ 56' \text{ E}$ ,  $41^\circ 82' \text{ N}$ , 43 m above sea level), China, and the soil type was brown soil. The basic physical and chemical properties of the soil are shown in Table 1, which were determined according to the method of the literature [30]. The soil composition and content are shown in Table 1.

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

Soil Type	pH	Organic Matter ( $\text{g}\cdot\text{kg}^{-1}$ )	Alkali-Hydrolyzable Nitrogen ( $\text{mg}\cdot\text{kg}^{-1}$ )	Available Phosphorus ( $\text{mg}\cdot\text{kg}^{-1}$ )	Available Potassium ( $\text{mg}\cdot\text{kg}^{-1}$ )	Total Phosphorus ( $\text{g}\cdot\text{kg}^{-1}$ )	Total Cd ( $\text{mg}\cdot\text{kg}^{-1}$ )
Brown soil	6.73	26.93	50.02	71.27	183.59	0.63	0.18

Natural nano zeolite and natural nano serpentine were obtained from Liaoning Province, China, and were crushed into 600 nm powder by high-energy nano impact grinding. The main composition and content of the natural nano zeolite and serpentine were tested by a Philips MagiX X-ray fluorescence spectrometer (PANalytical B.V, Almelo, The Netherlands) and are shown in Tables 2 and 3, respectively.

**Table 2.** The main components and content of zeolite.

Composition	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3$
Content in zeolite (wt. %)	76.32	12.49	3.78	3.24	2.30	1.29	0.58

**Table 3.** The main components and content of serpentine.

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>
Content in serpentine (wt. %)	57.24	0.11	37.97	3.20	0.18	1.30

The 600 nm natural nano serpentine powder was put into a crucible and calcined in a muffle furnace at 350, 550, 700, and 850 °C for 2 h at constant temperature [31]. After the serpentine cooled to room temperature, it was put in zip-lock bags and stored in a desiccator. The resulting thermally activated nano serpentine was briefly recorded as nS<sub>T</sub>, namely nS<sub>350</sub>, nS<sub>550</sub>, nS<sub>700</sub>, and nS<sub>850</sub>, where n represented nano-treated, S represented serpentine, T represented activation temperature, and natural nano serpentine was recorded as nS<sub>0</sub>. In the same way, thermally activated nano zeolite was produced. The resulting thermally activated nano zeolite was simply noted as nZ<sub>T</sub>, namely nZ<sub>350</sub>, nZ<sub>550</sub>, nZ<sub>700</sub>, and nZ<sub>850</sub>, where n represented nano-treated, Z represented zeolite, T represented activation temperature, and natural nano zeolite was recorded as nF<sub>0</sub>. The phosphate for testing was KH<sub>2</sub>PO<sub>4</sub> (Analytical Reagent), denoted as P.

## 2.2. Experimental Design

The simulated cadmium-contaminated soil without added phosphate and silicate was recorded as the reference (CK) treatment. The simulated cadmium-contaminated soil was supplemented with 0.5%, 1.0%, 2.0% low, medium, and high soil weight doses of KH<sub>2</sub>PO<sub>4</sub>, and the mixture of thermal-activated nano serpentine (KH<sub>2</sub>PO<sub>4</sub>: different nano serpentine = 1:2), denoted as nPS<sub>T</sub>-0.5, nPS<sub>T</sub>-1.0, and nPS<sub>T</sub>-2.0, respectively, was mixed thoroughly. In the same way, 0.5%, 1.0%, 2.0% low, medium, and high soil weight doses of KH<sub>2</sub>PO<sub>4</sub> and mixtures of thermal-activated nano zeolite (KH<sub>2</sub>PO<sub>4</sub>: different nano zeolite = 1:2) were denoted as nPZ<sub>T</sub>-0.5, nPZ<sub>T</sub>-1.0, and nPZ<sub>T</sub>-2.0, respectively. There was a total of 31 samples, each repeated 3 times.

## 2.3. Sample Analysis

The air-dried soil had CdCl<sub>2</sub> · 2.5H<sub>2</sub>O (AR) added in the form of a solution, and the exogenous Cd content in the soil reached 10 mg·kg<sup>-1</sup>. An accurate weight of 50.0 g of each of the above-mentioned soils with different treatments was put into jars. The jars were placed in a thermotank and cultivated at 25 ± 2 °C, and the soil water content was maintained at 70.0% of the field water-holding capacity by using deionized water every other day, according to the weighing method. At 0, 7, 14, 28, and 56 days (d) of culture, an appropriate amount of naturally air-dried and ground soil samples were weighed, and the pH and available Cd content of the soil were determined.

The soil pH was measured by a pH meter (SCHOTT Group, Mainz, Germany) with a 1:2.5 water/soil ratio [32]. Soil available Cd was extracted by the DTPA method [33] and measured by an atomic absorption spectrophotometer (HITACH, Tokyo, Japan). The exchangeable Cd content in soil used the Tessier continuous extraction method [34] and was measured by an atomic absorption spectrophotometer (HITACH, Japan).

## 2.4. Data Processing and Analysis

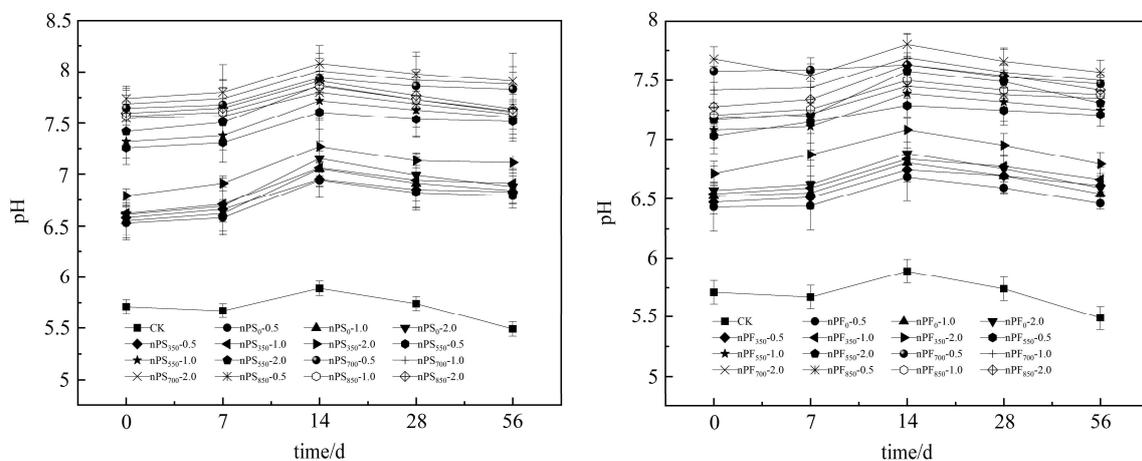
Microsoft Excel 2003, SPSS 19.0 (Duncan test) and origin 8.0 software were used for analysis and to graph data.

## 3. Results and Analysis

### 3.1. Effect on Soil pH

Soil pH affected the ionic composition and various chemical reactions, changes in the occurrence forms of heavy metals, and the bioavailability of heavy metals [35–37]. In Figure 1, compared to CK, with the increase of the dose level, after 56 d, for the culture with the combined KH<sub>2</sub>PO<sub>4</sub> and thermally activated nano zeolite, the soil pH presented

an uptrend, and that with the thermally activated temperature showed first a rising and then a falling trend. Compared to CK, the soil pH increased by 0.82–1.30, 0.84–1.35, and 0.90–1.39 units after the application of nPS0-0.5, nPS0-1.0, and nPS0-2.0, respectively; it increased by 0.87–1.34, 0.91–1.42, and 1.08–1.62 units after applying nPS350-0.5, nPS350-1.0, and nPS350-2.0, respectively; it increased by 1.55–2.03, 2.11–2.57, and 1.61–1.83 units after applying nPS550-0.5, nPS550-1.0, and nPS550-2.0, respectively; and it increased by 1.84–1.91, 1.86–2.12, and 1.89–2.15 units after applying nPS850-0.5, nPS850-1.0, and nPS850-2.0, respectively. After applying nPS700-0.5, nPS700-1.0, and nPS700-2.0, the soil pH increased by 1.94–2.34, 1.98–2.39, and 2.03–2.42 units, respectively, which obtained the highest growth rate. Natural serpentine contains a large amount of  $\text{OH}^-$  with strong chemical activity. After high-temperature thermal activation, much of the  $\text{OH}^-$  was lost, and the maximum loss happened at 700 °C; the alkalinity is enhanced when entering the environment. Another reason is that the Mg-OH bond in the soil solution undergoes proton migration to form new Mg-OH and MgO [38], and MgO hydrolyzes and enhances the pH value.



**Figure 1.** Changes of pH in Cd-contaminated soil with different treatments. Error bars ( $n = 3$ ).

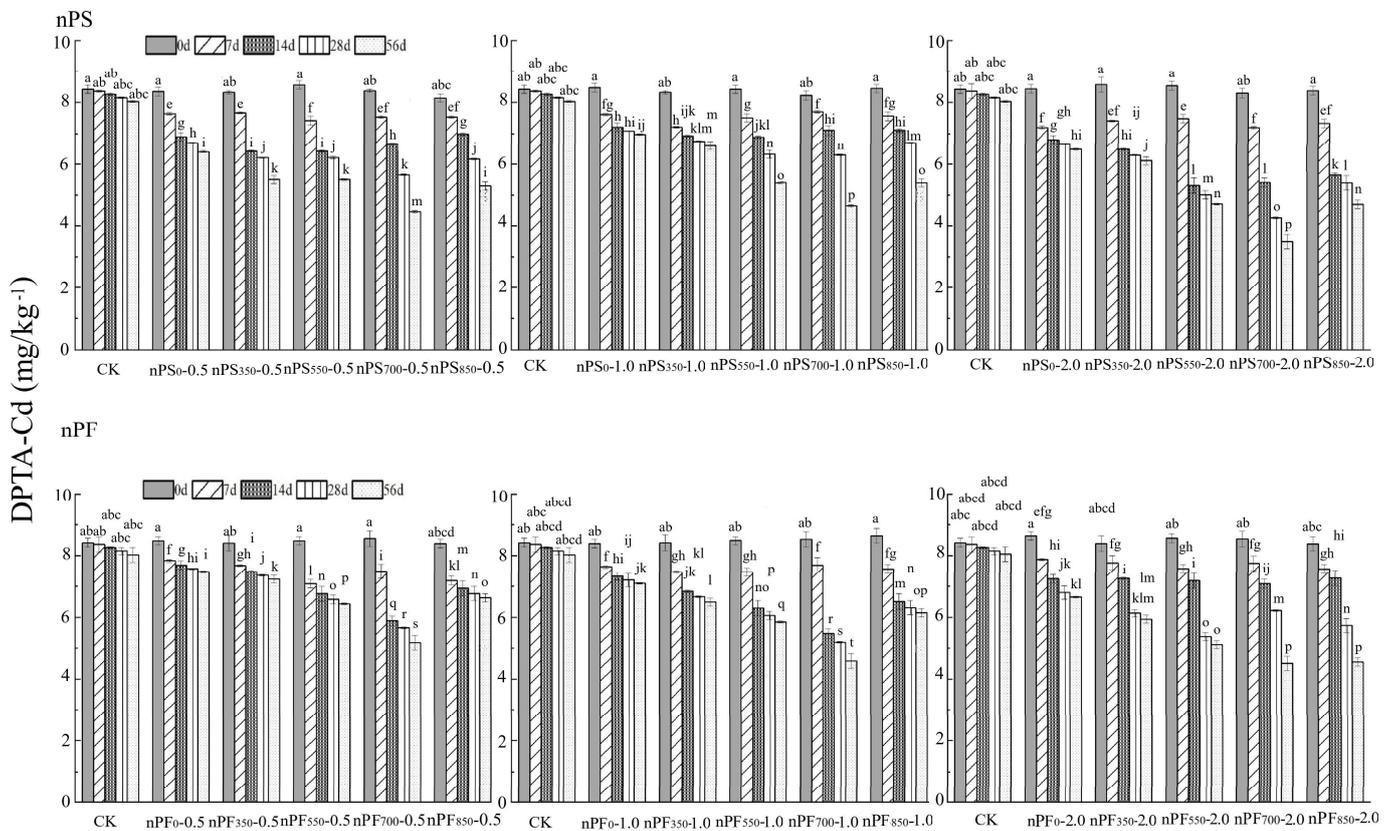
With the increase of dose level and thermally activated temperature, pH showed an uptrend during the combined application of  $\text{KH}_2\text{PO}_4$  and thermally activated nano zeolite. After 56 d of culturing, the maximum increase of pH value was nPF700; however, there was no significant difference with nPF850. The soil pH increased by 1.74–1.98, 1.71–2.01, and 1.87–2.08 units, respectively, after applying nPF700-0.5, nPF700-1.0, and nPF700-2.0. Compared to CK, the soil pH value increased by 0.72–0.97, 0.81–1.05, and 0.86–1.10 units after applying nPF0-0.5, nPF0-1.0, and nPF0-2.0, respectively; it increased by 0.76–1.12, 0.83–1.17, and 0.90–1.20 units after applying nPF350-0.5, nPF350-1.0, and nPF350-2.0, respectively; it increased by 1.32–1.72, 1.37–1.76, and 1.46–1.82 units after applying nPF550-0.5, nPF550-1.0, and nPF550-2.0, respectively; and it increased by 1.47–1.86, 1.50–1.89, and 1.57–1.93 units after applying nPF850-0.5, nPF850-1.0, and nPF850-2.0, respectively. At the same temperature, the pH value increased with the increase of zeolite dosage.

In general, under the same conditions, the combined application of  $\text{KH}_2\text{PO}_4$  with thermally activated nano serpentine was better than  $\text{KH}_2\text{PO}_4$  with thermally activated nano zeolite in improving the soil pH value.

### 3.2. Effect on Soil DTPA-Cd and Exchangeable Cd by Different Modifiers

DTPA-Cd is the easiest to transform and migrate, and it is absorbed and utilized by plants to enter the food chain, which causes harm to the environment, animals, and plants, as well as human beings. In the nPS treatments in Figure 2, the content of DTPA-Cd gradually decreased with the increase of thermal activation temperature, except over 700 °C, and the highest reduction of DTPA-Cd was shown in nPS700 treatments (nPS700-0.5, nPS700-1.0, nPS700-2.0). After 56 d, compared to nPS0-0.5, the DTPA-Cd decreased

by 14.06%, 14.06%, 30.16%, and 17.19%, respectively, in nPS<sub>350</sub>-0.5, nPS<sub>550</sub>-0.5, nPS<sub>700</sub>-0.5, and nPS<sub>850</sub>-0.5. Compared to nPS<sub>0</sub>-1.0, DPTA-Cd decreased by 5.31%, 22.67%, 21.51%, and 22.53%, respectively, in nPS<sub>350</sub>-1.0, nPS<sub>550</sub>-1.0, nPS<sub>700</sub>-1.0, and nPS<sub>850</sub>-1.0. Compared to nPS<sub>0</sub>-2.0, DPTA-Cd decreased by 5.86%, 27.43%, 46.07%, and 27.58%, respectively, in nPS<sub>350</sub>-2.0, nPS<sub>550</sub>-2.0, nPS<sub>700</sub>-2.0, and nPS<sub>850</sub>-2.0. Compared to CK, the DPTA-Cd contents of nPS<sub>0</sub>-0.5, nPS<sub>0</sub>-1.0, and nPS<sub>0</sub>-2.0 treatments were reduced by 0.81–20.33%, 0.62–13.22%, and 0.24–19.24%, respectively; nPS<sub>350</sub>-0.5, nPS<sub>350</sub>-1.0, and nPS<sub>350</sub>-2.0 were reduced by 1.19–17.81%, 1.19–23.91%, and 1.78–31.51%, respectively; the contents of nPS<sub>550</sub>-0.5, nPS<sub>550</sub>-1.0, and nPS<sub>550</sub>-2.0 were reduced by 2.73–31.51%, 0.12–32.88%, and 1.31–41.34%, respectively; and the contents of nPS<sub>850</sub>-0.5, nPS<sub>850</sub>-1.0, and nPS<sub>850</sub>-2.0 were reduced by 3.32–33.40%, 0.24–32.75%, and 0.59–41.47%, respectively. In the same treatment, with the increase of cultivation time, the reduction rate of soil DPTA-Cd was higher. With the higher doses of KH<sub>2</sub>PO<sub>4</sub> and the mixture of thermal-activated nano serpentine, the removal rates rose steadily, such as nPS<sub>700</sub>-2.0 becoming 25.05% higher than nPS<sub>700</sub>-0.5. The final DPTA-Cd removal of nPS<sub>700</sub>-2.0 was 57.80%, well above the rate of single serpentine [28].

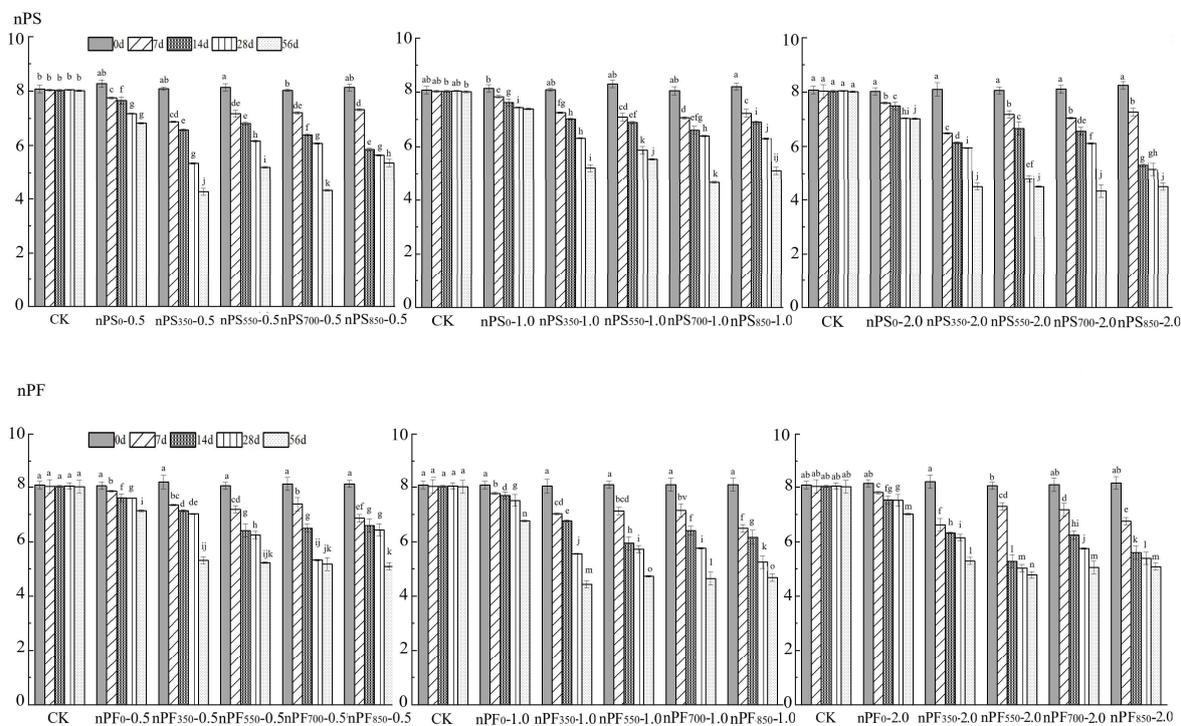


**Figure 2.** Effect of different treatments on the soil’s DPTA-Cd content. *n* = 3, Different lower-case letters marked in Figure 2 indicate a significant difference across different treatments (*p* < 0.05). Error bars (*n* = 3, Mean ± SD).

In the nPF treatments, after 56 d of culturing, we found 700 °C was also the best thermal activation temperature, regardless of the concentration of mixed additives. It had the highest removal rate of DPTA-Cd. Compared to CK, the DPTA-Cd of nPF<sub>0</sub>-0.5, nPF<sub>350</sub>-0.5, nPF<sub>550</sub>-0.5, nPF<sub>700</sub>-0.5, and nPF<sub>850</sub>-0.5 treatment decreased by 6.85%, 9.84%, 19.93%, 35.49%, and 17.43%, respectively. DPTA-Cd decreased by 11.58%, 19.18%, 27.15%, 40.97%, and 23.54%, respectively, in nPF<sub>0</sub>-1.0, nPF<sub>350</sub>-1.0, nPF<sub>550</sub>-1.0, nPF<sub>700</sub>-1.0, and nPF<sub>850</sub>-1.0, and it decreased by 6.65%, 5.94%, 5.11%, 44.17%, and 43.42%, respectively, in nPF<sub>0</sub>-2.0, nPF<sub>350</sub>-2.0, nPF<sub>550</sub>-2.0, nPF<sub>700</sub>-2.0, and nPF<sub>850</sub>-2.0. The removal rate became higher significantly as the added dose of KH<sub>2</sub>PO<sub>4</sub> and the mixture of thermal-activated nano

zeolite increased. Compared to nPF<sub>0</sub>-0.5, DPTA-Cd decreased by 3.21%, 14.04%, 30.88%, and 11.36%, respectively, in nPF<sub>350</sub>-0.5, nPF<sub>550</sub>-0.5, nPF<sub>700</sub>-0.5, and nPF<sub>850</sub>-0.5. Compared to nPF<sub>0</sub>-1.0, DPTA-Cd decreased by 8.59%, 17.61%, 38.50%, and 13.52%, respectively, in nPF<sub>350</sub>-1.0, nPF<sub>550</sub>-1.0, nPF<sub>700</sub>-1.0, and nPF<sub>850</sub>-1.0. Compared to nPF<sub>0</sub>-2.0, DPTA-Cd decreased by 10.68%, 23.16%, 40.28%, and 31.43%, respectively, in nPF<sub>350</sub>-2.0, nPF<sub>550</sub>-2.0, nPF<sub>700</sub>-2.0, and nPF<sub>850</sub>-2.0.

The content changes of exchangeable Cd via different treatments are shown in Figure 3. The heavy metal Cd forms used consisted of five forms: exchangeable, carbonate bound, organic bound, iron-manganese oxide bound, and residue. Among them, the higher the content of exchangeable Cd, the greater its instability, activity, and harm to the soil [39,40]. Compared to CK, the contents of exchangeable Cd decreased significantly after adding different mixtures of KH<sub>2</sub>PO<sub>4</sub> and thermal-activated nano serpentine or nano zeolite, the amounts of which were dependent on the activation temperature. Moreover, the decreasing tendency became prominent as the incubation time and the dosage of the mixture increased. After 56 d, compared to nPS<sub>0</sub>-0.5, the exchangeable Cd decreased by 28.01%, 25.03%, 33.69%, and 19.35%, respectively, in nPS<sub>350</sub>-0.5, nPS<sub>550</sub>-0.5, nPS<sub>700</sub>-0.5, and nPS<sub>850</sub>-0.5. Compared to nPS<sub>0</sub>-1.0, exchangeable Cd decreased by 23.61%, 25.81%, 29.33%, and 26.17%, respectively, in nPS<sub>350</sub>-1.0, nPS<sub>550</sub>-1.0, nPS<sub>700</sub>-1.0, and nPS<sub>850</sub>-1.0. Compared to nPS<sub>0</sub>-2.0, exchangeable Cd decreased by 39.32%, 37.61%, 41.03%, and 39.36%, respectively, in nPS<sub>350</sub>-2.0, nPS<sub>550</sub>-2.0, nPS<sub>700</sub>-2.0, and nPS<sub>850</sub>-2.0. Compared to CK, the exchangeable Cd content of nPS<sub>0</sub>-0.5, nPS<sub>0</sub>-1.0, and nPS<sub>0</sub>-2.0 treatments reduced by 0.78–7.86%, 2.35–12.47%, and 7.43–14.96%, respectively; the content of nPS<sub>350</sub>-0.5, nPS<sub>350</sub>-1.0, and nPS<sub>350</sub>-2.0 reduced by 0.25–33.67%, 1.24–35.04%, and 0.25–46.88%, respectively; the content of nPS<sub>550</sub>-0.5, nPS<sub>550</sub>-1.0, and nPS<sub>550</sub>-2.0 reduced by 2.72–30.92%, 0.62–36.91%, and 0.25–45.39%, respectively; and the content of nPS<sub>850</sub>-0.5, nPS<sub>850</sub>-1.0, and nPS<sub>850</sub>-2.0 reduced by 1.61–25.69%, 0.62–39.90%, and 1.98–48.38%, respectively.



**Figure 3.** Effect of different treatments on the soil’s exchangeable Cd content. Different lower-case letters marked in Figure 3 indicate a significant difference across different treatments ( $p < 0.05$ ). Error bars ( $n = 3$ , Mean  $\pm$  SD). In the nPF treatments, compared to nPF<sub>0</sub>-0.5, the exchangeable Cd decreased by 25.53%, 26.65%, 28.75%, and 28.61%, respectively, in nPF<sub>350</sub>-0.5, nPF<sub>550</sub>-0.5, nPF<sub>700</sub>-0.5, and nPF<sub>850</sub>-0.5. Compared to nPF<sub>0</sub>-1.0, exchangeable Cd decreased by 24.54%, 27.96%, 31.81%, and

27.53%, respectively, in nPF<sub>350</sub>-1.0, nPF<sub>550</sub>-1.0, nPF<sub>700</sub>-1.0, and nPF<sub>850</sub>-1.0. Compared to nPF<sub>0</sub>-2.0, exchangeable Cd decreased by 34.47%, 31.36%, 42.01%, and 41.72%, respectively, in nPF<sub>350</sub>-2.0, nPF<sub>550</sub>-2.0, nPF<sub>700</sub>-2.0, and nPF<sub>850</sub>-2.0. Compared to CK, the exchangeable Cd content of nPF<sub>0</sub>-0.5, nPF<sub>0</sub>-1.0, and nPF<sub>0</sub>-2.0 treatments reduced by 0.25–11.10%, 0–12.59%, and 0.74–15.71%, respectively; the content of nPF<sub>350</sub>-0.5, nPF<sub>350</sub>-1.0, and nPF<sub>350</sub>-2.0 reduced by 1.36–33.79%, 0.50–34.04%, and 1.49–44.76%, respectively; the content of nPF<sub>550</sub>-0.5, nPF<sub>550</sub>-1.0, and nPF<sub>550</sub>-2.0 reduced by 0.37–34.79%, 0.12–40.40%, and 0.37–44.39%, respectively; and the content of nPF<sub>850</sub>-0.5, nPF<sub>850</sub>-1.0, and nPF<sub>850</sub>-2.0 reduced by 0.50–36.53%, 0.12–36.66%, and 0.99–46.47%, respectively.

The nPS700 additions reduced exchangeable Cd by 39.36–48.76% compared to CK, and nPF reduced it by 35.89–42.57%. The nPS was higher than previous results, such as a palygorskite addition that reduced exchangeable Cd by 11–32% [41] and single serpentine that reduced it by around 39% [28].

## 4. Discussion

### 4.1. pH

The pH value was found to have a negative correlation with DPTA-Cd [42]; thus, in our study, the increasing soil pH (Figure 1) led to the increase of the negative charge of colloid, and it increased the electrical adsorption of Cd<sup>2+</sup>. Cd<sup>2+</sup> can combine with CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>, and PO<sub>4</sub><sup>3-</sup> to form insoluble CdCO<sub>3</sub>, Cd(OH)<sub>2</sub>, and Cd<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> precipitation, with the increase of OH<sup>-</sup> concentration in soil solution. This reduces the availability of heavy metals [43,44]. On the one hand, the pH values of serpentine and zeolite themselves are higher; on the other hand, both of them contain K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, which increase the soil pH [45]. Furthermore, natural serpentine contains a large amount of OH<sup>-</sup> with strong chemical activities. The Mg-OH<sup>-</sup> bond in the soil solution undergoes proton migration to form new Mg-OH and MgO [38], and MgO hydrolyzes and improves pH value.

### 4.2. Cd Content

Reducing the content of exchangeable Cd and DTPA-Cd can reduce the pollution of heavy metals to the soil. The exchangeable Cd is bioavailable, it has great mobility, and it is most easily absorbed and utilized by organisms. Studies have found that natural zeolites can absorb heavy metals due to its porous structure [46]. In our study, zeolite was still effective in the reduction of Cd bioavailability. The serpentine unit was composed of a six square mesh of the silicon-oxygen tetrahedron, with an eight-surface layer of magnesium hydroxide [47]. Cd ions can be adsorbed in the unit layer and combined with hydroxyl to enrich the mineral surface. Therefore, after adding serpentine, the content of DTPA-Cd in soil was significantly decreased (Figure 2). The O-Si-O bond of serpentine is broken in thermal activation, which leads to the increase of the active adsorption point and the increase of the surface area [31]. When serpentine was activated by 700 °C, the surface increased by two times due to the original layered structure collapsing to form a slit-shaped pore-like structure [31], which further increased its adsorption capacity of heavy metal in soil. This is why we added thermal-activated serpentine compared to natural serpentine. Phosphate is a cheap and effective chemical fixative used for the remediation of Cd-contaminated soil [29]. We found the effect of decreasing exchangeable Cd using phosphate (KH<sub>2</sub>PO<sub>4</sub>) combined with thermal-activated serpentine was better than only using thermal-activated serpentine. The removal rate of the latter was only 23.76–36.49% [28], less than what we obtained in Section 3.2. Therefore, the combined application of KH<sub>2</sub>PO<sub>4</sub> and thermally activated nano serpentine is a better method to remove cadmium pollution in soil.

## 5. Conclusions

Adding KH<sub>2</sub>PO<sub>4</sub> + thermally activated nano serpentine and KH<sub>2</sub>PO<sub>4</sub> + thermally activated nano zeolite could significantly increase soil pH, and the improvement of pH

depends on the thermal activation temperature, dosage, and soil incubation time. The removal rate of DTPA-Cd and exchangeable Cd became higher significantly with the added dose of the mixture. The best removal performance dosage was 2.0%, and the best thermally activated temperature was 700 °C in both serpentine and zeolite treatment. In our study, zeolite and serpentine exhibited different immobilization capabilities for Cd soils. The best treatment was nPS<sub>700</sub>-2.0; the removal rates of DTPA-Cd and exchangeable Cd were 57.80% and 48.76%, respectively, 13.63% and 6.19% higher than nPF<sub>700</sub>-2.0. The mixture of KH<sub>2</sub>PO<sub>4</sub> + thermally activated nano serpentine could effectively convert the bioavailable Cd speciation to have less bioavailable speciation, accounting for the reduction of Cd bioaccessibility.

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