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EFFECTS OF ACID MODIFIED MINERAL MATERIALS ON SOIL CADMIUM POLLUTION AND PLANT REMEDIATION

JINYANG ZHANG[1,2,3*], PENGXIN JIN[1,2,3], NA LEI[1,2,3] AND YIN LI[1,2,3]

Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Shaanxi, China

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Abstract

In response to the problem of soil heavy metal pollution, acid modified mineral materials were used to study the changes in adsorption performance, surface charge, and other indicators of four clay mineral materials, vermiculite, arsenic sandstone, shale, and zeolite, under acid modified conditions. The changes in soil physicochemical properties, heavy metal content, and plant growth before and after remediation were analyzed. The study showed that the introduction of acid modified adsorption materials increased the specific surface area and cation exchange capacity, enhanced adsorption performance, and provided theoretical reference for the mechanism and effect of remediation of cadmium contaminated soil. To optimize the application amount of remediation materials and develop cheap, effective, and scalable heavy metal remediation materials, it has important practical significance.

Introduction

The exceeding rate of pollutants of farmland soil in our country is 19.4%, and the main pollutants exceeding the standard are Cd, As, Cu, Hg, Pb, Cr, Zn, and Ni which account for 7.0, 2.7, 2.1, 1.6, 1.5, 1.1, 0.9, and 4.8% of the total pollution, respectively (Chen *et al.* 2016, Chen *et al.* 2018). In soil heavy metal pollution, Cd pollution is a prominent problem due to its high bioavailability. Clay minerals were a type of soil conditioning agent with low cost, high efficiency, and good environmental compatibility (Chuan 2020). Among them, zeolite, kaolin, bentonite, attapulgite, illite, vermiculite, and sepiolite have also been widely used in soil heavy metal pollution remediation in recent years. However, due to the inherent structure of natural minerals, their soil remediation ability and performance are still insufficient (Di *et al.* 2019, Fang *et al.* 2021). Except for a small amount of minerals such as montmorillonite, bentonite, and sepiolite, most natural materials have low reactivity and small specific surface area. According to Guo *et al.* 2006), activation modification could help fully explore the potential efficacy of materials, reduce dosage, and achieve better and more lasting remediation effects. There are various modification methods, and according to current reports, the commonly used modification methods include heat treatment, ion exchange modification, acid treatment, alkali treatment, organic modification, polymer intercalation, etc. (Han *et al.* 2014, Hang *et al.* 2007). Ren *et al.* (2018) found that high-temperature modified attapulgite on heavy metals could effectively passivate copper and zinc in soil studied the removal effect of heavy metal $Cd^{2+}$by hydrochloric acid modification of attapulgite, and found that due to 3mol/L of acid concentration, the removal effect of hydrochloric acid modified attapulgite on Cd^{2+} in water could reach over 90%. Adebowale *et al.* (2005) found that phosphate modified kaolin had a higher adsorption capacity for heavy metal ions than sulfate

[*] *Author for correspondence: <961230358@qq.com>. [1]Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd, China. [2]Key Laboratory of Degraded and Unused Land Consolidation Engineering, Ministry of Natural Resources, China. [3]Shaanxi Engineering Research Center of Land Consolidation, Land Engineering Technology Innovation Center, Ministry of Natural Resources, Shaanxi, China.

modified kaolin. Both modified kaolin methods had higher adsorption capacity than unmodified kaolin, especially for Cd^{2+} adsorption. Introducing inorganic modifiers into the interlayer of clay minerals, the compounds formed by separating the layers, changing the interlayer structure, improving surface activity, and enhancing adsorption capacity (Ye *et al.* 2013, Zhao *et al.* 2019). At present, the passivation effect of a single remediation material on heavy metals in farmland is widely studied, and there is a lack of comparison between the remediation effects of different remediation materials. At the same time, the dosage of remediation materials is relatively high, which is not conducive to cost savings and maintaining the original physical and chemical properties of soil. Most of them were applied in water treatment research, and there was relatively little research in the remediation of polluted soil. This study explored the changes in adsorption performance, surface charge, and other indicators of four clay mineral materials, vermiculite, arsenic sandstone, shale, and zeolite, under acid modification conditions through indoor and potted experiments. It analyzed the changes in soil physicochemical properties, heavy metal content, and plant growth before and after remediation, and explored the mechanism and effect of the four materials in remediation of cadmium contaminated soil. The results of the research could provide reference for the remediation of heavy metal cadmium in soil.

Materials and Methods

The soil sample (type - loess) was taken from a farmland in Chuyuan Village, Fuping County, Shaanxi Province. After crushing it through a 1 mm sieve, every 60 g of soil was used as the soil sample. 10 ml of cadmium chloride solution with a concentration of 10 μM was added to each soil sample, stirred evenly, and allowed to dry naturally (the pollutant concentration refers to the GB15618-2018 agricultural soil pollution risk screening value, and other agricultural risk values of $6.5 < pH \leq 7.5$ are selected as 0.3 mg/kg).

The raw materials were rinsed with tap water for about 3 times, soaked in deionized water for 24 hrs, changed the water every 4 hrs, and then dried at 90ºC in an electric drying oven for 12 hrs. A certain mass (5 g) of pretreated raw materials was kept into a conical flask containing HCl solutions of different concentrations (0.001, 0.1, 0.25, 0.50, 1.00 mol/l), added stoppers and shaked at room temperature (25ºC) and 160r/min for 12 hrs, and allowed to stand for about 12 hrs. The upper liquid was poured out and the solid phase was washed multiple times with deionized water until Cl^- (tested with $AgNO_3$) was removed completely, filtered, dried at 80 ℃ for about 10 hrs in an oven, and sealed the sample bag for use.

To compare the passivation effects of four modified materials on cadmium in soil, the remediation materials were added at dosages of 0.1, 0.2, and 0.3% (m/m), namely 0.6, 1.2, and 1.8g, respectively. Each sample contained 60g of contaminated soil. Two replicates were set for each treatment Referring to the method of diethylenetriamine pentaacetic acid (DTPA) extraction - eight effective elements were prepared. The extractant was added in a soil liquid ratio of 1: 2 and reacted in a 180 ± 20 r/min shaker for 2 hrs before extracting the extract. The filtrate was used to detect the bioavailability of heavy metals and analyze the physicochemical properties of the remediated soil.

Four sets of potted plant experiments were conducted. The experimental plant was *Solanum nigrum*. The changes in cadmium content in the rhizosphere soil of the plants at different growth stages, and the growth status of the plants was observed. Three potted plants were arranged in parallel for each group, with the same number of control groups.

For the determination of soil physicochemical parameters soil pH, organic matter, available phosphorus, available potassium, total nitrogen, water content and other indicators were carried out using conventional methods. The soil pH was measured using a pH meter method, the soil organic matter was measured using the potassium dichromate volumetric method, and the available phosphorus was measured using the 0.5 mol/L $NaHCO_3$ extraction colorimetric method. The UV visible spectrophotometer (TU-1810PC) was used for measurement.Rapid potassium was extracted using 1mol/L NH_4OAc and measured using a flame photometer (FP650); Soil total nitrogen was measured using the $K_2Cr_2O_7$-H_2SO_4 digestion method and the Kjeldahl nitrogen analyzer (KDN-1); Cadmium content refers to the determination of eight effective elements in diethylenetriamine pentaacetic acid extraction. The prepared extraction agent was added in a soil liquid ratio of 1:2 and reacted in a 180 ± 20r/min shaker for 2 hours before extracting the extraction solution. The bioavailability of cadmium was detected by an inductively coupled plasma mass spectrometer (Agilent, 7700e).

For the determination of specific surface area of materials, nitrogen adsorption experiment was conducted on a fully automatic specific surface area analyzer (AntonPaar, NOVA4000e), mainly to obtain pore size distribution, specific surface area, and pore volume of 3-100nm. Approximately 0.5 g of crushed sample powder was taken to 100 mesh and 0.1-0.2/g for instrumental analysis.

For the measurement of surface charge of materials, extraction of soil colloids involved dispersing the air-dried soil into a soil suspension after removing organic matter, and then separating soil clay particles (smaller than 2 μ m) according to Stokes' law. Soil colloid (25 mg) was taken into a 250 mL plastic bottle and sonicated for 30 minutes; the Zeta potential of (Brookhaven, NanoBrookOmni, NY, USA) colloids was measured using a Zeta potential analyzer.

Results and Discussion

This study analyzed and tested the specific surface area and pore structure of different biomaterials after acid modification (Table 1). The acid modified material achieved a D_{ap} of 60.334, indicating that after modification, some micropores of the biomaterials were masked, while mesopores increased. The higher the cation exchange capacity of soil, the higher the proportion of soil colloids, and the corresponding negative charge amount. After exogenous heavy metals enter the agricultural soil environment, they are easily adsorbed by soil colloids at low concentrations. Acid modified mineral materials increase soil cation exchange capacity and specific surface area to varying degrees (Fig. 1). The higher the surface soil cation exchange capacity, the stronger the soil's adsorption effect on heavy metals. The larger the specific surface area, the greater the adsorption area for heavy metals, which can reduce the absorption of heavy metals by agricultural crops. Therefore, soil cation exchange capacity and specific surface area are key indicators for guiding agricultural fertilization and soil remediation.

Table 1. The influence of acid modified clay mineral materials on comparative surface area and pore structure parameters.

Adsorbent material	LangmuirSA (m^2/g)	S_{micro} (m^2/g)	V_{total} (m^2/g)	D_{ap} (A)
Vermiculite	1.3835	0.0181	0.195	29.241
Arsenicsandstone	1.2775	0.0203	0.196	60.334
Shale	1.1708	1.2985	0.015	30.321
Zeolite	1.7234	0.0817	0.193	32.176

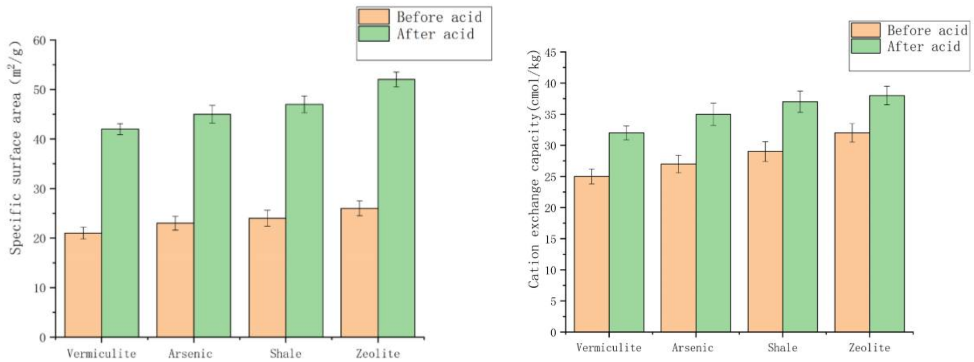

Fig. 1. Comparison of surface area and cation exchange capacity of clay mineral materials before and after acid modification

The study on the physical and chemical properties of soil using different acid modified materials showed that under acid modified conditions, four types of clay mineral materials had an impact on soil physical and chemical properties. Table 2 showed that organic matter, available potassium, available phosphorus, and total nitrogen all increased to varying degrees. After acid modification, the organic matter of shale clay mineral materials increased by 6.68g/kg, and the available phosphorus increased by 8.98mg/kg. After acid modification, the available potassium of arsenic sandstone increased by 40.85mg/kg. The changes in total nitrogen content and Ph content were not significant. The cadmium content in soil after acid modification showed a decrease of 8.25, 12.34, and 4.25%, respectively (Fig. 2).

Table 2. Effects of clay mineral materials on soil physical and chemical properties before and after acid modification.

Nutrient indicators	Statistical indicators	Vermiculite		Arsenic sandstone		Shale		Zeolite	
		Before acid	After acid	Before acid	After acid	Before acid	After acid	Before acid	After acid
Organic matter	mean value (g/kg)	3.41	4.12	8.62	8.65	10.97	17.65	9.27	10.21
	CV	0.32	0.20	0.15	0.07	0.32	0.17	0.16	0.23
Quick acting potassium	mean value (mg/kg)	65.56	97.53	127.10	167.95	78.24	113.47	90.47	110.78
	CV	0.29	0.14	0.53	0.15	0.12	0.05	0.21	0.32
Effective phosphorus	mean value (mg/kg)	2.78	9.95	3.44	15.68	13.95	22.93	12.21	15.78
	CV	0.51	0.26	0.27	0.11	0.59	0.15	0.14	0.17
Total nitrogen	mean value (g/kg)	0.48	0.51	0.51	0.48	0.59	0.56	0.65	0.73
	CV	0.09	0.03	0.09	0.04	0.13	0.06	0.02	0.03
Ph	mean value	1.31	1.21	1.33	1.32	1.24	1.21	1.35	1.33
	CV	0.01	0.02	0.01	0.03	0.02	0.01	0.02	0.03

The application of vermiculite, arsenic sandstone, shale, and zeolite to farmland soil could effectively reduce the content of cadmium in the soil. However, it was not clear whether it could further enhance the inhibitory effect of sunflower roots, stems, and leaves on cadmium, and reduce the accumulation and distribution of cadmium in sunflowers. Therefore, pot experiments were conducted to study the effects of adding vermiculite, arsenic sandstone, shale, and zeolite on the distribution of heavy metal cadmium content in various parts of sunflower (i.e. roots, stems, and leaves), and to explore the rules of cadmium transport and accumulation in different parts of wheat by applying different clay mineral materials, providing support for the remediation of heavy metal cadmium farmland soil.

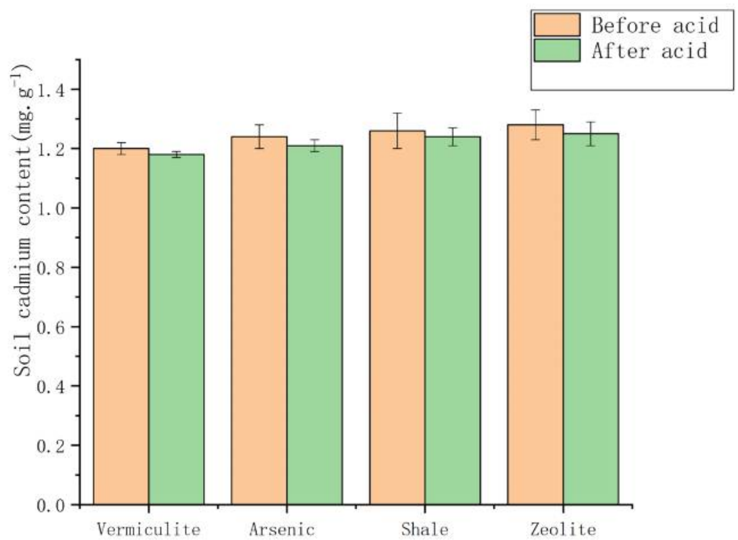

Fig. 2. Effect of acid modification on soil cadmium content of clay mineral materials before and after acid modification.

The total accumulation of cadmium in different parts of *Solanum niger* was as follows: root >leaf > stem. The distribution of cadmium in different parts of *S. niger* treated with different clay mineral materials also showed different results (Figs. 3-5). The four clay mineral materials showed an upward trend in cadmium content in *S. niger* roots, stems, and leaves, indicating that the addition of mineral materials promoted the absorption of heavy metal cadmium in wheat stems. Compared with the control CK, the cadmium content in vermiculite mineral materials increases by 2.25, 3.32, and 1.15% in the roots, leaves and stems, respectively;. The cadmium content of arsenic sandstone mineral materials increased by 2.24, 4.35, and 2.15% in the roots, leaves and stems, respectively; Similarly, the cadmium content of shale mineral materials increased by 5.21, 2.36, and 2.45% in the roots, leaves and stems, respectively;. The cadmium content of zeolite vermiculite mineral materials increased by 2.21, 7.37, and 8.25% in the roots, leaves and stems, respectively. As a result, surface acid modified clay mineral materials increased the absorption of heavy metal cadmium content by plants.

Acid modified mineral materials increased soil cation exchange capacity and specific surface area to varying degrees. The higher the surface soil cation exchange capacity, the stronger the adsorption of heavy metals by the soil itself. The larger the specific surface area, the greater the adsorption area for heavy metals, which could reduce the absorption of heavy metals by agricultural crops. Therefore, soil cation exchange capacity and specific surface area are key indicators for guiding agricultural fertilization and soil remediation. Acid modified materials make D_{ap} reached 60.334, indicating that after modification, some micropores of the biomaterials were covered, while mesopores increased. The higher the cation exchange capacity of soil, the higher the proportion of soil colloids, and the corresponding negative charge amount.

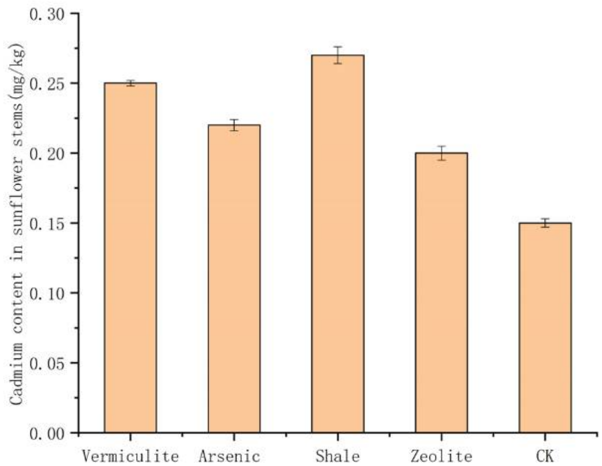

Fig. 4. Effect of clay mineral materials on cadmium content in sunflower stem after acid modification

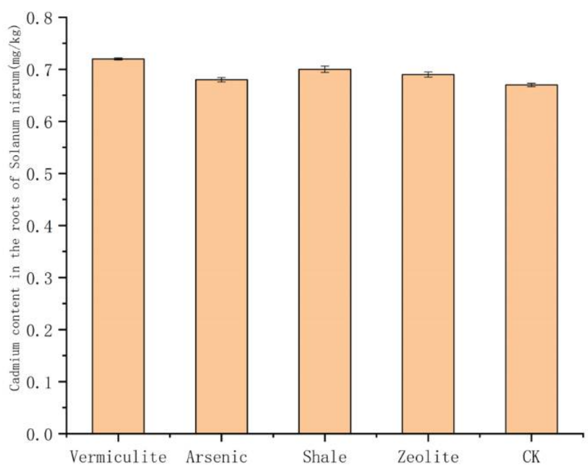

Fig. 5. Effect of clay mineral materials on cadmium content in sunflower leaves after acid modification.

At present, there is a widespread study on the passivation effect of a single remediation material on heavy metals in farmland. There is a lack of comparison between the remediation effects of different remediation materials, and the dosage of remediation materials is relatively high, which is not conducive to cost savings and maintaining the original physical and chemical properties of the soil. Therefore, this article used modified clay minerals as remediation materials, compared and analyzed the passivation effect of different remediation materials on cadmium in farmland soil, explored the bioavailability of cadmium in soil after remediation materials were applied, and changed in soil physicochemical properties. The amount of remediation materials applied was optimized, providing scientific basis and method reference for the remediation of cadmium contaminated farmland soil in China.

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