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RESEARCH ARTICLE

Restoration effect of sulfhydryl-modified sepiolite on cadmium in contaminated soil and its effect on the growth of spinach (*Spinacia oleracea L*)

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Abstract

Coal mining has produced a large amount of coal gangue. It makes the soil around the mining area seriously polluted by heavy metals, affects the growth of crops, and endangers human health. Therefore, there is an urgent need to develop new materials for remediation of Cd in soil. In this study, mercaptosilane-modified sepiolite (Q-Sep) was used as a basic passivator, and it was pretreated with acid (H-Q-Sep) and high temperature (R-Q-Sep) respectively. By analyzing the forms of Cd and pH values in soil after adding modified sepiolite, we compared the remediation effects of two modified methods on Cd in soil. The enrichment of spinach (*Spinacia oleracea* L) to Cd and changes in physiological and biochemical indexes of spinach were determined, and the effect of modified sepiolite on the growth of spinach was judged. The experimental results showed that the addition of modified sepiolite could significantly increase the soil pH values ($p < 0.05$); the content of exchangeable Cd in soil decreased by 60.4%; and the maximum increase of residual state was 32.9%. The absorption of Cd in soil by spinach decreased, and root length, plant height, and biomass of spinach all increased. It was proved that the addition of modified sepiolite can improve the productivity of soil, reduce toxicity of heavy metals in soil, and promote growth of plants. As a result, the addition of H-Q-Sep and R-Q-Sep can effectively repair Cd in gangue filled soil, which provides a certain theoretical basis for the passivation remediation of Cd in soil.

Keywords Cadmium · Passivation repair · Mercaptosilane · Sepiolite · Spinach

Introduction

China is the largest producer and consumer of coal in the world; a large amount of solid waste including coal gangue will be produced in the process of coal mining; heavy metal is one of the typical pollutants of coal gangue (Gao et al. 2021; Sun et al. 2020). The long-term accumulation of coal gangue and the filling of coal mining subsidence areas with coal gangue will lead to the surrounding soil to be polluted by heavy metals in coal gangue, including a variety of heavy metal elements, such as Cd, Hg, Mn, Pb, and Zn (Sun et al. 2021; Zhang et al. 2019). Heavy metal pollution of cultivated land in China is relatively serious, among which Cd pollution is the most serious, with the national point exceeding the standard rate of 7%(Lu et al. 2019; Zhang et al. 2018). Cd is a heavy metal with silver luster, which has strong biological toxicity and mobility, and is very harmful to plants, animals, and microorganisms in soil. It is considered by most scholars an element with serious toxic effects. Cd pollution is nondegradable and persistent. On the one hand, it can poison plant tissues; on the other hand, after being absorbed by plant roots, it will be directly transported to the aboveground parts and in grains, vegetables, stems, leaves, and fruits of food crops, which will reduce yields of

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crop and endanger human health through the food chain (Shi et al. 2009; Wang et al. 2022).

Because of the seriousness of Cd pollution in soil and the urgency to solve it, it has been widely studied. Soil remediation refers to use methods of transfer, absorption, degradation, and transformation to reduce the concentration of pollutants to an acceptable level of the soil or to convert toxic and harmful pollutants into harmless substances (Hossain et al. 2010). The remediation of heavy metal Cd in soil is generally carried out from two aspects: removal of heavy metals by leaching or phytoremediation. Passivation changes the existing forms of heavy metals in soil and reduces mobility and bioavailable toxicity of heavy metals to organisms (Houben et al. 2013). The technology of in situ passivation for heavy metals has the advantages of quick effect, convenient operation, high repair efficiency, and low cost. It can generally meet the application of heavy metal remediation and agricultural production (Xu et al. 2017). Currently, clay minerals (Liang et al. 2013), phosphate compounds, basic compounds (Ma et al. 2012), biochar, etc. are considered as effective passivators. Zhang et al. (2021) showed that the addition of biochar and steel slag could reduce the content of Cd in soil, reduce the absorption of Cd by rice, and increase the yield of rice. Huang et al. (2020) proved that the addition of slaked lime and sepiolite to Cd contaminated soil can reduce the content of exchangeable Cd by 42.66%, and the content of Cd in brown rice decreased by 49.03%.

Sepiolite is a clay mineral with good adsorption properties, and it has the advantages of low cost and large output. However, the adsorption capacity of natural sepiolite is limited by its narrow internal channels and low self-loading capacity (Sun et al. 2016). Therefore, it is necessary to modify sepiolite properly to improve its repair effect on heavy metals. Existing research had shown that thiol groups can be loaded on the surface of organic and inorganic materials through hydrolytic condensation reactions (Gan et al. 2016). By covalent and electrostatic binding, sulfur-containing groups can form stable complexes with heavy metals to achieve the purpose of adsorption (Yusuke et al. 2009). Karlsson et al. (2007) found that Cd in soil mainly forms complexes with active groups such as sulfhydryl and carboxyl groups on the surface of soil organic matter, to reduce the mobility and bioavailability of Cd. When sepiolite is roasted at high temperature, its crystal water will be taken away, thereby enlarging the internal pores of the sepiolite and enhancing the adsorption performance of sepiolite (Valentin et al. 2007; Kuang et al. 2003). Activation with acid can reduce content of iron and aluminum in clay minerals and increase their specific surface area and porosity, thus enhancing their adsorption capacity (Rusmin et al. 2016). At present, the adsorption properties of sepiolite can be optimized by using acid, heat, and thiol-modified sepiolite, which can enhance the ability of sepiolite to adsorb heavy metals. However, the results of combining acid modification and thermal modification with sulfhydryl modification are unknown.

The study showed that the average concentration of Cd in soil around the Xinzhuangzi mine exceeded the soil background value in Huainan city and it was 2.9 times larger than the soil background value of Huainan city (You et al. 2016). Therefore, this study selected the cultivated soil near the Xinzhuangzi coal mining subsidence area in Huainan as the research samples. Spinach is a leafy vegetable with strong Cd enrichment ability. At present, spinach has been selected as the research object for the experiment (Bakhshayesh et al. 2014). In this study, the combination of acid treatment, heat treatment, and mercaptosilane was used to modify sepiolite; the existing forms of Cd in soil and the physiological indexes of spinach after the addition of two modified sepiolite were analyzed and compared to verify their passivation effect on Cd in soil and their effect on the growth of spinach. The purpose of this study is to clarify the effect of two modified sepiolite on soil environment, compare the passivation effects of two modified sepiolite on Cd in soil, and analyze their effect on the growth of spinach.

Materials and methods

Chemicals

All chemicals used in this study were of analytical grade. 3-Mercaptopropyltrimethoxysilane and anhydrous ethanol were purchased from Shanghai Boyle Chemical Co., Ltd. (Shanghai China). Hydrochloric acid (HCl), nitric acid (HNO_3), and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). National mineral soil standard material (GSS-3) was supplied by Wuhan Zhong Chang Guo Yan Biao Wu Technology Co., Ltd. (Wuhan, China). Spinach seeds were obtained from Xingyun Vegetable Seed Breeding Center in Qingxian County, Hebei Province. Sepiolite was obtained from Xinlei Mineral Powder Processing Plant, Xingtang County, Shijiazhuang, Hebei Province.

Preparation of modified sepiolite

Sulfhydryl-modified sepiolite

First, 3-mercaptopropyltrimethoxysilane, ethanol, distilled water were mixed in a volume ratio of 1:8:0.5 to obtain a sulfhydryl mixed solution. Then, natural sepiolite was immersed into the sulfhydryl mixed solution at a ratio of 1:1 (g to ml). After shaking for 6 h at a shaker speed of 300 rpm and 25 °C, the mixture was filtered with 0.45-μm filter paper and dried in an oven at 40 °C to obtain sulfhydryl-loaded sepiolite (Q-Sep) (Han et al. 2019).

Acid-sulfhydryl modified sepiolite

The natural sepiolite was mixed with HCl at a ratio of 1:10 (g to ml) (1 g sepiolite:10 ml HCl). After shaking for 8 h at a shaker speed of 300 rpm and 25 °C, the mixture was filtered with 0.45-μm filter paper and then dried in an oven at 40 °C to obtain acidified sepiolite. The concentrations of HCl were 2 M, 3 M, 4 M, and 5 M (Su et al. 2014). Acidified sepiolite and sulfhydryl mixed solution were mixed at a ratio of 1:1 (g to ml). After shaking for 6 h at a shaker speed of 300 rpm and 25 °C, the mixture was filtered with 0.45-μm filter paper and dried in an oven at 40 °C to obtain acidified sulfhydryl-loaded sepiolite (H-Q-Sep).

Thermo-sulfhydryl-modified sepiolite

The natural sepiolite was roasted in a tube furnace (SX-GO7102, Zhonghuan Experimental Electric Furnace, China) at high temperature for 2 h, and the temperature settings were 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C (Biswas et al. 2016). The thermally modified sepiolite was immersed into the sulfhydryl mixed solution at a ratio of 1:1 (g to ml). After shaking for 6 h at a shaker speed of 300 rpm and 25 °C, the mixture was filtered with 0.45-μm filter paper and dried in an oven at 40 °C to obtain sulfhydryl-loaded sepiolite after thermal treatment (R-Q-Sep).

Sample collection and experiment setup

Soil samples were collected from Xinzhuangzi coal gangue filling area, Huainan city, Anhui Province. Soil samples were collected at a depth of 0–20 cm from the soil surface. Soil samples were collected from five different locations within 100 m^2 and composited in one sample bag to make representative soil samples. When samples were brought back to the lab, stones and debris in soil were removed. Sep, Q-Sep, H-Q-Sep, and R-Q-Sep at 15 $g\cdot kg^{-1}$ were mixed with 3-kg soil and placed in flowerpots. After soil in the flowerpots was balanced for 1 week, 30 spinach seeds were sown in each pot. The duration of the whole growth period was 60 days. Three duplicates per processing were set.

Analysis of soil properties

Physiochemical properties and heavy metals in the collected soil and spinach matured (60 days) soil were determined. Soil was air-dried at room temperature (25 °C) and sieved with 2-mm sieve. The soil pH value was measured with a pH meter (MP220, Mettler Toledo, USA) after shaking 5 g of soil and 25 ml of distilled water for 1 h at a shaker speed of 300 rpm and 25 °C. Total nitrogen in soil was determined by the Kjeldahl method (HJ 711-2014), total phosphorus in soil was determined by molybdenum-antimony resistance colorimetry soil (HJ 632-2011), and organic matter (OM) was determined by oxidation potassium dichromate colorimetric method (Nelson et al. 1996). The basic properties of soil are shown in Table 1.

After soil samples were digested with aqua regia (HNO_3 to HCl (v to v) =1:3) (Yoon et al. 2019), their content of Cd was measured by an atomic absorption spectrophotometer (Analyst 100, PerkinElmer, USA). The Tessier five-part extraction method (Tessier et al. 1979) divides heavy metals in soil into five forms according to their biological activities, which are exchangeable Cd, carbonate-bound Cd, iron–manganese oxide–bound Cd, organic matter–bound Cd, and residual Cd. Various forms of Cd in soil were extracted and the content of Cd was determined by an atomic absorption spectrophotometer (Analyst100, PerkinElmer, USA). In order to ensure the accuracy of the test process and data, quality control and quality assurance measures were taken. During the test, blank reagents, three samples, and national mineral soil standard material (GSS-3) were included, to verify the accuracy of the digestion and analysis method, and the analysis error was less than 10%.

Plant sample measurement

Measurement of plant height, root length, biomass, and Cd content

After 60 days of culture cycle, three spinach plants of uniform size were selected for each treatment. Plant height and root length were measured after washing with distilled water. Then, the plants were put in an oven at 105 °C for 40 min and dried at 80 °C to constant weight. The dried weights of plants were recorded.

The dried spinach was divided into stems, leaves, and roots; after grinding the 2-mm sieve, they were digested with aqua regia (HNO_3 to HCl (v to v) =1:3). After that, the content of Cd in spinach was measured by an atomic absorption spectrophotometer (Analyst 100, PerkinElmer, USA).

Table 1 Basic physical and chemical properties of gangue-filled soil

Properties	Soil value
pH	6.87
OM ($g\cdot kg^{-1}$)	33.31
Total N ($g\cdot kg^{-1}$)	5.28
Total P ($g\cdot kg^{-1}$)	0.44
Total Cd ($mg\cdot kg^{-1}$)	0.57

OM stands for soil organic matter; total N, total P, and total Cd are the concentrations of total nitrogen, total phosphorus, and total cadmium in soil, respectively

Determination of chlorophyll, malondialdehyde content, and antioxidant enzyme activity

The blotted fresh leaves of the plants were used for the estimation of chlorophyll. The leaves were ground into powder with liquid nitrogen in the dark. Absolute ethanol and acetone were mixed with a volume ratio of 1:2 to obtain the extract solution. The extract solution was added to the plant powder, and the mixture was stored in the dark for more than 3 h to extract chlorophyll. Then, the supernatant was measured at 645 nm and 663 nm by an ultraviolet-visible spectrophotometer (UV-5500, Shanghai Metash Instruments, China), and the absorbance value was read for calculation.

Leaf samples (0.2 g) were ground with liquid nitrogen and homogenized with 1.8 ml phosphate buffer. Then, the homogenate was centrifuged at 6000 rpm and 4 °C for 15 min. This supernatant was used to measure the activities of superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) and the content of malondialdehyde (MDA) (Huang et al. 2020). These steps were followed by a kit (Nanjing Jiancheng Bioengineering Institute).

Data analysis

There were three duplicates in all processing, and the statistical analysis of experimental data was performed with SPSS (Version 20.0) software. And all values are expressed as mean ± standard deviation (SD). One-way analysis of variance (ANOVA) was used to analyze the statistical characteristic differences of sample data, When a significant ($p < 0.05$) difference was observed between treatments, multiple comparisons were made by the Duncan test. The graphical work was performed with Origin 2022b.

Results

Effects of modified sepiolite on soil pH values

According to Fig. 1, sepiolite modified by HCl and mercaptosilane can increase the pH in soil significantly ($p < 0.05$) compared with the control group. And with the increase of the concentration of HCl, it showed a trend of first increasing and then decreasing. The highest increase in soil pH (7.65) was observed when the concentration of HCl was 3 M, which was 0.78 higher than the control group. In the group of thermal treatment as pretreatment, the highest increase in soil pH (7.71) was observed when the temperature was 300 °C, which was 0.84 higher than the control group.

When Q-Sep and Sep were added to soil the pH values of the soil increased by 0.54 and 0.46, respectively. This is because sepiolite contains a large amount of calcium

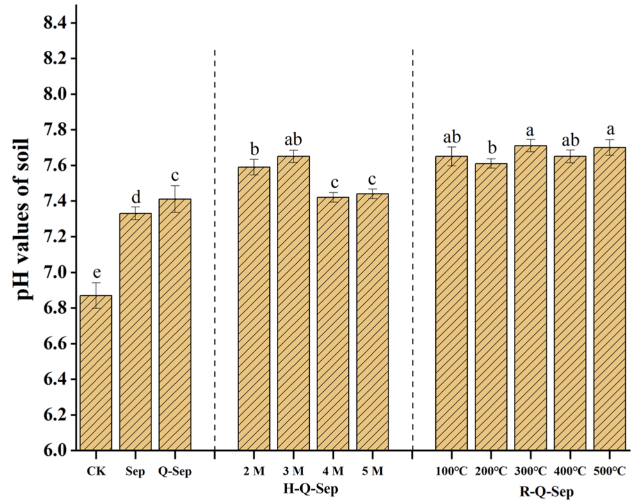

Fig. 1 Effects of different hydrochloric acid concentration and temperature modified sepiolite on pH values of soil. Letters above the bar diagram refer to the difference at significance level $p < 0.05$ among different treatments of sepiolite. Note:Sep stands for sepiolite, Q-Sep stands for sulfhydryl modified sepiolite, H-Q-Sep is sulfhydryl modified sepiolite after acidification, and R-Q-Sep is sulfhydryl modified sepiolite after high temperature. In this experiment, the number of samples n= 3, and the level of significance test was $p < 0.05$

carbonate, which has a certain neutralization effect on the hydrogen ions in the soil (Tang et al. 2016). It can be seen from Fig. 1 that the addition of H-Q-Sep and R-Q-Sep can increase the pH values of soil. However, R-Q-Sep can increase pH values to a greater extent than H-Q-Sep, probably due to the increased concentration of HCl in the H-Q-Sep treatment, which resulted in a similar increase of hydrogen ions in soil, resulting in a slight drop in pH values. Hence, R-Q-Sep increased pH values of soil more significantly.

Wang et al. (2015) added serpentine and lime to contaminated soil, which significantly increased pH values of the soil. The reason was that there existed a large number of internal and external hydroxyl groups in the serpentine structure with strong chemical reactivity. The hydrogen atoms could covalently bond to highly electronegative atoms such as O, F, and N to form hydroxyl groups and then generate an alkaline solution, resulting in an increase of soil pH values (Sharma et al. 2009). In this experiment, sepiolite also contained internal and external hydroxyl groups; the same reaction as serpentine can occur and improve soil pH values. The rise of soil pH values can also convert Cd in soil from exchangeable state to residual state through coordination, precipitation, etc. It is conducive to the substitution of magnesium in the edge structure of sepiolite octahedral sheets, which is beneficial to the adsorption of heavy metals in soil by sepiolite (Biswas et al. 2016). Therefore, increasing soil pH value is also one of the main methods of soil heavy metal remediation.

Effects of modified sepiolite on the occurrence form of Cd in soil

The effects of adding H-Q-Sep and R-Q-Sep to soil with different concentrations of HCl and temperatures on the forms of Cd in soil are shown in Fig. 2. The addition of H-Q-Sep can significantly improve the passivation effect of Cd in soil. In this treatment, the content of exchangeable state Cd was significantly reduced and the content of residual state was increased compared with the control group.

Among them, the most significant effect was observed when the concentration of HCl was 3 M. Compared with the control group, the content of exchangeable Cd decreased by 60.4% and the residual content increased by 32.9%. The content of exchangeable Cd in soil decreased by 21.9% and 34.2%, when Sep and Q-Sep were added. The content of residual state increased by 4.69% and 16.4%, respectively. On the one hand, this is due to the increase of soil pH values, which converts Cd in soil from the more active exchangeable state to the residual state through coordination, precipitation, etc. (Liang et al. 2014). On the other hand, there are certain pores in sepiolite, which can convert exchangeable and carbonate-bound Cd into residual state by adsorption (Lu et al. 2018). In addition to combining with hydroxyl groups on the surface of sepiolite, active Cd can also complex with sulfhydryl groups, thereby changing its morphology (Liang et al. 2011).

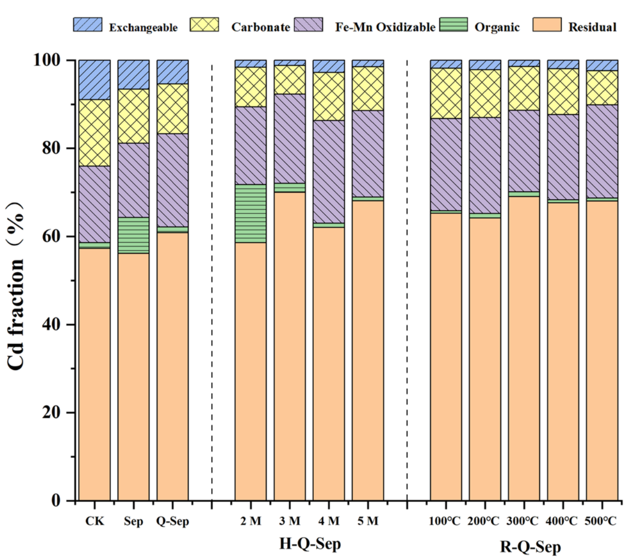

Fig. 2 Effects of different hydrochloric acid concentration and temperature modified sepiolite on the speciation of cadmium in soil. Note:Sep stands for sepiolite, Q-Sep stands for sulfhydryl modified sepiolite, H-Q-Sep is sulfhydryl modified sepiolite after acidification, and R-Q-Sep is sulfhydryl modified sepiolite after high temperature. In this experiment, the number of samples n= 3

It can be seen from Fig. 2 that the sepiolite modified by high temperature and mercaptosilane also has a passivation effect on Cd in soil, the content of exchangeable Cd decreased, and the content of residual state was also significantly increased. Among them, the best passivation effect was produced when the R-Q-Sep temperature was 300 °C. Compared to the control group with the treatment of additional Sep and Q-Sep, its content of exchangeable state decreased by 58.9%, 47.1%, and 37.5%, respectively. The increase of residual state was 31.2%, 28.0%, and 20.0%, respectively. After high-temperature roasting and HCl activation, the excess water in the sepiolite was lost, the purity was improved, its internal pores were enlarged, and the specific surface area became larger (Liang et al. 2014). The sulfhydryl group was more easily attached to the surface of sepiolite, and the adsorption effect was better. However, when the temperature was too high, a large amount of crystal water in sepiolite may come out, which would lead to the destruction of the structure of sepiolite and the collapse of its internal pores, making its specific surface area smaller. Therefore, too high temperature will lead to a decrease of passivation effect of R-Q-Sep on soil. The results showed that the addition of H-Q-Sep and R-Q-Sep can reduce the content of exchangeable Cd in soil and reduce toxicity of Cd to the environment and organisms.

The chemical forms of heavy metals in soil vary significantly in terms of their effectiveness and harmfulness to organisms (Kim et al. 2003). Among them, the higher the exchangeable content is, the stronger the toxic effect on organisms. The mutual transformation of different forms of heavy metal Cd in soil is the main process of passivation remediation. The addition of H-Q-Sep and R-Q-Sep can transform Cd from a more active form to a less active form or a form that is difficult for biology to use, thus achieving the purpose of heavy metal remediation.

Effects of modified sepiolite on physiology and biochemistry of spinach

Effects of modified sepiolite on Cd absorption of spinach

The effect of different modified sepiolite on the absorption of Cd by spinach is shown by Fig. 3. The addition of passivating agents can reduce the absorption of Cd by spinach, and there were significant differences ($p < 0.05$) compared with the control group. The addition of Q-Sep can reduce the content of Cd in the aboveground and underground parts of spinach by 35.83% and 47.76%, respectively. In the treatment of H-Q-Sep, when the concentration of HCl was 3 M, spinach had the lowest concentration of Cd. The content of Cd in aboveground and underground parts of spinach

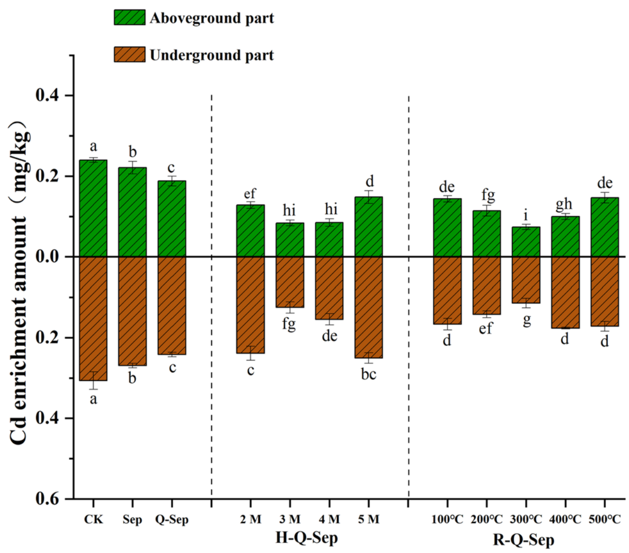

Fig. 3 Effects of different hydrochloric acid concentration and temperature modified sepiolite on cadmium accumulation in spinach. Letters above the bar diagram refer to the difference at significance level $p < 0.05$ among different treatments of sepiolite. Note:Sep stands for sepiolite, Q-Sep stands for sulfhydryl modified sepiolite, H-Q-Sep is sulfhydryl modified sepiolite after acidification, and R-Q-Sep is sulfhydryl modified sepiolite after high temperature. In this experiment, the number of samples n= 3, and the level of significance test was $p < 0.05$

decreased by 65.0% and 59.2%, respectively. The content of Cd in the aboveground part decreased from 0.24 mg·kg^{-1} in the control group to 0.08 mg·kg^{-1}; the content of Cd in the underground part decreased from 0.30 mg·kg^{-1} to 0.12 mg·kg^{-1}.

In the group with R-Q-Sep addition, spinach had the lowest concentration of Cd when the modified temperature was 300 °C, in which the content of Cd in aboveground part decreased to 0.07 mg·kg^{-1}, and the content of Cd in the underground part was reduced to 0.11 mg·kg^{-1}, with the declines of 69.2% and 60.7% respectively. The transfer coefficient of spinach was lower than other groups and the content of Cd in leaves was lower when the modified temperature of sepiolite was 400 °C, which might be due to the randomness of sampling. The location of spinach young leaves was determined by sampling; when the modified temperature was 500 °C, the available content of Cd in soil was greater, and plants enriched more Cd, so the content of aboveground part was lower than at 500 °C (Shamshad et al. 2018).

The absorption of heavy metals by plants mainly occurs when heavy metals in the form of ions are adsorbed by the roots of plants and transferred to other parts such as stems, leaves, and fruits. During the process of enrichment, the uptake of heavy metals by roots depends on soil properties, such as soil pH values, soil content of organic matter, and soil nutrients (Zulfiqar et al. 2019). In general, the increased soil pH value promotes the formation of heavy metal carbonate and hydroxide precipitation, thereby reducing the utilization of heavy metals by organisms (Qin et al. 2020). Bashir et al. (2018) added straw biochar to soil, which significantly increased pH value and reduced availability of Cd in soil and absorption of Cd by water spinach. Hong et al. (2020) showed that the concentration of Cd in lettuce was negatively correlated with soil pH, and an increase of soil pH could promote the immobilization of Cd in soil.

Effects of modified sepiolite on plant height, root length, and biomass of spinach

The effects of adding modified sepiolite to soil under different conditions on the root length, plant height, and biomass of spinach are shown in Table. 2. The root length, plant height, and biomass of spinach in each group had different degrees of improvement. In the group pretreated with HCl, when the concentration of HCl was 3 M, the root length, plant height, and biomass increased by 43.8%, 63.3%, and 88.2%, respectively. In the group pretreated at high temperature, when the temperature was 300 °C, the growth index of spinach increased most. And compared to H-Q-Sep and Q-Sep, the addition of R-Q-Sep can reduce toxicity of Cd and increase pH values of soil to a greater extent; it also increases productivity of soil and growth of spinach. HCl can improve the purity of sepiolite and high-temperature roasting can remove the excess crystal water in sepiolite (Rusmin et al. 2016). It can increase the specific surface area of sepiolite and expand its porosity. Therefore, it is more convenient for sulfhydryl to load and more conducive to the adsorption of heavy metals in soil by sepiolite, thus reducing toxicity of Cd to organisms in soil. Anjum et al. (2011) found that the dried weight of mung bean seedlings was reduced by 59.8% in soil containing 100 mg·kg^{-1} Cd. Gu et al. (2020) confirmed that adding passivating agents can increase the nutrients in soil, reduce toxicity of Cd to plant roots, and increase the biomass of beet roots by 267%.

Effects of modified sepiolite on chlorophyll content of spinach

Photosynthesis is the basis of plant growth. When heavy metal Cd contaminates plants, it will affect photosynthetic pigments of plants and thus affect the photosynthesis of plants (Qin et al. 2018). As shown in Fig. 4, the addition of H-Q-Sep and R-Q-Sep increased the total amount of chlorophyll in spinach leaves. The highest points were at a concentration of HCl which was 3 M and modified temperature which was 300 °C, and there was a significant difference between them and the control group ($p < 0.05$). This is due to the excessive stress of Cd in the control group, and heavy metal ions were absorbed by plants and accumulated

Table 2 Effects of different modified methods of sepiolite on plant height, root length, and biomass of spinach

Group		Plant height (cm)	Root length (cm)	Biomass (g)
	CK	6.0 ± 0.65e	4.9 ± 0.25bc	0.0399 ± 0.0012e
	Sep	6.7 ± 0.36e	5.4 ± 0.49abc	0.0532 ± 0.0021cde
	Q-Sep	9.5 ± 0.41bc	5.6 ± 0.68abc	0.0576 ± 0.0021bcde
H-Q-Sep	2 M	9.1 ± 0.93bcd	4.6 ± 0.86c	0.0452 ± 0.020e
	3 M	9.8 ± 2.20bc	7.0 ± 1.38ab	0.0751 ± 0.0082abcd
	4 M	7.8 ± 2.11cde	6.1 ± 1.05abc	0.060 ± 0.028bcde
	5 M	7.4 ± 1.81cde	5.6 ± 0.50abc	0.047 ± 0.012de
R-Q-Sep	100 °C	11.3 ± 0.69ab	4.8 ± 0.63bc	0.083 ± 0.012ab
	200 °C	10.3 ± 0.36ab	7.6 ± 1.33a	0.065 ± 0.0092bcde
	300 °C	12.1 ± 0.40a	7.5 ± 2.95a	0.102 ± 0.021a
	400 °C	7.1 ± 1.76de	6.2 ± 0.30abc	0.056 ± 0.0070bcde
	500 °C	9.5 ± 1.21bc	5 ± 0.55bc	0.0781 ± 0.025abc

The same letters are not significantly different at $p < 0.05$ according to Duncan multiple comparisons. The statistical analysis was a one-way ANOVA

in plants continuously, resulting in destruction of chloroplast structure. The addition of modified sepiolite reduced toxicity of Cd in soil to plants and increased the content of chlorophyll in plants. It can weaken the effect of Cd on plant photosynthesis and improve the ability of plant photosynthesis and promote growth of plant (Lu et al. 2018). Singh et al. (2006) found that heavy metals can replace magnesium ions in chlorophyll, decrease the activity of chlorophyll synthase, and cause chlorophyll synthesis to be blocked. At the same time, the activity of chlorophyll decomposing enzymes is increased and the decomposition of chlorophyll is accelerated. The decrease of chlorophyll content had an adverse effect on growth of plants, which was consistent with the previously recorded indicators of plant growth.

Effects of modified sepiolite on antioxidant enzyme activity and malondialdehyde content of spinach

When plants are subjected to external stress, they produce oxidative stress and a large amount of reactive oxygen species (Soares et al. 2019). Reactive oxygen species can interact with proteins, lipids, and nucleic acids in cells to change their structure and function and eventually lead to membrane lipid peroxidation. The content of MDA is an

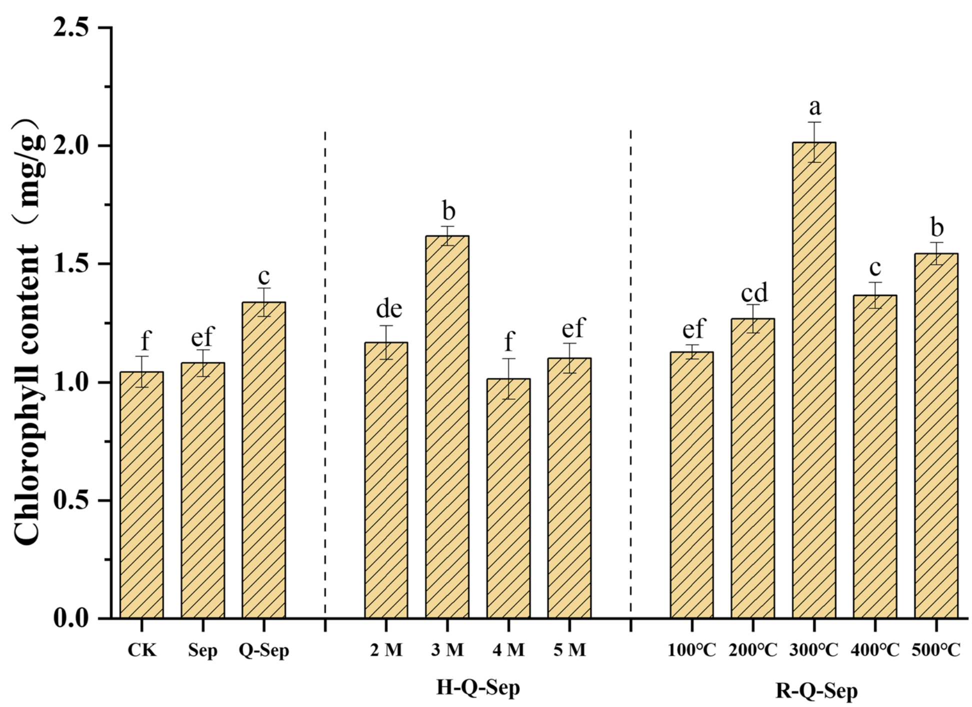

Fig. 4 Effects of different concentrations of hydrochloric acid and temperature modified sepiolite on chlorophyll content of spinach. Letters above the bar diagram refer to the difference at significance level $p < 0.05$ among different treatments of sepiolite. Note:Sep stands for sepiolite, Q-Sep stands for sulfhydryl modified sepiolite, H-Q-Sep is sulfhydryl modified sepiolite after acidification, and R-Q-Sep is sulfhydryl modified sepiolite after high temperature. In this experiment, the number of samples n= 3, and the level of significance test was $p < 0.05$

important index that reflects the strength of membrane lipid peroxidation (Zhang et al. 2007). Studies have shown that when plants are under stress, the activities of antioxidant enzymes in plants will increase rapidly to maintain their vitality under stress (Yadhu et al. 2017). According to Fig. 5, the activities of SOD, POD, CAT, and the content of MDA in the control group were highest, while those in other treatments decreased to varying degrees and there were significant differences from the control group ($p < 0.05$). The most significant effect was observed when the concentration of HCl was 3 M and the modified temperature was 300 °C, because the stress of Cd on spinach was the lowest at this time. The addition of modified sepiolite reduced the stress of Cd to spinach to different degrees. Therefore, the activity of antioxidant enzymes and the content of MDA also decreased to varying degrees.

Discussion

Spinach is a common and nutritious leafy vegetable (Zubair et al. 2019). Cd pollution in agricultural land poses a threat to growth of crop and human health. Cd in farmland is easily absorbed by plants and transferred to edible parts of plants. The concentration of Cd in spinach in the control group exceeded the Chinese national standard GB 2762-2012 (the highest level of pollutants in food) by 0.2 mg·kg^{-1} (Fig. 3). Hence, two different modified sepiolite were added to contaminated soil, and the chemical forms of Cd in the treated soil and the growth of spinach were analyzed and compared by pot experiment. The results showed that the addition of modified sepiolite could reduce toxicity of Cd in soil, inhibit the stress of Cd on spinach, and promote the growth of spinach.

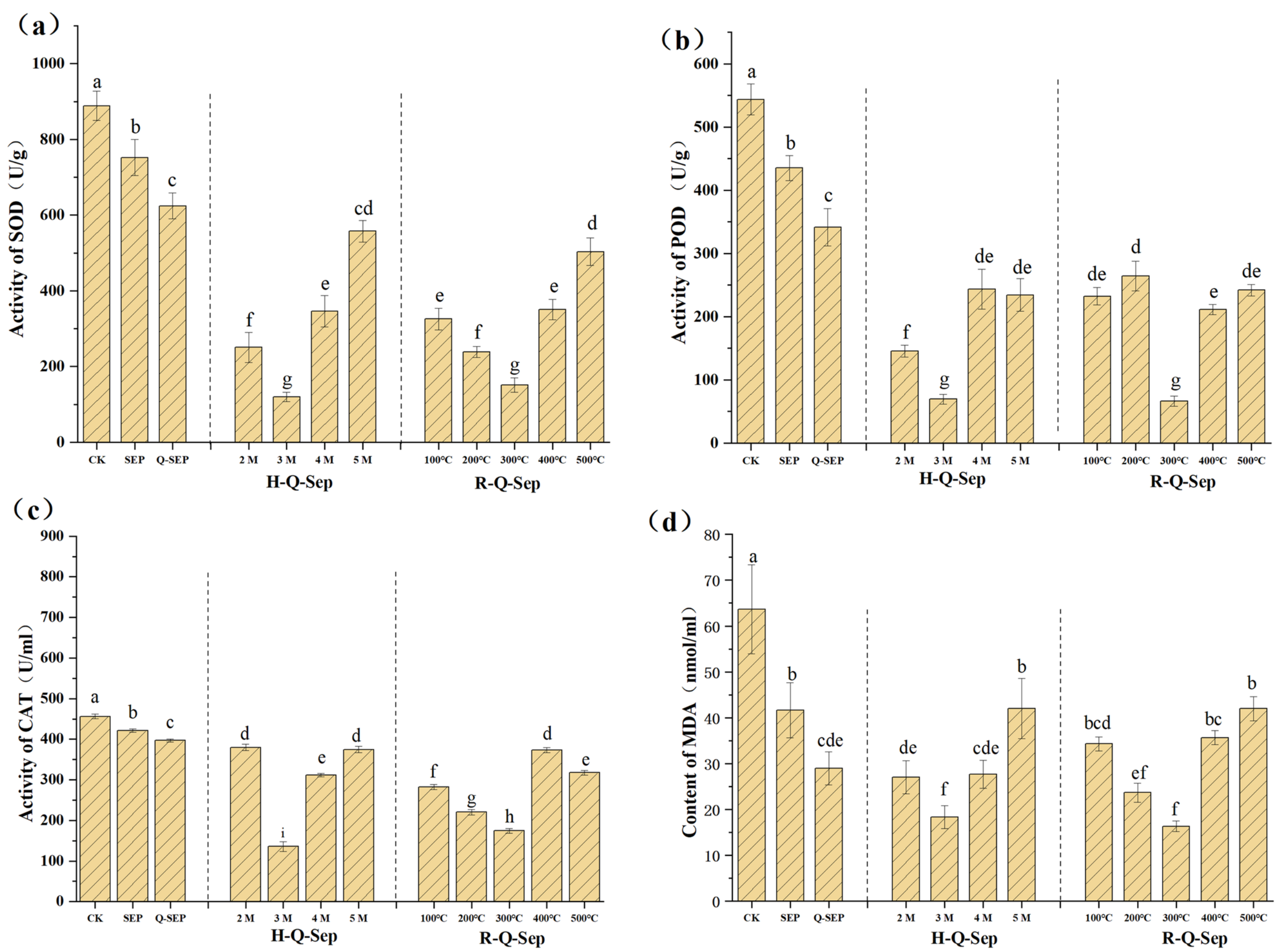

Fig. 5 Effects of different hydrochloric acid concentration and temperature modified sepiolite on antioxidant enzyme activity and malondialdehyde content of spinach. Letters above the bar diagram refer to the difference at significance level $p < 0.05$ among different treatments of sepiolite. Note:Sep stands for sepiolite, Q-Sep stands for sulfhydryl modified sepiolite, H-Q-Sep is sulfhydryl modified sepiolite after acidification, and R-Q-Sep is sulfhydryl modified sepiolite after high temperature. In this experiment, the number of samples n= 3, and the level of significance test was $p < 0.05$

Soil pH value can affect the absorption of Cd by plant roots (Huang et al. 2020). Sepiolite is an alkaline substance that can be hydrolyzed to release hydroxide ions to raise soil pH value and thus fix Cd in the soil (Inkham et al. 2019). We used sulfhydryl to modify sepiolite and loaded the sulfhydryl functional group on the surface of sepiolite to form a stable complex, thus enhancing the adsorption performance of sepiolite. Sepiolite pretreatment work (acidification or high temperature) was performed to improve its purity. Our results showed that the addition of passivating agents can reduce the content of exchangeable Cd in soil and reduce the toxicity of Cd (Fig. 2). By using modified sepiolite as a passivating agent, pH values in soil can be significantly increased, thus reducing the content of Cd in spinach roots and leaves (Fig. 3) (Shangguan et al. 2019; Sanderson et al. 2015). Many studies have shown that the addition of passivating agents can reduce the enrichment of heavy metals by plants in heavy metal polluted soil. For example, the addition of hydrated lime and sepiolite significantly reduced the content of Cd in rice grains (Huang et al. 2020). The addition of passivating agents increased the soil pH values (Fig. 1) and reduced the content of exchangeable Cd in the soil. The results showed that a higher soil pH value would make the Cd in the soil fixed, thus reducing the absorption of Cd by plants in soil.

The most common plant response to stress is growth slowdown. Root is the first part of plants to contact pollutants in the soil environment, which can most obviously reflect the absorption of heavy metals in plants. Pollutants also have a relatively obvious inhibitory effect on roots, so the root length can better reflect the toxic effect of Cd on spinach (Xu et al. 2019). After the addition of modified sepiolite, the plant height, root length, and biomass of spinach in each treatment were significantly higher than those in the control group (Table 2) because the stress of Cd on spinach was relieved to some extent, which made the growth of spinach tend to be normal. We analyzed on the correlation between plant height and root length, and there was a certain correlation between them, but the correlation was not significant. We analyzed the main reason why the correlation between them was not significant, mainly because the root length of spinach was shorter when the concentration of modified HCl was 2 M and the modified temperature was 100 °C. In the measurement, we found that the fibrous roots of the two groups of spinach were relatively exuberant and therefore, the straight roots were shorter (Liu et al. 2006). After the two groups of data had been removed, we conducted correlation analysis on the plant height and root length of spinach again and found a significant correlation between them ($p < 0.05$). We analyzed the correlation between plant height and biomass of spinach and found a significant correlation, which was related to the variety of spinach. The variety of spinach planted in this study was large-leaf spinach, so for biomass, the aboveground part accounted for the dominant biomass, and there was a significant correlation between plant height and biomass ($p < 0.05$).

Chlorophyll is essential for plants to capture light energy and plays a central role in photosynthesis. Its content can directly affect the photosynthesis of plants and therefore affect the accumulation of net photosynthetic energy of plants, thus affecting the yield and biomass of plants (Golan et al. 2015). The stress of Cd is not conducive to the synthesis of photosynthetic pigments, resulting in the decrease of the photosynthetic rate of plants. Therefore, the synthesis of chlorophyll under the stress of Cd has a significant inhibitory effect (Zhang et al. 2021). In this experiment, the addition of modified sepiolite to the soil can improve the pH values and reduce the toxicity of Cd in soil, thus promoting the synthesis of chlorophyll in spinach (Fig. 4). The results showed that when two kinds of modified sepiolite were added, the content of chlorophyll in spinach was the highest when the concentration of HCl and the temperature were 3 M and 300 °C, respectively. This is because at this time, the stress of Cd in soil to plants was the lowest, and the accumulation of heavy metals in spinach body was the lowest. Therefore, the addition of modified sepiolite is beneficial to improve plant photosynthesis and promote the accumulation of carbohydrates in plants, which is necessary to reduce the stress of Cd on plants.

Malondialdehyde is the product of peroxidation of plant membrane lipids. Studies have shown that content of MDA in plants can be significantly increased under Cd stress (Zhang et al. 2021). In our study, the addition of modified sepiolite significantly reduced the content of MDA in spinach (Fig. 5a). Antioxidant enzymes (SOD, POD, CAT) are substances produced by plants to resist various external stresses. They protect plants from oxidative stress by removing reactive oxygen species (Geslin et al. 2001). Under heavy metal stress, plants produce excessive reactive oxygen species, which stimulates the production of antioxidant enzymes. Our results showed that the activities of SOD, POD, and CAT in spinach decreased after passivating agent was added (Fig. 5b–d), indicating that the addition of modified sepiolite increased soil pH value and inhibited the absorption of Cd by spinach roots, and plant roots did not need to produce more antioxidant enzymes to resist the stress of Cd (Huang et al. 2020).

Conclusion

Sepiolite is a good material for passivation and remediation of heavy metals in soil. The sulfhydryl group can be loaded on the surface of sepiolite modified by mercaptosilane to enhance its adsorption capacity. The purity of sepiolite can be increased by HCl and high-temperature pretreatment, the internal pores become larger, and the specific surface area increases, which is more conducive to the loading of sulfhydryl groups. The modified sepiolite has stronger adsorption and passivation ability for heavy metals. The following conclusions are drawn from the experimental results: (1) the addition of modified sepiolite can change the soil environment and increase the pH values of soil; (2) the addition of modified sepiolite can transform Cd in soil from exchangeable state to residual state, thus reducing the toxicity of Cd in soil; and (3) The addition of modified sepiolite can reduce the absorption of Cd in the soil by spinach, promote the growth of spinach, increase the content of chlorophyll in spinach, and reduce the activity of antioxidant enzyme and the content of MDA in spinach. Therefore, the addition of sepiolite modified by acid, heat, and sulfhydryl is an effective method to remediate Cd in soil and can promote the growth of spinach.

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Author contribution All authors contributed to the study conception and design. Yuchen Li: methodology, formal analysis, software, formal analysis, writing original draft, and visualization. Xing Chen and Liqun Zhang: data curation, validation, writing, review, and editing. Jie Hu and Chunlu Jiang: writing, review, and editing. Yongchun Chen and Shikai An: supervision. Liugen Zheng: conceptualization, resources, project administration, and funding acquisition.

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Data availability The data collected are property of our research center but will be made available by the corresponding author when requested.

Declarations

Ethics approval Not applicable.

Consent to participate All authors equally participate in the study.

Consent for publication All authors allow the publication of the paper.

Competing interests The authors declare no competing interests.

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