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Study of the Effects on Mn, Pb, and Zn Solidification in Soil by a Mixed Curing Agent of Modified Diatomite

Zhixian Li,* Limei Chen, Zhang Chen, Guoliang Chen, Jianlin Zhou, and Xiling Liu

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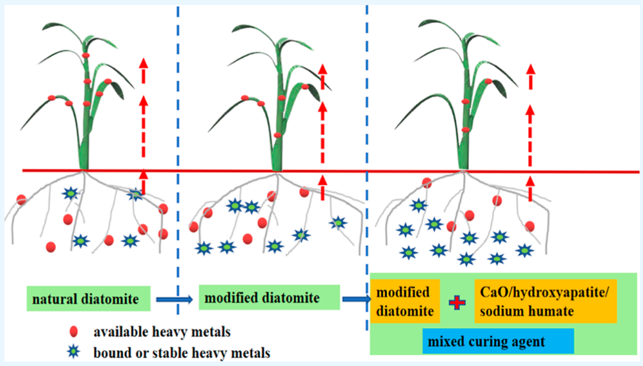
ABSTRACT: In order to improve the application scale of diatomite in the remediation of heavy metal-contaminated soil in non-ferrous metal mining areas, the preparation of the modified diatomite-combined curing agent and its stabilizing effect on manganese (Mn), lead (Pb), and zinc (Zn) were systematically studied in non-ferrous metal tailing soil in this paper. The results showed that compared with that in natural diatomite (DE), the contents of available Mn in soil treated by acid- and alkali-modified diatomite samples (C-D and Na-D) were 18.82 and 25.93% lower, respectively, and the content of available Zn in Na-D was significantly lower, 6.71%, than that in DE. Further research showed that modified diatomite combined with quicklime (CaO) and hydroxyapatite (HAP) could significantly improve the solidification effect of soil heavy metals. Compared with that in single modified diatomite, the contents of available Mn, Pb, and Zn in the mixed curing agent-treated soil decreased by 23.59−46.32, 5.88−47.93, and 5.37−10.68%, respectively. The final pot test showed that the mixed curing agent of modified diatomite had no significant effect on the growth of plants, but it could reduce the Mn, Pb, and Zn accumulation in the upper and lower parts of plants, which is because the acid-soluble and reducible heavy metals in soil transform into an oxidizable and residual state, which reduces the mobility of heavy metals.



1. INTRODUCTION

In recent years, the non-ferrous metal industry of China has developed rapidly, resulting in increasingly serious soil heavy metal pollution in China.[1] At present, about 20 million hm^2 of cultivated land in China is polluted by heavy metals such as Cd, Pb, and Mn, of which nearly 3.333 million hm^2 is heavily polluted by heavy metals.[2] Therefore, the soil environmental quality of cultivated land in China is degraded, and the soil pollution problem of the industrial and mining wasteland is also very prominent.[3] As the heavy metals in the soil are stable, hidden, irreversible, easy to accumulate, and difficult to degrade by microorganisms, once the soil is polluted by heavy metals, it is difficult to repair in a short time,[4,5] which will not only reduce crop yield[6] but also have a serious impact on human health.[7] Therefore, exploring green, economic, and efficient remediation methods for heavy metal-contaminated soil[8] has become one of the urgent directions at this stage.

The remediation methods of heavy metal pollution soil mainly include physical remediation, chemical remediation, and phytoremediation. In situ solidification remediation is one of the simple, efficient, and widely used remediation methods of heavy metals in soil at present,[9] which consists of applying solidified materials into the heavy metal-polluted soil to change the availability of heavy metals in soils by changing the physical and chemical properties of the soils (ion exchange, adsorption, and precipitation)[10−12] and reducing the bioavailability and mobility of heavy metals, thus reducing the environmental risk of heavy metals.[13] Clay materials such as zeolite, bentonite, and sepiolite have been widely used in in situ solidification and remediation of heavy metal-contaminated soil because of their large specific surface area, rich reserves, low price, stable chemical properties, and environmental friendliness.[14,15] Studies have shown that sepiolite could improve the pH of soil, which transforms the Pb and Cd from the extractable state with high activity to a more stable state, and significantly reduce the availability of Pb and Cd.[16] Liang et al. found that adding the mixture of dolomite, diatomite, montmorillonite, bentonite, alginate, and zeolite as the remediation material of heavy metal-contaminated soil can significantly change the dehydrogenase and β-glucosidase activity and effectively reduce the potential bioavailability of Pb, Zn, Cu, and Cd.[17] However, due to the different physical and chemical environments of the soil and the heavy metal

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compound pollution of soil, the use of natural clay still has some limitations due to low or incomplete solidification efficiency of heavy metals in soil. The modification of natural clay can achieve the purpose of more efficient and stable solidification and adsorption of heavy metals in soil.[18,19] Liu[20] researched that the modified biochar had richer surface properties and better adsorption effects on heavy metals than natural biochar. Liu et al.[21] applied hydrochloric acid-modified palm biochar to the soil and monitored the occurrence forms of heavy metal arsenic in the soil. It was found that compared with that in the soil without biochar, the acid extracted content of arsenic in the soil with modified biochar decreased by 23.6%, and the content of arsenic decreased by 71.4%, reducing the harm of heavy metal pollution in the soil. The above research studies indicated that there are great differences in the structure between the modified solidified material and the natural material, and the modified solidified material can effectively improve the adsorption effect and adsorption capacity of heavy metals. Diatomite was also a preferred heavy metal solidified material with a porous structure, easy modification, high adsorption capacity, wide distribution, and low cost. However, the solidification efficiency of single diatomite for heavy metal ions, especially for heavy metal compound-polluted soil, is not sufficient enough.[22,23] At present, the discussion on the remediation of heavy metals in soil by diatomite mostly focuses on improving the solidification efficiency of diatomite to single polluted heavy metals through different modification methods.[24,25] In view of the current situation of compound pollution of heavy metals in soil, there are few studies on the efficient modification of diatomite, the preparation of a mixed curing agent of modified diatomite, and its application in the remediation of heavy metal compound pollution soil.

Based on the above analysis, this study selected diatomite as the adsorption natural material of soil heavy metals, modified diatomite with acids and alkalis, explored the adsorption and solidification effect of acid- and alkali-modified diatomite on Mn, Pb, and Zn in soil. The modified diatomite was further combined with quicklime and hydroxyapatite in two-phase and three-phase processes, respectively, to screen the advantages of mixed modified diatomite and analyze the high-efficiency solidification effect of mixed modified diatomite on soil heavy metal. A synchronous design pot experiment was performed to verify the effect of the dominant mixed modified diatomite on the bioavailability of heavy metals in soil, and its mechanism is revealed. This study can provide the technical support for the large-scale application of diatomite in the remediation of heavy metal compound pollution of soil and also provide a theoretical basis for the efficient solidification and remediation of heavy metal compound pollution of soil.

2. MATERIALS AND METHODS

2.1. Test Soil. The soil samples used in this study were obtained from a manganese ore tailing soil. The soil at a depth of 0−20 cm was collected from five different locations and mixed evenly. After the treatment, the heavy metal content of the soil was determined (Table 1). Compared with the standard documents related to heavy metals in soil, the contents of Zn, Mn, and Pb in the tailing soil of the Xiangtan manganese mine far exceeded the standard values of heavy metal content in soil (Table 2).

Table 1. Heavy Metal Content in Soil ($mg \cdot kg^{-1}$)

soil type	total heavy metal content		
	Mn	Pb	Zn
red soil	200 275	695	1130

Table 2. Executive Standard

standard documents	standard values ($mg \cdot kg^{-1}$)			
	pH	Pb	Zn	Mn
“soil environmental quality standard”	6−9	350	300	
“soil remediation standard for heavy metal-contaminated sites”	6−9	280	500	
national soil background value		26	74	
soil background value in a manganese mining area				583

2.2. Experiment Design. *2.2.1. Selection of Modified Diatomite.* According to the author’s previous experimental results of diatomite modification, the modified diatomite with heavy metal adsorption advantages, which was successfully modified in the early stage,[19] was selected as the composite material in this study. The specific modification treatments and the corresponding identifiers are shown in Table 3.

Table 3. Treatments and Identifiers of Modified Diatomite

number	treatment
CK	blank
DE	natural diatomite
C-D	diatomite + acetic acid (1 mol/L)
Na-D	diatomite + sodium hydroxide (3 mol/L)

2.2.2. Combination Experiment of Modified Diatomite. In view of the current situation of compound pollution of heavy metals in soil, to overcome the singleness and incompleteness of diatomite’s solidification and adsorption of heavy metals in soil, the modified diatomite is mixed and screened with other reagents in different types and different quantities, and then, it is cured under normal temperature, dry, and ventilated conditions for 7 days. The combination method of modified diatomite and the corresponding identifiers are shown in Table 4.

Table 4. Treatments and Identifiers of the Combination Experiment

number	treatment
D	C-D ($4\ g \cdot kg^{-1}$) + CaO ($2\ g \cdot kg^{-1}$) + hydroxyapatite ($2\ g \cdot kg^{-1}$)
E	C-D ($4\ g \cdot kg^{-1}$) + CaO ($4\ g \cdot kg^{-1}$) + hydroxyapatite ($4\ g \cdot kg^{-1}$)
F	C-D ($8\ g \cdot kg^{-1}$) + CaO ($4\ g \cdot kg^{-1}$) + hydroxyapatite ($4\ g \cdot kg^{-1}$)
G	Na-D ($4\ g \cdot kg^{-1}$) + CaO ($4\ g \cdot kg^{-1}$)
H	Na-D ($8\ g \cdot kg^{-1}$) + CaO ($4\ g \cdot kg^{-1}$)
I	Na-D ($4\ g \cdot kg^{-1}$) + CaO ($2\ g \cdot kg^{-1}$) + hydroxyapatite ($2\ g \cdot kg^{-1}$)
J	Na-D ($4\ g \cdot kg^{-1}$) + CaO ($4\ g \cdot kg^{-1}$) + hydroxyapatite ($4\ g \cdot kg^{-1}$)

2.2.3. Potted Validation Test of the Effectiveness of Heavy Metals. The pot experiment of heavy metal bioavailability was conducted in a randomized block design. A total of 12 treatments with three repetitions for each treatment were set. First, the non-polluted soil and heavy metal-polluted soil were mixed in the ratio of 3:1, where the non-polluted soil was vegetable garden soil, which belonged to red soil, and the contents of heavy metals Mn, Pb, and Zn were 625.2, 75.0, and 108.7 $mg \cdot kg^{-1}$, respectively. Second, the modified diatomite and quicklime and hydroxyapatite were added in mixed soil by two-phase or three-phase processes and in a certain proportion. After 14 days of balance, Shanghai Qing was sown in the soil and watered regularly. When the plant was mature (growth period 25 days), the content of heavy metals in the aboveground and underground parts of the plant and the content of different forms of heavy metals in rhizosphere soil were measured. The design of pot experiments is shown in Table 5.

Table 5. Treatments and Identifiers of Pot Experiments

number	treatment
1	CK
2	DE (8 g·kg^{-1})
3	C-D (8 g·kg^{-1})
4	Na-D (8 g·kg^{-1})
5	C-D (8 g·kg^{-1}) + sodium humate (4 g·kg^{-1})
6	C-D (8 g·kg^{-1}) + CaO (4 g·kg^{-1}) + hydroxyapatite (4 g·kg^{-1})
7	C-D (8 g·kg^{-1}) + CaO (4 g·kg^{-1}) + hydroxyapatite (4 g·kg^{-1}) + sodium humate (4 g·kg^{-1})
8	Na-D (8 g·kg^{-1}) + CaO (4 g·kg^{-1})
9	Na-D (8 g·kg^{-1}) + sodium humate (4 g·kg^{-1})
10	Na-D (4 g·kg^{-1}) + CaO (4 g·kg^{-1}) + hydroxyapatite (4 g·kg^{-1})
11	Na-D (8 g·kg^{-1}) + CaO (4 g·kg^{-1}) + sodium humate (4 g·kg^{-1})
12	Na-D (4 g·kg^{-1}) + CaO (4 g·kg^{-1}) + hydroxyapatite (4 g·kg^{-1}) + sodium humate (4 g·kg^{-1})

2.3. Index Measurement. *2.3.1. Soil pH Index.* The soil and distilled water were evenly mixed in the proportion of 1:2.5, and the pH value of the solid liquid mixed solution was measured using a pH meter after the mixture was left standing for 30 min. In order to explore the influence of modified diatomite on the soil pH value, the soil mixed with modified diatomite was cultured for 1 week, and the soil samples were analyzed to measure the pH value according to the above method.

2.3.2. Total Heavy Metals in the Soil and Plant. First, 0.2 g of the sample soil was accurately weighed and put into the digestion tube, 10 mL of aqua regia (hydrochloric acid/nitric acid = 3:1) was added into the digestion tube, and the digestion tube was sealed and put into the microwave digestion instrument (PYNN140899, CEM) for soil digestion. Then, the fully digested soil solution was filtered to a certain volume. Finally, the total amount of heavy metals in soil was determined and calculated using a flame atomic absorption spectrophotometer (SOLAAR M6, USA).

2.3.3. Different Forms of Heavy Metals in Soil. The different forms of heavy metals in soil were extracted using the BCR method. First, 0.5 g of the soil sample accurately weighed and put into a triangular flask. 20 mL of 0.1 mol/L acetic acid was added to the soil, and the soil solution was shaken at 22 °C for 16 h. Then, the soil solution was centrifuged (3000 rpm) for 20 min, and the supernatant was collected after centrifugation. The content of acid-soluble heavy metals in soil was calculated by testing the content of heavy metals in the supernatant. Then, 20 mL of 0.5 mol/L hydroxylamine hydrochloride was added to the residue after centrifugation. The soil solution was shaken at 22 °C for 16 h and centrifuged (3000 rpm) for 20 min. The supernatant was collected to test and calculate the content of reducible heavy metals in the soil. Then, 5 mL of hydrogen peroxide (30%) was added to the above centrifuged residue, and the soil solution was left standing at 25 °C for 1 h and heated in an 85 °C boiling water bath for 1 h. 25 mL of 1 mol/L ammonium acetate (pH = 2) was added, and the soil solution was shaken for 16 h and then centrifuged (3000 rpm) for 20 min. The supernatant was collected, and the content of oxidizable heavy metals in the soil was tested and calculated. Finally, 1.5 mL of deionized water, 3.75 mL of 6 mol/L hydrochloric acid, and 1.25 mL of 14 mol/L nitric acid were added to the above centrifugal residue. The soil mixed solution was allowed to stand overnight and refluxed for 2 h. The content of heavy metals in the filtrate was determined as the content of residual heavy metals.

3. RESULTS AND DISCUSSION

3.1. Effects of Modified Diatomite on Heavy Metals in Soil. *3.1.1. Effects of Modified Diatomite on the Soil pH Value.* The results (Figure 1) showed that compared with the blank treatment (CK), the application of natural diatomite (DE) did not significantly change the soil pH, while acid-modified diatomite (C-D) could significantly reduce the soil pH and alkali-modified diatomite (Na-D) could significantly increase the soil pH.

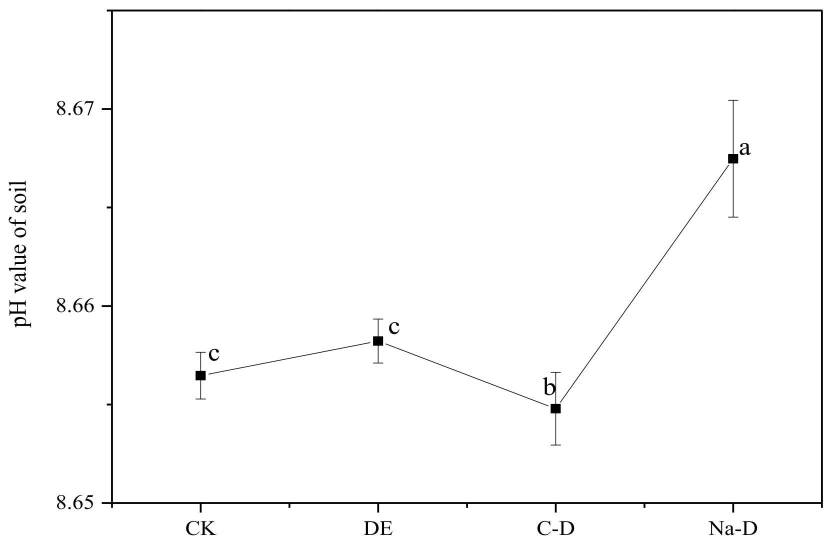

Figure 1. Effects of modified diatomite on the soil pH value.

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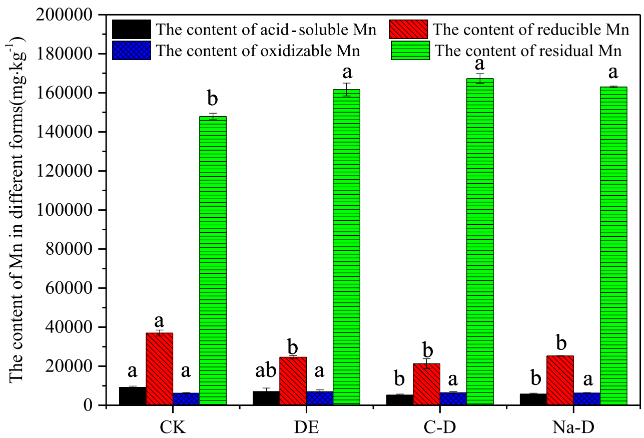

Figure 2. Effects of modified diatomites on the contents of Mn in different forms.

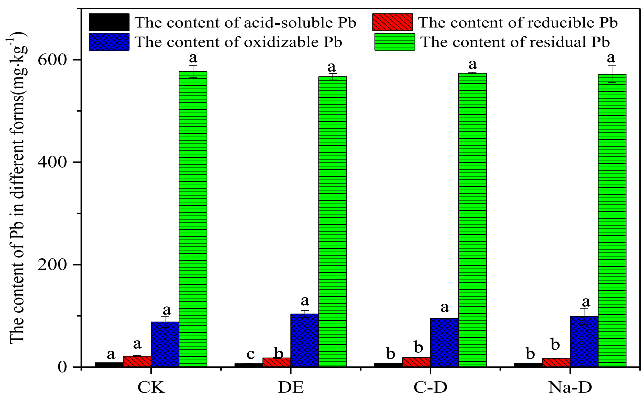

Figure 3. Effects of modified diatomites on the contents of Pb in different forms.

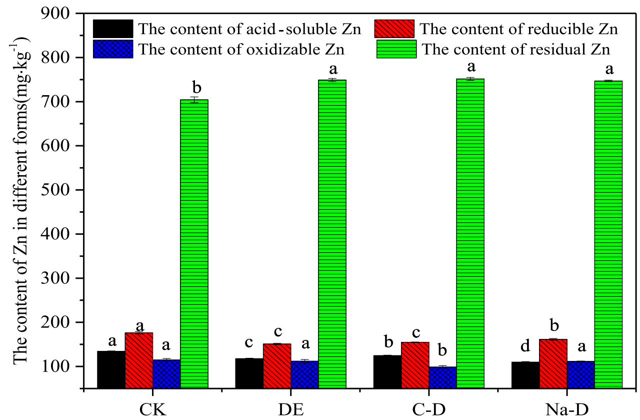

Figure 4. Effects of modified diatomites on the contents of Zn in different forms.

3.1.2. Effects of Modified Diatomite on the Contents of Different Forms of Mn, Pb, and Zn in Soil. Natural diatomite and modified diatomite showed obvious solidification ability to heavy metals Mn, Pb, and Zn in soil. The results (Figures 2−4) showed that compared with that in CK soil, the contents of acid-soluble available Mn, Pb, and Zn and reducible Mn, Pb, and Zn in soils of DE, C-D, and Na-D decreased by 7.25−43.30 and 8.45−42.46%, respectively. In general, the order of the solidifying efficiency of diatomite to Mn, Pb, and Zn was as follows: Mn > Pb > Zn. Compared with that of natural diatomite, the solidification ability of acid- and alkali-modified diatomite to Mn was significantly enhanced. Acid- and alkali-modified diatomites could transform acid-soluble Mn and reducible Mn in soil to oxidizable and residual Mn and stabilize the Mn existing forms in soil. The results in Figure 2 show that the contents of acid-soluble available Mn in soils of C-D and Na-D treatments were 18.82 and 25.93% lower than that in DE treatment, respectively. The content of residual Mn in soils of C-D and Na-D treatments were 3.51 and 0.86% higher than that in DE, respectively. Alkali-modified diatomite could significantly enhance the solidification ability to Zn. The results in Figure 4 show that the content of acid-soluble available Zn in the soil of Na-D treatment was significantly lower, 6.71%, than that in DE, the content of residual Zn in soil of Na-D treatment was 0.36% higher than that in DE. However, acid- and alkali-modified diatomites did not significantly improve the solidification ability to Pb (Figure 3).

The solidification ability of diatomite to heavy metals could be attributed to the physical and chemical properties. The high

Table 6. Effects of the Combined Curing Agent on the Solidification Efficiency of Different Heavy Metals

combined curing agent treatments	heavy metal	reduction rate (%)
D	Mn(II)	51.61
	Pb(II)	47.37
	Zn(II)	63.15
E	Mn(II)	65.58
	Pb(II)	42.11
	Zn(II)	77.76
F	Mn(II)	56.08
	Pb(II)	57.89
	Zn(II)	72.38
G	Mn(II)	61.34
	Pb(II)	47.37
	Zn(II)	97.06
H	Mn(II)	60.93
	Pb(II)	47.37
	Zn(II)	78.08
I	Mn(II)	56.31
	Pb(II)	42.11
	Zn(II)	68.31
J	Mn(II)	59.17
	Pb(II)	89.47
	Zn(II)	62.59

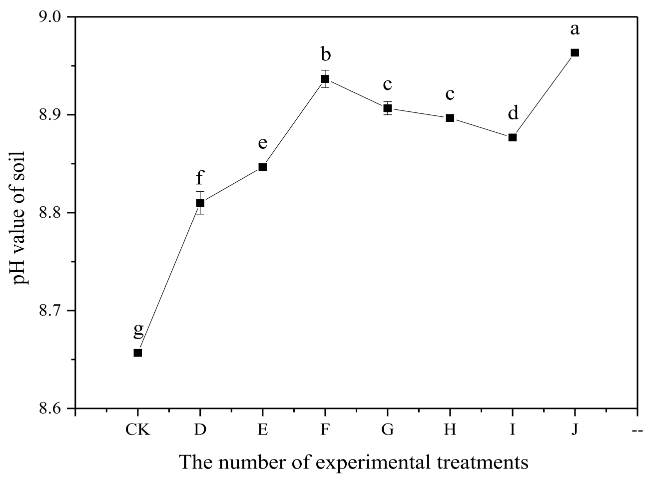

Figure 5. Effects of the combined curing agent on the soil pH value.

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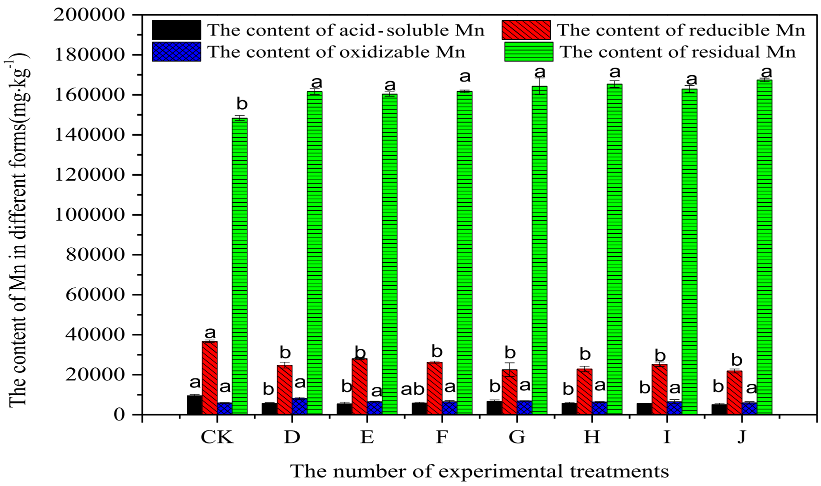

Figure 6. Effects of the combined curing agent on the content of different forms of Mn in soil.

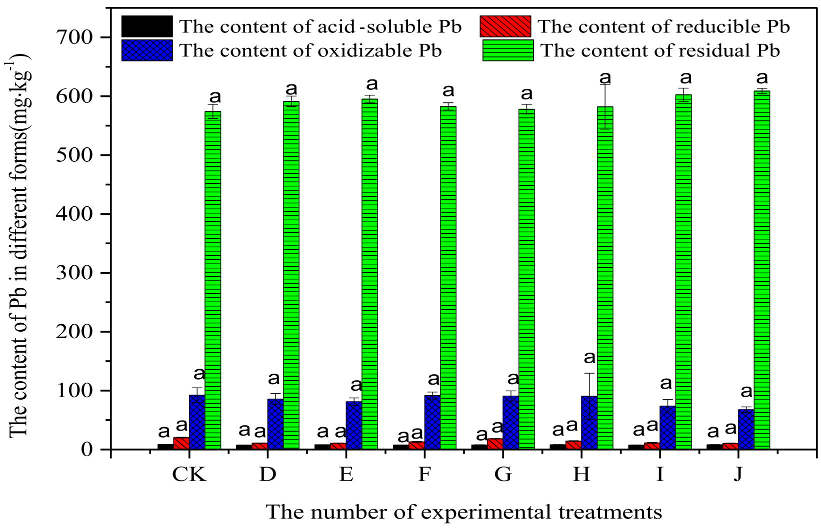

Figure 7. Effects of the combined curing agent on the content of different forms of Pb in soil.

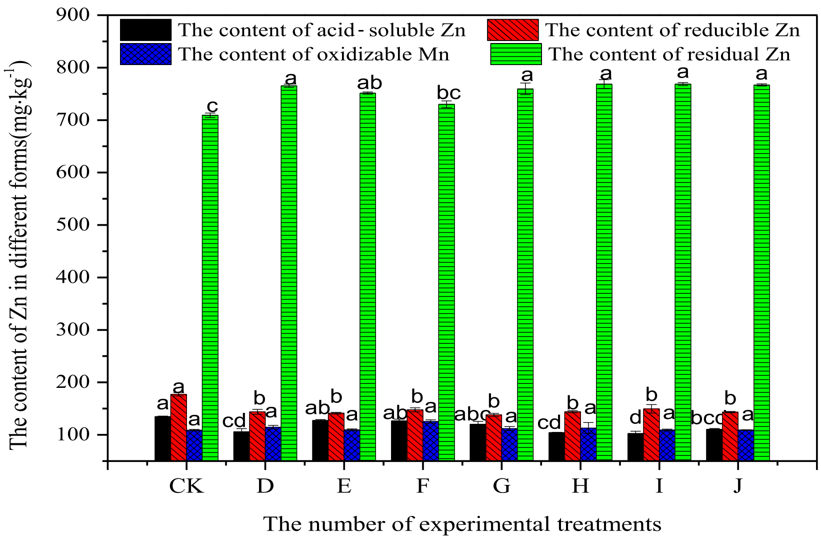

Figure 8. Effects of the combined curing agent on the content of different forms of Zn in soil.

porosity, small particle structure, and large specific surface area of diatomite enable it to show a significant adsorption effect on heavy metal ions.[26] Moreover, there were more silicon hydroxyl groups (Si−OH) on the surface of diatomite, and H^+ could be separated from silicon hydroxyl groups, which results in the surface of diatomite having a certain negative charge and a

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Figure 9. Growth of *Brassica chinensis.*

certain attraction to heavy metal ions and cations.[27] The silicon hydroxyl group (Si−OH) on the surface of diatomite could also show surface complexation adsorption with heavy metal cations,[28] which promoted the adsorption efficiency of heavy metal ions by diatomite. The content of increased anions (CH_3COO^-) in acetic acid-modified diatomite enhanced the adsorption capacity of heavy metal cations. Moreover, acetic acid is an organic acid, and the hydroxyl group on diatomite may react with the thiol group of acetic acid to form residual organic components esters.[29] The residual organic components in the process of acetic acid-modified diatomite could react with heavy metal cations, through processes such as complexation and chelation, to enhance the solidification ability of acetic acid-modified diatomite to heavy metals. The anion content in sodium hydroxide-modified diatomite also increased, which enhanced the adsorption capacity of sodium hydroxide-modified diatomite to heavy metal cations. Moreover, the presence of OH^- in the process of sodium hydroxide modification of diatomite could result in precipitation with heavy metal ions, which would also enhance the solidification effect of sodium hydroxide-modified diatomite on heavy metals. Alkaline substances could lead to the following effects, such as rapidly increasing the pH value of the soil, increasing the negative charge on the soil surface, improving the affinity of the soil to heavy metals, and improving the adsorption capacity of the soil to heavy metal ions. At the same time, alkaline substances could also promote the formation of heavy metals in soil into heavy metal hydroxide, heavy metal carbonate-bound sediment, and heavy metal cosediments.[30] The results of the BCR extraction method in this study also showed that acid-modified diatomite and alkali-modified diatomite could effectively reduce the acid-soluble and reducible content of Mn and Zn in soil and increase the oxidizable and residual content of Mn and Zn in soil.

3.2. Effects of Modified Diatomite Combined with a Curing Agent on Heavy Metals in Soil. *3.2.1. Effects of the Modified Diatomite Combined with a Curing Agent on the Solidification Efficiency of Mn, Pb, and Zn in Soil.* In order to improve the application scope of modified diatomite in heavy metal compound-polluted soil and its remediation effects on heavy metals, modified diatomite was mixed with quicklime and hydroxyapatite according to different components and proportions. The results (Table 6) showed that the mixed curing agent composed of two or three phases of modified diatomite, quicklime, and hydroxyapatite had significant solidification effects on soil heavy metals Mn, Pb, and Zn, among which the combination of acid-modified diatomite with quicklime and hydroxyapatite (D, E, and F) and alkali-modified diatomite with quicklime (G and H) had a particularly significant solidification effect on soil heavy metals. The solidification efficiencies of Mn, Pb, and Zn in soil treated with D, E, F, G, and H reached 51.61−65.58, 42.11−57.89, and 63.15−97.06%, respectively. The combined curing agent had a particularly obvious solidification effects on Mn and Zn in soil. At the same time, the combination of alkali-modified diatomite, quicklime, and hydroxyapatite (I and J) could result in the solidification efficiencies of soil Mn, Pb, and Zn reaching 56.31−59.17, 42.11−89.47, and 62.59−68.31%, respectively, among which the solidification effect of treatments I and J on Pb in soil was particularly obvious. However, among the combined curing agents, modified diatomite, quicklime, and hydroxyapatite were combined in different proportions, and the combined curing agents had different solidification effects on soil heavy metals Mn, Pb, and Zn. For the mixed curing agent treatments (D, E, and F) of acid-modified diatomite, quicklime, and hydroxyapatite, if the proportion of quicklime and hydroxyapatite was increased, the solidification effect of the combined curing agent on Mn and Zn could be improved. Compared with treatment E, increasing the proportion of acid-modified diatomite in treatment F could significantly improve the solidification effect of the combined

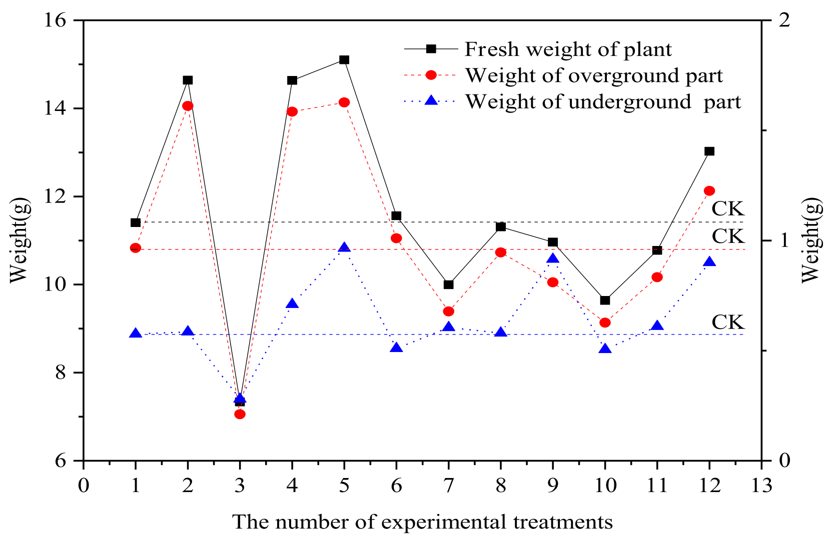

Figure 10. Effects of curing agents on fresh weight of the plant.

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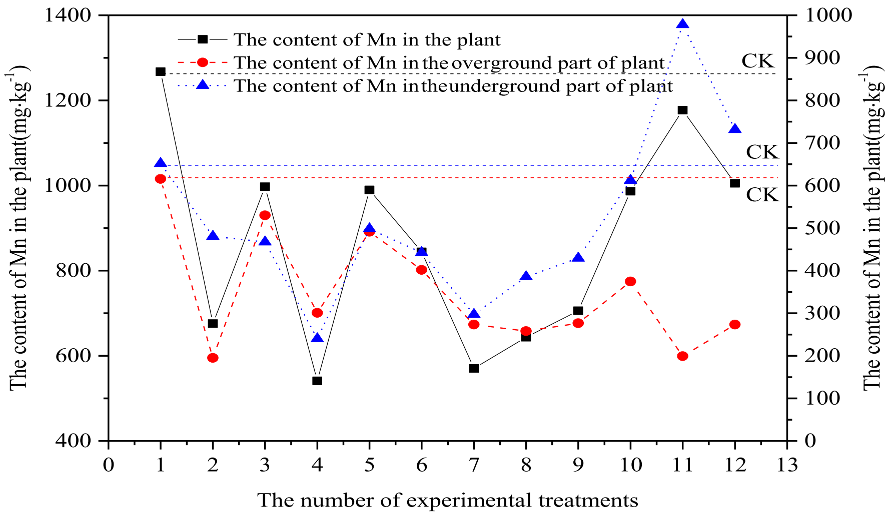

Figure 11. Mn contents in different parts of the plant.

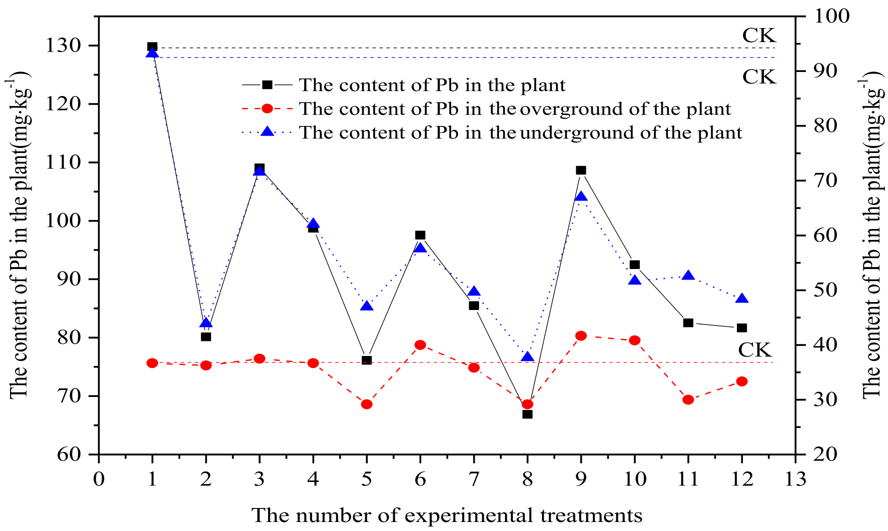

Figure 12. Pb contents in different parts of the plant.

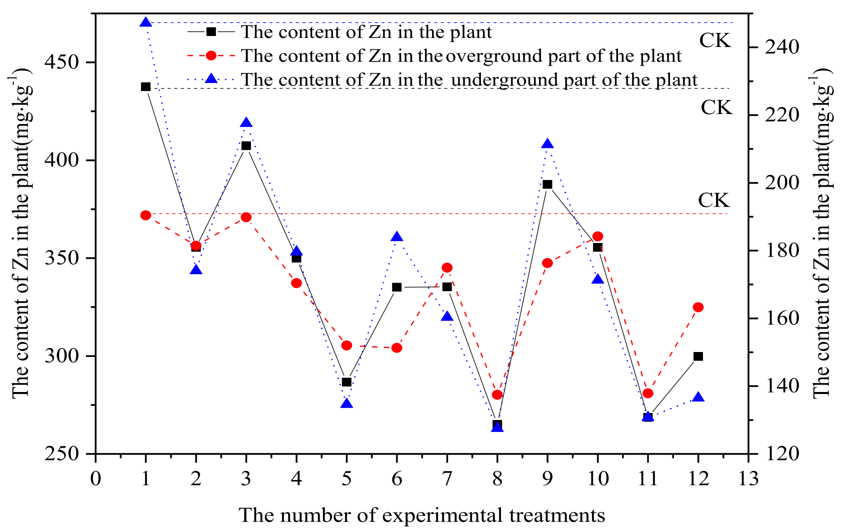

Figure 13. Zn contents in different parts of the plant.

curing agent on Pb. In the mixed curing agent treatments of alkali-modified diatomite with quicklime and hydroxyapatite (I and J), increasing the proportion of quicklime and hydroxyapatite in the combined curing agent could improve the

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solidification efficiency of Mn and Pb. Therefore, in the practical application of the combined curing agent, the modified diatomite could be combined in different doses and groups according to the category and degree of heavy metal pollution of the soil so that the combined curing agent could achieve a more efficient curing effect.

3.2.2. Effects of Modified Diatomite-Combined Curing Agents on the Soil pH Value. The combined curing agent of modified diatomite had a significant effect on the pH value of soil. The results (Figure 5) showed that compared with that of CK treatment, the soil pH value of the combined curing agent treatment (D, E, F, G, H, I, and J) increased significantly ($P < 0.05$), and the range of the pH value increase was 0.15−0.31, among which the increase range of the soil pH value in treatment J was the largest. At the same time, the soil pH value of the treatments (D, E, and F) of acid-modified diatomite mixed with quicklime and hydroxyapatite increased when the proportion of quicklime and hydroxyapatite increased, among which the soil pH value increase of the F treatment was the largest. In the combined curing agent treatments (G, H, I, and J) of alkali-modified diatomite mixed with quicklime and hydroxyapatite, mixing the same amount of alkali-modified diatomite and increasing the proportion of quicklime and hydroxyapatite could significantly increase the pH value of the soil.

3.2.3. Effects of the Modified Diatomite-Combined Curing Agent on the Contents of Different Forms of Mn, Pb, and Zn in Soil. The efficient solidification of heavy metals in soil of modified diatomite-combined curing agent treatments was mainly realized by changing the occurrence forms of soil heavy metals. The modified diatomite-combined curing agent could significantly affect the forms of Mn, Pb, and Zn in soil. The results (Figure 6) showed that compared with CK treatment, the contents of acid-soluble and reducible Mn in soil could be significantly reduced ($P < 0.05$) 23.59−46.32% by the combined curing agent treatment, and the contents of residual Mn could be significantly increased ($P < 0.05$) 8.11−12.88%. At the same time, the results (Figure 7) showed that compared with CK treatment, the contents of acid-soluble, reducible, and oxidizable Pb in the soil of the combined curing agent treatment decreased, 5.88−47.93%, and the contents of residual Pb increased, 0.67−6.04%, but the difference was not significant. Compared with CK treatment, the contents of acid-soluble and reducible Zn in the soil of the combined curing agent treatment decreased significantly ($P < 0.05$), 5.37−23.84%, and the contents of oxidizable and residual Zn increased significantly ($P < 0.05$), 5.97−5.24% (Figure 8). Based on the above results, it is indicated that modified diatomite combined curing agents promote the transformation of available heavy metals (acid-soluble and reducible) to stable heavy metals (residual) in soil and thus enhance the remediation and solidification effects of heavy metals in soil.

The reasons for the above results were as follows: first, the modified diatomite improved the adsorption performance of heavy metals in soil and enhanced the adsorption capacity of heavy metals in soil, and second, the modified diatomite combined curing agent could significantly improve the soil pH value, and the application of quicklime and hydroxyapatite had a certain impact on the increase of the soil pH value. The increase of the soil pH value would increase the adsorption capacity of the negatively charged soil colloid to positively charged heavy metal ions,[31] and the increase of the soil pH value also increases the contents of OH^- ions in soil, which made it easy for heavy metal cations in soil to form hydroxide precipitation, so as to reduce the mobility of heavy metals in soil. The research of Xue et al.[32] showed that the hydrated product of quicklime could solidify Pb and Cr in polluted soil by surface adsorption and physical migration. Quicklime could also enhance the fixation of heavy metals in soil by increasing the exchange capacity of cations in soil.[33] At the same time, the rapid surface adsorption of hydroxyapatite in the modified diatomite combined curing agent and the available adsorption sites on the surface could complexate with heavy metals,[34] and hydroxyapatite could also form stable and insoluble phosphate precipitation with heavy metals.[35] The results of BCR speciation classification of heavy metals in this study also showed that the combination of modified diatomite and hydroxyapatite could reduce the content of acid-soluble and reducible Mn, Pb, and Zn in soil and increased the content of residual Mn, Pb, and Zn in soil so as to effectively reduced the bioavailability of heavy metals Mn, Pb, and Zn.

3.3. Effects of the Modified Diatomite-Combined Curing Agent on the Bioavailability of Heavy Metals.

3.3.1. Effects of the Modified Diatomite-Combined Curing Agent on Plant Growth. The results (Figures 9 and 10) showed that the Shanghai Qing could grow well in the treatments of the modified diatomite curing agent. Compared with the blank treatment (CK), except treatments 3, 7 and 9, the fresh weight of the whole plant and the aboveground in the solidification treatment were 16.37−35.25 and 13.06−39.47% higher than that in the CK treatment, respectively. Therefore, modified diatomite and the modified diatomite-combined curing agent could promote the growth of plants.

3.3.2. Effects of the Modified Diatomite-Combined Curing Agent on the Content of Heavy Metals in Plants. Modified diatomite and the modified diatomite-combined curing agent could not only solidify soil heavy metals but also effectively prevent the absorption and accumulation of heavy metals by plants. Compare with the CK treatment, the Mn, Pb, and Zn contents in the plants of modified diatomite and the modified diatomite-combined curing agent treatment were lower by 7.13−57.29, 5.99−48.49, and 89−39.44%, respectively (Figures 11−13). Compared with the treatments of modified diatomite, the modified diatomite curing agent treatments had a more obvious prevention effect on the absorption of Mn, Pb, and Zn by plants. The amounts of Mn, Pb, and Zn absorbed by plants in the treatments of acid modified diatomite curing agent were significantly lower, 0.75−42.80, 10.55−30.21, and 17.70−29.64%, respectively, than that in the acid-modified diatomite treatments. The amount of Pb and Zn absorbed by plants in the treatments of alkali-modified diatomite curing agent was significantly lower, 6.32−32.27 and 14.35−24.29%, respectively, than that in the treatments of alkali-modified diatomite. The prevention effect of the combined curing agent of alkali-modified diatomite and quicklime on the absorption of heavy metals by plants was particularly significant. According to the above analysis, if applied to the soil, the modified diatomite and the modified diatomite-combined curing agent, which could change the forms of heavy metals in the soil without affecting the growth of crops,[36,37] could also effectively prevent the crops from absorbing heavy metals so that the accumulation of heavy metals by crops could be significantly reduced. The modified diatomite-combined curing agent could more effectively prevent the absorption of heavy metals by crops.

4. CONCLUSIONS

(1) Acid−alkali modification of diatomite could enhance the transformation trend of heavy metal forms in soil from acid-soluble and reducible to oxidizable and residual and effectively improved the curing efficiency of the heavy metals in soil. Compared with that in natural diatomite (DE), the contents of available Mn in soil modified by an acid and an alkali (1 mol/L acetic acid, C-D and 3 mol/L sodium hydroxide, Na-D) were 18.82 and 25.93% lower, respectively. The content of available Zn in soil modified by Na-D was significantly lower than that of DE 6.71%, but C-D and Na-D did not significantly improve the curing performance of Pb.

(2) Compared with single modified diatomite, the combination of modified diatomite with quicklime and hydroxyapatite in two or three phases could significantly improve the curing efficiency of available heavy metals Mn, Pb, and Zn in soil. The content of available heavy metals Mn, Pb, and Zn in soil could be reduced by 23.59−46.32, 5.88−47.93, and 5.37−10.68%, respectively, by combining modified diatomite with a curing agent.

(3) The effect of modified diatomite on the bioavailability of heavy metals Mn, Pb, and Zn in soil was further verified by the pot experiment. The results showed that the application of modified diatomite and modified diatomite combined with a curing agent had no significant effect on plant growth. However, the application of modified diatomite and modified diatomite combined with a curing agent could effectively prevent and control the absorption of heavy metals by crops by changing the form of heavy metals in soil.

AUTHOR INFORMATION

Corresponding Author

Zhixian Li − *Hunan Province Key Laboratory of Coal Resources Clean Utilization and Mine Environment Protection, Hunan University of Science and Technology, Xiangtan 411201, China*; orcid.org/0000-0002-5793-0052; Email: 36529146@qq.com

Authors

Limei Chen − *Hunan Province Key Laboratory of Coal Resources Clean Utilization and Mine Environment Protection, Hunan University of Science and Technology, Xiangtan 411201, China*

Zhang Chen − *Hunan Province Key Laboratory of Coal Resources Clean Utilization and Mine Environment Protection, Hunan University of Science and Technology, Xiangtan 411201, China*

Guoliang Chen − *Hunan Province Key Laboratory of Coal Resources Clean Utilization and Mine Environment Protection, Hunan University of Science and Technology, Xiangtan 411201, China*

Jianlin Zhou − *Hunan Province Key Laboratory of Coal Resources Clean Utilization and Mine Environment Protection, Hunan University of Science and Technology, Xiangtan 411201, China*

Xiling Liu − *School of Resources and Safety Engineering, Central South University, Changsha 410083, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02135

Notes

The authors declare no competing financial interest.

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