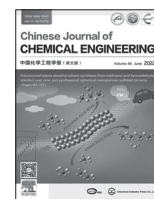




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Full Length Article

Synergistic effects of phosphoric acid modified hydrochar and coal gangue-based zeolite on bioavailability and accumulation of cadmium and lead in contaminated soil

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ABSTRACT

In this paper, a novel compound was developed by mixing H₃PO₄-modified cauliflower leaves hydrochar (CLH) and coal gangue-based Na-X zeolite (ZL). An alkaline soil contaminated with cadmium (Cd) and lead (Pb) was amended through the individual and synergistic application of CLH and ZL (1%CLH, 2% CLH, 1%ZL, 2%ZL and 1%CLH + 1%ZL), and Chinese cabbage was grown on it. Individual application of CLH was superior to ZL on decreasing the pH of alkaline soil and increasing soil available phosphorus (Olsen-P) and soil organic matter (SOM). In contrast, their combined application significantly improved the soil cation exchange capacity (CEC). Besides, the 1%CLH + 1%ZL was the most efficient treatment in decreasing diethylenetriamine pentaacetate (DTPA)-extractable Cd/Pb and concentrations of these two metals in cabbage root and shoot. Their synergistic application could better increase Cd and Pb immobilization and cabbage yield than their alone application. Furthermore, the immobilization of Pb for all treatments was higher than that of Cd. The synergistic immobilization mechanism of CLH and ZL reflected that the CLH precipitated and complexed with these two metals, which may block the pores of hydrochar or wrap on the surface of hydrochar. So the continuous adsorption and complexation were prevented. Nevertheless, ZL could probably alleviate this obstacle. This finding provides helpful information about using CLH combined with ZL as a soil stabilizer to immobilize heavy metals in contaminated alkaline soil.

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1. Introduction

As the largest coal consumption country globally, China accounts for nearly 50% of world coal production [1,2]. It is well-known that coal exploration and washing have negative impacts on the environment. Coal gangue, a hazardous solid by-product generated from the coal mining and washing industry, contributes about 10%–15% of the total coal yield. In China, the accumulation of coal gangue is over 5 billion tons and increases at 300–350 million tons per year [3]. The considerable coal gangue occupies lots of lands and causes eco-environmental issue, such as air and soil pollution. Owing to the heat accumulation, the spontaneous combustion of coal gangue will release large quantities of harmful and dangerous gases (e.g. CO, SO₂ and NO_x) [4]. Commonly, according

to previous researches [5,6], the main compositions of coal gangue are Al₂O₃ and SiO₂, which is suitable for preparing zeolite, a porous aluminosilicates material. As an inorganic amendment, zeolite can immobilize the heavy metals in soil because of the special porous structure and surface negative charges [7]. Therefore, to realize high added value utilization of massive coal gangue. Using zeolite prepared from coal gangue to stabilize heavy metals in soil may be a favorable choice. Several studies have reported about the input of nature zeolite into heavy metal contaminated soils. However, the knowledge about the impacts of coal gangue-based zeolite (ZL) on heavy metal immobilization in the soil is lacking.

The high concentration of cadmium (Cd) and lead (Pb) in soil introduced by human activities (e.g. coking, mining, electroplating, pesticides and atmospheric deposition) has also posed risks to the worldwide soil environment, plant growth, human and animal health [8]. Due to the contaminated wastewater irrigation, mine exploration and their non-biodegradable characteristic, these two metals are usually detected in agricultural farmlands and

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mining area [9,10]. About 10.87% of the Chinese farmland area has been subjected to heavy metal pollution [11]. Various diseases, including skin cancer, joint sore, kidney and lung dysfunction, are caused by long-term Cd and (or) Pb exposure (e.g. eating rice containing more than $0.2 \text{ mg} \cdot \text{kg}^{-1}$ cadmium element) [12]. To reduce this threat, much attention has been paid to *in-situ* stabilization with additives on account of the time-saving and low-cost of this technique [13,14]. Several soil amendments have been developed for the heavy metals immobilization in soil [15,16]. Recently, phosphorus-rich biochar prepared by dry pyrolysis with sufficient P-containing groups on their surface has a good performance of Cd and Pb immobilization mainly by forming more stable precipitation (e.g. pyromorphite, metal-phosphate) in most cases, although the improvement of soil physicochemical and biological properties also play a key role [1,17,18]. However, the dry pyrolysis method always needs high temperature (usually above 500°C) and anaerobic conditions, which is high energy consumption and uneconomical [19]. The previous studies have found that numerous phosphorus and P-containing functional groups are also loaded in the internal pore and on the surface of hydrochar by H_3PO_4 -impregnation hydrothermal carbonization (namely wet pyrolysis) method at low temperature (lower than 250°C) under air atmosphere [19–21]. Moreover, another advantage of hydrothermal carbonization is the utilization of feedstock containing high moisture content (e.g. cauliflower leaves, banana peel, pomelo peel). Among these fresh biomasses, cauliflower leaves, a typical vegetable residue, are generated during cauliflower production. For China, a large amount of cauliflower leaves piled up around the county, which leaves a burden on the local eco-environment [22]. Due to the rich in lignin and cellulose, these leaves are the preferred pristine material for hydrochar preparation. To date, limited literature has reported the efficiency of biochar combined with natural zeolite [13]. However, there is no attempt to study the synergistic effect of phosphorus-rich hydrochar with or without artificial zeolite on soil physicochemical properties and metals bioavailability in contaminated soil.

Furthermore, few attentions have been given to heavy metals immobilization in alkaline contaminated soil. Although the labile fractions of these metals in alkaline soil are less than them in neutral or acidic soil, their pollution also threatens plant and animal health, especially for North China [23]. The most representative province is Shanxi, located in North China. Many mining and coking contaminated sites exist in this area due to the eradication of high energy-consumption and pollution equipment/techniques in the past decade or so when both the coke and mining industry was undergoing unprecedented energy and technology transformation [24]. More serious is that plants are nonviable at these multi-contaminated sites. Unlike the popular alkaline biochar prepared through dry pyrolysis, phosphorus-rich hydrochar prepared by hydrothermal carbonization always show weak acidic (e.g. H_3PO_4 -modified hydrochar), which can be used to neutralize the pH of the alkaline soil to make it more suitable for crop growth [25].

Therefore, we hypothesis that heavy metals bioavailability and plant yield are probably dominated by the co-application of H_3PO_4 -modified cauliflower leaves hydrochar (CLH) and coal gangue-based zeolite (ZL). So before applying to the field area, a pot experiment was designed in this study to obtain information about the metals immobilizing behavior of CLH, ZL and their co-application in soil. Four aims of the present work are as follow: (1) The effects of CLH, ZL and their combination on bioavailability and immobilization of Cd and Pb in alkaline soil were evaluated; (2) The influences of adding CLH and ZL separately and together on plant growth and physicochemical properties of Cd and Pb contaminated soil were investigated; (3) The content of Cd and Pb in the root and shoot of the plant was determined; (4) The individual and synergistic immobilization mechanisms of CLH and ZL were explored.

2. Materials and Methods

2.1. Preparation and characterization of hydrochar and zeolite

Cauliflower leaves were obtained from the rural farmland in Shijiazhuang City ($38^\circ06'54''\text{N}$, $114^\circ47'37''\text{E}$, Hebei province, China). The CLH were prepared via the hydrothermal carbonization method following our previous and other relevant studies [20,21]. The detailed description of the preparation process of CLH is shown in Supplemental Materials (Supporting methods about the preparation of CLH). The sample prepared with the same process without H_3PO_4 addition marked as CL.

In parallel, coal gangue was obtained from the Longquan coal mine ($38^\circ10'31''\text{N}$, $111^\circ46'48''\text{E}$, Shanxi, China). Zeolite was synthesized through the alkaline-hydrothermal method according to our previous study [5]. The detailed description of the preparation process of ZL is provided in Supplemental Materials (Supporting methods about the preparation of ZL).

The cation exchange capacity (CEC) values of CLH and ZL were detected through the modified compulsive exchange method and the ammonium acetate saturation standard method, respectively [26,27]. The pH of CLH was identified by pH meter (Leici pH-3C, Shanghai, China) after stirring the slurry for 0.5 h, in which the ratio of CLH to water was 1:20 (w/v). The element compositions of CL and CLH were detected with an Elemental Analyzer (Vario EL cube, Elementar, Germany). Moreover, scanning electron microscopy (SEM, JSM-IT200, Japan), X-ray diffraction (XRD, ULTIMA IV, Japan), Fourier transform infrared spectroscopy (FTIR, TENSOR27, Germany) and X-ray photoelectron (ESCALAB 250Xi, USA) were carried out to the relevant materials. The details were identical to our previous reports [20]. The content of Cd and Pb in all amendments can be neglected due to below the detection line.

2.2. Soil sample collection and characterization

The polluted soil samples (0–20 cm depth) were collected from an agricultural field ($35^\circ42'39''\text{N}$, $110^\circ41'42''\text{E}$), which was close to a coal mine in Hejin county, Yuncheng city, Shanxi Province, China. The soil samples were stored in polyethylene bags. To obtain a relatively average sample, the sub-sample was bulked together. After being air-dried and crushed manually, the sample was ground, sieved through the sieve (2 mm). Soil electrical conductivity (EC) and pH were examined in soil/water (1:2.5 w/v) slurry. NaHCO_3 -NaOH was used to extract Olsen-P. The extracting solution was measured by the molybdenum antimony colorimetric method (NY/T1121.7-2014). Soil CEC was identified through the compulsive exchange method [28]. Soil organic matter (SOM) was detected using the potassium dichromate oxidation spectrophotometric method (HJ 615-2011). Besides, heavy metal concentrations of soil sample were detected by Flame Atomic Absorption Spectrometer (FAAS) (AA-1800C, Shanghai, China) after digestion with HNO_3 -HCl-HClO₄ mixture. Basic properties of the soil sample were Sand 65%, silt 21% and clay 14%, pH (8.26 ± 0.13), EC (0.25 ± 0.04) $\text{dS} \cdot \text{m}^{-1}$, CEC (9.77 ± 0.97) $\text{cmol} \cdot \text{kg}^{-1}$ and SOM (9.87 ± 1.17) $\text{g} \cdot \text{kg}^{-1}$, Total N (0.34 ± 0.03) $\text{g} \cdot \text{kg}^{-1}$ and Olsen-P (4.30 ± 0.21) $\text{mg} \cdot \text{g}^{-1}$. The soil was heavily contaminated with Cd and Pb. The total content of them was (5.12 ± 0.27) $\text{mg} \cdot \text{kg}^{-1}$ and (837.25 ± 67.6) $\text{mg} \cdot \text{kg}^{-1}$, respectively, which were 8.53 and 4.92 times higher than the risk screening values (0.6 and 170 $\text{mg} \cdot \text{kg}^{-1}$ for Cd and Pb, respectively) for the agricultural area, according to Chinese soil environmental quality risk control standard for soil contamination of agricultural land (GB 15618–2018). Besides, based on this standard, other total content of other metals (e.g. Cu (18.11 ± 2.23) $\text{mg} \cdot \text{kg}^{-1}$, Ni (39.62 ± 3.43) $\text{mg} \cdot \text{kg}^{-1}$) in soil was far below these corresponding

risk screening values. It can be ignored due to the low risk for crop growth or soil ecological environment.

2.3. Adsorptive selectivity experiment

Competitive adsorption experiments were carried out to compare the selective property of CLH, ZL and their mixture (marked as CLH + ZL). Adding 0.5 g CLH, 0.5 g ZL and 0.25 g CLH + 0.25 g ZL, respectively, into 200 ml binary solution containing Pb(II) (200 mg·L⁻¹) and Cd(II) (200 mg·L⁻¹). The sample without adsorbent was selected to distinguish between metal precipitation and adsorption. After shaking 24 h at 25 °C, all samples were filtered, and the filtrates were used to determine the metal concentration by FAAS [29].

2.4. Pot experiment

In the pot experiment, Chinese cabbage (*Brassica Chinensis*) was chosen as an experimental crop due to the easy growth and resistance to disease with a growing period of 42–49 days. Referring to relevant studies, five treatments [1%CLH, 2%CLH, 1%ZL 2%ZL and 1% CLH + 1%ZL (hydrochar/zeolite to soil), respectively] with three replicates were arranged [1]. Briefly, 3.0 kg air-dried soil sample was uniformly mixed with a corresponding proportion of additives. The mixture was placed into every pot (20 cm height and 25 cm diameter). To reach the moisture level and activate soil microbes, all the pots were soaked with deionized water (18 MΩ) and then incubated in a greenhouse at 15–25 °C for 20 days. Ten uniform seeds (the detailed description of seeding preparation was presented in Supplementary Material) were planted in each pot, which followed by thinning five plants after two weeks. During the incubation period, soil moisture content was maintained at about 70% of water holding capacity through weighting the pots every two days and adding deionized water [12]. The soil sample was fertilized with 6.68 g urea and 4.58 g potassium sulfate per pot [13,16]. After seven weeks, the mature cabbages were harvested. About 50 g soil samples were ground and stored for further analysis. Another 20 g remaining soil samples were collected and transformed into a centrifuge tube (100 ml) with deionized water (60 ml). To obtain the upper additives-water suspension, the tube was centrifuged at 3500 r·min⁻¹ for 15 min [30]. The additives were filtrated (0.2 μm syringe filter), dried (at 90 °C for about 3 h) and characterized by SEM-EDS, XRD, FTIR, XPS. Detailed methods of these analyses were identical to the description in Section 2.1.

2.5. Diethylenetriamine pentaacetate (DTPA) extraction and Bureau Community (BCR) sequential extraction

The bioavailable Cd and Pb was determined by measuring DTPA extractable metals content released from the mixture of soil and remediation agents. BCR sequential extraction was used for metal fractions analysis. Corresponding to sequential extraction steps, each metal fraction was defined as follow: (i) acid-soluble fraction, (ii) reducible fraction, (iii) oxidizable fraction and (iv) residual fraction [11]. The detailed descriptions of each step of DTPA and BCR extraction are demonstrated in Table S1 and Table S2 (Supplementary Material), respectively.

2.6. Determination of dry mass and metals content of plant

All the harvested cabbages were cautiously uprooted from each pot and divided into the root (underground parts) and shoot (surface parts). After washing with deionized water, the harvested plants were put into paper bags and air-dried for recording fresh mass. Then dried at 80 °C and weighed until the mass did not

change. The dried plant root and shoot were ground into the powder and digested using HNO₃ + HClO₄ (3:1) for measuring total concentrations of heavy metal by FAAS [13].

2.7. Quality control and statistical analyses

To certify the reliability of the BCR sequential extraction, the sum of various fractions was compared with wet digestion. The recoveries of Cd and Pb were 94.5%–101.7% and 95.6%–104.7%, respectively. Besides, the soil reference sample (GBW07498) brought from the National Research Center for Certified Reference Materials (Beijing, China) was used to control quality. For the standard soil sample, the recovery rate of heavy metals ranged from 96.7% to 103.5%.

Immobilization rate of heavy metal =

$$[1 - (\text{DTPA extracted amounts of heavy metal in soil with the remediation agents addition} / \text{DTPA extracted amounts of corresponding heavy metal in soil without the remediation agents addition})] \times 100\%$$

Experimental data were calculated as the standard deviation of the means values of the three replicates. Analysis of variance (ANOVA) in SPSS (Version 24.0, IBM) was used to perform statistical significance. The least-significant difference (LSD) ($P < 0.05$) was used to compare the mean values. The correlations among different factors, such as soil physicochemical characteristics, heavy metal bioavailability, plant weight and content of heavy metal in the plant, were also reflected by SPSS. Origin 8.0 software was chosen to perform all figures.

3. Results and Discussion

3.1. Characteristics of CLH and ZL

Compared with SEM images of CL (Fig.S1(a) and S1(b)), a block structure with a smooth surface and numerous pores were formed in CLH (Fig.S1(c) and S1(d)). Besides, combined with XRD patterns (Fig.S2(a)) and FTIR spectra (Fig.S2(b)), a mass of O-containing (—OH (3428 cm⁻¹), —COOH (1701 cm⁻¹)) and P-containing (P=OOH or P=O (1220 cm⁻¹)) functional groups were formed on the CLH after H₃PO₄ impregnation [31,32]. The selected chemical composition and physicochemical properties of CLH and CL were presented in Table 1, from which the decline of pH was observed for CLH (from 6.47 to 4.51), and CEC of CLH increased about 2.0 times due to the effect of H₃PO₄ impregnation on hydrochar microstructures [20]. As seen in Table 1, the increase in the carbon content of CLH was possibly attributed to the complex influences

Table 1
Elemental composition, pH and CEC of CLH and CL.

Parameters	CLH	CL
C/(% (mass))	67.13 ± 0.14	59.71 ± 0.11
H/(% (mass))	5.37 ± 0.03	7.02 ± 0.03
O/(% (mass))	15.47 ± 0.05	23.57 ± 0.07
N/(% (mass))	1.97 ± 0.01	1.79 ± 0.01
S/(% (mass))	0.34 ± 0.01	0.27 ± 0.01
Mg/(% (mass))	0.21 ± 0.02	0.17 ± 0.01
Si/(% (mass))	0.27 ± 0.01	0.51 ± 0.01
P/(% (mass))	1.83 ± 0.03	0.21 ± 0.01
Fe/(% (mass))	0.21 ± 0.01	0.12 ± 0.01
C/H	12.50	8.51
C/O	4.34	2.53
C/P	36.68	284.33
pH	4.51 ± 0.04	6.47 ± 0.07
CEC/cmole·kg ⁻¹	40.27 ± 1.46	19.61 ± 1.03

Table 2

Summary of immobilization rate of Cd and Pb in soil.

Materials and Dose	Experiment type	Immobilization rate/%		Refs.
		Cd	Pb	
1% BC + 1% PFA	pot	50.52	41.41	[1]
1% GSA-4	field	about 35	about 34	[8]
1% CA2	field	about 46	about 67	[33]
3% BCP	pot	65.39	24.93	[34]
3% BC	pot	58.54	46.53	[34]
4% ANHP	pot	84.0	42.6	[35]
6% WB + 2% SS	pot	59.55	18.20	[36]
1% CLH + 1% ZL	pot	59.93	70.04	This study

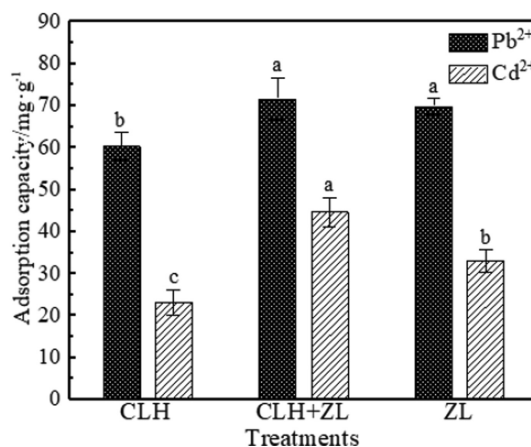
Note: BC+PEA: Co-application of bamboo biochar and hydrothermal treated fly ash; GSA-4: Combined application of manure, lime and sepiolite; CA2: Synergistic application of manure, lime and sepiolite; BCP: KH_2PO_4 modified biochar derived from palm tree leaves; BC: Biochar derived from palm tree leaves; ANHP: *Aspergillus niger*-based nanocomposite; WB + SS: Co-application of Wood biochar and sewage sludge biochar.

of phosphoric acid on catalyzing carbonization of organics and keeping small molecular substances into the solid phase. Conversely, the decrease in oxygen and hydrogen content was probably due to the dehydration reaction, which could remove oxygen and hydrogen from biomass, and this reduction was enhanced by H_3PO_4 impregnation [19]. Furthermore, the ratio of C/P in CLH was also much lower than that of CL, suggesting that more P compounds were formed on the CLH compared with CL [29].

The characteristics of zeolite prepared from coal gangue were as follows: CEC (427 ± 5.0) $\text{mol} \cdot \text{kg}^{-1}$, pH (8.1 ± 0.05), Al_2O_3 ($28.57 \pm 0.52\%$), SiO_2 ($48.73 \pm 0.11\%$), Fe_2O_3 ($1.57 \pm 0.02\%$), CaO ($0.41 \pm 0.01\%$), TiO_2 ($0.73 \pm 0.01\%$), K_2O ($0.77 \pm 0.01\%$) and Na_2O ($18.97 \pm 0.17\%$). Microscope images of the synthetic sample presented in Fig.S3 demonstrated regular and distinct pyramidal octahedron structures. The XRD patterns illustrated the disappearance of coal gangue powder (Fig.S4(a)) and the formation of Na-X zeolite (Fig.S4(b)) ($2\theta = 6.2^\circ, 15.5^\circ, 23.4^\circ, 26.8^\circ, 31.2^\circ$). Moreover, FTIR spectra (Fig.S5) also confirmed that the transmittance peaks of synthetic and commercial grade zeolite were almost identical, indicating that both of them contained the same active functional groups such as $-\text{OH}$ (3467 cm^{-1}), Si-O/Ai-O (463 cm^{-1}) and TO_4 ($\text{T} = \text{Si or Al}$) (671 cm^{-1}) [5]. The comparison result suggested that coal gangue powder was successfully converted into Na-X zeolite.

3.2. Adsorption selectivity

Concerning the studied soil was heavily polluted by Pb and Cd, heavy metals selectivity was investigated by competitive adsorption experiments in the dual-metal solution of these two metals. Overall, Fig. 1 presented that the order of selectivity sorption in all treatments was $\text{Pb(II)} > \text{Cd(II)}$, which was probably controlled by several factors, such as hydrated radius, electronegativity, hydrolysis constant and charge heavy metals carry [37]. Because the valences of these two metals were identical, the hydrate radius, electronegativity and hydrolysis constant dominated their adsorption. The hydrolysis constants of Pb(II) and Cd(II) are $10^{-7.6}$ and $10^{-10.1}$, respectively, and the electronegativities of them are 2.33 and 0.69, respectively. Generally, the metal ions with higher values of hydrolysis constants and electronegativities are preferred to be adsorbed than the metals with lower corresponding values [29]. Besides, in comparison to the hydrated radius of Cd(II) (0.426 nm), the lower value of Pb(II) (0.401 nm) also intensify this selectivity [38]. Moreover, the comparison result also suggested that the adsorption capacity of the sample with both CLH and ZL added for Cd(II) was much better than that of their individual addi-

**Fig. 1.** The adsorption capacity of CLH, CLH + ZL and ZL for Pb(II) and Cd(II) .

tion in the dual-metal solution system, and the adsorption capacity of Pb(II) was slightly higher than ZL addition alone (Fig. 1). So the inhibition effect of Cd(II) adsorption on zeolite and hydrochar was significantly stronger than that of Pb(II) . The degree of this competitive adsorption could be possibly relieved when CLH combined with ZL was added.

3.3. Effects of treatments on post-experimental soil

Soil properties (e.g. pH, Olsen-P, CEC and SOM) were improved by the mono- and co-application of CLH and ZL. The addition of 1% CLH, 2%CLH and 1%CLH + 1%ZL treatments decreased ($P < 0.05$) the soil pH from 8.26 to 7.01, 6.42 and 7.45, respectively, while ZL treatment had no significant effect on the soil pH (slightly reduced to 8.17 and 8.09) (Fig. 2(a)). Therefore, the CLH could lead to a remarkable decrease in soil pH, which attributed to the phosphoric acid participation in hydrochar preparation and mitigation of the soil pH. It is well-known that hydrochar prepared through hydrothermal carbonization, especially with phosphoric acid, exhibit slight acidity. A similar study has been reported by Zhou *et al.* [19], who explained that numerous acid O-containing functional groups would be increased by the dehydration and degradation of polysaccharides with the addition of H_3PO_4 . In parallel, zeolite synthesized via the fusion-hydrothermal method commonly presents weak alkalinity because of the NaOH participation during the synthesis of zeolite.

The addition of CLH with or without ZL remarkably improved ($P < 0.05$) the soil Olsen-P (Fig. 2(b)) because phosphate and phosphate groups were fixed on the surface and internal pore walls of CLH [20,30]. Interestingly, ZL was also helpful for slightly increasing Olsen-P in the soil, although it contained almost no phosphorus. The study of Zhu *et al.* [39] explained that adsorptive cations (Na^+) in the ZL could exchange with free cations (e.g. Ca^{2+} , Al^{3+}) in soil. So the fixed amount of phosphorus in soil was decreased, and then more soluble phosphorus was released.

The increase ($P < 0.05$) of soil CEC after 1%CLH, 2%CLH, 1%ZL, 2% ZL and 1%CLH + 1%ZL treatments (11.71, 13.57, 14.27, 16.01 and 18.20 $\text{cmol} \cdot \text{kg}^{-1}$, respectively) were found after 49 days of plant growth in comparison to control (9.53 $\text{cmol} \cdot \text{kg}^{-1}$) (Fig. 2(c)), because sufficient active functional groups mentioned above (Section 3.1) appeared on the surface of CLH and ZL. Moreover, the highest value of soil CEC was observed in 1%CLH + 1%ZL treatment probably because the right amount of ZL contained lots of hydroxyl functional groups and improved negative charges on soil particles surface [40]. The CLH could provide enough functional groups and adequate organic matter for improving soil CEC [41].

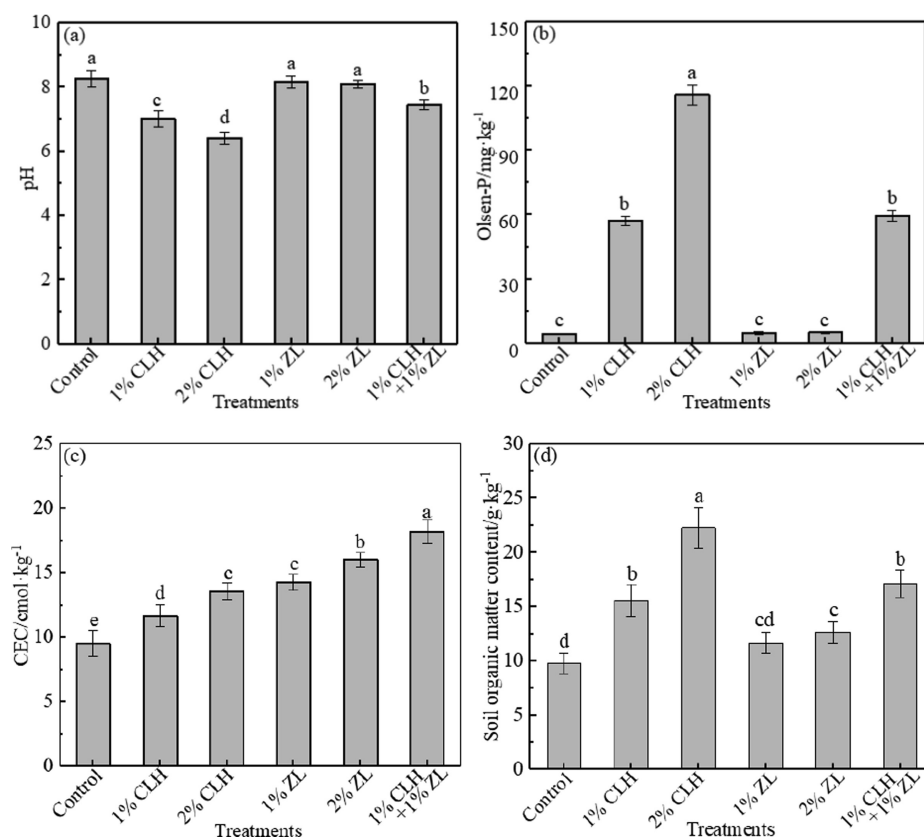


Fig. 2. Effects of different treatments on soil pH (a), Olsen-P (b), CEC (c) and SOM (d) after 49 days incubation. Different letters above the column represented a significant difference ($P < 0.05$) among control and different treatments. Error bars indicated the standard deviation of the mean ($n = 3$).

Additionally, the SOM significantly increased ($P < 0.05$) in 1% CLH, 2%CLH and 1%CLH + 1%ZL treatments from $9.77 \text{ g}\cdot\text{kg}^{-1}$ (in control) to 15.56 , 22.28 and $17.13 \text{ g}\cdot\text{kg}^{-1}$, respectively (Fig. 2 (d)), because of the high carbon content in CLH (Table 1). ZL slightly improved SOM. The reason might be that it prolongs the time of soil fertilization and maintain the soil structure [42]. Overall, the results suggested that the utilization of CLH along with ZL improved soil properties, which finally promoted the plant yield. CLH application with ZL was also related to the improvement of SOM, possibly due to the help of ZL for improving the fertilizer efficiency of CLH and stabilizing carbon by the formation of the organic-mineral compound in soil [1,12].

3.4. Effect of treatments on bioavailability and speciation of Cd and Pb in soil

According to previous studies [8,34], DTPA-extraction can be seen as indicators for metals bioavailability in soil, and the result was shown in Fig. 3(a). Without the addition of amendments (control), the extraction percentages of Cd and Pb were 16.41% and 23.53%, respectively. Similar phenomena were found by Hussain *et al.* [13], who suggested that soil alkalinity was more conducive to Cd retention than Pb retention. As presented in Fig. 3(a), the immobilization rates of DTPA-extractable Cd and Pb in all treatments changed significantly. The corresponding values were 40.90% and 45.37% for 1%CLH treatment, 53.39% and 57.67% for 2%CLH treatment, 30.95% and 26.10% for 1%ZL treatment, 36.90% and 37.45% for 2%ZL treatment, 59.93% and 70.04% for 1%CLH + 1%ZL treatment, respectively, suggesting that mono- and co-application of CLH and ZL could reduce the bioavailability of Cd and Pb in soil. Adding ZL alone could immobilize Cd and Pb due

to the unique pore structure, large specific surface area and high content of O-containing functional groups of synthetic zeolite [5]. Nevertheless, CLH was more effective on metal immobilization than ZL. The comparison result indicated that physical adsorption was not the only mechanism governing heavy metal immobilization in the soil, although the adsorption capacities of CLH were lower than that of ZL. Probably because the number of interactions mainly affected CLH behavior of immobilizing Cd and Pb, such as Cd/Pb-P precipitation and complexation between Cd/Pb and the functional groups in CLH [43]. Moreover, in comparison to individual application treatments, the influence of their combination on decreasing the bioavailability of Cd and Pb were more effective. DTPA-extractable concentrations of Cd and Pb reduced to their lowest value (0.34 and $58.93 \text{ mg}\cdot\text{kg}^{-1}$, respectively), which showed the great potential of co-application in retarding the adverse effects of heavy metals on the soil properties and planting. The mechanisms, including ion metal exchange, various functional groups, surface precipitation, complexation and physical adsorption, which lead to metals adsorption onto CLH and ZL, might well explain the decreasing metal bioavailability [14,43]. Besides, another good reason is that Cd and Pb tend to complex with the SOM, especially under water holding capacity conditions which enhance the opportunities of Cd and Pb combining with SOM [12]. The result of the collection (Table S3) in this study demonstrated that there were strong negative correlations between DTPA-extractable Cd and Pb concentrations and SOM. Several studies have explained that organic amendments combined with inorganic amendments improve the SOM and nutrients (e.g. available N, P and K), increase the soil properties and promote plant yield [1,44]. Moreover, the microbial activities are boosted, and metals solubility is decreased, which cause the lower metals uptake by the plant.

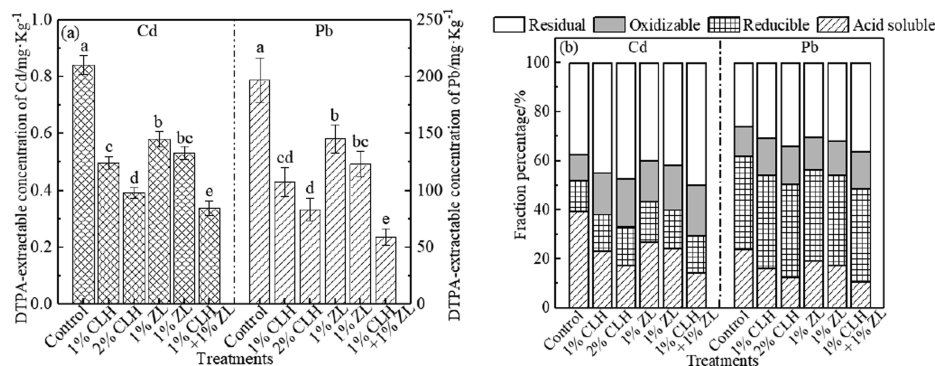


Fig. 3. DTPA-extractable concentration (a) and fractions percentage (b) of Cd and Pb in soils after 49 days incubation. Different letters above the bars indicated significant differences ($P < 0.05$) among treatments.

1%CLH + 1%ZL treatment kept higher immobilization rates of Cd (59.93%) and Pb (70.04%) compared with previous literature (Table 2). Although several studies showed higher immobilization rates than this study, the addition of amendments was usually greater than or equal to 3%. Xu *et al.* [45] reported that biochar application in contaminated soil was not only beneficial to carbon reserves but also could stabilize Cd and Pb by complexation and precipitation reactions in soils. Besides, for CLH and CLH + ZL treated soils, the availability of Cd and Pb was decreased because of the formation of the phosphate precipitation [46]. Moreover, the moderate ZL also helped to reduce the availability of Cd and Pb, because ZL could improve the surface negative charge in both CLH and soil components [13]. Lateef *et al.* [47] had also explained that ZL could temporarily adsorb soil nutrient, such as low molecular organic matter and moisture, into the crystal and stored them in the pore space, avoiding fertilizer weathering, volatilization, leaching and penetration. Then slowly released again when the crop needed. So ZL could extend the fertilizer action time, improve the utilization rate of fertilizer, and even reduce the pollution of fertilizer and pesticide to the soil.

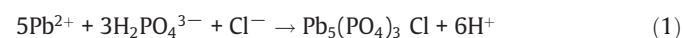
Among four existing fractions in the BCR sequential extraction experiment, both acid-soluble and reductive fractions are more easily absorbed by a plant than the other two fractions, so the sum of these two fractions is identified as the bio-effective state. Inversely, oxidizable and residual fractions may be bioavailable only under a given condition, resulting in difficulty for plants to uptake [11,12]. The distribution of Cd and Pb fractions in different amended soils was presented in Fig. 3(b). Compared with control (without amendments), Most Cd and Pb were transformed from the acid-soluble forms to the other three states after 49 days incubation. Among the five treatments, the best immobilization behavior of Cd and Pb could be observed after synergistic application followed by 2%CLH treatment, which was consistent with the results of DTPA-extraction. For example, for 1%CLH, 2%CLH, 1%ZL and 2%ZL and 1%CLH + 1%ZL treatment, the acid-soluble fractions of Cd were reduced by 16.03%, 21.93%, 12.33%, 15.33% and 24.93%, respectively. While the reducible fraction of Cd slightly increased by 1.97%, 2.86%, 3.51%, 3.21% and 2.36%, respectively. Meanwhile, the oxidizable fractions of Cd were increased by 6.63%, 9.29%, 6.31%, 7.91% and 10.29%, respectively. And the residual fractions also went up by 7.43%, 9.78%, 2.51%, 4.21% and 12.28%, respectively. The chemical fractions of Pb showed a similar trend to that of Cd. Apart from that, the percentages of reducible Pb remained almost stable during the incubation period. The collection analysis (Table S3) also presented that acid-soluble fractions of Cd and Pb were positively correlated to their DTPA-extractable concentration, suggesting that acid-soluble and bioavailable concentrations of these two metals in soil were decreased. Probably

due to the rich in P-containing (e.g. $P=OOH$, $P=O$) and O-containing (e.g. $-COOH$, $-OH$) groups on the surface of CLH (Section 3.1), the organic-bound Cd/Pb were formed through the reaction between these groups and Cd/Pb [48]. Besides, maybe due to the H_3PO_4 -impregnation in the hydrochar preparation, the phosphorous compounds which newly formed and wrapped on the surface of CLH precipitated with Cd/Pb [49]. Furthermore, the appropriated amount of ZL could not only enhance the formation of soil aggregates and preservation of SOM as discussed above (Section 3.3) but also converted humus to organic-inorganic compound [42]. Then the decomposition of organic matter was slowed down. The elevated levels of SOM could contribute to the ion exchange reaction of the soil and reduce the bioavailability of Cd/Pb by forming organic-bound Cd/Pb [45].

3.5. The main synergistic immobilization mechanisms

SEM-EDS semi-quantitative analysis reflected that the appearance of precipitation was found on the surface of CLH in CLH treated soil, which blocked the pores of CLH (Fig. 4(a)). Moreover, for CLH + ZL treatment, the precipitation could also be seen on the surface of both CLH and ZL (Fig. 4(b)). However, no precipitation was observed on the surface of ZL after ZL alone treatment (Fig. 4(c)). Corresponding EDX data revealed that Cd and Pb were absorbed by these amendments after incubation. The content of Pb was higher than that of Cd in all treatments after incubation. This selective order could be explained by the joint action of their electronegativity, hydrolysis constant and hydrated radius, which has been discussed in Section 3.2. Furthermore, the content of P on the surface of ZL in CLH + ZL treatment was much larger than that in ZL treatment, possibly due to the adsorption of P compounds and/or ions released by CLH onto ZL.

Pouliot *et al.* [50] indicated a strong association between phosphate and adsorption in Cd contaminated soil with the addition of manure-derived biochar. Gao *et al.* [37] also reported that phosphate was of great importance for Pb and Cd immobilization by forming phosphate precipitations. These assumptions were further confirmed by XRD patterns presented in this study (Fig. 5(a), (b) and (c)). A new peak of SiO_2 was found in all treatments may be due to the existence of a little soil which was not separated with amendments completely. Compared with the XRD patterns before incubation, the appearance of $Pb_5(PO_4)_3Cl$ ($2\theta = 20.49^\circ$, 21.50° , 26.35° , 27.25° , 29.91° , 30.17° , 30.97°) could be seen after CLH and CLH + ZL treatments (Fig. 5(a) and (b)), probably because Pb in soil reacted directly with the phosphorous substances on the hydrochar according to Eq. (1):



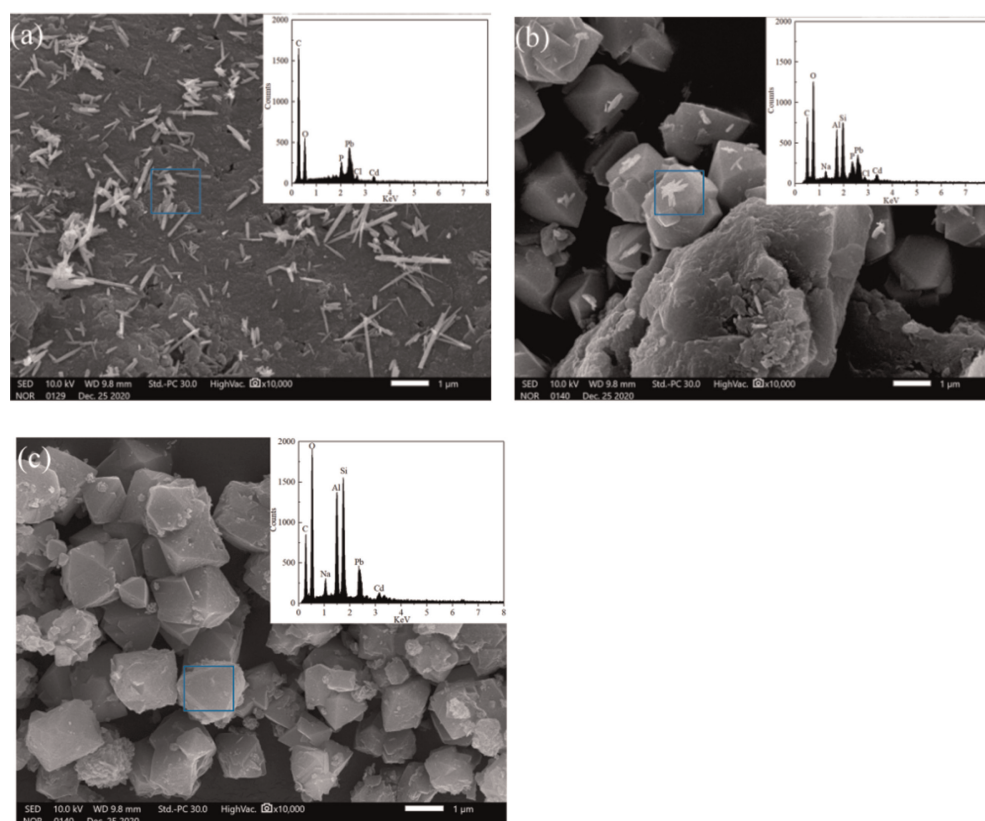


Fig. 4. SEM-EDS images of amendments (1%CLH (a), 1%CLH + 1%ZL (b) and 1%ZL (c)) after incubation. The solid blue box represented the EDS test area.

Several studies have revealed that that acidic biochar could promote the formation of Pb-P precipitation [17], which was in accordance with this study. Besides, chloridion might play a significant role in Pb immobilization. Because the percentage of Cd-P precipitation was lower than the detection limits of these analysis methods, the Cd-P precipitation was not found in the XRD pattern. It was worth noting that the peaks of these precipitations after CLH + ZL treatment did not decrease with the addition of ZL compared with the peaks in CLH treatment. The reason may be that adding the appropriate amount of ZL could not only adsorb exchangeable Cd and Pb onto its surface but also possibly adsorb the precipitation, which relieved the pore blocking and inhibition of the groups on the surface of CLH [51–53]. Then the formation of the precipitation was enhanced. Another reason may be that phosphorus ion (such as PO_4^{3-} , $\text{H}_2\text{PO}_4^{3-}$) released from the CLH was firstly adsorbed by ZL, and the precipitation was formed afterwards on the surface of ZL [54]. Without the hinder of these precipitations, more phosphorus ion released from the inner pore of CLH could form precipitation with metals. Conversely, for ZL treatment, no new peak was formed after incubation (except the peak of SiO_2) (Fig. 5(c)), indicating that precipitation was not the predominant mechanisms in ZL treated soil.

A peak shift of FTIR spectra could be found from 1069 cm^{-1} ascribed to $\text{P}^+\text{-O}^-$ (acid phosphate esters)/ P-O-P (polyphosphate) before incubation to 1080 cm^{-1} corresponding to PO_4^{3-} after incubation in CLH and CLH + ZL treated soil (Fig. 5(d) and (e)), which might because the formation of metal-phosphate precipitations discussed above [31,51]. Additionally, the intensity of the peak at 1080 cm^{-1} was higher in CLH + ZL treatment than that after CLH treatment, suggesting the favorable effect of ZL on promoting the formation of these precipitations. Besides, concerning the complexation mechanisms, in comparison to the spectra of amendments before incubation, the peak of at $2500\text{--}3500\text{ cm}^{-1}$ (-OH) remarkably decreased

after CLH, CLH + ZL and ZL incubation (Fig. 5(d), (e) and (f)), because heavy metals reacted with -OH during incubation [5,11]. In parallel, the decrease of peaks at 1701 cm^{-1} (C=O), 2920 cm^{-1} ($\text{-CH}_2\text{-}$), 1616 cm^{-1} (aromatic C=C) and 1220 cm^{-1} (P=OOH or P=O) could also be found after CLH and CLH + ZL treatment due to the reaction between metals and these functional groups (Fig. 5(d) and (e)) [31,37]. The results indicated that these groups on amendments complexed with Cd and Pb.

XPS analysis revealed that the new peak of Pb 4f (143.2 eV , 138.1 eV) observed and the peak of P 2p (134.1 eV) formed through H_3PO_4 -modification disappeared due to the formation of metal-P precipitation after CLH treatment (Fig. 6(a)). Besides, the peak intensity of Pb 4f after synergistic application of CLH and ZL was higher than that in their individual treatments (Fig. 6 (a), (b) and (c)). The peak of P 2p decreased but did not diminish (Fig. 6(b)), possibly because part of Cd-P/Pb-P precipitation, phosphate radical and (or) groups were adsorbed onto ZL containing little phosphorus that could be neglected [5]. Then more P compounds and groups were released from the internal pores of CLH. This finding was corresponding to the analysis results of XRD and FTIR. Combined with the description of complexation discussed above, the precipitation of metals with inorganic P compound in soil possibly took precedence over the complexation and the cation exchange. A similar result was reported by Zhang *et al.* [30], who applied K_3PO_4 -modified rice husk and cornstalk biochar on Cd and Cu immobilization in a copper mine-contaminated soil. Based on these characterization analyses, the primary immobilization mechanisms of Cd and Pb in soil with the co-application of CLH and ZL could be summarized in Fig. 6(d).

3.6. Plant growth and Cd/Pb content in root and shoot

The effects of different treatments on cabbage growth and Cd/Pb content were presented in Table 3. Overall, the higher fresh

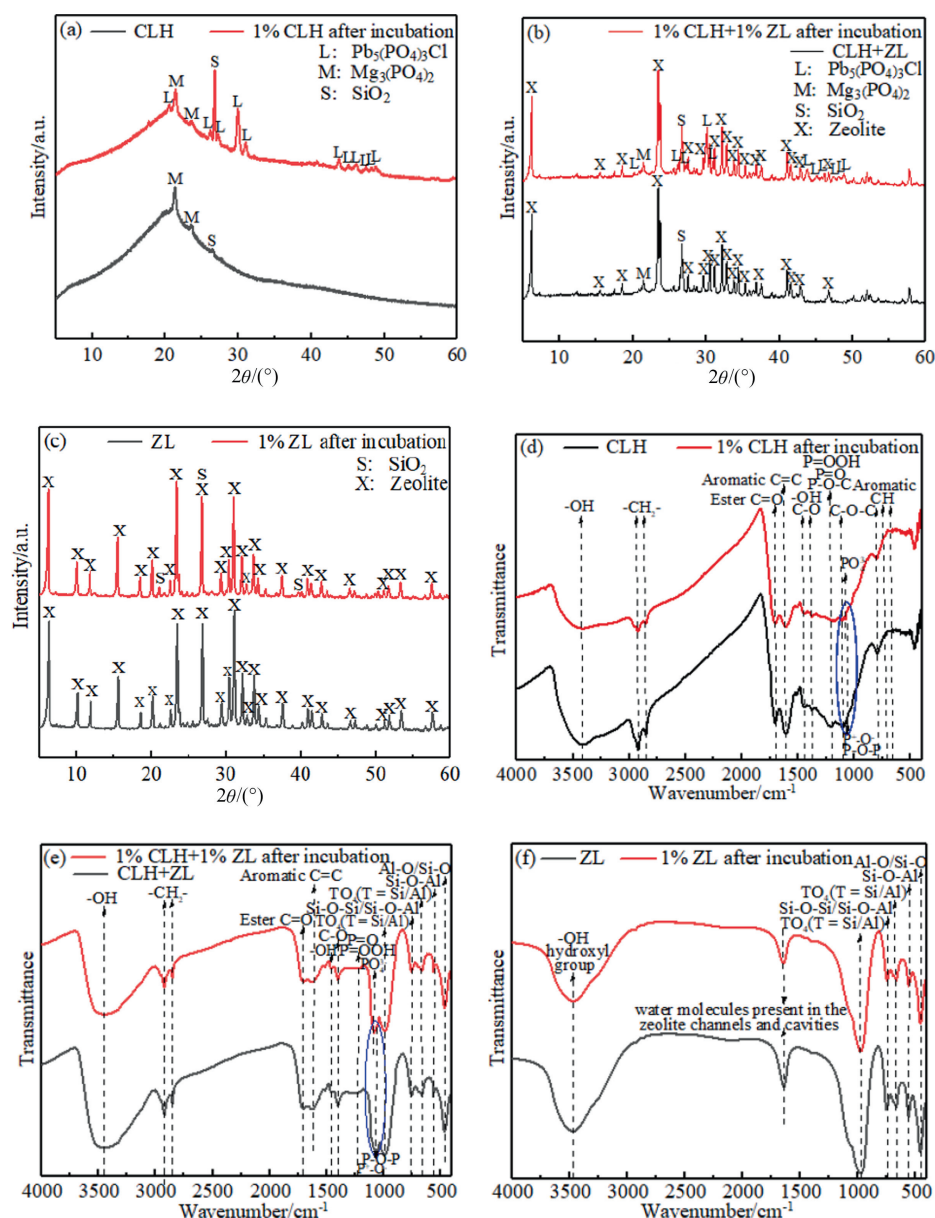


Fig. 5. XRD patterns ((a), (b) and (c)) and FTIR spectra ((d), (e) and (f)) of amendments (1%CLH, 1%CLH + 1%ZL and 1%ZL) before and after incubation in soil.

and dry mass of root and shoot in five treatments than that in control could be found ($P < 0.05$), except that ZL treatment did not significantly improve root fresh and dry mass ($P > 0.05$). Adding 1%CLH, 2%CLH, 1%ZL, 2%ZL and 1%CLH + 1%ZL amendments increased root fresh mass by 69.71%, 39.43%, 14.86%, 21.14% and 112.00%, respectively, and root dry mass by 85.71%, 42.86%, 4.76%, 23.81% and 147.62%, respectively. Several studies have reported that combined application of biochar and natural zeolite (or processed fly ash) at a lower rate can enhance the plant growth and nutrient uptake better than the individual application at a higher rate [1,13]. In parallel, the application of 1%CLH, 2%CLH, 1%ZL, 2%ZL and 1%CLH + 1%ZL also improved the shoot fresh mass by 79.43%, 65.86%, 39.34%, 47.88% and 176.62%, respectively, and shoot dry mass by 108.59%, 94.16%, 62.54%, 74.23% and 193.13%, respectively. So cabbage produced the highest root and shoot biomass after 1%CLH + 1%ZL treatment. This observation was consistent with the previous study of Shahbaz *et al.* [55], in which the co-application of miscanthus biochar and natural zeolite in contaminated soil decreased nickel concentration in roots and shoots

of sunflower and maize due to the decrease of heavy metal bioavailability to plants, the supply of plant nutrition, and controlled-release of fertilizers [52]. Moreover, compared with 1% CLH treatment, 2% CLH treatment significantly reduced ($P < 0.05$) the biomass mass of cabbage. The reason was that soil pH decreased ($P < 0.05$) with the addition of 2%CLH and reached acidity (Fig. 2(a)), which was not advantageous to cabbage growth [56]. Hence, co-application of CLH and ZL could be suggested as the optimum for cabbage productivity.

Cd and Pb concentrations in cabbage root were much higher than those in cabbage shoot (Table 3). By adding 1%CLH + 1%ZL, the concentrations of Cd and Pb in root reduced by 58.54% and 73.05%, respectively, compared with control. The significant decrease ($P < 0.05$) was also higher than other treatments, except 2%CLH treatment. Application of CLH with ZL could increase the soil binding and adsorption capacity because of the large surface area of these two amendments. Then metals retention capacity in soils was improved, and finally, these metals concentration in cabbage root/shoot was decreased. Another explanation was that the

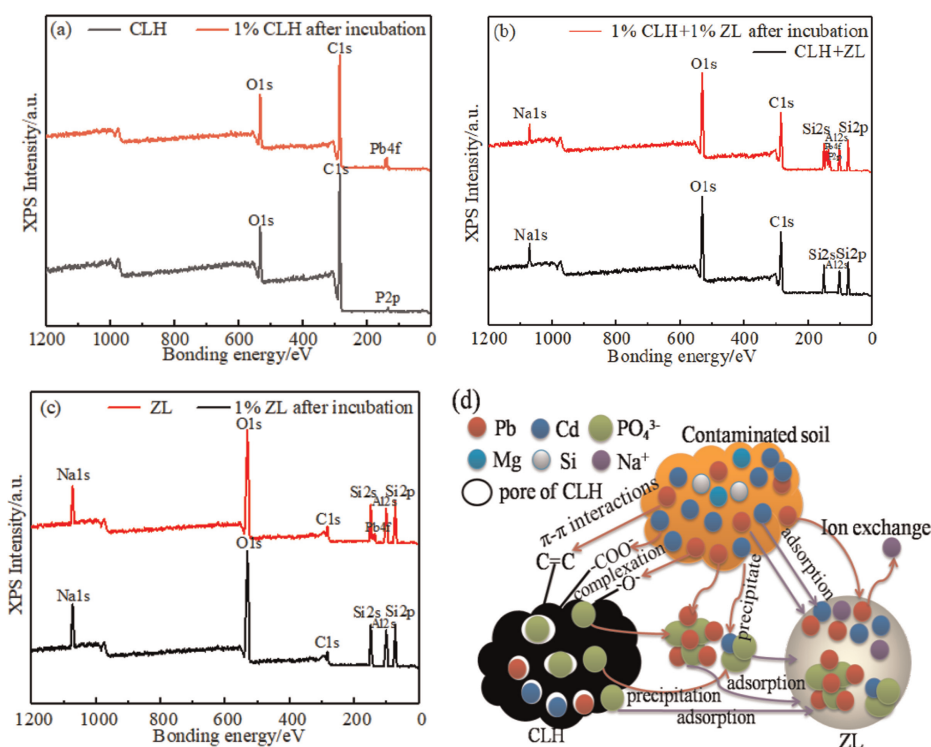


Fig. 6. XPS spectra ((a), (b) and (c)) of amendments (1%CLH, 1%CLH + 1%ZL and 1%ZL) before and after incubation in contaminated soil. Summarized primary immobilization mechanisms (d) of Cd and Pb with the co-application of CLH and ZL in soil.

Table 3

Effect of different treatments on fresh and dry mass (g) and metals contents(mg·kg⁻¹) fresh mass of cabbage root and shoot after 49 days incubation.

Treatments	Fresh mass	Root			Fresh mass	Shoot		
		Dry mass	Cd	Pb		Dry mass	Cd	Pb
Control	1.75 ± 0.21d	0.21 ± 0.03d	0.82 ± 0.12a	1.67 ± 0.11a	24.25 ± 3.13d	2.91 ± 0.13e	0.42 ± 0.04a	0.72 ± 0.09a
1%CLH	2.97 ± 0.24b	0.39 ± 0.05b	0.57 ± 0.08bc	0.84 ± 0.08c	43.49 ± 4.11b	6.07 ± 0.21b	0.25 ± 0.02 cd	0.26 ± 0.02c
2%CLH	2.44 ± 0.21c	0.30 ± 0.04c	0.49 ± 0.07 cd	0.59 ± 0.04d	40.22 ± 3.11bc	5.65 ± 0.18c	0.21 ± 0.02de	0.22 ± 0.02c
1%ZL	2.01 ± 0.19 cd	0.22 ± 0.03 cd	0.68 ± 0.12ab	1.23 ± 0.19b	33.79 ± 5.02bc	4.73 ± 0.15d	0.34 ± 0.03b	0.63 ± 0.08ab
2%ZL	2.12 ± 0.17 cd	0.26 ± 0.03 cd	0.62 ± 0.10bc	1.10 ± 0.09b	35.86 ± 4.92bc	5.07 ± 0.17d	0.30 ± 0.02bc	0.55 ± 0.06b
1%CLH + 1%ZL	3.71 ± 0.34a	0.52 ± 0.07a	0.34 ± 0.06d	0.45 ± 0.05d	67.08 ± 6.47a	8.53 ± 0.17a	0.16 ± 0.02e	0.19 ± 0.02c

Note: All the values were the mean of three replications. ± stands for standard deviation. Different letters suggested a significantly different ($P < 0.05$) among various treatments.

more metals in amended soil were immobilized, and the acid-soluble fractions of these metals were reduced (Section 3.4). Furthermore, compared to the contaminant limits of national standards for food safety (GB 2762–2017), in control, Cd and Pb concentrations of cabbage shoot (edible parts) in the contaminated soils were over the limit values (Cd 0.2 mg·kg⁻¹ fresh mass and Pb 0.3 mg·kg⁻¹ fresh mass, respectively). After incubation, for 1%CLH + 1%ZL treatment, the Cd and Pb concentrations measured in cabbage shoot were both below the corresponding limit value. For 1%CLH and 2%CLH treatment, only Pb concentration was lower than the limit value. While for 1%ZL and 2%ZL treatment, both Cd and Pb concentrations were not up to these standards. The comparison results suggested a strong synergistic effect of CLH and ZL on cabbage growth and metals immobilization, making it suitable for human consumption. As discussed above (Section 3.3), the co-application of CLH and ZL increased soil CEC, Olsen-P and SOM, which were beneficial for metals immobilization. The bioavailability of heavy metals in soil decreased because of the increased adsorption, precipitation and complexation under higher CEC, Olsen-P and SOM levels [34,37]. A significantly negative correlation between Cd and Pb concentrations in cabbage root and shoot with SOM was found in this work (Table S3), suggesting that the mobility of these two metals might be reduced by SOM. Small

molecular organic matter and functional groups in the SOM could form less soluble and stable metal–organic complexed with these metals, which immobilized metals in soil [1,57]. Similar effects of biochar and natural zeolite on metals availability and uptake by the plant were found in several studies, in which the ability of biochar along with zeolite for the decrease of metals availability and the increase of micronutrients for plants was concluded [13,55]. Then the concentrations of heavy metals in plant root and shoot were reduced. This reduction might also be explained by higher biomass production and plant selectivity [44]. This work is a short-term inquiry into heavy metals immobilization in soil by this novel compound (CLH + ZL). Further study should pay more attention to the long-term influences of this mixture. Due to the strong stability, the formation of Pb₅(PO₄)Cl was helpful for long-term validness [17]. However, the eco-environmental risks of abundant phosphorus need further research before co-application of H₃PO₄-modified hydrochar and coal gangue-based zeolite.

4. Conclusions

This study reflected the excellent performance of CLH and ZL as the sole and combined treatments to stabilize Cd and Pb in contaminated soil and reduce their bioavailability with Chinese cabbage

grown on it. Although CLH was superior to ZL on decreasing the pH of alkaline soil and increasing soil Olsen-P and SOM, their combination was favorable rather than their sole application for improving soil CEC. The best performance on immobilizing Cd and Pb (the immobilization ratios of Cd and Pb were 59.93% and 70.04%, respectively) in soil and reducing the content of these two metals (reduced by 58.54% and 73.05% for Cd and Pb, respectively) in cabbage root was observed after 1%CLH + 1%ZL treatment. Meanwhile, the decrease of Cd and Pb from 0.42 (control) to 0.16 mg·kg⁻¹ fresh mass and 0.72 (control) to 0.19 mg·kg⁻¹ fresh mass, respectively, in cabbage shoot was also found after 1%CLH + 1%ZL treatment, which was suitable for human consumption. Besides, due to the negative charge and larger specific surface area of ZL, the blocking pores of hydrochar caused by the metal-P precipitation and metal-organic complexation might be slowed down by ZL. Then more P compounds and groups were released from the internal pores of CLH. Therefore, the co-application of H₃PO₄-modified hydrochar and synthetic zeolite from coal gangue is superior to their application alone in the contaminated alkaline soil for enhancing soil physicochemical properties, immobilizing heavy metals and finally decreasing the concentration of these heavy metals in the plant.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.03.029>.

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