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RESEARCH ARTICLE

Stabilization of Cd and Pb in the contaminated soils by applying modified fly ash

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HIGHLIGHTS

• After modification, the adsorption capacity of fly ash on heavy metals is enhanced.
• Modified fly ash has significant effect on stabilization of Cadmium and lead.
• The activity of heavy metals stabilized after 6 months of operation of the column.
• DOC, pH, and organic matter play an important role in heavy metal remediation.

GRAPHICAL ABSTRACT
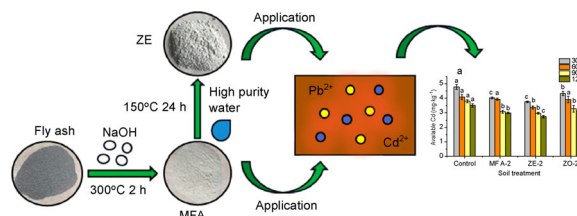
ABSTRACT

This study investigated the stabilization of heavy metals by adding modified fly ash (FA) to contaminated soils, and two similar materials, NaOH-zeolite (ZE) and natural zeolite (ZO) were introduced into the soils for comparison. Column leaching tests were conducted to analyze the difference of stabilization effects between the three materials. Leaching columns were run for 6 months, and a considerable stabilization of heavy metals in the soils was observed. The concentration of cadmium (Cd) and lead (Pb) in the amended soil substantially decreased ($p < 0.05$). The results indicated that after 11 weeks of column leaching, Cd and Pb concentrations in the soil leachate decreased to below the detection limit due to amendment stabilization. Among the three amendments, the ZE amendment showed the optimum capacity for heavy metal immobilisation in the soils. In addition, after 6 months of leaching, Pb and Cd concentrations in the soils with the three different amendments decreased to various degrees. The amendments of modified FA and ZE were better than those of natural ZO. Coal FA, after modification, is a useful amendment for the remediation of heavy metals in the contaminated soil.

1 Introduction

Soil heavy metal pollution is one of the most serious global environmental problems (Zhao et al., 2015; Huang et al.,

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2016). Most heavy metals in contaminated soils have been introduced through metal smelting or the release of metal ions in agricultural fields over decades or even centuries (Shao et al., 2016; Alicja et al., 2018). This contamination adversely affects not only plant growth but also human health through food chains (Mukherjee et al., 2020). Among these contaminants, Cd and Pb present the most serious environmental hazards. Rice has a strong enrichment effect on Cd. Ingesting contaminated rice is likely to cause severe chronic celiac disease, poisoning, renal insufficiency, osteoporosis, cancer, and other symptoms (Xu et al., 2020). Pb is one of the most toxic heavy metals that pose a direct threat to organisms. Pb cannot be degraded through microbial activities or chemical reactions (Zeng et al., 2017).

The soil environment complexity leads to the difficulty of heavy metal control. Studies (Xu et al., 2006; Fest et al., 2008) have shown that some physical and chemical properties of soil, such as pH, DOC, organic matter, redox potential, carbonate content, and cation exchange capacity, directly or indirectly affect the migration behavior of heavy metals. However, if heavy metals are bound with inactive compounds, their toxicity and mobility are decreased (Houben et al., 2012) and their hazards to the environment is minimised. The *in situ* stabilization of heavy metals has been reported (Pani and Singh, 2019; Wang et al., 2021). The purpose of this technique is to reduce metal activities by using soil amendments to immobilise metals. The stabilization technology has a wide application in many studies. Sneddon et al. (2006) showed that bone-meal amendment substantially reduced the release of Pb, Cd, and Zn in the soil leachate. Simultaneously, the exchangeable amount of Zn, Pb, Cu, and Cd in the polluted soil evidently decreases when hydroxyapatite is added (Li et al., 2020; Nag et al., 2020).

Coal fly ash (FA), as an industrial by-product, was widely used in soil heavy metals stabilization. FA primarily comprises silica and alumina (Leelarungroj et al., 2018). Due to its large bulk density, particle size, porosity, and specific surface area, FA is suitable to be used as an adsorbent (Ahmaruzzaman, 2010). A study reported that FA can reduce the heavy metal bioavailability in soils due to its surface functionalisation and complexation. (Lee et al., 2006). Although FA has been applied to stabilize heavy metals in most cases, most stabilization measures only use raw ash (Lee et al., 2008; Nayak et al., 2015). Due to the limited adsorption capacity of raw ash toward heavy metal ions, some researchers have explored many physical and chemical methods to stimulate

the adsorption potential of FA (Wu et al., 2012; Deng et al., 2018; Qi et al., 2019). The modified FA has been widely used, but most of its applications are limited to adsorbing heavy metal ions in the waste-water environment (Astuti et al., 2017; Huang et al., 2020b). Limited studies have focused on the application of modified FA to soils as a heavy metal amendment. In this study, column leaching tests were performed and the immobilising effect of FA-based modified materials was investigated, which may provide useful information for low-cost heavy metal removal.

Moreover, alkali (NaOH) was used as an activator, and a low-temperature roasting method was introduced. NaOH-zeolite (ZE) was synthesized from FA by using two-step hydrothermal roasting. This study determined the capacity of modified FA on metal-polluted soils and explored the leaching effect and mechanism of soil pH, dissolved organic carbon (DOC), and soil organic matter (SOM) on Cd and Pb. Moreover, we explored whether the performance of the modified FA is better than that of similar materials.

2 Materials and methods

2.1 Soils

The soil samples were collected at a depth of 0–20 cm from the campus of the Shaanxi University of Technology in Hanzhong, Shaanxi (33°07′ N, 107°05′ E). This sampling site was selected because the Hanzhong area was polluted with heavy metals throughout the year. The soil samples were air-dried and sieved through a coarse sieve (size < 2 mm) to remove impurities such as stones. However, a certain amount of Cd and Pb were added to the collected soils to increase metal concentrations to a set level. The available Cd and Pb concentration after manual configuration was 5.06 and 515 mg kg^{-1}, respectively. Table 1 presents the soil properties. The soils were sieved through a 1-mm sieve and stored in polyethylene bags.

2.2 Amendment preparation

Coal FA, a product of coal combustion, was obtained from Datong Thermal Power Plant. Coal FA was oven-dried at 105°C for 3 h; the dried FA was passed through a 0.3-mm mesh sieve and then was completely mixed with NaOH (powder) in the 5:8 ratio. The resultant mixture was calcined in a nickel crucible for 3 h at 300°C, and the sample was

Table 1 Basic physical and chemical properties of soils and materials.

	pH	SOM (g kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Fe (mg kg^{-1})
Soil	8.11	32.1	5.06	515	134	47	597	18600
FA	7.81	2.57	0.52	47.7	58.7	46.3	153	16500
MFA	8.14	—	0.37	2.37	39.6	40	131	13500
ZE	8.86	—	0.31	3.82	25.3	34.5	90	9220
ZO	7.95	—	0.40	8.20	45.8	0.36	62.7	5020

naturally cooled to normal atmospheric temperature after the reaction. Finally, the sample was washed with deionised water until pH stabilized and was dried to obtain NaOH-modified FA (MFA) at 105°C for 4 h. Subsequently, MFA and high-purity water were mixed in the ratio of 1:6 in a high-pressure reactor at 150°C for 24 h. Similarly, the samples were washed with deionised water until pH stabilized to acquire ZE. The third amendment was natural zeolite (ZO) purchased from a material market (AR) and originated from Gongyi City, Henan Province. Table 1 presents the basic characteristics of the amendments. The micromorphology and chemical elements of amendments were investigated using field scanning electron microscopy (SEM, S-4800, Hitachi Limited, Japan).

2.3 Leaching column set-up

Figure 1 illustrates the scheme of the leaching column set-up. The outer diameter and height of the Polyvinyl chloride (PVC) columns designed were 10 and 30 cm. The column was divided into three layers, and one sampling port was set at each 10 cm. A polyamide mesh (size 50 μm) was placed at the bottom of the column, and 2 cm of the quartz sand (size < 0.5 mm) was filled for leachate filtration. The lowest end of the column was connected to a funnel to collect the leachate, and a stopcock was placed on the funnel to adjust the flow from the column. 1 cm of the quartz sand was filled at each sampling port, and remaining space inside the column was filled with the soil samples (size < 1 mm). Similarly, the top of the column was filled with 2 cm of quartz sand (size < 0.5 mm) to ensure that no soil was lost during leaching.
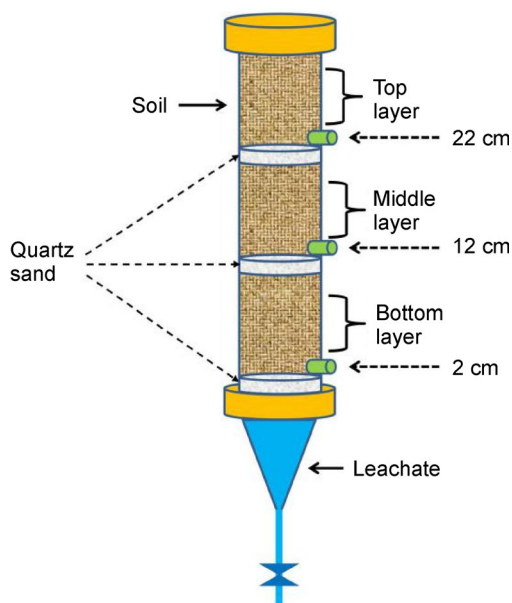
Fig. 1 Schematic view of leaching column.

2.4 Column experiments

MFA, ZE, ZO, and the tested soils were thoroughly mixed together to ensure homogeneity. Approximately 1800 g of the air-dried soil was added to each column Three amendments of 0.5%, 1%, and 2% (w/w) were prepared. Each treatment (0.5%, 1% or 2%) was performed in 3 replicates, and as control, the untreated soil sample treatment was conducted in three replicates. Before irrigation, the columns were equilibrated at 25°C and 60% water-holding capacity was maintained for 5 weeks. After the equilibrium period, the columns were irrigated with deionised water at a flow rate of 200 mL per week, and the leachate and soil samples were collected weekly and monthly.

2.5 Chemical analysis

2.5.1 Leachate analyses

After each leachate collection, the solution volume was measured with a graduated cylinder. The pH of the solution was simultaneously determined using a pH meter. Subsequently, the leachate was filtered with a 0.45-μm membrane, and then each solution sample was divided into two subsamples. One of these subsamples was used to measure DOC by using a total organic carbon analyzer (Shimadzu TOC-L CPH), and the other sample was used to determine the Pb and Cd concentrations of the leachate by using a Graphite furnace atomic absorption spectrometer (PinAAcle 900H).

2.5.2 Soil analyses

The collected soil samples were divided into two subsamples; the first subsample was temporarily stored in an ultra-low-temperature refrigerator, and the other subsample was air-dried in a drying room. The soils were sieved through a 0.15-mm mesh and kept in polyethylene bags after crushing. Potassium dichromate oxidation was conducted to measure the organic matter content in soils. The total amount of Cd, Pb, Cu, Zn, Fe, and Mn was digested with triacid (HNO_3, $HClO_4$, and HF). The available heavy metals were extracted using the M3 method, the solution analyzed using flame atomic absorption spectroscopy (PinAAcle 900H).

3 Results and discussion

3.1 Amendment characterization

Figure 2A–C present the SEM images of FA, MFA, and ZE. FA reacted and fused with alkaline substances (Fig. 2B), which promoted the dissolution of an amorphous glass phase in FA, and the surface of the spherical glass phase became extremely rough and irregular agglomerates, with a highly increased specific surface area and microporous structure, were formed, which resulted in an increase in adsorption capacity of FA for heavy metals. Under alkaline hydrothermal

conditions, the sample exhibited a basic ZO structure, and FA dissolved in the alkaline solution (Fig. 2C), so that the silicon–oxygen and aluminum–oxygen bonds were broken and reorganised in the presence of an alkaline catalyst, indicating that geo-polymerisation reactions were involved in modification (Jaarsveld et al., 1999). Terzano et al. (2005) observed that geo-polymerisation can deactivate heavy metals in the solid phase, and under these conditions, heavy metals can lose certain mobilisation capacity through adsorption and precipitation or by chemical bonding with amorphous.

3.2 Analysis of components in the soil leachate

3.2.1 pH in the soil leachate

Figure 3A–C present the leachate pH profile. Compared with control, the pH of the leachate with ZE and MFA amendments was considerably higher and increased with an increase in the rate of amendment application (Fig. 3A and B). Mainly because FA absorbed a large amount of sodium hydroxide during modification and bonded with it; hence, numerous
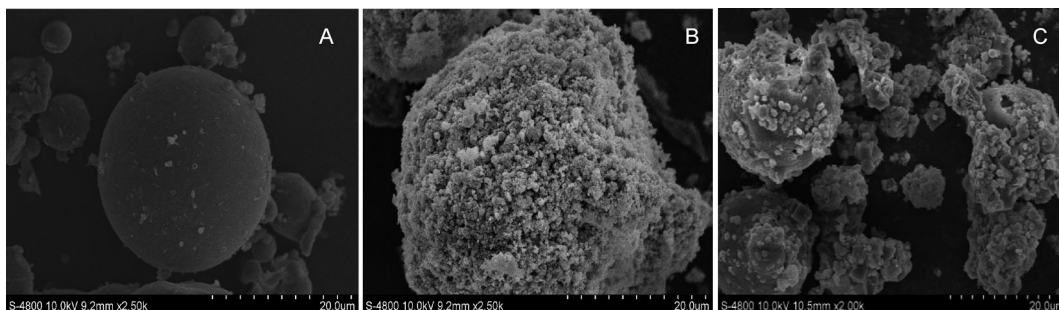

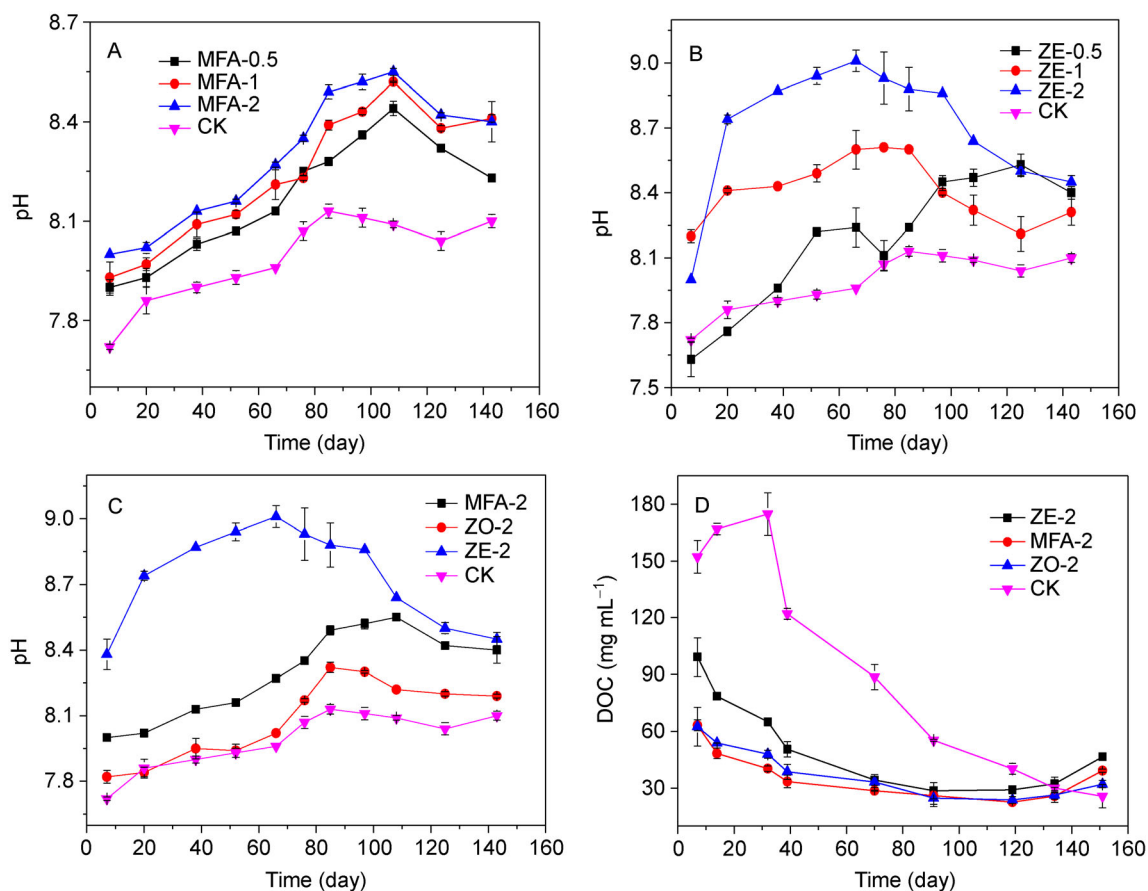**Fig. 2**   SEM images of FA (A), MFA (B), and ZE (C) .

Fig. 3   Soil column pH of the leachate with different amendments and gradient (A–C), and the concentrations of DOC (D). MFA-*x*, ZE-*x*, ZO-*x* indicates that the amount of amendments is *x*% of the soil weight. Error bars represent a standard deviation on either side of the mean.

hydroxide ions were released into the soil medium, neutralising most hydrogen ions present in the original soil solution. Furthermore, this result might be contributed to the available surface negative charges of amendments and amendment addition, which led to and increase in the negative charges at the edges of clay particles and change in the soil acidity to alkaline. This behavior was beneficial to the metallic ions adsorbed on the active sites of amendments for reducing the mobility of metal ions. When the treatments of 2% MFA and ZE were performed, pH increased by 0.65 and 1.25, respectively. The treatment of 2% ZO showed no considerable statistical significance in pH change, which indicated that ZE and MFA exhibited a greater effect than ZO on soil pH. pH for the soil leachate with MFA and ZE amendments reached the peak in 15 and 8 weeks, respectively, indicating the ZE amendment had stronger effect on pH than the MFA amendment. After the peak, the effect of these amendments on pH decreased and then became stable. A speculation is that alkaline substances leached continually to a low level. Additionally, the soil played an important role as a buffer through the ion exchange process of colloids to subsequently stabilize pH.
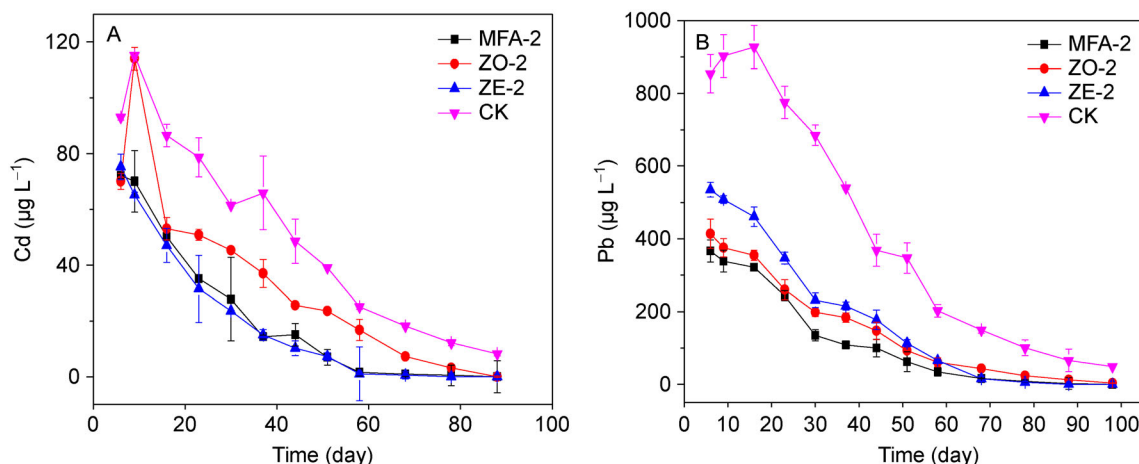
3.2.2 DOC in the leachate

Figure 3D presents the DOC concentrations. Compared with the control profiles, DOC profiles crucially decreased with the addition of the three amendments. The results indicated that when three 2% amendments were added, MFA provided the optimal control on DOC and DOC leached from the ZE-added soil primarily because after FA reacted with NaOH, the glass phase on the sample surface was dissolved by an alkaline attack to form irregular agglomerate structures (Fig. 2B–C); thus, the specific surface area increased, which ultimately improved the adsorption and fixation of DOC in the soil solution. Another study showed that the DOC amount in the leachate increased at higher pH (Christ and David, 1996); the

DOC concentration of the ZE treatment was higher than that of MFA treatment. DOC concentrations decreased considerably in the initial stage of the experiment, indicating that amendment application increased the stabilization effect on DOC. DOC comprises various low-molecular-weight organic compounds such as mono fatty acids, amino acids, and sugar acids (Antoniadis and Alloway, 2002). By contrast, some studies (Brunner and Blaser, 1989; Christ and David, 1996) have shown that an increase in pH leads to an increase in DOC solubility. However, the phenomenon presented in this study indicated that soil amendments have a greater impact on DOC than pH. Moreover, DOC solubility depends on many factors, such as the size of organic molecules, pH, charge density, and cation concentration (Andersson et al., 2000). After 10 weeks, with the continuous leaching of deionised water, DOC concentrations finally stabilized (Fig. 3D) most likely due to amendment consumption and the strong buffering capacity of the soil (Sneddon et al., 2006). Furthermore, a lack of input of organics may lead to a limited carbon source into the leachate (Andersson et al., 2000). After approximately 20 weeks, the DOC concentration slightly increased, indicating that in addition to pH and the stabilization capacities of amendments, other factors influenced DOC solubility. We inferred that it may be a function of microbial activities; microorganism apoptosis can lead to the release of soluble carbon and nitrogen (Morel et al., 2009), resulting in an increase in the DOC concentration.

3.2.3 The Pb and Cd dissolved in the leachate

Figure 4A and B shows the concentrations of Cd and Pb dissolved in the leachate. Compared with the control, when 2% ZE amendment was used, the concentrations of dissolved Cd leaching from soil were the lowest (Fig. 4A), and for the 2% MFA treatment, this concentration was slightly higher than that for the ZE treatment, which might be attributed to the effect of higher pH. Some studies have shown that pH plays an

Fig. 4 Concentrations of dissolved Cd (A) and Pb (B) in the leachate. Error bars represent a standard deviation on either side of the mean.

important role in heavy metal stabilization and dissolution (Smolyakov et al., 2010; Huang et al., 2017). Another study (Bradl, 2004) showed that an increase in the pH value induces heavy metal stabilization through several processes in soil, including the increased precipitation of heavy metals in the soil environment. For example, Cd ions precipitate in the $Cd(OH)_2$ form. In addition, FA mainly comprises Al_2O_3- and SiO_2-related compounds. Si available in MFA was dissolved, and the dissolved silicate ions combined with acid exchange component Cd to form insoluble cadmium silicon and metal silicate cadmium. Moreover, the tetrahedron of aluminum oxides formed through Al and O elements combined a part of Cd ions (Lin et al., 2019). Therefore, the concentration of dissolved Cd in the leachate highly decreased. By the end of week 9, dissolved Cd in the soil with MFA and ZE amendments continued to decrease to below the detection limit, and dissolved Cd in the soil with the ZO amendment remained at detectable level. On one hand, the amount of soluble heavy metals was relatively small in the overall amount of heavy metals. By contrast, only a small amount of heavy metals dissolved in the amended soil, and their concentrations became relatively stable after long-term leaching. In summary, MFA and ZE have a high capacity for Cd stabilization.

Figure 4B presents the concentration profiles of Pb dissolved in the leachate.The Pb concentration shows a trend similar to The dissolved Cd concentration with the application of the three amendments, and the Pb concentration substantially decreased when the soil was treated with 2% of the amendments. The MFA 2% treatment, which led to heavy metal stabilization mainly due to an increase in the specific surface area of FA under alkaline modification conditions, was the most effective. The specific surface area of FA and MFA was 1.45 cm^2 g^{-1} and 31.6 m^2 g^{-1}, respectively; this finding was reported in our previous study (Huang et al., 2020a). However, under the ZE treatment condition, dissolved Pb and Cd showed a different trend

(Fig. 4). Titeux and Delvaux (2009) reported that DOC and Pb can form a strong complex, and therefore the increase in the Pb concentration in the leachate may be resulted from the higher DOC concentration with the ZE amendment. Table 2 presents a strong positive Pearson's correlation coefficient ($r = 0.94$, $p < 0.001$) between dissolved Pb and DOC concentrations. Furthermore, under the action of amendments, some Pb ions existed in the form of $Pb(OH)_2$, an amphoteric compound, and in a certain pH range, their solubility increased with the increase in pH, which can explain the increase in dissolved Pb when the ZE amendment was applied to the soil. Moreover, during the 11th week of the experiment, the dissolved Pb level decreased to below the detection limit due to the reason similar to the Cd level decrease below the detection limit. Another reason for this phenomenon could be that the dissolved Pb concentration was correlated to the DOC concentration, which must be investigated in the future.

Table 2 Pearson's correlation coefficients *r* between dissolved Pb and Cd and DOC concentration and pH in leachates (*n* = 140).

	Cd	Pb	DOC	pH
Cd	1	0.93[***]	0.78[***]	−0.57[**]
Pb	0.93[***]	1	0.94[***]	−0.45[*]

[***] $p < 0.001$. [**] $p < 0.01$. [*] $p < 0.05$.

3.3 Profiles of Cd, Pb, and soil organic matter in the soil matrix

3.3.1 Bioavailability of Cd and Pb

The bioavailable (available) heavy metals are the fraction of those easily absorbed by plants in soils and are the most harmful to the soils (Semple et al., 2004). Compared with the control, the available Cd (Fig. 5A and B) was considerably decreased in the amended soil, which suggested that
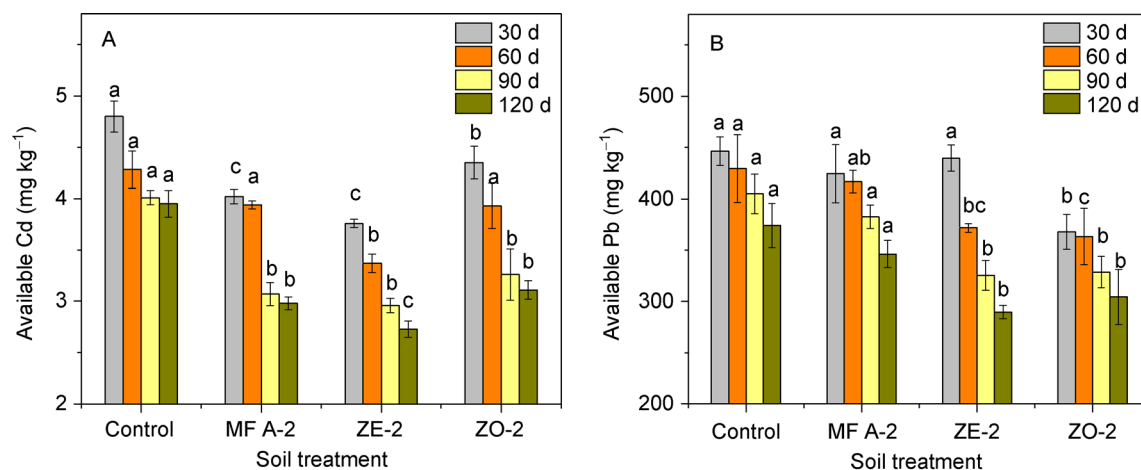
Fig. 5 Concentrations of available Cd (A) and Pb (B) in the soil column in different time periods with the addition of the three different amendments. MFA-2, ZE-2, and ZO-2 indicate that the amount of amendments is 2% of the soil weight. The data are the average of the three columns, the error bars represent a standard deviation on either side of the mean. Different lower-case letters indicate significant differences among treatments at *p* < 0.05.

deionised water transferred a small amount of heavy metals into the leachate. In addition, the application of the amendments led to a decrease in the mobility of heavy metals. Adsorption and precipitation play an important role in controlling Cd levels in the contaminated soils (Bradl., 2004). Compared with the ZO 2% treatment, MFA 2% and ZE 2% treatments showed a higher capacity to immobilise Cd, which can be explained by the fact that NaOH-modified FA comprised more alumino silicates and most particles showed a porous honeycomb structure with a large specific surface area (Fig. 2C). Studies have shown that the adsorption capacity for heavy metals is positively related to the specific surface area of adsorbents (Stötzel et al., 2009), which indicated soil amendments adsorbed the inorganic pollutants present in the soil well and therefore reduced the mobility and biological toxicity of Cd. In conclusion, MFA and ZE amendments have an effective immobilisation effect on Cd in the soil.

The ZE amendment reduced Cd uptake in the soil more effectively than the MFA amendment (Fig. 5A). Numerous researchers have reported soil pH as the most important factor that affects the metal solution and soil surface chemistry (Bradl., 2004; Zeng et al., 2011). The absorption capacity for various heavy metals on the solid phase of the soil was enhanced by increasing the pH value. The pH of the ZE 2% treatment was 0.45 higher than that of the MFA 2% treatment (Fig. 2C), which is consistent with the finding that when pH increases by approximately 0.5, the soil's capacity to adsorb Cd becomes twice (Khan et al., 2008). Furthermore, an increase in pH in the soil causes metal fixation through several processes: numerous anions are adsorbed on heavy metal surfaces or heavy metals are precipitated in the form of oxides, hydroxides, carbonates, and phosphates (Houben et al., 2012). Compared with the ZE amendment, MFA and ZO amendments did not evidently affect the Cd concentration in the first two months may be because the effect of pH on these two amendments in the initial stage was moderated due to the soil buffering effect (Duan et al., 2018). However, under the ZE amendment, pH increased sharply at the beginning of the experiment and remained stable for a long time, which led to a decrease in Cd mobilisation. Moreover, SEM images showed that ZE has porous aluminosilicate crystals to form a framework structure and a rougher surface than MFA does, indicating that ZE has high capacity to adsorb Cd ions. Furthermore, high pH affects the concentration of inorganic carbon and leads to carbonate buffering, which results in the formation of carbonate precipitates, complexes, and secondary minerals with heavy metals (Basta and McGowen, 2004). Raw FA contains a large amount of silicon, which can substantially increase silicon available in the soil that combines with Cd to form compounds and thus Cd mobility decreases. Studies have shown that the introduction of silicon improves soil attributes (Ahmaruzzaman, 2010). Our results indicated that NaOH-modified FA highly immobilised Cd in the contaminated soil.

Compared with the control, available Pb amounts significantly decreased when the three amendments were added (Fig. 5B). The ZE 2% treatment led to a drastic decrease in the available Pb concentration, which can be attributed to combined action of pH and amendments. Griffin and Au (1977) showed that Pb can be hydrolysed at low pH and can undergo multiple hydrolysis reactions where $Pb(OH)_2$ is the main form when pH is >9 and $Pb(OH)^+$ mainly exists in pH of 6–10 (Tian et al., 2018). High pH with the ZE amendment leads to small metal solubility or highly stable metal compound precipitates, which may be an important reason for the decrease in the Pb concentration. The microporous structure of ZE has a strong capacity for Pb adsorption; its pore volume can reach approximately 50%, and the pore size of ions is obviously larger than the hydration radius of lead ions, which enhances the adsorption capacity of Pb. Additionally, the special physical structure of ZE provided it a strong ion exchange capacity: Si^{4+} in ZE was replaced with Al^{3+}, resulting in excessive negative charges, for which monovalent or divalent cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) compensated. Because these cations were exchangeable in the soil environment, they can be replaced with H^+, H^+, and Pb^{2+} in the soil, and consequently, the heavy metal ions can be immobilised. In the final stage of the column experiment, no considerable change was observed in the Pb concentration with the addition of three different amendments. Throughout the experiment, the stabilization ratio of available Pb was approximately 53%. Overall, due to the biological toxicity and non-degradability of Pb, Pb stabilization in the contaminated soil mainly depends on its chemical form transformation (Zeng et al., 2017). In this study, the direct adsorption of Pb onto the amendments was considered an important mechanism for Pb stabilization in the soil. Simultaneously, adsorption, complexation, surface complexes, and co-precipitation also play an important role (Mavropoulos et al., 2002). However, MFA and ZE lead to higher soil pH, and whether it results in soil salinisation must further be investigated.

3.3.2 SOM analysis

SOM plays a critical role in the heavy metal concentration and morphological transformation because it is a rich source of negative charge (Kabata-Pendias, 2011). A study found that the adsorption of heavy metals on SOM is 6–13 times higher than that on soil minerals (Lair et al., 2007); SOM also improves the soil structure and provides better binding to heavy metal cations (Oste et al., 2002).

Figure 6A presents the concentration profile of SOM. At the beginning of experiment, soil amendments and control did not show considerable differences. However, with the progress of the experiment toward middle and late stages, the differences became larger. The loss of the organic matter in the control soil was higher than that in the amended soils may be because of the leaching effect of deionised water on macromolecular insoluble complexes present in organic
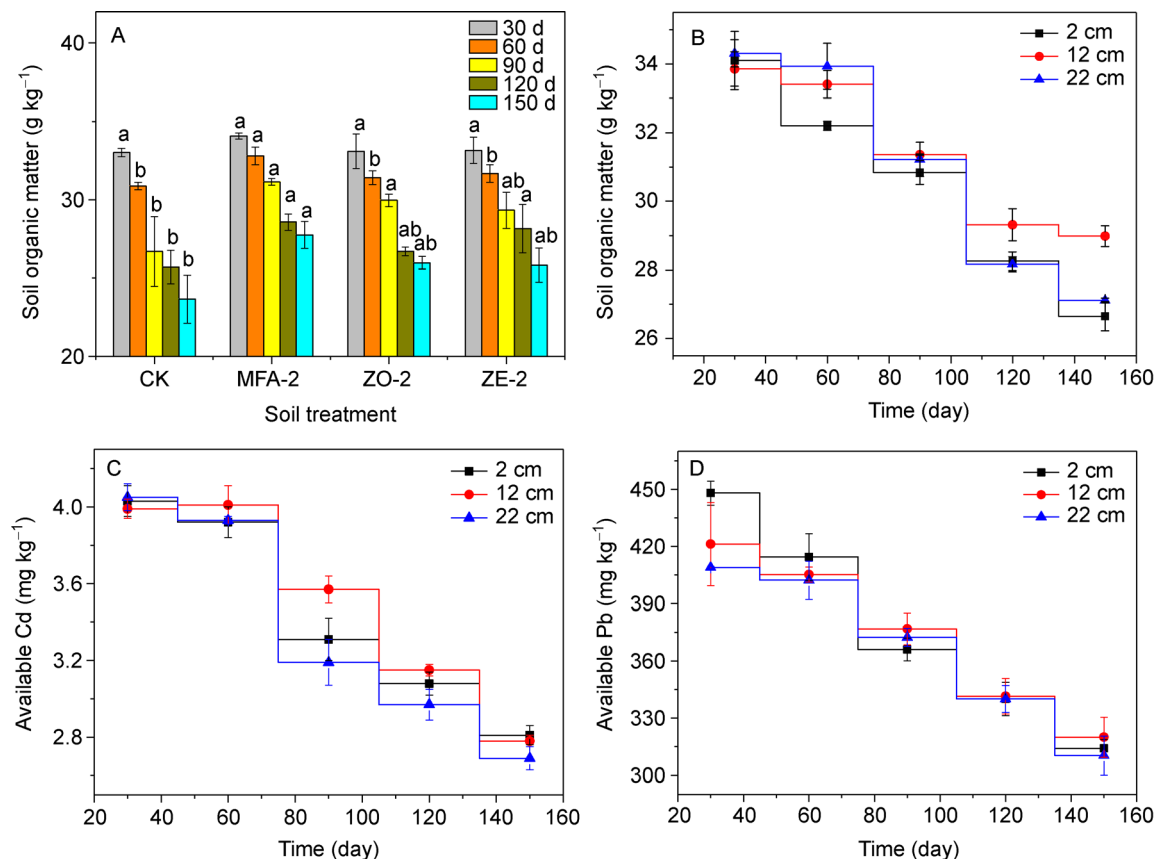
Fig. 6 (A) Concentration of SOM at different times and under different treatments. (B–D) Concentrations of SOM, available Cb, and available Pd at different soil column depths under the 2% MFA treatment. The data are the average of the three columns, the error bars represent a standard deviation on either side of the mean. Different lower-case letters indicate significant differences among treatments at $p < 0.05$.

components. Furthermore, a long-term suitable temperature leads to an increase in the microbial activity, thereby increasing SOM mineralisation (Davidson and Janssens, 2006). We can infer that the use of soil amendments leads to an increase in the accumulation and sequestration of organic matters. The MFA amendment had the most significant effect on the organic matter due to two reasons: FA modification increased its adsorption capacity and iron–aluminum oxide present in FA formed a stronger bond with the organic matter, which improved the adsorption of organic compositions (Oste et al., 2002). The retention mechanism of organic components for heavy metals includes multiple aspects, such as weak physical forces, ion exchange, and the formation of internal spherical complexes (Lair et al., 2007; Ju et al., 2019). Soil amendments accelerated organic matter sequestration, thereby improving the capacity of the organic matter to immobilise heavy metals.

3.3.3 Heavy metals and organic matter at different depths in soil columns

Heavy metal mobilisation in the soil matrix is considered to

strongly depend on parameters, such as SOM, DOC, and pH (Kalbitz and Wennrich, 1998). Figure 6B–D present the distribution profile of SOM, available Pb, and available Cd with the soil depth. At the beginning of the experiment, the distribution of SOM, Pb, and Cd in the soil column was roughly uniform and no obvious differences were observed at three different depths. However, with the proceeding of the experiments, the soil showed a clear concentration gradient across the three different layers: they appeared to mobilise to the lower layer of the soil.

SOM was mainly transported to the middle of the soil column, which could result from an uneven flow of deionised water and the microbial activity in the soil matrix (Lehmann et al., 2018). The migration of available Cd was similar to that of SOM and it mobilised toward the deeper soil (2 cm), indicating that Cd has a strong capacity of migration and mobilisation in the soil environment. In addition to complexing with SOM, pH is an important factor that influences Cd (Cruz-Paredes et al., 2017). Compared with Cd, Pb has a lower migration capacity in the soil column, which followed the SOM distribution, indicating that Pb was substantially influenced by the microbial community and organic matter reduced the toxic

effect of heavy metals on the microbial activity (Stefanowicz et al., 2020). Thus, SOM is partial to spatially and temporally affect the mobilisation of heavy metals.

4 Conclusions

Our investigation showed that the internal structure of FA considerably changed after low-temperature roasting and hydrothermal syntheses. The specific surface area highly enlarged after the modification with NaOH, and the capacity to adsorb heavy metal ions substantially increased. The leaching column experiments showed that MFA and ZE used as soil amendments exhibited positive immobilisation effects on heavy metals.

The leachate and soil composition analyses showed that the input of amendments stimulates an increase in pH, the leaching amount of soluble Cd and Pb in the leachate gradually decreases, and pH is an important factor for heavy metal immobilisation. Moreover, DOC stability is related to the special structure of amendments. Furthermore, DOC stability may be affected through the microbial activity, indicating that long-term experiments are necessary. SOM exhibits a principal effect on the migration and adsorption of heavy metals. The experimental results indicated that the addition of amendments substantially stabilizes the organic matter and improves the soil structure. The study indicated that modified FA as an amendment is an effective remediation measure for the application and management of heavy metal pollution.

Acknowledgments

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