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The preparation of paddy soil amendment using granite and marble waste: Performance and mechanisms

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ABSTRACT

The wastes generated from the mining and processing of granite and marble stone are generally regarded as useless. However, these waste materials were used as the soil amendments for the first time. The functional groups, crystalline structure and micro-morphology of granite and marble wastes amendments (GMWA) were different from the original wastes demonstrated by X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FT-IR) and Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) analyses. With the addition of the amendments, the cation exchange capacity, electrical conductivity and nutrient availability of the soil increased, and the extractable heavy metals of the soil reduced significantly. Under the condition of the addition of 3% amendments, 7.0%, 99.9%, 99.7% and 70.5% of Cu, Pb, Zn and Cd in exchangeable fractions in soil were transformed to the more stable Fe-Mn oxides- or carbonates-bounded fractions. Tessier method and correlation analysis showed that the reduction of extractable metals in the acidic paddy soil can be attributed to the adsorption of available SiO_2, the co-precipitation induced by the elevated pH value, the complexation induced by Fe-Mn oxides and the cation exchange induced by mineral nutrients. This study provides a new strategy for resource recovery of waste stones and remediation of heavy metal-contaminated soil.

Introduction

As the most consumed natural stone, granite and marble wastes (GMW) are produced more than 8.59 million tons in China, accounting for 31.4% of the global GMW in total (Rana et al., 2016; Bai et al., 2020; Qian et al., 2022). These stone wastes have very poor valueless and the huge swathes of land are encroached by the accumulation of stone waste (Amani et al., 2019). In addition, the stone wastes adversely affect the porosity and permeability of topsoil, and the fine stone powder particles entering the air after drying would cause air pollution (Mashaly et al., 2016; Sarici and Ozdemir, 2018; Cao et al., 2022). Therefore, it is of great environmental signifi-

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cance to explore the comprehensive utilization of these stone wastes (Vijayalakshmi et al., 2013; Sarici and Ozdemir, 2018; Lopes et al., 2019; Qian et al., 2022).

The main components of GMW are silicon (Si) and calcium (Ca). Various silicon-rich solid wastes such as red mud (Li et al., 2018), steel slag (Ning et al., 2016; He et al., 2017; Yang et al., 2022) and fly ash (Lee et al., 2019) have been already introduced to acidic paddy soil in which the bioavailability of heavy metals (HMs) could be reduced (NaziaTahir et al., 2021; Stein et al., 2021). However, little attention has been paid for GMWs. Granite is an typical acidic igneous rock that is mainly composed of quartz (SiO_2), potash feldspar ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), plagioclase ($Na(AlSi_3O_8)$-$Ca(Al_2Si_2O_8)$) and biotite ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$). Although these minerals are rich in silicate components, these Si exists in the form of stable phase and cannot reduce the solidification of the heavy metals (Tombeur et al., 2020). However, the silicon dioxide lattice could be cracked and the available silicon in the solid phase could be produced during the alkali-activated roasting process (Lei et al., 2018; Du et al., 2022, Qian et al., 2022). Different from granite, marble is a metamorphic rock with high level of calcium carbonate ($CaCO_3$), which is just the typical alkaline for silicon activation. Thus, the combination of granite and marble provides a latent capacity to be used as a soil amendment. In addition, previous studies have shown that the silicon-rich amendments to acidic soils could induce precipitation of Cd and Cu in the form of silicates, phosphates and hydroxides (Gu et al., 2011). In the soil solution, Si in the form of monomer silicic acid (H_4SiO_4) or polysilicic acid could potentially adsorb on the soil Fe or Al oxide/hydroxide. The coatings of amorphous silica may form in acidic soils minerals, and these different Si forms may interact with potentially toxic pollutants (PTEs) in soil (Schaller et al., 2021). In the polymerization process of H_4SiO_4 interacting with Pb^{2+}, Cd^{2+} and Cu^{2+}, Cu^{2+} promotes the polymerization of Si, while Cd^{2+} promotes the formation of larger SiO_2 polymer particles. Besides that, Cu^{2+} is integrated into the polymeric silica network structure, or forms inner-sphere surface complexes, or is blocked in the aggregates after diffusion (Stein et al., 2020). Although there are many reports on the mechanism of HMs immobilization by silicon, the Si based-amendment prepared from granite and marble stone powder have not been studied yet.

Fe and Mn in soil are important components that have strong adsorption capacity (Lian et al., 2020). A number of biochar (BC)-based composites (e.g., BC-FeOx, BC-MnOx), clay-based composites (ferric modified sepiolite (NIMS)) and iron–manganese modified sepiolite (FMS) have been investigated as novel adsorbents with enhanced adsorption/oxidation properties to increase the efficiency of paddy soil remediation (Kou et al., 2021; Wu et al., 2018; Lin et al., 2018; Wang et al., 2019; Zhou et al., 2022). For example, the application of Fe-single bond Mn modified sepiolite composites successfully reduced the content of As and Cd in contaminated-soil and rice grown thereon (Zhou et al., 2022). Wang et al. (2019) reported that Fe-Mn-modified biochar could alleviate the availability of Sb and Cd in soil and their transfer from soil to *Lolium multiflorum* Lam. Recent studies also showed that Fe/Mn modified biochar or clay, as a soil amendment, affect many soil physiochemical properties (Wang et al., 2019; Zhou et al., 2022). As typical soil supplements, they can also significantly alter microbial communities. However, the effects of the soil amendment made of waste stones have not been investigated.

This study used granite and marble stone powder as the raw material to prepare a new type of green improver (granite and marble wastes amendments, GMWA) by means of alkali activation roasting. In addition, Fe/Mn modified materials (GMWA-Fe and GMWA-Mn) were synthesized by doping Fe and Mn, and the remediation effects of the three materials on contaminated soil were compared. The purposes of this study are as follows: (1) to identify the effectiveness of these amendments prepared by the NaOH-activated roasting method through Thermogravimetric-differential scanning calorimetry (TG-DSC), X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FT-IR) and Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) characterization, (2) to investigate the effects of these amendments on soil properties and nutrient availability, as well as their ability to stabilize Cu, Pb, Zn and Cd, and (3) to explore the interaction mechanisms between the amendments and HMs. This study may provide a technical support for the resource utilization of GMW and a practical foundation for the remediation of HM-contaminated paddy soil.

1. Materials and methods

1.1. *The raw material and amendments preparation*

The GMW used in this experiment was collected from a Yunfu stone processing plant, Guangdong, China, and its basic chemical compositions were listed in **Appendix A Table S1**. The raw materials (granite and marble) were air-dried and milled to pass through a 0.15 mm sieve. The GMWA was prepared by low-temperature calcination with sodium hydroxide (NaOH, AR, Macklin, China) as an activator. The GMW was mixed with different rations of NaOH and the mixture was impregnated with deionized water (18 MΩ × cm, 25°C, PLUS-E3-30TH, Nanjing EPED Technology Development Co., Ltd., China) to reach homogeneous, and further the mixture was oven-dried at 65°C (101 type electric blast drying oven, Beijing Yongguangming Medical Appliance Factory, China). Then, the mixture was roasted at different conditions with a muffle furnace (SX2-4-10, Shenzhen yibaishun Technology Co., Ltd., China). After roasting, the sample was immediately removed from the muffle furnace and rapidly cooled with water quenching. After been dried at 65°C, the sample was ground to pass through a 0.15 mm sieved for the further use. Different from the preparation of the GMWA, the water impregnating stages for the GMWA-Fe and GMWA-Mn used 10 mL of 0.2 mol/L $FeCl_3$ (AR, Tianjin kermel Chemical Reagent Co., Ltd., China) solution and 10 mL of 0.2 mol/L $KMnO_4$ (AR, Tianjin kermel Chemical Reagent Co., Ltd., China) solution respectively. Extra alkaline could be washed with the quenching process either. The optimal process parameters were shown in **Appendix A Table S2**. The content of available Si in the amendment samples was used to evaluate the efficiency of the NaOH-activated roasting method. GMWA was prepared under the optimal roasting conditions.

Table 1 – Physicochemical properties of the initial soil and amendments. The data are expressed as means ± standard deviation (n = 3).

Parameter	Initial soil	GMWA	GMWA-Fe	GMWA-Mn
pH	5.52 ± 0.01	13.10 ± 0.01	13.10 ± 0.01	13.20 ± 0.01
Cu (mg/kg)	481.02 ± 3.05	44.8 ± 0.4	53.1 ± 1.1	46.2 ± 0.7
Pb (mg/kg)	669.13 ± 4.29	ND	ND	ND
Zn (mg/kg)	439.35 ± 8.33	48.5 ± 1.8	51.2 ± 2.6	57.3 ± 2.1
Cd (mg/kg)	0.54 ± 0.06	ND	ND	ND
Cr (mg/kg)	50.14 ± 1.63	208.9 ± 2.9	199.3 ± 1.5	156.9 ± 17.4
Mn (mg/kg)	260.26 ± 6.30	451.2 ± 1.8	517.1 ± 10.0	12,392 ± 214
Fe (%)	11.38 ± 0.10	1.65 ± 0.01	3.35 ± 0.01	1.71 ± 0.04
Available Si (g/kg)	0.015 ± 0.002	89.66 ± 0.32	121.71 ± 1.36	115.39 ± 1.62
Available K (g/kg)	0.108 ± 0.001	10.72 ± 0.16	18.11 ± 0.12	20.96 ± 0.13
Available Ca (g/kg)	0.181 ± 0.002	96.63 ± 0.25	132.36 ± 1.37	130.58 ± 0.14
Available Mg (g/kg)	0.077 ± 0.002	2.59 ± 0.02	2.79 ± 0.04	2.78 ± 0.06
Available N (mg/kg)	33.25 ± 0.33	nd	nd	nd
Available P (mg/kg)	8.38 ± 0.07	nd	nd	nd
BET (m^2/g)	nd	9.92	4.09	7.46
EC (mS/cm)	0.118 ± 0.01	51.25 ± 0.03	42.60 ± 0.04	56.20 ± 0.03
CEC ($cmol^+$/kg)	3.90 ± 0.05	12.54 ± 0.05	9.54 ± 0.09	21.04 ± 0.04
Organic matter (g/kg)	19.06 ± 0.23	nd	nd	nd

ND: not detected; nd: no data.
GMWA: granite and marble wastes amendments; GMWA-Fe: granite and marble wastes amendments + Fe modified materials; GMWA-Mn: granite and marble wastes amendments + Mn modified materials.

1.2. *Soil collection and preparation*

The initial soil was collected from the surface layer (0-20 cm) of a paddy field, its properties were presented in **Table 1**. To simulate the contamination, the solution containing Cu, Pb, Zn and Cd was mixed with the initial soil and the mixture was placed for 15 days. Then, the HM-spiked soil was air-dried and grounded to pass through a 2-mm sieve. The contents of Cu, Pb, Zn and Cd in soil reached (706.05 ± 7.63) mg/kg, (1128.91 ± 11.72) mg/kg, (927.90 ± 7.79) mg/kg and (4.64 ± 0.54) mg/kg, respectively. These contents were above the risk screening values for agricultural land (50, 80, 200 and 0.3 mg/kg, respectively) (CMEE, 2018).

1.3. *Soil incubation and seed germination*

The effects of prepared amendments (GMWA, GMWA-Fe and GMWA-Mn) on the amelioration of paddy soil and immobilization of Cu, Pb, Zn and Cd were tested in soil incubation. Specifically, the prepared amendments were mixed with HM-spiked soil (500 g) in plastic pots with the addition ratios of 0.5% and 3% (wt./wt.) respectively. Meanwhile, the initial soil and HM-spiked soil without any amendments were designated as the negative control (Soil) and positive control (Soil&HM), respectively. The water content of all soil samples was kept at 70% of the field water holding capacity and then all pots were covered with plastic caps to minimize water loss. The pots were incubated at 25°C and weighed daily to compensate for water loss by adding deionized water. After 45 days incubation, the soil samples were collected to determine the relevant physicochemical parameters. Each test was repeated for 3 times.

The sample is cultured for 120 days after applying amendments in order to reduce the negative impact on soil pH increased by adding soil amendment at the preliminary germination. Then seeds were grown in natural soils with pH values lower than 8. Since the concentrations of heavy metal (Cu, Cd, Pb and Zn) in HM-spiked soil were higher than the risk screening values of agricultural land, the rice in the controls cannot grow. All the samples were incubated at constant temperature, once the germination was observed, the seeds would be calculated as survival. The growth status of seedlings in the early stage (14 days) was determined by measuring the shoot length of 5 randomly selected seedlings.

1.4. *Analysis methods*

Soil cation exchange capacity (CEC) was determined by the Hexamminecobalt Trichloride Solution-Spectrophotometry Method (CMEE, 2017). Soil pH and electrical conductivity (EC) were measured using a glass electrode with the mixed solution of soil/water ratio of 1:5 (g:mL) (CMEE, 2016, 2018). Soil available Ca, K and Mg in soil were extracted with 1.0 mol/L ammonium acetate (AR, Aladdin Technology Co., Ltd., China), and the concentration of filtrates were determined by Atomic Absorption Spectrophotometer (AAS; ZA3000 Series Polarized Zeeman, Japan). Soil available Si was extracted with 0.025 mol/L citric acid (AR, Aladdin Technology Co., Ltd., China) solution, masked with oxalic acid (AR, Aladdin Technology Co., Ltd, China), and determined by ammonium molybdate(AR, Aladdin Technology Co., Ltd., China) spectrophotometry at 700 nm (Huang et al., 2019). The diethylenetriaminepentaacetic acid dianhydride (DTPA, 99%, Aladdin Technology Co., Ltd., China) solution (0.005 mol/L DTPA + 0.01 mol/L $CaCl_2$ + 0.1 mol/L triethanolamine (TEA, 99.5%, Aladdin Technology Co., Ltd., China), pH 7.3) was adopted to evaluate the effect of amendments on the extractability of HMs in soil (Lindsay and Norvell, 1978). The concentrations of HMs in soil pore water were determined by 0.01 mol/L $CaCl_2$ (AR, Aladdin Technology

Co., Ltd., China) solution extraction method (Gao et al., 2017a). The HM fractions were divided into exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual using Tessier five-step sequential extraction procedure (Tessier et al., 1979). All soil samples were digested according to the U.S. Environmental Protection Agency Method 3051A (USEPA, 1998), and the filtrates were analyzed for Cu, Pb, Zn and Cd via AAS (detection limits for Cu, Pb, Zn and Cd are 1, 2, 0.1 and 0.01 μg/L).

TG-DSC was carried out in a thermal analyzer (NETZSCH STA 449 F3, Germany). About 10 mg of raw material was heated at 10°C/min from room temperature to 1000°C under a 40 mL/min flow rate of N_2. The mineralogical composition was analyzed using a Powder XRD (Bruker D8 Advance, Germany) with Cu-$K\alpha$ radiation ($\lambda = 1.5405$Å) generated at a power of 60 kV and 80 mA, equipped with a Vantec-1 detector. The XRD patterns were collected in the angular range from 0° to 90°, with a scan rate of 8°/min and a step size of 0.02°; the solid phases were identified using the software of Jade 6.0 (Material Data, Inc., USA). FT-IR (Thermo Nicolet 6700, USA) was performed to analyze the functional groups at a wavelength range of 650−4000 cm^{-1} by 105 scans at a resolution of 0.4 cm^{-1}. Prior to FT-IR characterization, the amendment samples were prepared with KBr and manually reground with a pestle and mortar. The morphology and microstructure were examined using a SEM-EDS (Hitachi SU8000 series, Japan).

All results were analyzed using the software of IBM SPSS Statistics Version 25.0, and the experimental values represent mean ± standard deviation. One-Way ANOVA and Duncan's Post-Hoc Multiple Comparisons were performed to explore the effects of amendments and their treatment rate (0.5% and 3%) on soil quality, nutrient availability and HM immobilization capacity at a 95% confidence level, i.e., with a significance level of $p < 0.05$. Pearson's correlation analysis (Pearson correlation coefficient: r) was performed to check the relationships among the soil physicochemical properties, nutrient availability and metal extractability.

2. Results and discussion

2.1. Characterizations of the prepared amendments

In the preparation process of the amendments, the content of available Si in the amendments can be promoted by adding marble waste, adjusting the Si/Ca ratio in the raw material (**Appendix A Fig. S1a**), and controlling the amount of NaOH added (**Appendix A Fig. S1b**). Moreover, with the increase of roasting temperature from 650 to 800°C, the available Si content increased rapidly and tended to be stable at 800°C (**Appendix A Fig. S1c**). Similarly, the roasting time also promoted the conversion of crystalline-Si, and it stabilized after 1 hr roasting process (**Appendix A Fig. S1d**). The optimal conditions for the NaOH-activated roasting method were a granite/marble/NaOH ratio of 5/4/1.5, a roasting temperature of 800°C and a holding time of 1 hr, resulting in about 90 mg/g of available Si in the amendment (i.e., GMWA).

Table 1 showed the physicochemical parameters of the prepared amendments. pH of the prepared amendments reached 13. Fe/Mn modification process had no effect on pH, while, other properties such as CEC, EC and contents of available nutrient were different with GMWA. CEC and EC decreased with the Fe-modification process, but these values increased with the Mn-modification process. The contents of available nutrient increased considerably in both cases (**Table 1**). It is worth mentioning that GMWA-Fe (available Si of 121.71 mg/g, corresponding to available SiO_2 of 26.04%) and GMWA-Mn (available Si of 115.39 mg/g, corresponding to available SiO_2 of 24.69%) reach the standard of silicate fertilizer (CMARA., 2004).

As shown in **Fig. 1a**, granite is primarily consisted of quartz (SiO_2), albite ($Na(Si_3AlO_8)$) and orthoclase ($K(AlSi_3O_8)$), while the composition of marble is mainly calcite magnesian ($(Mg_{0.064}Ca_{0.936})CO_3$). The diffraction peaks of raw material disappeared or remarkedly weakened after roasting process, followed by the appearance of new peaks corresponding to calcium silicate ($CaSiO_3$), calcium iron oxide ($CaFeO_3$, $CaFe_2O_4$, $CaFe_3O_5$), calcite ($CaCO_3$) and magnesite ($MgCO_3$) (**Fig. 1b**). The calcium silicate is the typical soluble silicon compared to SiO_2. During the roasting process, there are two major weight loss process (**Fig. 2**). The weight loss at 355-400°C is 2.55%, and the endothermic peak on the heat flow curve is mainly related to the decomposition of NaOH to form Na_2O and lose water molecules. The second step weight loss is 16.71% at 600-830°C, and the endothermic peak is mainly related to the decomposition of marble and release CO_2 (Grela et al., 2016).

The FT-IR analysis results (**Appendix A Fig. S2**) indicated considerable spectroscopic changes between the raw material and amendments. Granite performs an obvious bridge Si-O bond at around 1084 and 995 cm^{-1}, which refers to the crystalline phases within the granite; the vibration bonds are observed at 776, 722 and 694 cm^{-1}, indicating the presence of asymmetric stretching Si-O-T (T means tetrahedral Si or Al) bonds with slight structural differences (Gao et al., 2017b; Lu et al., 2016). In the spectrum of marble, the bands at 1394, 871 and 712 cm^{-1} are the characteristic bands of carbonates (CO_3^{2-}), i.e., doubly degenerate asymmetric stretching vibrations, out-of-plane bending vibrations and doubly degenerate in-plane bending vibrations, respectively (Kuriyavar et al., 2000; Wan et al., 2017). After roasting, an intense and broad band at around 3400 cm^{-1} and a weak band at 1648 cm^{-1} appear in the spectra of amendments, which are associated with O-H stretching and H-O-H bending vibrations, corresponding to the bound water adsorbed in silicates or carbonates and the free water trapped in structure cavities (Lu et al., 2016). Moreover, a weak band is observed at around 3640 cm^{-1}, which can be attributed to the OH^- stretching (Kuriyavar et al., 2000; Ashraf and Olek, 2016), indicating the formation of little $Ca(OH)_2$ during the roasting reaction. The Si-O-T peaks at 776, 722 and 694 cm^{-1} in granite migrated to a higher wavenumber, which led us to infer that roasting process facilitated the transformation of Si-O-Al to Si-O-Si and promoted the formation of silicates. In addition, the residual CO_3^{2-} absorption peaks of amendments were still detectable at 1440 cm^{-1} and 1408 cm^{-1}, but their relative intensities were lower than that of marble, especially for GMWA-Fe and GMWA-Mn, indicating that Fe/Mn-modification enhanced the use of marble and made the conversion of SiO_2 more thorough.

The SEM micrographs (**Appendix A Fig. S3**) exhibited variations in size-scale and micromorphology from the raw mate-

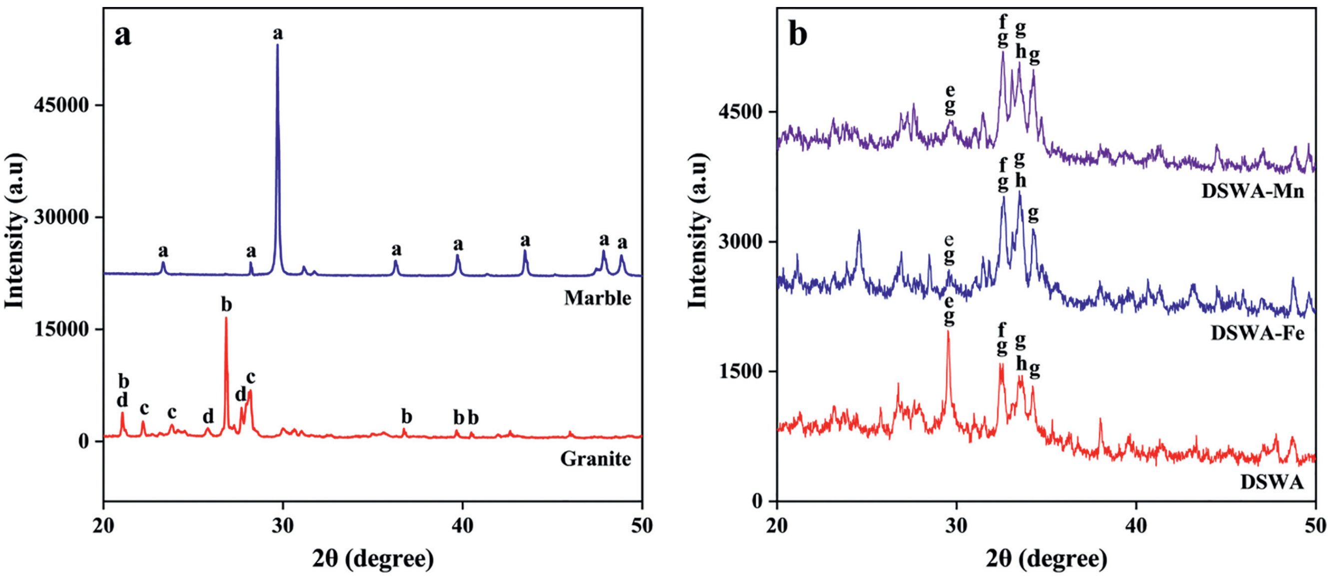

Fig. 1 – XRD analysis results of raw material (a) and amendments (b). In figure (a), a: Calcite magnesian (PDF# 86–2335), b: Quartz (PDF# 85–0865), c: Albite (PDF# 99–0001), d: Orthoclase (PDF# 86–0438); In figure (b), e: Calcite (PDF# 17–0763), f: Magnesite (PDF# 08–0479), g: Calcium silicate (PDF# 36–0642, PDF# 33–0303, PDF# 49–0442), h: Calcium iron oxide (PDF# 41–0753, PDF# 32–0168, PDF# 31–0274).

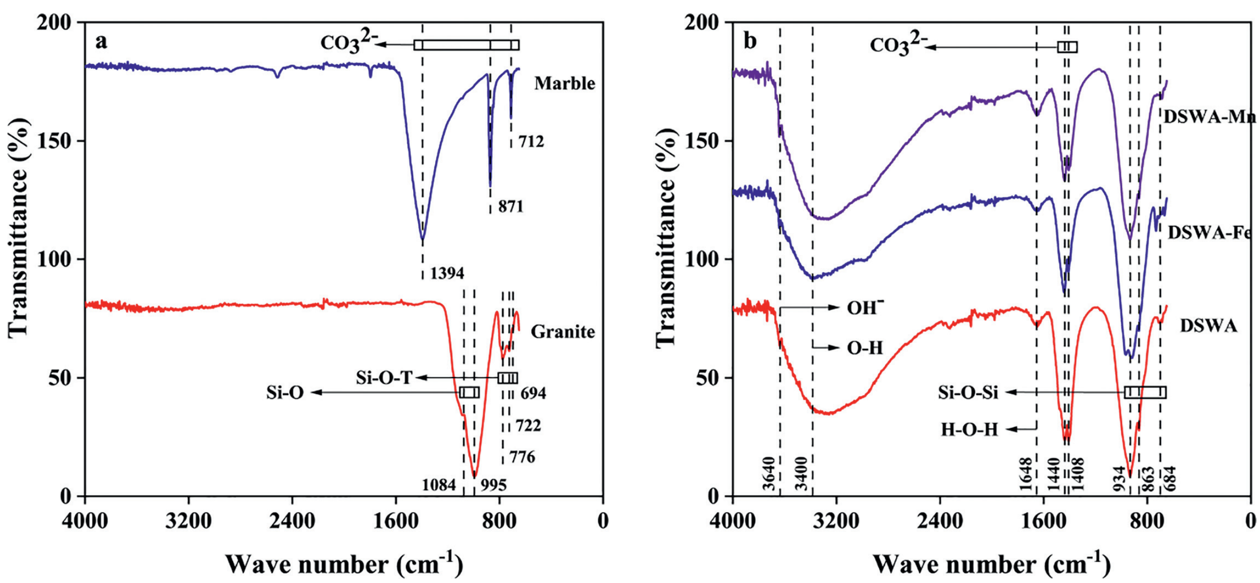

Fig. 2 – FT-IR analysis results of raw material (a) and amendments (b).

rial particles to amendment particles. A variety of granite and marble particle sizes were observed, with diameters spanning from a few microns to around 10 µm. In contrast, the amendments were roughly characterized by irregular flocculent or cotton-like particles with rough surfaces in shape. Additionally, the amendments showed visible craters on the surface, with a certain degree of particle aggregation. The EDS spectrums (Appendix A **Fig. S4**) performed the dominance peaks of Ca, Si, and O on the amendments surface, which could be associated with the main product (i.e., calcium silicate) of the roasting reaction.

2.2. *Changes in soil properties and nutrient availability with amendments*

With an increasing addition of GMWA from 0.5% to 3%, the soil pH significantly ($p < 0.05$) increased from 5.55 and 9.01 relative to the Soil&HM control (4.57), respectively, and the treatment effects of GMWA-Fe and GMWA-Mn were slightly higher than that of soil amended with the corresponding level of GMWA (**Table 2**). The high contents of alkali and alkaline earth element give GMWA a strong alkalinity and a high capacity to neutralize the acidic soil media (**Table 1**). Apart from

Table 2 – pH, CEC, EC and contents of available nutrients and extractable metals from the initial soil (Soil), HM-spiked soil (Soil&HM), and HM-spiked soil incorporated with 0.5% and 3% of amendments (GMWA, GMWA-Fe and GMWA-Mn).

Treatment	pH	CEC ($cmol^+/kg$)	EC (μS/cm)	Available nutrients (mg/kg)				Extractable metals (mg/kg)	
				Si	Ca	K	Mg	Fe	Mn
Soil	5.52 ± 0.01g	3.90 ± 0.05e	118.0 ± 0.5h	15.33 ± 1.76g	181.38 ± 1.65e	107.76 ± 1.18e	77.16 ± 1.94e	47.03 ± 1.67a	33.94 ± 1.53b
Soil&HM	4.57 ± 0.01h	3.89 ± 0.05e	379.9 ± 0.4g	15.38 ± 1.05g	170.60 ± 2.95e	151.59 ± 3.59d	72.68 ± 1.21e	38.77 ± 2.62b	36.43 ± 1.75a
0.5%GMWA	5.55 ± 0.01f	7.38 ± 0.06b	466.9 ± 0.8e	202.39 ± 1.45f	508.09 ± 12.62d	204.75 ± 5.95c	84.18 ± 1.97d	6.28 ± 0.26c	25.21 ± 1.75c
0.5%GMWA−Fe	5.70 ± 0.01e	6.98 ± 0.06d	435.1 ± 0.5f	240.55 ± 0.88d	523.04 ± 4.98cd	211.25 ± 6.26c	85.02 ± 1.18cd	7.81 ± 0.22c	23.63 ± 1.00c
0.5%GMW−Mn	5.74 ± 0.01d	7.71 ± 0.15c	494.5 ± 0.4d	220.15 ± 2.98e	552.68 ± 5.74c	201.69 ± 6.14c	88.61 ± 1.39bcd	7.09 ± 0.24c	25.47 ± 1.69c
3%GMWA	9.01 ± 0.01c	10.16 ± 0.10a	1059.3 ± 0.6c	2098.27 ± 10.16c	2190.91 ± 43.43b	248.67 ± 4.99b	89.74 ± 2.37bc	2.08 ± 0.22d	14.41 ± 0.78d
3%GMWA−Fe	9.11 ± 0.01b	10.21 ± 0.08a	1074.3 ± 0.6b	2176.03 ± 17.31a	2365.47 ± 48.53a	251.72 ± 6.62b	92.93 ± 4.92b	2.36 ± 0.14d	13.58 ± 0.45d
3%GMWA−Mn	9.15 ± 0.01a	10.06 ± 0.07a	1143.7 ± 1.5a	2123.80 ± 18.03b	2334.74 ± 9.74a	284.31 ± 7.47a	98.90 ± 3.54a	2.07 ± 0.28d	12.32 ± 0.66d

The data are expressed as means ± standard deviation ($n = 3$) with different lower-case letters in a column indicates significant ($p < 0.05$, Duncan's test) differences among the treatments. HM: heavy metal.

that, the dissolved silicates in the amendments reacted with Al^{3+} in soil to form stable amorphous hydroxyaluminosilicates, which also resulted in an increase of soil pH. As shown in **Table 2**, the available Si content in GMWA-Fe amended soil increased most significantly, with 14.6- and 140.5-fold increases at 0.5% and 3% treatment rate, respectively, followed by GMWA-Mn (13.3- and 137.1-fold) and GMWA (12.2- and 135.4-fold). The increase of silicates content in soil solution is another critical reason for the increase of soil pH due to the formation of metal-silicates, carbonates and hydroxides precipitation, resulting in a greater retention of HMs in soil solid phase (Mahar et al., 2016). Compared to GMWA, GMWA-Fe and GMWA-Mn showed a higher potential in elevating the storage and supply capacity of soil available Si.

Furthermore, the contents of available Ca, K and Mg in the soil increased with the amendment addition compared to the positive control, GMWA-Fe and GMWA-Mn are significantly better than that of GMWA (**Table 2**). The soil amended with 3% GMWA-Fe showed the highest Ca availability, which significantly ($p < 0.05$) increased the available Ca content from 170.60 to 2365.47 mg/kg; while 3% GMWA-Mn performed the highest available K and Mg amounts, with increases from 151.59 and 72.68 mg/kg to 284.31 and 98.90 mg/kg, respectively. This indicated that the performance of GMWA can be optimized by Fe/Mn-modification, enhancing the availability of multiple plant nutrients in soil. In general, the improvement of soil nutrient availability may provide a certain intensity of ion exchange for HMs, which is an important mechanism to reduce the mobility of HMs in soil (Mohamed et al., 2017; Zang et al., 2017). Meanwhile, the amendments led to a significant ($p < 0.05$) reduction of the DTPA-extractable Fe and Mn contents in soil (**Table 2**), suggesting that the amendments might be adsorbed on the surfaces of Fe-Mn oxides or formed precipitates with Fe and Mn. However, it is more likely that more HMs combined with Fe-Mn oxides due to the increased pH stimulated by amendments. Similarly, Zeng et al. (2020) reported that the concentrations of Fe and Mn in the pore water of paddy soil treated with hydrated lime at 0.6% rate decreased by 96% and 88%, respectively, indicating that alkaline amendments can promote the formation of Fe-Mn oxides or hydro oxides in the soil and make them adsorb and immobilize HMs.

CEC and EC values were improved compared to the positive control. With 0.5% and 3% GMWA, the soil CEC significantly ($p < 0.05$) increased from 3.89 cmol/kg to 7.38 and 10.16 cmol/kg, and EC increased from 379.9 μS/cm to 466.9 and 1059.3 μS/cm (**Table 2**). CEC and EC of the soil are related to the nutrient availability for both cations and anions, which are commonly used as indicators for predicting the ability of soil fertility retaining. Therefore, the abundant cations (Ca^{2+}, K^+, Mg^{2+} and Na^+) and anions (SiO_4^- and CO_3^{2-}) decomposed from the amendments (especially for GMWA-Fe and GMWA-Mn) are the direct cause of the improvement of soil CEC and EC. In fact, the introduction of several exogenous substances, such as clay minerals, lime, metal oxides and organic matter, commonly improves soil CEC due to the increased negative charges on the soil surface, thus enhancing HM adsorption and reducing HM mobility (Palansooriya et al., 2020). Yan et al. (2016) found that calcite, gypsum and hydrocalumite in the original alkaline residue (by-product of soda ash industry) could be decomposed into CaO and MgO after high-temperature calcina-

Table 3 – Changes in soil DTPA-extractable Cu, Pb, Zn and Cd contents under the different treatments.

Treatment	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
Soil	54.13 ± 0.51f	142.98 ± 0.73f	19.57 ± 0.51e	0.19 ± 0.01f
Soil&HM	188.84 ± 1.51a	518.98 ± 5.90a	291.24 ± 8.49a	3.14 ± 0.07b
0.5%GMWA	121.69 ± 1.37e	386.43 ± 6.06d	144.09 ± 1.52c	2.91 ± 0.07c
0.5%GMWA-Fe	152.26 ± 2.19b	443.16 ± 3.92b	179.47 ± 3.96b	3.31 ± 0.04a
0.5%GMWA-Mn	144.65 ± 0.74c	433.30 ± 1.89c	179.77 ± 2.11b	3.37 ± 0.03a
3%GMWA	127.96 ± 0.27d	246.66 ± 0.92e	125.54 ± 3.21d	2.54 ± 0.02e
3%GMWA-Fe	128.62 ± 2.48d	241.46 ± 5.16e	129.06 ± 1.35d	2.62 ± 0.05d
3%GMWA-Mn	129.61 ± 0.56d	247.41 ± 2.94e	124.06 ± 1.52d	2.52 ± 0.02e

The data are expressed as means ± standard deviation ($n = 3$) with different lower-case letters in a column indicates significant ($p < 0.05$, Duncan's test) differences among the treatments. DTPA: diethylenetriaminepentaacetic acid dianhydride.

tion, which was highly effective in improving soil CEC (i.e., 31.4%-116.7%). Lahori et al. (2017) applied lime blended with Ca-bentonite to soil at a treatment rate of 1%, resulting in a significant enhancement of soil CEC by 73.96%, even if lime alone caused a 67.61% increase. The above changes in soil properties implied a positive effect of the amendments, especially of the effect of Fe/Mn-modified amendments on soil quality and fertility.

2.3. *Effects of amendments on mobility and solubility of HMs in soil*

DTPA-extractable HMs are considered as the plant-available fractions in soil (Yang et al., 2021), thus, it is used as a factor for HMs immobilization. As listed in **Table 3**, the DTPA-extractable Cu, Pb, Zn and Cd varied among the treatment rate of amendments. The DTPA-extractable percentages were highest in the positive control, with 26.7% for Cu, 46.0% for Pb, 31.4% for Zn and 67.7% for Cd, which was the result of the intervention of exogenous HMs; whereas the percentage in the negative control were lower (11.3%, 21.4%, 4.5% and 35.2%, respectively). All treatments significantly ($p < 0.05$) decreased the soil DTPA-extractable Cu, Pb and Zn, and the DTPA-extractable Pb and Zn could be further reduced by increasing the treatment rate of amendments. For the 3% treatment, GMWA, GMWA-Fe and GMWA-Mn reduced 31.4%-32.2% of DTPA-extractable Cu, 52.3%-53.5% of Pb, 55.7%-57.4% of Zn and 16.6%-19.7% of Cd compared to the positive control (**Table 3**). Namely, the percentages of Cu, Pb, Zn and Cd in the plant-available fractions in soil were reduced to 18.1%-18.4%, 21.4%-21.9%, 13.4%-13.9% and 54.3%-56.5%, respectively. Recently, Mu et al. (2020) found that in Si-amended paddy soil, there were significant negative correlations among the contents of DTPA-extractable HMs (Pb and Cd) and soil pH as well as the concentrations of Ca and Si in the pore water ($p < 0.05$). Hence, soil pH, available Si content and mineral nutrients are closely related to the immobilization of HMs. Similar results has been obtained by Wang et al. (2020), who found that the EDTA-extractable Cd content decreased by 30.3% when the paddy soil was treated with 0.2% of Si-Ca-K-Mg amendment (prepared by calcining a mixture of phosphogypsum and potassium feldspar at 1000–1100°C). Further, He and Shi (2012) applied 1125 kg/ha of K, Ca, Mg and Si-rich ameliorant (prepared by calcining a mixture of flue gas desulfurization residue and potassium feldspar and/or limestone at 1000°C) to paddy soil, resulting in 89.7% and 76.8% reductions in EDTA-extractable Pb and Cd.

Compared with DTPA solution, $CaCl_2$ solution is a mild extractant that has been extensively used to extract the HMs from soil pore water, i.e., the most soluble fraction of HMs in the overall soil matrix (Houba et al., 2000). As shown in **Table 4**, the $CaCl_2$-extractable Cu, Pb, Zn and Cd contents were decreased in all treatments significantly ($p < 0.05$) compared with the positive control, especially for Pb and Zn. After the soil was amended with 0.5% GMWA, the $CaCl_2$-extractable contents of Cu, Pb, Zn and Cd decreased from 22.65, 35.73, 254.03 and 3.31 mg/kg to 1.00, 0.10, 6.22 and 0.24 mg/kg, respectively; with 3% GMWA substantially reduced to 6.28, 0.03, 0.05 and 0.02 mg/kg, respectively. In this sense, high treatment rate of amendments resulted in a better HM removal from pore water (almost reaching 100%), except for Cu (**Table 4**). In particular, the contents of Cu, Pb and Zn in the pore water of HM-spiked soil (positive control) could be reduced to below those of the initial soil (negative control) in the 0.5% GMWA treatment, but it needs 3% to achieve the same effect for Cd (**Table 4**), which was related to the high activity of Cd. The changes of $CaCl_2$-extractable HMs in soils proved that the pH value, available Si content and mineralogical composition of GMWA had a remarkable influence on HM concentrations in soil pore water. As He et al. (2017) reported, the reduction of $CaCl_2$-extractable Cd concentration in Si-amended paddy soil was largely attributed to the improvement of paddy soil acidity and the formation of metal-silicate precipitates. However, the immobilization capacity of HMs by GMWA-Fe and GMWA-Mn were consistent with GMWA.

2.4. *Changes in soil HMs fractions with amendments*

The Tessier sequential extraction results of Cu, Pb, Zn and Cd were presented in **Fig. 3**. In the positive control, there was a stark contrast among the fractions of HM. For Cu and Zn, approximately half of the total content occurred in the residual fraction (51.3% and 49.0%, respectively); the carbonates-bounded and residual fractions accounted for 64.8% of total Pb; and 64.4% of total Cd existed as exchangeable fraction. The sum of the first three fractions were 87.4% for Cd, 54.1% for Pb, 43.9% for Zn and 27.4% for Cu in the positive control, demonstrating that Cd and Pb had a stronger mobility and a higher dissolution capacity than Zn and Cu.

Table 4 – Changes in soil $CaCl_2$-extractable Cu, Pb, Zn and Cd contents under the different treatments.

Treatment	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
Soil	1.92 ± 0.02d	0.90 ± 0.08b	13.46 ± 0.13b	0.2 ± 0.04c
Soil&HM	22.65 ± 0.10a	35.73 ± 0.01a	254.03 ± 3.12a	3.31 ± 0.05a
0.5%GMWA	1.00 ± 0.02e	0.10 ± 0.01cd	6.22 ± 0.04d	0.24 ± 0.01c
0.5%GMWA-Fe	1.26 ± 0.03e	0.15 ± 0.01c	9.62 ± 0.05c	0.36 ± 0.01b
0.5%GMWA-Mn	1.08 ± 0.02e	0.15 ± 0.01c	9.88 ± 0.17c	0.36 ± 0.01b
3%GMWA	6.28 ± 0.13c	0.03 ± 0.00d	0.05 ± 0.02e	0.02 ± 0.00d
3%GMWA-Fe	6.91 ± 0.78b	0.03 ± 0.01d	0.02 ± 0.01e	0.02 ± 0.00d
3%GMWA-Mn	6.67 ± 0.22bc	0.05 ± 0.01d	0.02 ± 0.01e	0.02 ± 0.00d

The data are expressed as means ± standard deviation (n = 3) with different lower-case letters in a column indicates significant (p < 0.05, Duncan's test) differences among the treatments.

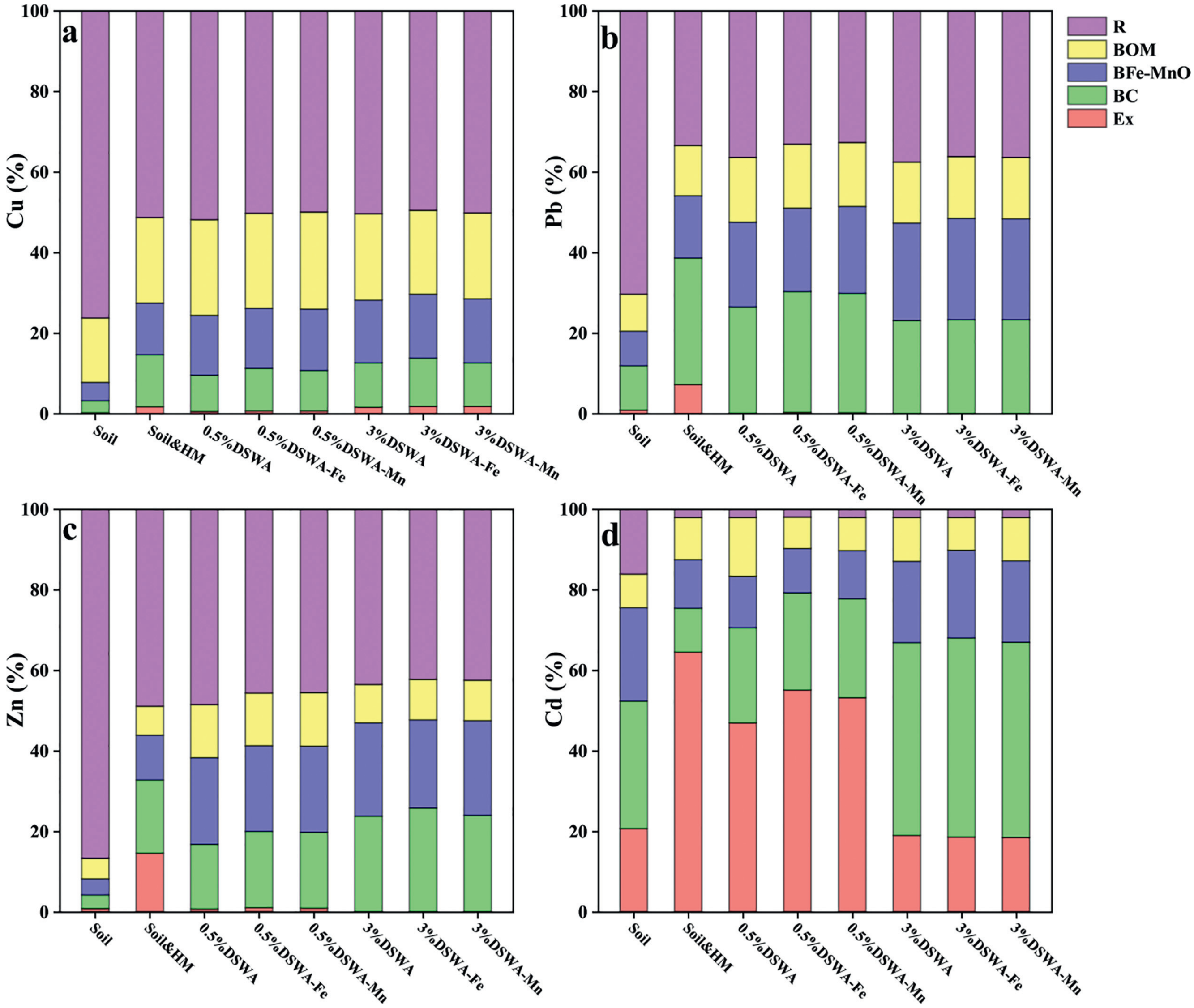

Fig. 3 – Variations of Cu (a), Pb (b), Zn (c) and Cd (d) fractions under different amendment treatments. R: residual; BOM: bond to organic matter; BFe-MnO: bond to Fe-Mn oxides; BC: bond to carbonates; Ex: exchangeable.

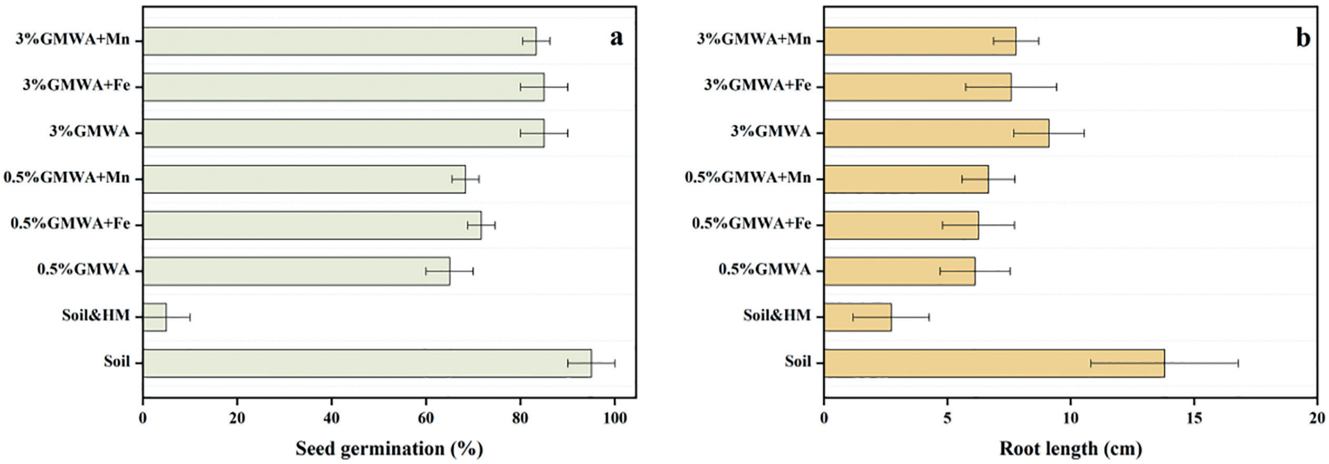

Fig. 4 – Comparison of rice seed germination rate (a) and the root length (b) in amendment soil.

Compared to the positive control, 0.5% GMWA treatment led to a 71.0%, 97.8%, 95.8% and 27.3% reduction in the exchangeable fraction for soil Cu, Pb, Zn and Cd, and the reduction in the 3% GMWA treatment were 7.0%, 99.9%, 99.7% and 70.5%, respectively (**Fig. 3**). This trend was consistent with the $CaCl_2$-extraction (**Table 4**). Moreover, in the 0.5% and 3% GMWA amended soil, the reduction of carbonates-bounded Cu and Pb were 29.9% and 14.9% as well as 16.4% and 26.7%, respectively, while the increase of carbonates – bounded Zn and Cd was 11.3% and 30.1% as well as 116.9% and 339.0%, respectively. Thus, the soil exchangeable and carbonates – bounded fractions of Cu and Pb reduced by GMWA were primarily transformed to Fe-Mn oxides – bounded and organic matter – bounded fractions. High treatment rate of GMWA resulted in a more transformation of Zn and Cd from the exchangeable fraction to carbonates-bounded, Fe-Mn oxides-bounded and organic matter – bounded fractions (**Fig. 3**). The above results indicate that the adsorption of Pb and Zn in soil was better than that of Cu and Cd. The difference in the immobilization effects for Cu, Pb, Zn and Cd by GMWA may be explained by the theory of “Hard-Soft-Acid-Base”. The theory defines that Pb^{2+}, Zn^{2+}, Cu^{2+} are the “Lewis borderline acid”, and Cu^{+}, Cd^{2+} are the “Lewis soft acid”, hence in the GMWA amended soil, Pb^{2+} and Zn^{2+} tend to form complexes with the “Lewis hard base” such as OH^{-}, $CO_3{}^{2-}$ and $SiO_4{}^{4-}$ than with Cu^{+} and Cd^{2+}. In addition, the comparison in **Table 3** shows that the solidification effect of the amendment prepared in this study on the available heavy metals in soil is better than the exogenous mineral silicon (Ma et al., 2021; Xiao et al., 2021), organosilicone (Xiao et al., 2021) and peanut shell biochar (Chao et al., 2018) used in previous studies.

2.5. *Effects of amendments on rice seedling growth*

Rice seed germination tests were performed in soil to evaluate the possible application of pretreated modified granite as soil amendments. The seed germination rate of rice and its seedling growth were shown in **Fig. 4**. The seed germination of rice was enhanced by the addition of GMWA, GMWA-Fe and GMWA-Mn. With the increasing amount of passivator added, the toxicity of heavy metals is effectively alleviated, which also better explained the reduction in the effective state of heavy metals (**Tables 3** and **4**). The above results suggested that the application of amendments could remarkably alleviate the stress of Pb, Cu, Zn, and Cd on rice in contaminated soil (Soil&HM). Similar results could be found in previous studies (Jiang et al., 2021). In addition, the very low germination rate and root length in the Soil&HM control indicated that heavy metals affect the physiological characteristics of rice seeds and destroyed normal physiological metabolic functions of plants (Qiu et al., 2022; Morales et al., 2012). This result suggests that the amendments (GMWA, GMWA-Fe and GMWA-Mn) could reduce the released risk of heavy metal in soil and improved soil quality.

2.6. *HMs immobilization mechanism*

Previous studies have demonstrated that the application of exogenous Si-compounds had consistent and beneficial effects on soil pH and available Si content, especially on soil extractable Cu (Ning et al., 2016), Pb (Ji et al., 2016; Mu et al., 2019; Zhao et al., 2017), Zn (Ning et al., 2016; Ji et al., 2016) and Cd (He et al., 2017; Ji et al., 2016; Mu et al., 2019) contents. In the present study, the effectiveness of Si-enriched amendments in reducing the mobility and dissolution of HMs were confirmed by applying GMWA, GMWA-Fe and GMWA-Mn to acidic paddy soil. Moreover, compared with DTPA-extraction, $CaCl_2$-extraction showed better correlation with the immobilization capacity of Cu, Pb, Zn and Cd in soil (**Fig. 5**). Based on our results and discussion, the mechanisms of paddy soil amelioration and HM immobilization by GMW amendments were presented in **Fig. 6**, which can be concluded as the following aspects:

(1) The $CaCl_2$ extracted Pb ($r = -0.477$, $p < 0.05$; $r = -0.572$, $p < 0.01$), Zn ($r = -0.514$, $p < 0.05$; $r = -0.603$, $p < 0.01$) and Cd ($r = -0.564$, $p < 0.01$; $r = -0.623$, $p < 0.01$) in soil showed significant negative correlations with soil pH and CEC values (**Fig. 5**), indicating that soil pH and CEC are the crucial factors affecting the mobility and dissolution of Pb, Zn and Cd. The improvement of soil pH and CEC by amendments seems to be one of the pos-

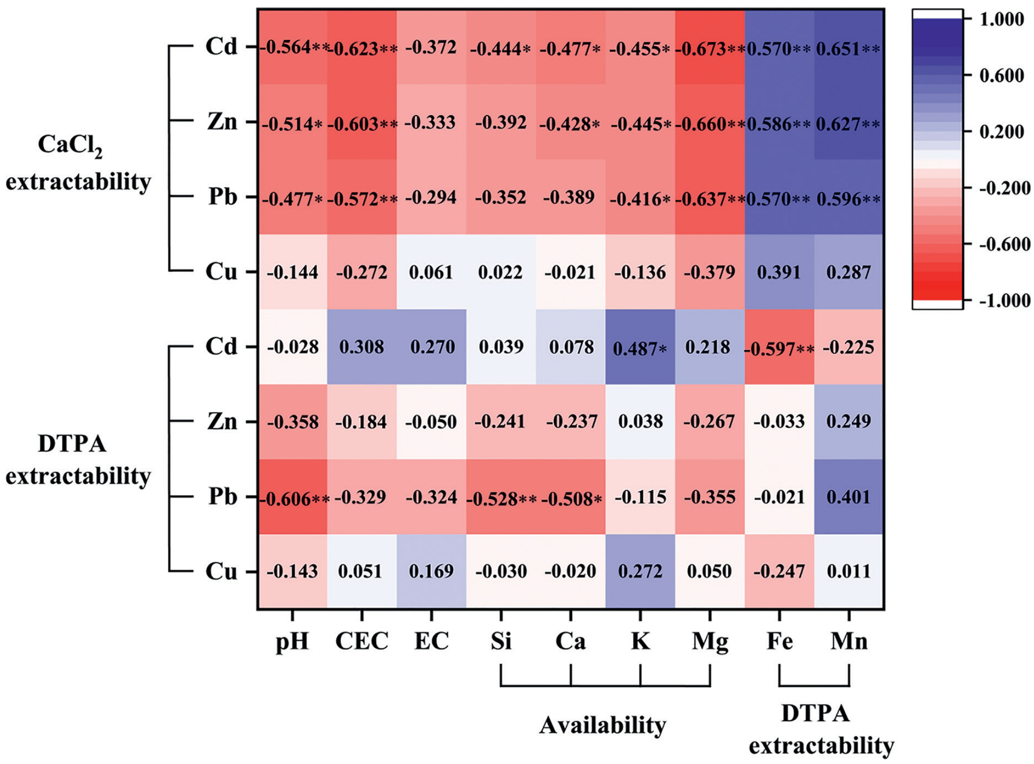

Fig. 5 – Heat map of Pearson correlation coefficients (*r*) among the soil physicochemical properties, nutrient availability and metal extractability ("*" means $p < 0.05$, "" means $p < 0.01$).**

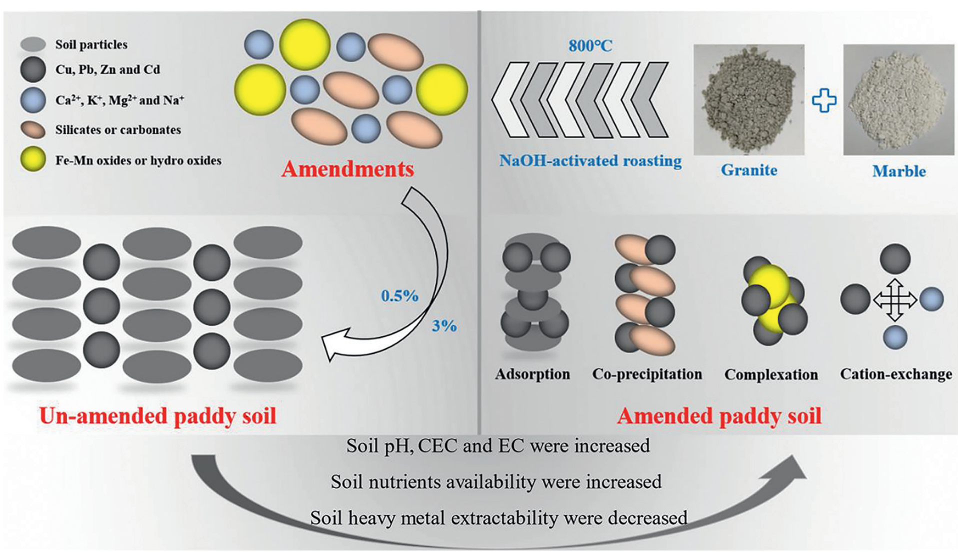

Fig. 6 – Remediation mechanisms of amendments on HM-contaminated paddy soil.

sible mechanisms for HM immobilization. It is reported that the elevated pH in acidic paddy soil enhanced the negative surface charges and pH-dependent cation exchange sites, further improving soil CEC (Mu et al., 2019; Chen et al., 2019), which achieved HM immobilization via adsorption, surface complexation and precipitation reactions of HMs by soil particles.

(2) Apart from the precipitability and alkalinity of CO_3^{2-} and $Ca(OH)_2$ or CaO, the amendments also released a large amount of available Si into paddy soil (**Table 2**), further promoting the solid solution encapsulation and precipitation reaction between HMs and Si. For example, the stability of Zn in Si-amended soil can be enhanced by the formation of Zn-Al layered double hydroxide and phyllosilicate-like precipitates (Gu et al., 2011). Similarly, Si can also induce Pb and Cd in soil to form the co-precipitation of metal–silicates to achieve the immobilization of HMs (Mu et al., 2020).

(3) The application of amendments significantly ($p < 0.05$) improved the contents of available Ca, K and Mg in soil (**Table 2**), and then enhanced the cation-exchange between nutrients and HMs, making HMs exist in a more stable form. The significant negative correlation between the availability of Ca, K, Mg and the extractable Pb, Zn, Cd in soil supports the corresponding conclusion (**Fig. 5**). In addition, the increase of available Ca content in soil facilitated the coagulation of dissolved organic carbon (DOC) and then reduced the solubility of DOC-HM (e.g., DOC-Cu and DOC-Cd) complex in soil pore water (Zeng et al., 2020; Römkens and Dolfing, 1998).

(4) The application of amendments significantly ($p < 0.05$) reduced the contents of DTPA-extractable Fe and Mn in soil (**Table 2**). As shown in **Fig. 5**, the $CaCl_2$ extractable Pb ($r = 0.570$, $p < 0.01$; $r = 0.596$, $p < 0.01$), Zn ($r = 0.586$, $p < 0.01$; $r = 0.627$, $p < 0.01$) and Cd ($r = 0.570$, $p < 0.01$; $r = 0.651$, $p < 0.01$) in soil displays significant positive correlations with the DTPA extractable Fe and Mn in soil. Therefore, due to the increase in soil pH caused by the amendments, the colloids of iron and manganese oxides in soil changed from a positive or zero charge to a negative charge, which enhanced the adsorption capacity of Fe-Mn oxides for HMs (Wen et al., 2020). This mechanism is also confirmed by the increase of Cu, Pb, Zn and Cd in the Fe-Mn oxides-bounded fraction in paddy soil (**Fig. 3**).

(5) For Cu in soil, the amendments can achieve significant immobilization capacity at both 0.5% and 3% treatment rate, but the capacity of high treatment rate is slightly decreased (**Table 4**). Therefore, it should be noted that the immobilization effect of amendments on Cu is different from that of Pb, Zn and Cd, i.e., higher treatment rate may not lead to better results.

3. Conclusions

In this work, soil amendments using GMW was successfully prepared. The results demonstrated that GMWA not only improved the physicochemical properties such as pH, CEC, EC and nutrient availability of acidic paddy soil, and also significantly reduced the DTPA- and $CaCl_2$-extractable Cu, Pb, Zn and Cd. Compared with GMWA, GMWA-Fe and GMWA-Mn showed better capability of ameliorating soil quality and fertility, especially higher storage and supply of available Si for soil. In general, the preparation and application of low-cost GMWA could be not only conducive to the resource utilization of GMW, and also benefit to solve the issues of acidification, nutrient loss and heavy metal contamination in soil .

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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Appendix A Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jes.2022.06.009.

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