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ORIGINAL ARTICLE

Influence of coal gangue aided phytostabilization on metal availability and mobility in copper mine tailings

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Abstract

Copper mine tailings without proper remediation deposited permanently in tailings ponds would pose adverse impacts to the environment. Coal gangue, with high nutrients, used in infertile soil, is investigated in microcosm trials to explore the possibility of immobilize metals within the copper mine tailing in this research. Therefore, a pot trial was conducted using coal gangue and *Vetiveria zizanioides* for phytostabilization of the metals in copper mine tailing. Results indicated that applying coal gangue not only increased the pH, organic matter content and nutrient contents of the amended tailings, but also decreased the DTPA-extractable concentrations of Zn, Pb, Cd, and Cu in the amended tailings. The application of coal gangue converted the exchangeable and carbonate fractions of Zn, Pb, Cd, and Cu into unavailable forms of Fe–Mn oxide and/or organic matter fractions, thus reducing those metal contents in mobile fractions of the amended tailings. This study shows that treatments with coal gangue inhibited Zn, Pb, Cd, and Cu translocation from tailings to *Vetiveria zizanioides*. In contrast, the accumulation of Cr in the plant was increased by the addition of coal gangue. Collectively, these results support the hypothesis that coal gangue is a potential waste-derived amendment with the ability to reduce the mobility of most of the studied metals in copper mine tailings. This study also proposed a new approach to dispose the waste of coal gangue as an amendment for phytostabilization of copper mine tailings.

Keywords Chemical fractionation · Phytoremediation · Phytostabilization · Waste-derived amendment · Coal gangue · Mine tailing

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Introduction

Copper mine tailings are a type of solid waste produced by the excavation of copper mines, and they are usually discharged and deposited in tailings ponds that are not managed after mine closure. Copper mine tailings contain high levels of Cu even several years after the tailings are abandoned (Li 2006). If copper mine tailings are left without proper remediation, some of the toxic metals such as Cu, Cd, and Cr in copper mine tailings are leached by water and wind and transferred to the surrounding environment (Conesa and Schulin 2010). As a result, copper mine tailings pose a potential risk to terrestrial and aquatic ecosystems (D'Emilio et al. 2013). Furthermore, copper mine tailings often affect plant colonization and growth, due to their poor physical properties, low pH and organic matter, lack of nutrient contents (N, P, and K) and high concentrations of toxic elements such as Cr, Pb, and Cd (Zhang et al. 2011, 2016). Therefore, it is necessary to remediate the copper mine tailings, but this task is arduous to achieve.

A number of techniques have been proposed and applied to remediate soils contaminated with mine tailing, including pneumatic fracturing, soil washing, vitrification, electrokinetics, chemical oxidation/ reduction and so on, but the above mentioned methods are often very expensive to implement (Rodríguez-Vila et al. 2014; Saleh 2015a, b; Saleh 2016a). Alternatively, in situ stabilization of metals in the substrate through application of soil amendments is less expensive and may provide a low-cost technique for the remediation of polluted soils (Basta and McGowen 2004; Asensio et al. 2013; Novo et al. 2013). The use of wastes as amendments to restore degraded sites is regarded as a feasible method (Chiu et al. 2006; Camps Arbestain et al. 2008; Das and Maiti 2009; Saleh et al. 2017a; Saleh et al. 2018; Soury et al. 2019). Technosol, biochar, manure, compost, industrial by-products (bentonite, red mud, and fly ash) and sewage sludge have been proposed to immobilize metals by the formation of low-solubility precipitates or minerals, stable complexes with organic ligands and adsorption to mineral surfaces, etc., in polluted soils (Novo et al. 2013; Rodríguez-Vila et al. 2014; Saleh 2018). If properly managed, using waste as the amendment for remediation could be recognized as an environmentally sustainable solution for the disposal of these wastes, as they would otherwise be deposited on the land at high cost. Coal gangue is an industrial solid waste that is produced from coal production and accounts for 10–15% of coal mining products. If coal gangue could be used as a kind of amendment, it will propose a resource utilization way to dispose of this waste.

Nowadays, coal gangue is also a kind of mine tailings and typically dumped on the land surface without any specific treatment. In recent years, coal gangue had been blended with coal for power generation. By applying specific processing methods, coal gangue can be used for constructing material, such as cement, brick and a substitute for clay. Coal gangue can also be used in many places as alternative aggregates in embankment, building construction, zeolites production and pyrites extraction (Xiaoyan and Changsheng 2007; Sun and Li 2008). In addition, coal gangue can be used as a kind of soil fertilizer (Liu and Liu 2010). It contains essential elements for plant growth, such as Cu, Zn, Mn, and B (Kang et al. 2011). Previous studies also revealed that the addition of coal gangue at a low rate can improve the nutrient content of infertile soil and accelerate plant growth (Hu et al. 2007). Tong et al. (2010) observed that the application of coal gangue to soilless culture substrates improved the growth of eight species of vegetables. Luo et al. (2015) found that applying coal gangue to infertile soil increased the biomass, root weight and shoot length of *Brassica rapa pekinensis* (pakchoi). Therefore, coal gangue is actually a useful waste product and could be regarded as an effective fertilizer when used in infertile soil (Kang et al. 2011). Further, coal gangue typically consists of sulfides and aluminosilicate minerals. The ferroalumino-silicates within the coal gangue could affect the adsorption of metals on their Al and Fe oxides or hydroxides. Therefore, previous works have found coal gangue is a kind of fertilizer, which can increase the plant growth at a low rate in infertile soil. However, whether coal gangue could be used for binding metals and improving the physical and chemical properties in copper mine tailings is unknown (Hu et al. 2007; Tong et al. 2010; Luo et al. 2015).

Phytoremediation is a less-cost method to alleviate the deleterious effects at high concentrations of metals in tailings (Prasad and Freitas 2003; Mendez and Maier 2008). Phytostabilization and phytoextraction are two main representative methods of phytoremediation, which are of particular interest in the mining restoration. Phytostabilization uses the combination of amendments and plants tolerant to toxic concentrations of metals and reduces the mobility of metals in soils (Mendez and Maier 2008). Currently, the application of amendment combined with planting vegetation can also help diminish the spread of pollutants by water or wind erosion and reduce the leaching of metals into groundwater (Lopareva-Pohu et al. 2011). However, the success of the phytostabilization combination depends on the choice of plant species. *Vetiveria zizanioides* (vetiver) is often used for the phytostabilization of metal contaminated soils and regarded as a tolerant plant that can grow and produce high biomass in harsh environments (Chen et al. 2004). Recently, a few studies have reported that *Vetiveria zizanioides* can thrive in the heavy metal contaminated soils, Pb/Zn mine tailings and copper tailings amended with sewage sludge or compost (Chiu et al. 2006; Mendez and Maier 2008; Lopareva-Pohu et al. 2011). Liu and Liu (2006) observed that *Vetiveria zizanioides* can also survive on coal gangue piles as well. As a result, *Vetiveria zizanioides* (vetiver) is a useful restoration plant which can thrive in the harsh environment. However, whether *Vetiveria zizanioides* could combine with coal gangue for phytoremediation of copper mine tailings is also unknown.

To sum up, previous works assessed the effects of waste-derived amendments combined with plants in contaminated soils or tailings (Chiu et al. 2006; Gondar and Bernal 2009; Lopareva-Pohu et al. 2011). There is hardly any information about the combination of coal gangue and *Vetiveria zizanioides* for the phytostabilization of copper mine tailings. In addition, little is known about the chemical distribution of metals in tailings mixed with coal gangue and vegetated with *Vetiveria zizanioides*. Therefore, a greenhouse experiment was adopted in this study to investigate the use of coal gangue and this plant on the chemical stabilization of metals in copper mine tailings. We hypothesized that amending with coal gangue and planting *Vetiveria zizanioides* could decrease the solubility and mobility of some metals in copper mine tailings. The aims of this study were to (1) evaluate the effects of coal gangue on the revegetation of copper mine tailings; (2) investigate the effects of coal gangue and vegetated with plants on the chemical fractions of metals in amended tailings; (3) to testify whether the coal gangue could be used as a potential waste-derived amendment for copper mine tailings.

Materials and methods

Copper mine tailings sampling

Copper mine tailings were collected in a tailing pond from a copper mine of Anhui Province. (30°54′36.89″N, 117°53′37.54″E) at a 0–20 cm depth. Coal gangue was sampled from a coal waste dump in Huainan coalfield (Anhui, China) (32°49′07.0″N, 116°34′23.5″E). The coal gangue and tailings were air dried, sieved through a 2 mm mesh sieve and homogenized before use. The physico-chemical properties of the coal gangue and tailings are presented in Table 1.

Experimental design and procedure

The tailings were mixed with coal gangue at different proportions (w/w) of 0% (CG 0), 1% (CG 1), 2.5% (CG 2.5), 5% (CG 5), 10% (CG 10), 15% (CG 15), 20% (CG 20), and 30% (CG 30) and subsequently placed in plastic pots (0.5 L) with a piece of 0.1 mm plastic sieve located at the bottom to retain the fine tailing particles in a greenhouse. These rates were predetermined, and each treatment was replicated three

Table 1 The physical and chemical properties of the copper mine tailings and coal gangue before the experiment

	Copper mine tailings	Coal gangue
pH	7.75 ± 0.1[a]	9 ± 0.2
EC(μS/cm)	254.8 ± 3.53	538.72 ± 11.17
OM(%)	0.27 ± 0.04	8.43 ± 0.72
N_{Total} (mg kg^{-1})	305.01 ± 33.48	2409.7 ± 107.89
P_{Total} (mg kg^{-1})	352.38 ± 22.68	1005.73 ± 143.74
K_{Total} (mg kg^{-1})	1754.52 ± 127.39	4143.97 ± 79.07
$Zn_{Pseudototal}$ (mg kg^{-1})	249.5 ± 15.99	105.03 ± 11.20
$Pb_{Pseudototal}$ (mg kg^{-1})	28.38 ± 3.75	21.74 ± 1.30
$Cd_{Pseudototal}$ (mg kg^{-1})	2.57 ± 0.34	0.33 ± 0.04
$Cr_{Pseudototal}$ (mg kg^{-1})	69 ± 2.42	76.29 ± 5.72
$Cu_{Pseudototal}$ (mg kg^{-1})	984.38 ± 66.14	179.2 ± 2.98
$Zn_{DTPA\text{-}Extractable}$(mg kg^{-1})	9.46 ± 0.79	4.58 ± 0.13
$Pb_{DTPA\text{-}Extractable}$(mg kg^{-1})	2.92 ± 0.6	1.48 ± 0.25
$Cd_{DTPA\text{-}Extractable}$ (mg kg^{-1})	0.43 ± 0.03	0.05 ± 0.01
$Cr_{DTPA\text{-}Extractable}$ (mg kg^{-1})	3.53 ± 0.55	4.48 ± 1.23
$Cu_{DTPA\text{-}Extractable}$ (mg kg^{-1})	59.41 ± 3.83	7.21 ± 1.2

[a]Mean ± SD values ($n = 3$)

times. The pots were incubated for 5 weeks prior to grow the plant, during which the amended tailings moisture was maintained. Seeds of *Vetiveria zizanioides* were soaked for five minutes with mercuric chloride (0.1%) then, washed with deionized water. Ten sterilized seeds were sown and allowed to germinate in each pot. When the *Vetiveria zizanioides* seedlings developed two leaves, half of the plants were thinned out to give five seedlings in each pot for uniformity. The pots in the greenhouse were arranged randomly, rotated regularly and watered daily. After 45 days, all the cultivated plants were harvested for the following analysis. The plants were carefully removed from the pots and washed with tap water then rinsed for 3 times with DW (deionized water). During the experiment, the relative air humidity and temperature were controlled at approximately 75% and 25 °C, respectively.

Tailings substrata analysis

Coal gangue, copper mine tailings and amended tailings were analyzed for electrical conductivity (EC), pH and organic matter (OM) content (Kalra and Maynard 1991). Total nitrogen was measured using the Kjeldahl method (Asensio et al. 2013), and total phosphorus was determined according to the molybdenum blue method (Rodríguez-Vila et al. 2014). Pseudototal Zn, Pb, Cr, Cd, Cu, and K in the tailings were determined after digestion with HCl and HNO_3 (3:1 v/v), and phytoavailable metals in the tailings were extracted by 0.5 M DTPA (diethylenetriamine-pentaacetic acid). Zn, Pb, Cr, Cd, Cu, and K concentrations in the solution were determined by ICP-OES (PerkinElmer Optima 2100 DV). A standard reference soil material (GBW 07,403 (GSS-3)) was analyzed to examine the accuracy of the metal determination.

The metal fraction in the coal gangue, copper mine tailings and amended tailings was extracted using the method suggested by Tessier et al. (1979). Briefly, the exchangeable fraction (F1) was extracted with 1 M $MgCl_2$ at pH 7, the carbonate fraction (F2) was extracted with 1 M NH_4OAc at pH 5, the Fe–Mn oxide fraction (F3) was extracted with hydroxylamine, the organic matter fraction (F4) was extracted with H_2O_2 in 1 M HNO_3, and the residual fraction (F5) was wet digested with $HClO_4$ and HF. Accordingly, the mobility factor (MF) of the metals in the amended tailings could be expressed by the ratio of $\left\{[\mathrm{Metal}]_{(F1+F2)}/[\mathrm{Metal}]_{(F1+F2+F3+F4+F5)}\right\} \times 100$ (Narwal et al. 1999).

Plant tissue analysis

After 45 days, the plants in each pot were carefully uprooted, washed, and weighted for fresh biomass. The plant was dried at 80 °C for 48 h. The dried plant was ground to powder, and then digested using a mix of HNO_3 and $HClO_4$ (5:1 v/v). The metal concentration was determined by ICP-OES. Meanwhile, GBW07603 (GSV-2) was analyzed as the certified reference plant material for quality control.

Statistical analysis

The analyses of the tailings properties and the metal concentrations were performed in triplicate. The data were subjected to ANOVA to compare the means of the different treatments and Duncan's and Tukey's test was employed for comparison between treatments. Pearson's correlation coefficients were calculated to assess the relationship between the metal concentrations in the amended tailings and those metals in the plant ($p<0.01$ and $p<0.05$).

Results and discussion

Properties of copper mine tailings and coal gangue

From Table 1, properties of copper mine tailings were poorer than coal gangue, which created a harsh environment compared with the coal gangue. Copper mine tailings used in this study had a nearly neutral pH with a mean value of 7.75 and low electrical conductance. The coal gangue was alkaline with high EC. Generally, the OM contents, and total N, P, and K in the tailings were lower than those in the coal gangue. High pseudototal and DTPA-extractable Zn, Pb, Cd, and Cu concentrations were observed in the tailings, while elevated pseudototal and DTPA-extractable Cr concentrations were found in the coal gangue. In general, soils containing more than 300 mg kg^{-1} and 20 mg kg^{-1} extractable Zn and Pb are regarded as toxic to plants (Chiu et al. 2006). Soils with total concentrations of 60–125 mg kg^{-1} Cu, 3–8 mg kg^{-1} Cd, and 75–100 mg kg^{-1} Cr are also considered to be toxic to vegetation (Deng et al. 2004). Therefore, the Cu content (984.38 mg kg^{-1}) in the tailings greatly exceeded the limits. Cu was the most abundant of the metals measured in the tailings and this level of Cu would exhibit toxic effects on the growth of remediation plants.

Additionally, organic matter is one of most valuable nutrient sources, which can affect metal adsorption, soil structure, nutrient supply and the retention and penetration of water, etc. (Sherameti and Varma 2010). Nitrogen is a vital nutrient for plants and microorganism. It is frequently available as nitrate and ammonium through the mineralization of the added fertilizers or organic compounds (Novo et al. 2013). Phosphorus is also a very important nutrient for soil organisms and plants, whose deficiency may inhibit the plant growth (Chiu et al. 2006). Low levels of nutrient elements (N, P, and K) and the relatively low OM content (0.24%) were observed in the copper mine tailings, which may denote that copper mine tailings created a nutrient-poor habitat for plant colonizing and growing (Rodríguez-Vila et al. 2014).

Effects of coal gangue on the chemical properties of copper mine tailings

The alterations in the chemical characteristics of copper mine tailings treated by different amendments are presented in Table 2. The addition of coal gangue to tailings significantly increased the pH and total N ($p<0.05$), especially at the highest application rate (30%), to give values 5.78% and 79.19% higher, respectively, than those of the control. In addition, the application of coal gangue in high proportions (5–30%) significantly increased the EC, OM, total P and K of the amended tailings by 9.25–49.69%, 113.64–431.82%, 59.21–101.53%, and 48.25–90.20%, respectively, compared with the treatments without coal gangue ($p<0.05$). Thus, the higher the amendment rate, the greater the levels of pH, EC, OM and nutrient elements (N, P, and K) in the amended tailings. Therefore, application of coal gangue to tailings corrected the pH, EC, OM and nutrient deficiencies of the copper mine tailings. The harsh environment of copper mine tailings was relieved by the addition of coal gangue (Rodríguez-Vila et al. 2014).

The waste-derived amendments often add the nutrients to the soils in which they applied, due to the origin of the waste material which composed these amendments. When properly conceived, these amendments can contribute to increase organic matter and nutrients (N, P, and K). Those organic

Table 2 Selected properties of amended copper mine tailings at 45 days of experiment

Treatment	pH	EC (μS cm^{-1})	OM (%)	N_{Total} (mg kg^{-1})	P_{Total} (mg kg^{-1})	K_{Total} (mg kg^{-1})
CG 0	7.79 ± 0.08a[†]	214.08 ± 5.35a	0.22 ± 0.02a	259.83 ± 55.95a	328.67 ± 28.31a	1215.54 ± 288.84a
CG 1	8.02 ± 0.04b[††]	222.46 ± 12.47ab	0.25 ± 0.04a	364.02 ± 7.27b	369.99 ± 36.49a	1529.54 ± 213.93ab
CG 2.5	8 ± 0.02b	228.34 ± 4.49abc	0.31 ± 0.03a	370.73 ± 18.18b	401.53 ± 34.57a	1676.35 ± 401.84abc
CG 5	7.99 ± 0.06b	233.89 ± 10.57bc	0.47 ± 0.02b	386.05 ± 11.21b	523.26 ± 38.73b	1802.02 ± 348.4bc
CG 10	8.04 ± 0.02b	241.08 ± 4.49c	0.71 ± 0.08c	395.28 ± 30.94bc	509.70 ± 55.07b	1917.33 ± 228.01bc
CG 15	8.1 ± 0.01b	293.02 ± 5.46d	0.81 ± 0.03cd	420.84 ± 19.71bcd	539.11 ± 23.72b	2269.6 ± 12.05c
CG 20	8.11 ± 0.01b	311.31 ± 5.40e	0.92 ± 0.05d	446.81 ± 12.49cd	575.48 ± 46.68b	2172.1 ± 191.32c
CG 30	8.24 ± 1.12c	320.46 ± 7.07e	1.17 ± 0.14e	465.59 ± 11.90d	662.36 ± 42.00c	2311.95 ± 32.05c

[†]Mean ± SD values ($n = 3$)

[††]Values followed by different letters differ significantly with $p < 0.05$

matter and nutrients are essential for promote microbial life, plant growth and make the trade-off balance clearly positive (Vega et al. 2009; Saleh 2017b, c). In this study, applying coal gangue significantly increased the pH, which may due to the 'alkalizing' effect of carbonate minerals in the coal gangue that increase the pH of the amended tailings (Park et al. 2013; Zhou et al. 2014). Due to the elevated OM content and total N, P, and K in the coal gangue, these indices all increased in the amended tailings. This is also consistent with numerous previous observations in which waste-derived amendments, such as technosols, sewage sludge, compost and biochar, can efficiently change the physiochemical properties of contaminated sites (Novo et al. 2013; Yang et al. 2013).

Effects of coal gangue on metal concentrations in copper mine tailings

Pseudototal concentrations of Zn, Pb, Cd, and Cu decreased gradually with an increase in the coal gangue amendment ratio, while the pseudototal Cr concentration increased slightly with increasing amounts of coal gangue (except for 1% coal gangue) (Fig. 1). In comparison with the control, pseudototal concentrations of Zn, Pb, Cd, and Cu were significantly reduced when the amendment ratio was over 15%, 5%, 20%, and 15% ($p < 0.05$), respectively. A significantly higher pseudototal Cr concentration was found only until 30% coal gangue was reached ($p < 0.05$). The addition of coal gangue also reduced the DTPA-extractable Zn, Pb, Cd, and Cu contents in the amended tailings, resulting in reductions of 4.61–40.22%, 4.56–50.12%, 8.20–50.82%, and 4.28–50.23%, respectively, compared with the control (Fig. 1). Nevertheless, the DTPA-extractable Cr contents were increased by 3.72–22.23% over the control after applying coal gangue to the tailings. However, no significant differences in the DTPA-extractable Cr contents were found between treatments ($p > 0.05$). Further, applying 1–30% coal gangue decreased DM/PT (DTPA -extractable metals versus Pseudototal concentrations) (Ünver et al. 2013) for Zn, Pb, Cd, and Cu in amended copper mine tailings from 0.037 to 0.030, 0.117–0.085, 0.172–0.137, and 0.055–0.031, respectively, which denoting the phytoavailable concentrations of Zn, Pb, Cd, and Cu were reduced in amended tailings by application of coal gangue.

Recently, numerous inorganic and organic waste materials have been examined for metal stabilization in tailings/soils (Zagury et al. 2016). In this study, the addition of coal gangue decreased the pseudototal and DTPA-extractable metal concentrations in the amended tailings (Fig. 1), which is in agreement with other reported results (Novo et al. 2013). However, applying coal gangue increased the pseudototal and DTPA-extractable Cr contents in the amended tailings, which may have resulted from the inherently high Cr content in the coal gangue (Rodríguez-Vila et al. 2015). Similar findings were also obtained by Rodríguez-Vila et al. (2016), who observed that waste amendment made of technosol and biochar lowered the total Cu and $CaCl_2$-extractable Cu, Ni, and Pb concentrations but increased the total Zn, Pb, and $CaCl_2$-extractable Zn concentrations in a polluted mine soil. Chiu et al. (2006) also found that the DTPA-extractable Pb and Cu concentrations in copper mine tailings were reduced, but the Zn content was increased ascribed to the high initial concentration of Zn in the sewage and manure that were used. Therefore, coal gangue is similar to other waste-derived amendments that can selectively reduce the contents of some metals but increase the contents of endogenous metals already accumulated in the contaminated substrate (Das and Maiti 2009).

The reduced concentrations of DTPA-extractable Zn, Pb, Cd, and Cu in the amended tailings could be attributed to increases in the pH and OM content. At high pH, H^+ can dissociate from the carbonyl, carboxyl, hydroxyl and phenolic groups, which would increase the affinity for metal cations (Rodríguez-Vila et al. 2015). Elevated levels of OM would lead to an increase in the surface charge, thus forming more metal-binding compounds, which may lead to the higher

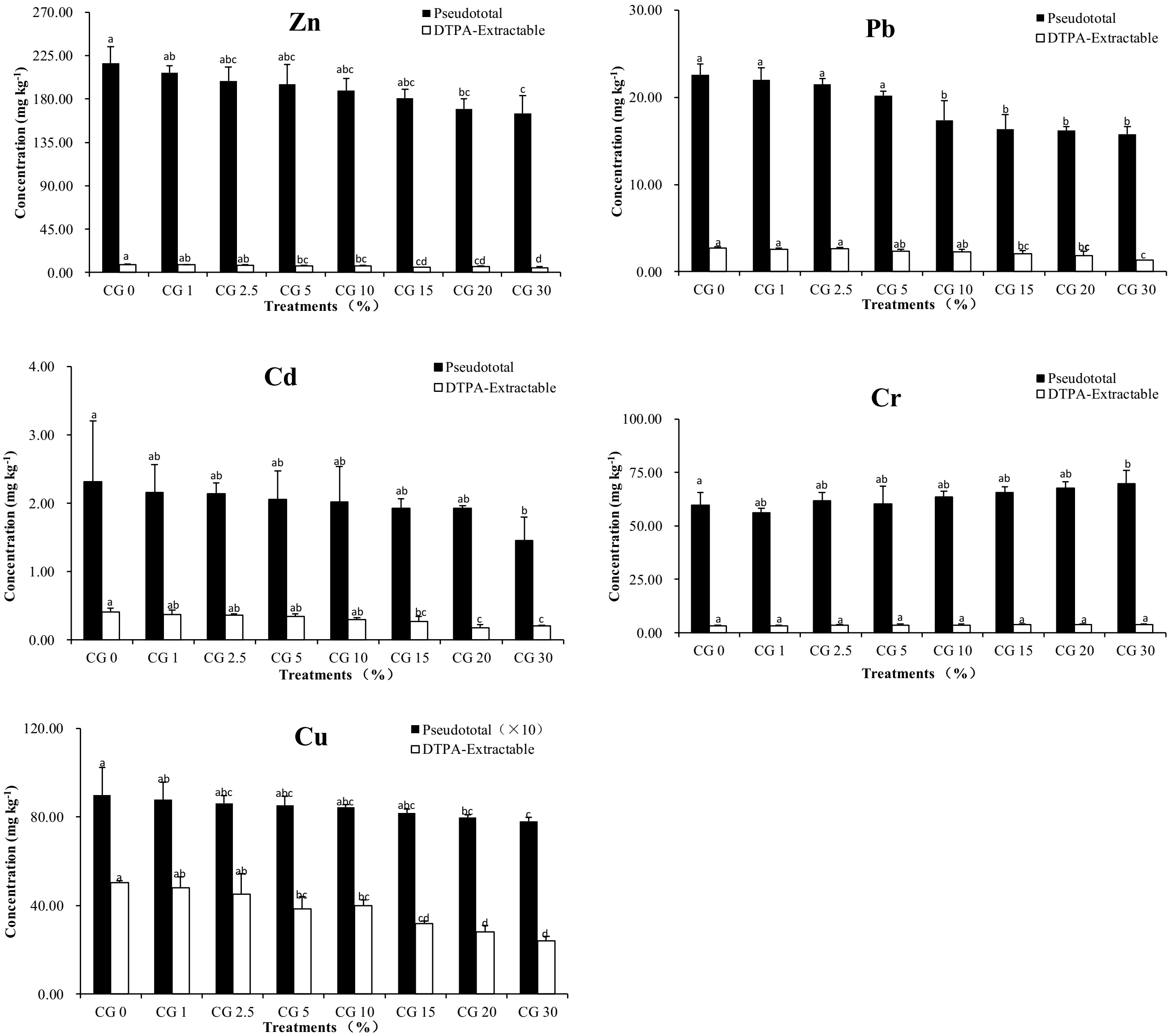

Fig. 1 Pseudototal and DTPA-extractable (phytoavailable) concentrations of heavy metals in the amended copper mine tailings at 45 days of experiment. Mean ± SD values ($n = 3$). Different letters in each column differ significantly with $P < 0.05$. (×10) indicates that values in the figures were reduced by ten times

retention of metals (Gondar and Bernal 2009). In this study, the DTPA-extractable Zn, Pb, Cd, and Cu concentrations were significantly negatively correlated with the pH/OM of the tailings (r^2 values were −0.711/−0.849, −0.724/−0.876, −0.661/−0.828 and −0.757/−0.875 for Zn, Pb, Cd, and Cu, respectively, all $p < 0.01$), thus suggesting that the increasing pH and OM levels in amended tailings by applying coal gangue essentially decreased the concentrations of available metals. Our findings are in agreement with those of Lee et al. (2011), who observed that industrial by-products or wastes, such as furnace slag and red mud, could increase the soil pH to reduce the DW (deionized water) extraction metal concentration. Park et al. (2011) also found that organic amendments (manure, municipal biosolids, compost, etc.) could decrease the availability of metals concentrations in polluted soil by the complexation and adsorption of metal due to the OM contained in the waste amendments.

Effects of coal gangue on the chemical fractionation of metals in copper mine tailings

The chemical fractions of metals in coal gangue, copper mine tailings and gangue amended copper mine tailings are given in Figs. 2 and 3. In this study, metals were classified into five fractions. The exchangeable and carbonate fractions of Zn, Pb, Cd, and Cr in coal gangue were lower than

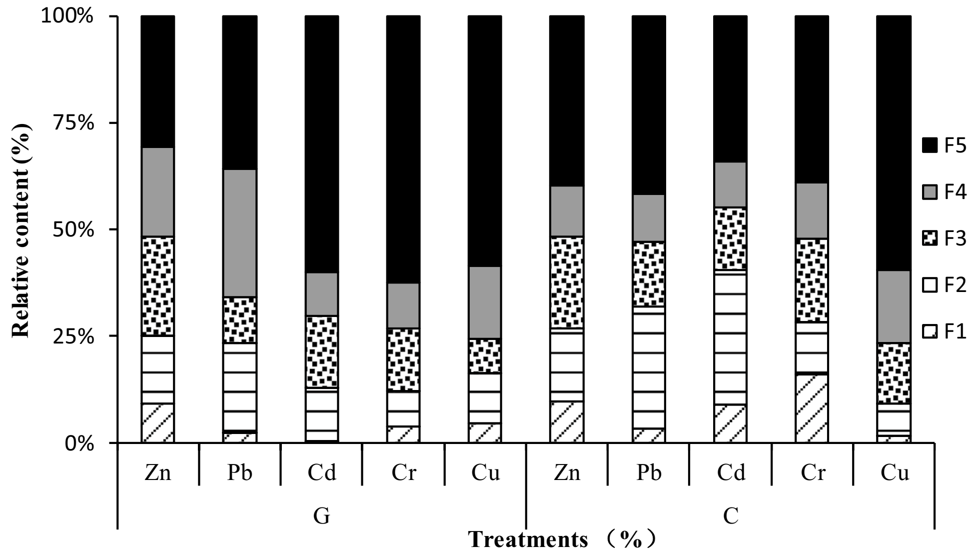

Fig. 2 Fractionation of heavy metals in coal gangue (G) and copper mine tailings (C) before experiment. Heavy metal fractions are F1 (exchangeable), F2 (carbonate bound), F3 (Fe–Mn oxides), F4 (organically bound) and F5 (residual)

those in copper mine tailings. Cu in with exchangeable and carbonate fractions were higher in coal gangue than that in copper mine tailings. The organic matter fraction of heavy metals in coal gangue was higher/roughly equal to those in copper mine tailings.

In different treatments, the maximum metal concentrations were found in the residual fraction. The lowest metal levels were observed in exchangeable fraction, except for Cr, which was associated with the carbonate fraction. Applying coal gangue decreased the sum of exchangeable and carbonate fractions of Zn, Pb, Cd, and Cu by 12.71–43.69%, 3.81–58.69%, 6.81–54.97% and 4.48–27.92%, respectively, but increased the sum of Fe–Mn oxide and organic matter fractions of Zn, Pb, and Cd by 3.97–43.51%, 31.89–82.44% and 1.15–89.87%, respectively. The addition of coal gangue also increased the percentage of Cu in the organic matter fraction by 1.60–41.70%, compared with no coal gangue. Conversely, the percentages of Cr bound in exchangeable and carbonate fractions in different amendments increased, but those of Cr in the Fe–Mn fraction decreased with an increase in coal gangue ratio. Therefore, most metals in amended tailings in the first and second fractions were reduced and converted into the Fe–Mn and/ or OM fraction by coal gangue addition.

Due to the variation in metal fractions in the amended tailings, applying coal gangue significantly decreased the mobility factors (MFs) of Zn and Cd by 12.66–43.75% and 7.05–54.58%, respectively, compared with the tailings treated without coal gangue ($p < 0.05$) (Table 3). In addition, the addition of coal gangue at 5–30% significantly reduced the MFs of Pb and Cu by 22.81–58.61% and 13.92–27.59%, respectively, in comparison with the control ($p < 0.05$). However, adding coal gangue to copper mine tailings significantly increased the MFs of Cr by 26.23–121.64% over the control ($p < 0.05$). Significantly lower MFs for Zn, Pb, Cd, and Cu in the amended tailings suggested that most heavy metals in the amended tailings were stabilized by the additions of coal gangue.

Sequential extraction procedures are often used to investigate the metal potential and actual ability of metals in soils by revealing the defined fractions of metals (Narwal et al. 1999). Our results revealed that the addition of coal gangue increased the organic matter content, which lead to an increase in the percentage of Zn, Pb, Cd, and Cu associated with the organic matter fractions. Meanwhile, coal gangue, which contains many reactive surface sites (Al and Fe oxides) able to bind metals (Zhou et al. 2014), resulted in more Zn, Pb, and Cd being bound to the Fe–Mn oxide fraction. As a result, low MFs for Zn, Pb, Cd, and Cu in the amended tailings were observed and could be explained by the higher metal extraction in the Fe–Mn oxide and organic matter fractions compared with the exchangeable and carbonate fractions. Numerous studies have been carried out on the sequence extraction of metals from waste-derived amendments (Narwal et al. 1999; Das and Maiti 2009). The additions of furnace slag and red mud shifted the As, Cd, Zn, and Pb distributions from the exchangeable fraction to the Fe–Mn oxide and/or carbonate fraction (Lee et al. 2011). Bentonite could shift the exchangeable Pb into carbonate, Fe–Mn oxide, organic and residual forms and convert exchangeable Cd into the residual form (Sun et al. 2015). Tannery sludge could increase the percentage of Zn bound to the Fe–Mn oxide fraction (Gupta and Sinha 2006). However, no study has reported the extraction of metals by the application of coal gangue. By comparing our findings with previous studies (Table 4), our results showed the mechanisms similar to the above mentioned waste-derived amendments (red mud, furnace slag, bentonite and sludge, etc.), i.e., that

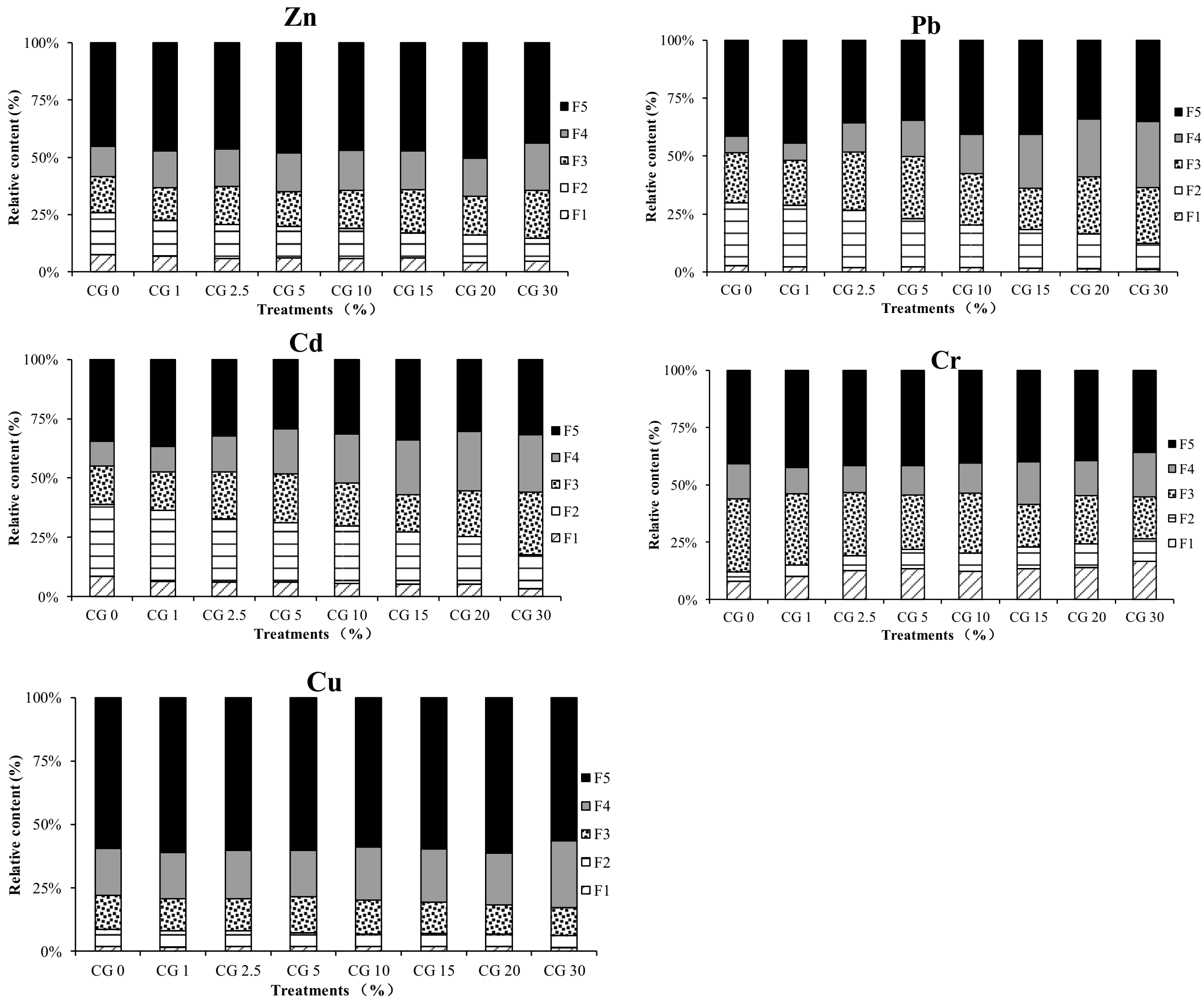

Fig. 3 Fractionation of heavy metals in copper mine tailings amended with coal gangue and vegetated with *Vetiveria zizanioides* at 45 days of experiment. Heavy metal fractions are F1 (exchangeable), F2 (carbonate bound), F3 (Fe–Mn oxides), F4 (organically bound) and F5 (residual)

Table 3 Mobility factors of heavy metals in copper mine tailings amended with coal gangue at 45 days of experiment

Treatment	Mobility factor				
	Zn	Pb	Cd	Cr	Cu
CG 0	25.76 ± 0.72a†	29.86 ± 1.65a	38.84 ± 0.26a	11.97 ± 0.89a	8.48 ± 3.86a
CG 1	22.5 ± 0.28b††	28.78 ± 2.98a	36.1 ± 1.69bc	15.11 ± 0.72b	8.12 ± 0.61ab
CG 2.5	20.62 ± 0.66c	26.47 ± 2.11a	33.01 ± 0.75b	19.22 ± 1.42c	8.06 ± 0.53ab
CG 5	19.78 ± 0.99cd	23.05 ± 0.33b	30.97 ± 0.64bcd	21.84 ± 2.37cde	7.3 ± 0.37bc
CG 10	18.94 ± 0.68c	20.22 ± 1.26bc	29.55 ± 1.09cd	20.14 ± 0.84cd	6.58 ± 0.15bc
CG 15	17.03 ± 0.5e	18.33 ± 2.08cd	27.12 ± 1.05d	22.95 ± 1.24de	6.82 ± 0.50bc
CG 20	16.02 ± 0.78e	16.37 ± 0.57cd	25.22 ± 0.59e	24.26 ± 1.53ef	6.69 ± 0.90b
CG 30	14.49 ± 0.47f	12.36 ± 0.67c	17.68 ± 0.48f	26.53 ± 1.36f	6.14 ± 0.89c

MF = (F1 + F2 / F1 + F2 + F3 + F4 + F5) × 100

†Mean ± SD values ($n = 3$)

††Values followed by different letters differ significantly with $p < 0.05$

Table 4 Comparative study of the heavy metal mobility in substrates amended by waste-derived amendments in the literature

Location	Substrate	Waste-derived amendments	Plant species	Plant available metals	Chemical fraction of metals	References
Lechang and Dabao Shan (China)	Lead/zinc (Pb/Zn) mine and Copper mine tailings	Manure compost and sewage sludge	*Vetiveria zizanioides* and *Phragmities australis*	DTPA-extractable Pb and Zn contents in Pb/Zn tailings and DTPA-extractable Cu contents in Cu tailings were decreased	–	Chiu et al. (2006)
Touro (Spain)	Copper mine tailings	Technosol (70% sewage sludge + 10% waste + 5% sand + 5% ashes) and biochar (holm oak wood)	*Brassica juncea* L	$CaCl_2$-extractable Cu, Ni and Pb concentrations were decreased	Water-soluble and exchangeable fractions were converted into organic matter and /or residual fractions	Rodríguez-Vila et al. (2015)
Touro (Spain)	Copper mine tailings	Compost (rabbit and horse manure + fruit wastes + pruning residues + seaweeds) and biochar (holm oak wood)	*Brassica juncea* L	$CaCl_2$-extractable Co, Cu and Ni concentrations were decreased	–	Rodríguez-Vila et al. (2014)
Parys Mountain (UK)	Copper mine tailings	Green waste compost (GC), GC + 30% sewage sludge, lime and diammonium phosphate	*Lactuca sativa* L	DTPA and $Ca(NO_3)_2$-extractable Cu, Fe, Zn and Pb concentrations were decreased	–	Khan and Jones (2009)
Tianjin (China)	Co-contaminated paddy soil	Bentonite	*Oryza- sativa* L	–	Exchangeable fractions of Cd and Pb were converted into carbonate, organic matter, Fe–Mn oxide and residual fractions	Sun et al. (2015)
Huayuan (China)	Pb/Zn mine tailings	Sweet sorghum vinasse, medicinal herb residues and spent mushroom compost	*Lolium perenne* L	DTPA-extractable Cd, Pb and Zn concentrations were decreased	–	Yang et al. (2013)

Table 4 (continued)

Location	Substrate	Waste-derived amendments	Plant species	Plant available metals	Chemical fraction of metals	References
Munbaek (Korea)	Gold mining soil	Limestone, red mud and furnace slag	*Lactuca sativa* L	$Ca(NO_3)_2$ -extractable As, Cd, Pb and Zn concentrations were decreased	Amendments shifted the As distribution from the nonspecifically sorbed fraction to the Fe- and Al-bound fraction; for Cd, Pb and Zn, the fraction changes were characterized by shifts from the exchangeable fractions to the carbonate- and/or Fe–Mn oxide bound fractions	Lee et al. (2011)
Tongling (China)	Copper mine tailings	Coal gangue	*Vetiveria zizanioides*	DTPA-extractable Zn, Pb, Cd and Cu concentrations were decreased	Exchangeable and carbonate fractions of Zn, Pb, Cd and Cu were converted into the Fe–Mn oxide and /or organic matter fractions	This study

– Not available

applying coal gangue converted some heavy metal fractions into non-labile forms thus control metal mobility in copper mine tailings (Saleh 2015c; Saleh et al. 2016b).

Effects of coal gangue on biomass, plant height and metal concentrations in *Vetiveria zizanioides*

As shown in Fig. 4, the biomass and plant height varied with increasing proportion of coal gangue. The addition of 10% coal gangue increased the biomass and plant height by approximately 16.12% and 19.24% in comparison with the control. While applying 30% coal gangue to the tailings reduced the fresh weight and height by 14.93% and 2.44% over the control. However, no significant differences in biomass were found between CG 30 and the control ($p > 0.05$).

Waste-derived amendments are effective at altering plant growth. Sewage, technosol and manure always increase the biomass due to the supply of additional nutrients and changes in the physical and chemical properties (Chiu et al. 2006). Gupta and Sinha (2006) observed that plant growth was improved by tannery sludge at lower amendment rates but inhibited at higher rates. In fact, when supplied in higher amendment rates, the excess toxic metals and soluble salts added by the waste-derived amendments prohibited plant growth (Rodríguez-Vila et al. 2014). In this study, the growth and plant height of *Vetiveria zizanioides* was increased at low amendment rate, which may be ascribed to the organic matter and nutrient elements supplied by the coal gangue. However, the elevated levels of EC and Cr in the amended tailings with the addition of a high proportion of coal gangue may result in excess soluble salts and Cr, which may be phytotoxicity to the plant and inhibit the plant growth (Sun et al. 2015).

The metal concentrations in *Vetiveria zizanioides* grew in amended tailings are shown in Table 5. The metal concentrations (except Cr) in the plant generally decreased with increasing proportion of coal gangue. Treatment with 10–30% coal gangue significantly decreased the Zn, Pb, Cd, and Cu concentrations in the plants by approximately 27.47–42.51%, 37.64–41.48%, 40.54–62.16%, and 28.11–42.07% ($p < 0.05$), respectively, but increased Cr concentrations in the plants by 45.30–148.72% ($p < 0.05$). Therefore, adding coal gangue at higher amendment rates actually inhibited the heavy metal (except Cr) uptake and translocation.

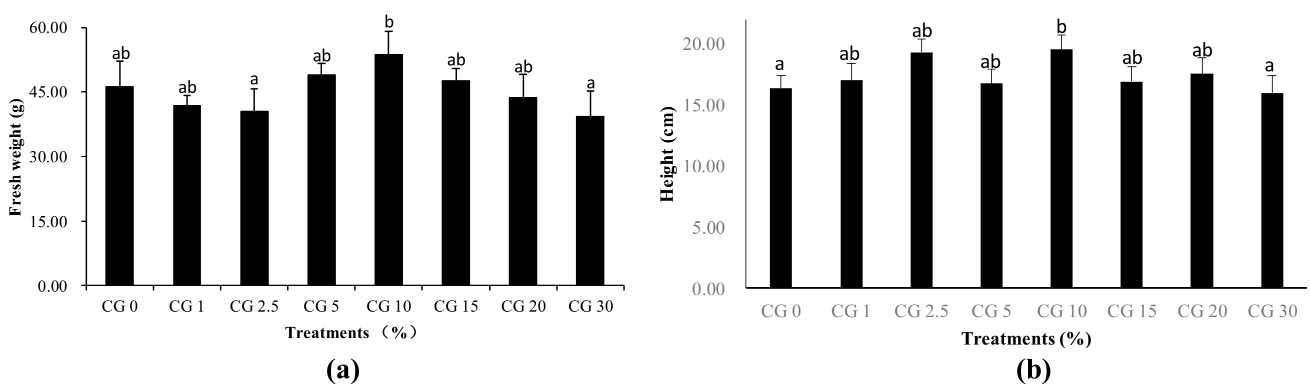

Fig. 4 Fresh weight (**a**) and plant height (**b**) of *Vetiveria zizanioides* (vetiver) grown in the amended copper mine tailings at 45 days of experiment. Mean ± SD values ($n = 3$). Different letters in each column differ significantly with $P < 0.05$

Table 5 Concentrations of heavy metals in *Vetiveria zizanioides* grown in copper mine tailings amended with coal gangue at 45 days of experiment

Treatment	Zn (mg kg^{-1})	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})
CG 0	69.52 ± 3.48a†	3.64 ± 0.66a	0.37 ± 0.03a	9.36 ± 0.90a	124.52 ± 25.21a
CG 1	65.54 ± 7.85a††	3.51 ± 0.48a	0.34 ± 0.02a	11.43 ± 1.68ab	121.09 ± 5.7a
CG 2.5	66.25 ± 1.58a	3.31 ± 0.52a	0.35 ± 0.02a	10.19 ± 0.77ab	115.42 ± 8.26a
CG 5	61.16 ± 2.13ab	3.20 ± 0.15a	0.32 ± 0.03a	11.48 ± 2.21ab	102.28 ± 10.48ab
CG 10	50.58 ± 0.7c	2.27 ± 0.29b	0.22 ± 0.02b	13.6 ± 1.32bc	89.52 ± 1.57bc
CG 15	55.68 ± 5.69bc	2.15 ± 0.25b	0.18 ± 0.02bc	15.74 ± 1.23c	84.23 ± 8.75bc
CG 20	36.34 ± 6.22d	2.11 ± 0.12b	0.19 ± 0.03bc	20.13 ± 2.22d	87.98 ± 6.66bc
CG 30	39.97 ± 2.25d	2.13 ± 0.08b	0.14 ± 0.03c	23.28 ± 0.89e	72.14 ± 9.98c

†Mean ± SD values ($n = 3$)

††Values followed by different letters differ significantly with $p < 0.05$

The levels of metals in *Vetiveria zizanioides* were also significantly and positively correlated the metals concentrations in the amended tailings ($p < 0.01$) (Table 6). The correlation coefficients were significantly higher between the metal concentrations in the plants and the sum of the F1 and F2 fractions than those between the metal concentrations in the plants and the DTPA-extractable/pseudototal concentrations of metals in the tailings. Thus, the decreased uptake of metals in the studied plants was due to the decrease in available and pseudototal metals in the amended copper mine tailings and mainly controlled by the available metals in the tailings. Lee et al. (2011) found similar results, in that the Zn, Pb, Cd, and As concentrations in *Lactvca saiva* L. (lettuce) were greatly decreased by the addition of industrial by-products (furnace slag, red mud and limestone) and the metal concentrations in the *Lactvca saiva* L. (lettuce) correlated closely with the first and second fractions, rather than the total concentrations of metals in the amended soil. Other similar works were also reported by Das and Maiti (2009) and Gupta and Sinha (2006), who found that metal uptake by plants was significantly affected by changing the available metal concentrations in the substrate with the addition of waste-derived amendments (chicken sludge and manure).

Therefore, by comparing with other researchers (Table 4), some mechanisms leading to the reduction of metal mobility in tailings mixed with coal gangue and vegetated with *Vetiveria zizanioides* can be determined. First, the pH increase induced by coal gangue resulted in a chemical alteration of the metal mobility and led to more metals being adsorbed on particles such as clays, Al and Fe oxides and aluminosilicates (Lee et al. 2009). Also, increase in the negative surface charge (pH dependent charge) with pH implies a corresponding increase in the availability of adsorption sites along with less competition from H^+ are the likely factors for increased metal sorption at higher pH (Sahoo et al. 2014). Raising the pH also caused the precipitation of metals with compounds present in the coal gangue (such as hydroxides, carbonates, phosphates, sulfates, etc.) (Gupta et al. 2002).

Table 6 Correlations coefficients between heavy metal concentrations of the amended tailings and heavy metal concentrations in *Vetiveria zizanioides* at 45 days of experiment

Heavy metals in plant	F1 + F2 fraction	DTPA-extractable	Pseudototal
Zn	0.836*	0.72*	0.713*
Pb	0.864*	0.666*	0.842*
Cd	0.804*	0.779*	0.547*
Cr	0.814*	0.585*	0.585*
Cu	0.87*	0.756*	0.704*

F1 + F2 fraction, exchangeable and carbonate-bound fraction for heavy metals in the amended tailings

*Significant at $p < 0.01$

Second, adding coal gangue increased the organic matter in the amended tailings. Organic matter contains many reactive groups (carboxyl, hydroxyl, phenoxyl, etc.) that can complex and adsorb more metals in the amended tailings (Gupta and Sinha 2006). Third, the large amounts of Al and Fe oxides in the coal gangue produced new sorptive surfaces, which stabilized the metals in the amended tailings via co-precipitation/chemisorption (Lombi et al. 2002). In addition, the rhizosphere environment of the plant may be altered by the indirect action of coal gangue via the improvement of organic matter and soil electrical conductivity, thus reducing the metal mobility by precipitation or absorption within the plant rhizosphere (Novo et al. 2013). Further, the combination of coal gangue and plant could also alter the conditions of rhizosphere through root exudates and bacterial exudates, which would precipitate and sequester the metals and thus convert the metal forms from mobile to non-mobile fractions (Mendez and Maier 2008; Rodríguez-Vila et al. 2015).

Conclusions

In this research, applying coal gangue to copper mine tailings improved soil conditions by increasing the pH, organic matter content and nutrient contents. Although the growth of *Vetiveria zizanioides* in the amended tailings was not significantly changed compared with the control. Application of 10% coal gangue significantly increased the plant height in comparison with the control. The used coal gangue generally decreased the DTPA-extractable concentrations of Zn, Pb, Cd, and Cu in the amended copper mine tailings and correspondingly decreased those metal levels in *Vetiveria zizanioides*. Sequential extraction indicated that coal gangue could convert the metals (except Cr) from the exchangeable and carbonate fractions into Fe–Mn oxide and /or organic matter fractions. The incorporation of coal gangue and *Vetiveria zizanioides* reduced the mobility factors for Zn, Pb, Cd, and Cu, denoting these metals were immobilized in the copper mine tailings. However, Coal gangue increased Cr uptake by *Vetiveria zizanioides*. Overall, the results of this study supported the usefulness of coal gangue aided phytostabilization of Zn, Pb, Cd, and Cu in copper mine tailings and proposed an alternative way to dispose of these solid wastes.

On balance, this short experiment suggests the potential for coal gangue use in Copper mine tailings, and the combination of amendment and plant could be a useful approach to deal with tailings remediation problems. However, long and large term researches are needed to fully understand the capabilities and limitations. Coal gangue characteristics also vary widely and depend on the source in which they are excavated. This means there is considerable scope to select the properties of coal gangue to target specific remediation problems, such as the appropriate coal gangue chosen to target metals existed in the tailings. Further, heavy metals were immobilized in the amended tailings and may be released again when the properties of the amended tailings changed. Accordingly, periodic monitoring of the application of coal gangue is needed to prevent the contamination to the environment.

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