Experimental Study on Different Phytoremediation of Heavy Metal Pollution in High-Density Sludge Sediment of Copper Mines

Ruoyan Cai
School of Energy and Mechanical Engineering, Jiangxi University of Science and Technology
Jinchun Xue (1023817019@qq.com)
School of Energy and Mechanical Engineering, Jiangxi University of Science and Technology
Min He
School of Software Engineering, Jiangxi University of Science and Technology
Jiajia You
School of Energy and Mechanical Engineering, Jiangxi University of Science and Technology
Weiwei Wang
School of Energy and Mechanical Engineering, Jiangxi University of Science and Technology
Huaqin Han
School of Energy and Mechanical Engineering, Jiangxi University of Science and Technology
Li Tan
Emergency Rescue Service Center of Haojiang District

Research Article

Keywords: copper mine, HDS sediment, phytoremediation, heavy metal

Posted Date: March 3rd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1357532/v1

Abstract

Purpose

HDS sediment is a type of solid waste produced when the high-concentration mud method (HDS) is adopted to treat acid wastewater from copper mines. It can rationally utilize sediment resources by using phytoremediation.

Methods

To reveal the effect of different phytoremediation on the heavy metal, enrichment capacity and microbial diversity of the HDS sediments of copper mines, in this experiment, the HDS sediments of a copper mine without phytoremediation were selected as the control group, while the sediments of black locust (*Robinia pseudoacacia*), slash pine (*Pinus elliottii* Engelmann) and Chinese white poplar (*Populus tomentosa* Carr.) were used as test groups to analyze the physical and chemical properties, heavy metal pollution and bioaccumulation capacity of HDS sediments under three phytoremediation.

Results

The results show that different phytoremediation can reduce the sediment's conductivity and adjust the sediment's pH value to the range suitable for plant growth. The BCF_{Shoot} and BTF values of Chinese white poplar to Cd and Zn and slash pine to Pb were both greater than 1.

Conclusions

As discovered from the bioconcentration coefficient and biotransport coefficient results, Chinese white poplar is an enriched plant of Cd and Zn, while slash pine is a plant full of Pb.

1 Introduction

With the rapid development of the world's economy and industrialization, the demand for copper resources has progressively increased[1]. At the same time, a large amount of acid wastewater will be generated during the mining of copper mines. In this context, the High-density Sludge (HDS) process is the main effective method used to treat acid mine wastewater and thus improve the recovery rate of mineral resources[2]. The HDS process flow is shown in Fig. 1. In the HDS treatment process, many heavy metal elements in the ore will enter the HDS sediment with the wastewater. After their introduction into HDS sediment, heavy metal elements affect the physicochemical properties and microorganisms of HDS sediment directly or indirectly. As the accumulation time of HSD sediment increases, the heavy metal elements in it will gradually transfer to the soil of the dumpsite. Then, the pollution caused by heavy metals is a severe risk to the surrounding ecosystem because of its toxicity[3], non-biodegradability, and bioaccumulation[4]. Heavy metals in soil may transport and accumulate in the human body along the food chain[5]. In this case, heavy metal pollution has become one of the most serious environmental problems in mining areas.

Nowadays, a variety of remediation approaches, including physical remediation (guest land methods, electro-remediation methods and thermal desorption methods), chemical remediation (Add fixative or acid-base leaching agents containing porous structure material, etc.), and biological remediation (microbial remediation and phytoremediation) approaches[6][7] have been developed to reclaim heavy metal-polluted soils. The physical repair method is widely used in engineering, but it is featured with a large amount of engineering, short-time effect, and high cost. The chemical remediation method has a large amount of precipitated sludge and is environmentally damaging. Whereas, phytoremediation adopts the ability of plants to remove the heavy metal of soil[8] which is regarded as the most cost-effective and environmentally friendly technique for remediation of heavy metal-contaminated soils[9]; besides, it uses plants to extract and transport elemental pollutants in the soil, thus stabilizing the fertility of plant growth substrates[10]. Actually, more than 400 plants have been found to have the ability to super-enrich heavy metals[11]. For example, the ryegrass possesses a strong cadmium ion enrichment ability, and there are differences between different types of ryegrass[12]. *B. papyrifera* has an excellent enrichment ability for lead, cadmium and zinc ions, and different ions feature different enrichment levels in different parts of the plant[13]. *Pteris vittata* L. is also called "As hyperaccumulator plant" due to its high ability to accumulate arsenic[14]. In recent years, applications of phytoremediation technology to the heavy metal pollution of solid waste in mining areas have been rapidly advancing. Solid waste in mining areas includes tailings generated during beneficiation and HDS sediment generated in mine wastewater treatment. *Solanum viarum* Dunal is used for solving heavy metal problems in tailings[15], and shows potential applicability for the treatment of areas contaminated by heavy metals in the mining area. *Quercus* spp. and *Salix* spp. were planted into the tailings containing lead and zinc ions. Due to the different mechanisms operated to confer tolerance of heavy metals, the root systems for heavy metals transhipment showed obvious differences[16]. When being planted in mine tailings containing copper, manganese, zinc and lead, even if the concentration of heavy metals in the tailings is different, ryegrass can still treat heavy metals there[17]. Clearly, it is found that little research is carried out on the use of phytoremediation techniques to repair HDS sediments contaminated by heavy metals.

As adaptability to the growth environment varies with plants, the growth environment has a great influence on the effect of phytoremediation[18]. Therefore, it is the key to phytoremediation technology to find heavy metal-rich plants suitable for growth in contaminated soil[19][20]. Native plant species are generally superior to introduced plants in terms of growth and reproduction under environmental stress[21][22]. The use of native plant species for phytoremediation is of great importance, which is a key element in the efficiency of phytoremediation strategies[23][24]. After testing and analysis, the bottom mud contains multiple heavy metals such as Cu, Cd, Zn, Pb, Cr and Hg, when four heavy metals namely Cu, Cd, Zn, and

Pb have the highest content, so that the subsequent tests are all about these four heavy metals. In fact, the heavy metals in the sediment are easy to form and accumulate, which will eventually threaten the ecological environment of the mining area. Considering that, in this experiment, three native plant species, including slash pine (*Pinus elliottii* Engelmann), Chinese white poplar (*Populus tomentosa* Carr.) and black locust (*Robinia pseudoacacia*), grown in the experimental area were used to remediate heavy metals in HDS sediments. Besides, the accumulation and transportation of heavy metals in different plants were analyzed, and its rules were also explored. At the same time, the thermogravimetric analysis on the sediments after different phytoremediation was carried out to identify the changes in the properties of the sediments before and after the improvement, which provides data support for the phytoremediation of heavy metals in the experimental area and similar areas.

2 Materials And Methods

2.1 Study area

The test area is located in a mining area in southeastern China and covers about 100 km^2. The mining area is a typical northwest low mountain and hilly region, featured with the topography of rolling hills in the southeast. It has a subtropical monsoon humid climate with a mean annual temperature of about 16–18°C, about 70–550 m, and its rainfall is abundant, and the mean annual precipitation is 1970–1990 mm, where around 70–90% of the precipitation is in May and June. The HDS sediments of this experiment were taken from the dumpsite of the mining area, the southwest direction of which was the test site with a total area of about 2620 m^2.

2.2 Materials

Plants selected in this experiment, including black locust (*Robinia pseudoacacia*), slash pine (*Pinus elliottii* Engelmann) and Chinese white poplar (*Populus tomentosa* Carr.), were obtained commercially from Muyangdou Seed Research Industry Co., LTD and all comply with Chinese phytosanitary regulations.

2.3 Experimental design and treatments

According to the climate conditions of the test area and the genetic resources of native plant species, in April 2017, a test area was established. Then, slash pine (*Pinus elliottii* Engelmann), Chinese white poplar (*Populus tomentosa* Carr.) and black locust (*Robinia pseudoacacia*) were planted there. The HDS sediment thickness in the test area was about 80 cm, and about 2000 cubic meters of HDS sediments were used. The species planted and plant root stem and leave samples grown in the experimental area are shown in Fig. 2. The root, stem, leaf and sediment of the above three plants were collected in July 2021. In this experiment, four groups of different treatments were set, when the sediment without planting any plant was employed as the control group (CK), while those planted with slash pine, Chinese white poplar and black locust were the test groups. Besides, these plants in the figures and tables in this study were marked as 1#, 2# and 3#, respectively. Before starting sample collection, the samplers such as garden shears and machetes were wiped with alcohol disinfection equipment. Here, it should be noted that this step should be repeated each time when the sample plot was replaced so as to reduce errors. Apart from that, these samples were collected in three randomly selected 2 m × 2 m quadrats, in each of which three plants have similar growth. Then, gardening shears and machetes were used to obtain plant branches and roots, and collect leaf, stem and root samples, while sediment samples were acquired within the range of 0–25 cm from the main plant stem. After that, all samples were put into a sealed sample bag and placed in a low-temperature incubator. Furthermore, the quality of all samples in the sealed sample bag was controlled to about 80 g, which was then brought back to the laboratory to determine the heavy metal content.

2.3 Sediment analysis and statistical analysis

The sediment and plant samples were put into a drying box and dried at 40°C for 48 hours. Then, the dried samples were crushed, thoroughly mixed, screened with a 40-mesh sieve and loaded into a sample vial. After that, heavy metal analysis was performed by weighing 0.2 mg of samples taken in a conical flask, and adding 5 ml nitric acid and 1 mol perchloric acid, followed by placing it on the Graphite Digestion Instrument at 200°C until the solution in the conical flask became colorless. Afterwards, it was poured into a 50ml volume. The volume was increased to 50 mL with distilled water. Other than that, the metal content was measured by ICP-MS. As for thermogravimetric analysis experiment, weigh 15–20 mg of samples; place them in an alumina crucible, and then put them into the WCT-122 thermogravimetric analyzer. Nitrogen was used as the protective gas, at a flow rate of 18mL min^{-1}, while the temperature range was from 25°C to 1000°C with a heating rate of 20°C min^{-1}. In order to eliminate experimental errors, a baseline calibration under the same conditions was performed before each sample test. Moreover, the pH and electrical conductivity of the sediment were determined by the water extraction potential method and the conductivity meter respectively.

The experimental data was processed, analyzed, and graphed by SPSS 22, Origin 8, and Microsoft Excel 2016 software.

The bioconcentration factor (BCF)[25] represents the ability of a certain metal in plant stems and leaves or roots[26][27]. The bioconcentration factor of plant aerial parts (stems and leaves) is calculated by formula (1), while that of the plant underground part (plant root) is by formula (2):

$$BCF_{Shoot} = \frac{[Metals]_{Shoot}}{[Metals]_{\mathrm{Sediment}}} \quad (1)$$

$$BCF_{Root} = \frac{[Metals]_{Root}}{[Metals]_{\mathrm{Sediment}}} \quad (2)$$

where $[Metals]_{Shoot}$ represents the total concentration of heavy metals in plant stems and leaves; $[Metals]_{Root}$ refers to the total concentration of heavy metals in the roots of the plant, and $[Metals]_{Sediment}$

indicates the concentration of heavy metals in the bottom silt of plants.

The biological transport factor (BTF)[28] reflects the ability of plants to transport heavy metals, and is the ratio of the concentration of heavy metals in the above-ground and underground parts of the plant[29][30]. The biological transport coefficient is calculated by formula (3):

$$BTF = \frac{[Metals]_{Shoot}}{[Metals]_{Root}} \quad (3)$$

where $[Metals]_{Shoot}$ represents the total concentration of heavy metals in plant stems and leaves, while $[Metals]_{Root}$ means the total concentration of heavy metals in the roots of the plant.

3 Results

3.1 Phytoremediation effects of different plants on the pH value and conductivity of HDS sediment

The pH of the plant growth substrate will directly affect its biochemical characteristics, thereby affecting plant growth. As shown in Fig. 3, the pH of the control group was 7.97, which was alkaline. After three kinds of phytoremediation, the pH value of the sediment decreased slightly. Among them, the pH of the sediment of the black locust group decreased most significantly, reaching 7.71, while the effect of other test groups on improving the pH value of sediment was: slash pine (7.81) > Chinese white poplar (7.86).

The conductivity of the sediment is a parameter of sediment salinity, which can indicate the salt content in the sediment and is an important factor that highlights the presence of nutrients in the soil. As shown in Fig. 2, after phytoremediation, the HDS sediment content showed a certain upward trend. The conductivity of the control group, the black locust group, the slash pine group and the Chinese white poplar was 213 ms s^{-1}, 241 ms s^{-1}, 226 ms s^{-1}, and 235 ms s^{-1}, respectively, when there was an increase of 13.1%, 6.1%, and 10.3% accordingly, compared with the control group.

3.2 Thermogravimetric analysis of sediment after different phytoremediation

Thermogravimetric (TG) profiles of selected samples together with the derivative thermogravimetric (DTG) curves are displayed in Fig. 4 and Fig. 5. Through the TG and DTG curves, each group of sediments at different stages of thermal weight loss, the maximum thermal weight loss rate and the corresponding peak temperature can be obtained. Table 1 shows the temperature range, quality change and peak temperature of each group of sediments at different stages of thermal weight loss. With the continuous increase of pyrolysis temperature, the sediments of the control group, the black locust group and the Chinese white poplar group mainly experienced four thermal weight loss stages, while the slash pine group was more complicated and featured with five thermal weight loss processes. The initial thermal weight loss of the four groups of samples occurred between 25°C and 136°C. In this stage, the peak temperature of the black locust group was 118.6℃, followed by the Chinese white poplar group, the slash pine group, and the control group with the peak temperature of 116.0°C, 109.7°C, and 109.2°C in sequence. At this stage, the quality loss of the control group, the black locust group, the slash pine group, and the Chinese white poplar group was 22.3%, 26.8%, 25.6%, and 26.8%, separately. The second-stage thermal weight loss process of the four groups of samples appeared between 128°C and 259°C. In this stage, the black locust group had the highest quality loss rate of 6%, followed by the Chinese white poplar group, the slash pine group, and the control group, with that of 4.4%, 3.7%, and 3.7% accordingly. The third-stage thermal weight loss process of the control group, the locust group and the Chinese white poplar group existed between 259℃-791℃. Within a similar temperature range, the Chinese white poplar group showed two thermal weight loss stages (stage III and IV), and the mass-loss rates were 1.5% and 11.4%, respectively, which was lower than that of the black locust group and higher than that of the control and slash pine groups. Furthermore, the quality loss rates of the control group, the black locust, the slash pine group, and the Chinese white poplar group in the last thermal weight-loss stage were 2.5%, 3.4%, 3.5%, and 3.4%, respectively. After the four groups of sediments were pyrolyzed at 25-1000℃, the unburned residues of the original sediments were the most, reaching 62.6%, followed by the slash pine group, the black locust group, and the Chinese white poplar group with that of 58%, 54.1%, and 52% in order.

Table 1
The temperature range, quality change and peak temperature of the sediment after phytoremediation at different stages of thermal weight loss. CK, the sediment without phytoremediation; T1, planted black locust; T2, planted slash pine; T3, planted Chinese white poplar.

Sample	Weight loss stages	Temperature ranges (℃)	Quality change rate (%)	Peak temperatures (℃)
CK	□	25.0-134.8	22.3	109.2
	□	134.8-249.6	3.7	167.5
	□	249.6-756.3	8.9	279.1
	□	756.3–1000.0	2.5	815.8
T1	□	25.0-135.4	26.8	118.6
	□	135.4-258.1	6.0	195.8
	□	258.1-790.1	15.7	667.1
	□	790.1–1000.0	3.4	854.4
T2	□	25.0-128.7	25.6	109.7
	□	128.7-241.4	4.4	171.3
	□	241.4-437.7	1.5	415.6
	□	437.7-767.8	11.4	457.6
	□	767.8–1000.0	3.5	807.1
T3	□	25.0-133.5	26.8	116.0
	□	133.5-246.2	3.7	193.8
	□	246.2-770.9	12.1	604.9
	□	770.9–1000.0	3.4	839.1

3.3 Plant heavy metal content under different phytoremediation

The contents of heavy metals in the sediments and plants of each group are shown in Table 2. The Cd, Cu, Zn, and Pb contents of the sediment after planting black locust were 1.47 mgkg^{-1}, 414.27 mg kg^{-1}, 272.09 mg kg^{-1}, and 15.55 mg kg^{-1}, respectively, while the contents of four heavy metals in the sediment after planting slash pine were 0.90 mg kg^{-1}, 561.69 mg kg^{-1}, 237.59 mg kg^{-1}, and 10.66 mg kg^{-1}, respectively. After planting Chinese white poplar, the contents of heavy metals in the sediments were 1.18 mg kg^{-1}, 594.20 mg kg^{-1}, 251.84 mg kg^{-1}, and 13.15 mg kg^{-1}, accordingly. In addition, the heavy metal content of the aerial parts of plants is equal to the addition of the heavy metal content of plant leaves and stems. As for the Cd content in the aerial parts of the three plants, it was Chinese white poplar (2.93

mg kg^{-1}) > slash pine (0.92 mg kg^{-1}) > black locust (0.57 mg kg^{-1}), while the Cu content was the black locust (233.65 mg kg^{-1}) > slash pine (82.16 mg kg^{-1}) > Chinese white poplar (44.16 mg kg^{-1}); the Zn content was Chinese white poplar (553.74 mg kg^{-1}) > slash pine (84.99 mg kg^{-1}) > black locust (57.69 mg kg^{-1}); and the Pb content was slash pine (17.59 mg kg^{-1}) > black locust (11.45 mg kg^{-1}) > Chinese white poplar (8.67 mg kg^{-1}). Different from that, the Cd content in the roots of the black locust, slash pine, and the Chinese white poplar was 0.67 mg kg^{-1}, 0.27 mg kg^{-1}, and 0.69 mg kg^{-1}; the Cu content was 148.78 mg kg^{-1}, 39.53 mg kg^{-1}, and 86.12 mg kg^{-1}, and the Zn content was 86.44 mg kg^{-1}, 27.86 mg kg^{-1}, and 93.89 mg kg^{-1}, separately, while Pb content was 4.99 mg kg^{-1}, 0.99 mg kg^{-1}, and 1.88 mg kg^{-1}, respectively. The data results show that the black locust has the strongest absorption capacity for Cu among the three plants, and the absorption of Zn by the Chinese white poplar group is more than 20 times that of other plants.

Table 2

The contents of heavy metals in the sediments and plants. Values are means ± standard error. According to Duncan's multiple range test, the data followed by a different letter are significantly different ($P \leq 0.05$). CK, the sediment without phytoremediation; T1, planted black locust; T2, planted slash pine; T3, planted Chinese white poplar.

Sample		Heavy content (mg kg^{-1})			
		Cd	Cu	Zn	Pb
T1	Sediment	1.47 ± 0.34	414.27 ± 87.69	272.09 ± 9.19	15.55 ± 0.50
	leaves	0.17 ± 0.06	37.96 ± 3.05	27.58 ± 6.81	2.09 ± 0.61
	rhizome	0.4 ± 0.15	195.69 ± 297.55	30.11 ± 3.31	4.37 ± 1.99
	root	0.67 ± 0.24	148.78 ± 33.05	86.44 ± 22.28	4.99 ± 1.65
T2	Sediment	0.99 ± 0.15	561.69 ± 131.92	237.59 ± 21.46	10.66 ± 2.96
	leaves	0.2 ± 0.05	19.87 ± 3.61	41.66 ± 10.21	3.99 ± 1.98
	rhizome	0.72 ± 0.15	62.29 ± 21.38	43.32 ± 26.72	12.62 ± 6.88
	root	0.27 ± 0.14	39.53 ± 11.65	27.86 ± 10.34	0.99 ± 0.58
T3	Sediment	1.18 ± 0.04	594.2 ± 80.13	251.84 ± 18.80	13.15 ± 1.82
	leaves	1.87 ± 0.30	20.35 ± 5.38	420.22 ± 132.12	4.25 ± 0.92
	rhizome	1.06 ± 0.12	23.81 ± 13.71	133.53 ± 6.99	2.53 ± 0.50
	root	0.69 ± 0.09	86.12 ± 44.12	93.89 ± 18.02	1.88 ± 0.84

3.4 Heavy metal enrichment and transport characteristics under different phytoremediation

The bioconcentration factor (BCF) and bio-transport factor (BTF) can evaluate the plant's ability to enrich and extract heavy metals from the plant substrate. From Table 2 and formulas (1), (2) and (3), the aboveground bioconcentration coefficient (BCF_{Shoot}), the underground bioconcentration coefficient (BCF_{Root}), and the transport coefficient (BTF) of the four heavy metals in each plant can be calculated. The calculation results are shown in Table 3, from which, it can be seen that the BCF_{Shoot} values of Chinese white poplar to Cd and Zn and slash pine to Pb are all greater than 1; the BTF value of the black locust to Cu and Pb is greater than 1; the BTF values of slash pine to Cd, Cu, Pb and Zn are all greater than 1, and the BTF value of slash pine to Pb is as high as 16.75; besides, the BTF values of Chinese white poplar to Zn, Cd and Pb were greater than 1, being 5.895, 4.244 and 3.608, respectively. Furthermore, the BTF values of the three plants to Cd were the Chinese white poplar group (4.244) > Slash pine group (3.403) > black locust group (0.311), to Cu being slash pine group (2.086) > black locust group (1.571) > Chinese white poplar group (0.510), to Zn being the Chinese white poplar group (5.895) > Slash pine group (3.060) > black locust group (0.670), and to Pb being the Slash pine group (16.750) > Chinese white poplar group (3.608) > black locust group (1.293).

Table 3

Bioconcentration coefficient and transport coefficient of various heavy metals in different plants. CK, the sediment without phytoremediation; T1, planted black locust; T2, planted slash pine; T3, planted Chinese white poplar. BCF_{Shoot} represents the total concentration of heavy metals in plant stems and leaves. BCF_{Root} represents the total concentration of heavy metals in the roots of the plant. BTF is the ratio of the concentration of heavy metals in the above-ground and underground parts of the plant.

Sample		Cd	Cu	Zn	Pb
T1	BCF_{Shoot}	0.143	0.564	0.213	0.415
	BCF_{Root}	0.456	0.359	0.318	0.321
	BTF	0.311	1.571	0.670	1.293
T2	BCF_{Shoot}	0.929	0.146	0.358	1.558
	BCF_{Root}	0.273	0.070	0.117	0.093
	BTF	3.403	2.086	3.060	16.750
T3	BCF_{Shoot}	2.483	0.074	2.199	0.516
	BCF_{Root}	0.585	0.145	0.373	0.143
	BTF	4.244	0.510	5.895	3.608

4 Discussion

As the HDS process is followed to treat acid mine wastewater, a certain amount of alkaline substances such as lime and calcium hydroxide will be used to recover Cu^{2+} in the mine acid wastewater, which also makes the HDS sediment alkaline[31]. After different phytoremediation, the pH of HDS bottom mud decreased slightly, maybe because the bottom mud is the product of acid wastewater treatment in the mining area, and it contains a lot of heavy metals, such as Cu, Zn, Cd and Pb[32]. When adopting phytoremediation technology to repair HDS sediment, each plant has a certain transport effect on the heavy metals in the sediment[33][34]. When the content of heavy metals in the sediment decreases, the pH value of the sediment will show a certain downward trend. Besides, by comparing the pH measurement results a year ago[35], it can be found that the pH value of the sediment without planting any plant ranges from 7.5 to 9.5. Regardless of whether phytoremediation increases or decreases the pH of the sediment, phytoremediation can always adjust the pH of the plant growth substrate to a range suitable for plant growth.

The conductivity of the sediment is an indicator of salinization degree of the sediment[36][37]. The increase in electrical conductivity of each group after phytoremediation may be because the water content of the sediment before remediation is much higher than that of the test group[38]. The decrease in water content of each group after phytoremediation affects the salinity of the sediment, which leads to the increase of the conductivity of each group after phytoremediation. As is known to all, water exists in clay in four forms: adsorbed water, interlayer water, crystal water and structured water[39], and their dehydration temperature is 0-100°C, 100–250°C, 200–500°C, and 600–1000°C accordingly[40]. The evaporation of adsorbed water mainly causes the initial thermal weight loss of the four groups of sediments in the sample[41]. The peak temperature of the black locust group is the highest at this stage, which indicates that the water retention performance of the bottom mud after restoration by the black locust is the best[42]. In addition, the peak temperature of the bottom sludge after phytoremediation is higher than that of the original bottom sludge at this stage, which reveals that the water retention capacity of the bottom sludge after phytoremediation has been improved to a certain extent. Other than that, volatile organic compounds play a key role in plant growth. Biological volatile organic compounds are derived from the release of soil bacteria, fungi and other rhizosphere microorganisms in plant-derived and plant growth substrates[43], a compound with a low melting point. The second stage thermal weight loss of the four groups of sediments may be caused by the volatilization and thermal decomposition of volatile organic compounds in the sediments[44]. In the second stage of thermal weight loss, the black locust group had the highest total mass loss rate, showing that the bottom sludge planted with black locust contained the highest content of low boiling point compounds non-biopolymer components[45], followed by the Chinese white poplar group, the slash pine group and the control group. Unlike the second stage, the third stage of weight loss in the control group, the black locust group, and the Chinese white poplar group may be due to the decomposition and volatilization of organic matter and stored organic carbon in the bottom mud after heating[46]. Here, it should be mentioned that the third and fourth stages of slash pine may be for the same reason. At this stage, the mass-loss rates of the three sediments after phytoremediation are higher than those of the control group, meaning that the organic matter and fixed carbon content of the sediments after phytoremediation have increased partly[47], which is in accordance with previous findings[48]. The final stage of the thermal weight loss of the four groups of bottom sludge may result from the further combustion of residual coke products produced during the previous pyrolysis process[49]. After the pyrolysis process, the unpyrolyzed residue of the original bottom mud is the largest, displaying that the original sediment contains higher mineral elements, and also verifying to a certain extent that phytoremediation has a transport effect on the mineral elements in the sediment[50].

Planting plants into heavy metal-contaminated plant growth substrates can be classified into enrichment plants, root hoarding plants and avoidance plants according to the characteristics of plants BCF_{Shoot}, BCF_{Root}, and BTF[51]. When the BCF_{Shoot} value and BTF value of a plant are greater than 1, the plant is considered an enriched plant[52]. When the BCF_{Root} value is greater than 1, and the BTF value is less than 1, the plant is considered a root hoarding plant[53]. When the BCF_{Shoot} value and the BCF_{Root} value are less than 1, the plant belongs to the evasive plant[54]. From Table 3, the BCF_{Shoot} value and BTF value of the Chinese white poplar for Cd and Zn are greater than 1, so the Chinese white poplar is an enriched plant of Cd and Zn. The BCF_{Shoot} of the slash pine to Pb > 1 and BTF > 1, so slash pine is a Pb-rich plant.

5 Conclusions

Phytoremediation is considered to be one of the friendliest methods of treating heavy metal pollutants. In summary, the results of this study show that phytoremediation can adjust the pH value of the plant growth substrate to a range suitable for plant growth, and it can also enhance the electrical conductivity of the plant growth substrate to a certain extent. In the treatment of heavy metals, phytoremediation has also shown a positive enrichment effect. Chinese white poplar is an enriched plant of Cd and Zn, and slash pine is an enriched plant of Pb. With the development of mineral resources, the problem of heavy metal pollution from mine waste will become increasingly serious, which will severely threaten the safety of global people and the development of the world economy. Considering that, this experimental method can solve the above problems from an environmentally friendly perspective and reduce the impact of heavy metals in mine waste.

Declarations

Acknowledgments

This work was supported by the Key R&D projects in Jiangxi Province, China (20212BBG73013).

Funding

This work was funded by the Key R&D projects in Jiangxi Province, China (20212BBG73013).

Conflicts of interest/Competing interests

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Availability of data and material

All data included in this study are available upon request by contact with the corrosponding author.

Code availability

Not applicable.

Authors' contributions

Ruoyan Cai performed the data analyses and wrote the manuscript;

Jinchun Xue and Min He contributed to the conception of the study;

Jiajia You and Weiwei Wang contributed significantly to the analysis;

Huaqin Han performed the experiment;

Li Tan helped perform the analysis with constructive discussions.

Ethics approval

Not applicable' for that section

Consent to participate

Not applicable' for that section

Consent for publication

Not applicable' for that section

References

1. Buayam N, Davey MP, Smith AG, Pumas C (2019). Effects of copper and pH on the growth and physiology of *Desmodesmus* sp. AARLG074. Metabolites, 9:84. https://doi.org/10.3390/metabo9050084
2. Mackie AL, Walsh ME (2015). Investigation into the use of cement kiln dust in high density sludge (HDS) treatment of acid mine water. Water Res, 85: 443–450. https://doi.org/10.1016/j.watres.2015.08.056
3. Pan LH, Wang ZQ, Yang Q, Huang RY (2018). Efficient removal of lead, copper and cadmium ions from water by a porous calcium alginate/graphene oxide composite serogel. Nanomaterials-basel,

8:957. https://doi.org/10.3390/nano8110957

4. Shehata EA, Liu YW, Feng Y, Cheng D, Li Z (2019). Changes in Arsenic and Copper Bioavailability and Oxytetracycline Degradation during the Composting Process. Molecules, 24: 4240. https://doi.org/10.3390/molecules24234240
5. Ma J, Quan Z, Sun Y, Du J, Liu B (2020). Excess sulfur and Fe elements drive changes in soil and vegetation at abandoned coal gangues, Guizhou China. Sci Rep-UK, 10. https://doi.org/10.1038/s41598-020-67311-z
6. Cheng S, Chen T, Xu WB, Huang J, Yan B (2020). Application research of biochar for the remediation of soil heavy metals contamination: a weview. Molecules, 25:3167. https://doi.org/10.3390/molecules25143167
7. Mcgrath SP, Chang AC, Page AL, Witter E (1994). Land application of sewage sludge: scientific perspectives of heavy metal loading limits in Europe and the United States. Environ Rev, 2: 108–118. https://doi.org/10.1139/a94-006
8. Fu Y, Mason AS, Zhang Y, Lin B, Yu H (2019). MicroRNA-mRNA expression profiles and their potential role in cadmium stress response in *Brassica napus*. BMC Plant Biol, 19. https://doi.org/10.1186/s12870-019-2189-9
9. Zhao JM, Xia B, Meng Y, Yang ZF, Zhang XQ (2019). Transcriptome Analysis to Shed Light on the Molecular Mechanisms of Early Responses to Cadmium in Roots and Leaves of King Grass (*Pennisetum americanum* × *P. purpureum*). Int J of Mol Sci, 20: 2532. https://doi.org/10.3390/ijms20102532
10. Jacob JM, Karthik C, Saratale RG, Kumar SS, Prabakar D, Kadirvelu K, Pugazhendhi A (2018). Biological approaches to tackle heavy metal pollution: A survey of literature. Journal Environ Manage, 217: 56–70. https://doi.org/10.1016/j.jenvman.2018.03.077
11. Baker AJM, Mcgrath SP, Sidoli C, Reeves RD (1994). In situ remediation of metal-contaminated soils using crops of hyperaccumulator plants: potentials and future prospects.
12. Li Y, Qin Y, Xu W, Chai Y, Feng D (2019). Differences of Cd uptake and expression of *MT* family genes and *NRAMP2* in two varieties of ryegrasses. Environ Sci Pollut R, 26: 13738–13745. https://doi.org/10.1007/s11356-018-2649-z
13. Zhao XL, Liu JF, Xia XL, Chu JM, Yuan W, Shi SQ, Chang EM, Yin WL, Jiang ZP (2014). The evaluation of heavy metal accumulation and application of a comprehensive bio-concentration index for woody species on contaminated sites in Hunan, China. Environ Sci Pollut R, 21: 5076–5085. https://doi.org/10.1007/s11356-013-2393-3
14. Chen T, Lei M, Wan X, Yang J, Zhou X (2018). Arsenic hyperaccumulator *Pteris vittata* L. and its application to the field. Twenty Years Res Dev on Soil Pollut Remediation in China. Springer Singapore, Singapore, pp. 465–476.
15. Afonso TF, Demarco CF, Pieniz S, Camargo F, Andreazza R (2019). Potential of *Solanum viarum* Dunal in use for phytoremediation of heavy metals to mining areas, southern Brazil. Environ Sci Pollut R, 26: 24132–24142. https://doi.org/10.1007/s11356-019-05460-z

16. Shi X, Wang SF, Sun HJ, Chen YT, Wang DX, Pan HW, Zou YZ, Liu JF, Zheng LY, Zhao XL (2017). Comparative of *Quercus* spp. and *Salix* spp. for phytoremediation of Pb/Zn mine tailings. Environ Sci Pollut Res, 24:3400–3411. https://doi.org/10.1007/s11356-016-7979-0
17. Mugica-Alvarez V, Cortés-Jiménez V, Vaca-Mier M, Domínguez-Soria V (2015). Phytoremediation of Mine Tailings Using *Lolium Multiflorum*. Int J Environ Sci Dev, 6: 246–251. https://doi.org/10.7763/IJESD.2015.V6.599
18. Pérez R, Tapia Y, Antilén M, Casanova M, Cornejo P (2021). Rhizosphere management for phytoremediation of copper mine tailings. J Soil Sci Plant Nut. https://doi.org/10.7763/IJESD.2015.V6.599
19. Ali H, Khan E, Sajad MA (2013). Phytoremediation of heavy metals: concepts and applications. Chemosphere, 91: 869–881. https://doi.org/10.1016/j.chemosphere.2013.01.075
20. Saxena G, Purchase D, Mulla SI, Saratale GD, Bharagava RN (2019). Phytoremediation of heavy metal-contaminated sites: eco-environmental concerns, field studies, sustainability issues and future prospects. Rev Environ Contam T, 249: 71–131. https://doi.org/.10.1007/398_2019_24
21. Cuevas JG, Quiroz M (2019). Screening of native and exotic tree species in Chile for element absorption from dairy slurry. J Soil Sci Plant Nut. https://doi.org/10.1007/s42729-018-0002-8
22. Kumari A, Lal B, Rai UN (2015). Assessment of native plant species for phytoremediation of heavy metals growing in the vicinity of NTPC sites, Kahalgaon, India. Int J Phytoremediat, 18: 592–597. https://doi.org/10.1080/15226514.2015.1086301
23. Fernández S, Poschenrieder C, Marcenò C, Gallego JR, Jiménez-Gámez D, Bueno A, Afif E (2017). Phytoremediation capability of native plant species living on Pb-Zn and Hg-As mining wastes in the Cantabrian range, north of Spain. J Geochem Explor, 174: 10–20. https://doi.org/10.1016/j.gexplo.2016.05.015
24. Marrugo-Negrete J, Marrugo-Madrid S, Pinedo-Hernandez J, Durango-Hernandez J, Diez S (2016). Screening of native plant species for phytoremediation potential at a Hg-contaminated mining site. Sci Total Environ, 542: 809–816. https://doi.org/10.1016/j.scitotenv.2015.10.117
25. Souza S, Andrade S, Souza L, Schiavinato MA (2012). Lead tolerance and phytoremediation potential of Brazilian leguminous tree species at the seedling stage. J Environ Manage, 110: 299–307. https://doi.org/10.1016/j.jenvman.2012.06.015
26. Mellem JJ, Baijnath H, Odhav B (2009). Translocation and accumulation of Cr, Hg, As, Pb, Cu and Ni by *Amaranthus dubius* (Amaranthaceae) from contaminated sites. J Environ Sci Heal A, 44: 568–575. https://doi.org/10.1080/10934520902784583
27. Zacchini M, Pietrini F, Mugnozza GS, Iori V, Pietrosanti L, Massacci A (2009). Metal Tolerance, Accumulation and Translocation in Poplar and Willow Clones Treated with Cadmium in Hydroponics. Water Air Soil Poll, 197: 23–34. https://doi.org/10.1007/s11270-008-9788-7
28. Mellem JJ, Baijnath H, Odhav B (2012). Bioaccumulation of Cr, Hg, As, Pb, Cu and Ni with the ability for hyperaccumulation by *Amaranthus dubius*. Afr J Agr Res, 7: 591–596. https://doi.org/10.5897/AJAR11.1486

29. Hammad DM (2011). Cu, Ni and Zn phytoremediation and translocation by water hyacinth plant at different aquatic environments. Aust J Basic Applied Sci, 5: 11–22.
30. Yoon J, Cao XD, Zhou QX, Ma LQ (2006). Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ, 368: 456–464. https://doi.org/10.1016/j.scitotenv.2006.01.016
31. Kalin M, Fyson A, Wheeler WN (2006). The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. Sci Total Environ, 366: 395–408. https://doi.org/10.1016/j.scitotenv.2005.11.015
32. Tangahu BV, Sheikh Abdullah SR, Basri H, Idris M, Anuar N, Mukhlisin M (2011). A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. Int J Chem Eng, 2011: 1–31. https://doi.org/10.1155/2011/939161
33. Emenike CU, Barasarathi J, Pariatamby A, Hamid FS (2018). Biotransformation and removal of heavy metals: a review of phyto and microbial remediation assessment on contaminated soil. Environ Rev, 26. https://doi.org/10.1139/er-2017-0045
34. Ruqaya, Jabeen, Altaf, Ahmad, Muhammad, Iqbal (2009). Phytoremediation of Heavy Metals: Physiological and Molecular Mechanisms. Bot. Rev, 75:339–364. https://doi.org/10.1007/s12229-009-9036-x
35. Cai RY, Xue JC, Tan L, Zhao ZY, Zhang ZY (2021). Study on physicochemical properties of High-density sludge sediment in copper mine after phytoremediation. J Soil Sci Plant Nut. https://doi.org/10.1007/s42729-021-00575-0
36. Afonso S, Arrobas M, Rodrigues MN (2020). Soil and plant analyses to diagnose hop fields irregular growth. J Soil Sci Plant Nut, 20: 1999–2013. https://doi.org/10.1007/s42729-020-00270-6
37. Pan C, Liu C, Zhao H, Wang Y (2013). Changes of soil physico-chemical properties and enzyme activities in relation to grassland salinization. Eur J Soil Biol, 55: 13–19. https://doi.org/10.1016/j.ejsobi.2012.09.009
38. Jampasri K, Pokethitiyook P, Poolpak T, Kruatrachue M, Kumsopa A (2019). Bacteria-assisted phytoremediation of fuel oil and lead co-contaminated soil in the salt-stressed condition by *chromolaena odorata* and *Micrococcus luteus*. Int J Phytoremediat, 22: 1–12. https://doi.org/10.1080/15226514.2019.1663482
39. Cases JM (1997). Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite: 3. the Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} exchanged forms. Clay Clay Miner, 45: 8–22. https://doi.org/10.1346/CCMN.1997.0450102
40. Schuttlefield JD, Cox D, Grassian VH (2007). An investigation of water uptake on clays minerals using ATR-FTIR spectroscopy coupled with quartz crystal microbalance measurements. J Geophys Res-Atmos, 112. https://doi.org/10.1029/2007JD008973
41. Tang P, Zhao Y, Xia F (2008). Thermal behaviors and heavy metal vaporization of phosphatized tannery sludge in incineration process. J Environ Sci, 20: 1146–1152. https://doi.org/10.1016/S1001-0742(08)62162-2

42. Opatokun SA, Yousef LF, Strezov V (2017). Agronomic assessment of pyrolysed food waste digestate for sandy soil management. J Environ Manage, 187: 24–30. https://doi.org/10.1016/j.jenvman.2016.11.030
43. Naznin HA, Kimura M, Miyazawa M, Hyakumachi M (2013). Analysis of volatile organic compounds emitted by plant growth-promoting fungus *Phoma sp.* GS8-3 for growth promotion effects on tobacco. Microbes Environ, 28: 42–49. https://doi.org/10.1264/jsme2.ME12085
44. Kruse J, Eckhardt KU, Regier T, Leinweber P (2011). TG–FTIR, LC/MS, XANES and Py-FIMS to disclose the thermal decomposition pathways and aromatic N formation during dipeptide pyrolysis in a soil matrix. J Anal Appl Pyrol, 90: 164–173. https://doi.org/10.1016/j.jaap.2010.12.002
45. Shen J, Igathinathane C, Yu M, Pothula AK (2015). Biomass pyrolysis and combustion integral and differential reaction heats with temperatures using thermogravimetric analysis/differential scanning calorimetry. Bioresource Technol, 185: 89–98. https://doi.org/10.1016/j.biortech.2015.02.079
46. Mayer LM, Schick LL, Hardy KR, Wagai R, Mccarthy J (2004). Organic matter in small mesopores in sediments and soils. Geochim Cosmochim Ac, 68: 3863–3872. https://doi.org/978-3-319-10394-5
47. Yamamoto T, Goto I, Kawaguchi O, Minagawa K, Ariyoshi E, Matsuda O (2008). Phytoremediation of shallow organically enriched marine sediments using benthic microalgae. Mar Pollut Bull, 57: 108–115. https://doi.org/10.1016/j.marpolbul.2007.10.006
48. Xue JC, He M, Wu CF, Zhang ZY, Tan L (2020). Adaptable plants for acidic wastewater sediment of copper sulfide mines. Environ Eng Manage J, 19:1475–1480. https://doi.org/10.30638/EEMJ.2020.137
49. Li Y, Luo C, Lin X, Li K, Pu WF (2020). Characteristics and properties of coke formed by low-temperature oxidation and thermal pyrolysis during in situ combustion. Ind Eng Chem Res, 59: 2171–2180. https://doi.org/10.1021/acs.iecr.9b05635
50. Magdziak Z, Gąsecka M, Goliński P, Mleczek M (2015). Phytoremediation and environmental factors. Phytoremediation, pp: 45–55
51. Bai Y, Zhou Y, Gong J (2021). Physiological mechanisms of the tolerance response to manganese stress exhibited by *Pinus massoniana*, a candidate plant for the phytoremediation of Mn-contaminated soil. Environ Sci Pollut R, 28: 45422–45433. https://doi.org/10.1007/s11356-021-13912-8
52. Zhu GG, Xiao HY, Guo QJ, Song B, Zheng GD, Zhang ZY, Zhao JJ, Okoli CP (2018). Heavy metal contents and enrichment characteristics of dominant plants in wasteland of the downstream of a lead-zinc mining area in Guangxi, Southwest China. Ecotox Environ Safe, 151: 266–271. https://doi.org/10.1016/j.ecoenv.2018.01.011
53. Wpc A, Wvdsp A, Damg A, Ommt B, Cbda C, Arf A (2020). Phytoremediation potential of *Khaya ivorensis* and *Cedrela fissilis* in copper contaminated soil. J Environ Manage, 268. https://doi.org/10.1016/j.jenvman.2020.110733
54. Karimyan K, Alimohammadi M, Maleki A, Yunesian M, Foroushani AR (2020). The mobility of arsenic from highly polluted farmlands to wheat: Soil–Plant transfer model and health risk assessment.

Land Degrad Dev. https://doi.org/10.1002/ldr.3552

Figures

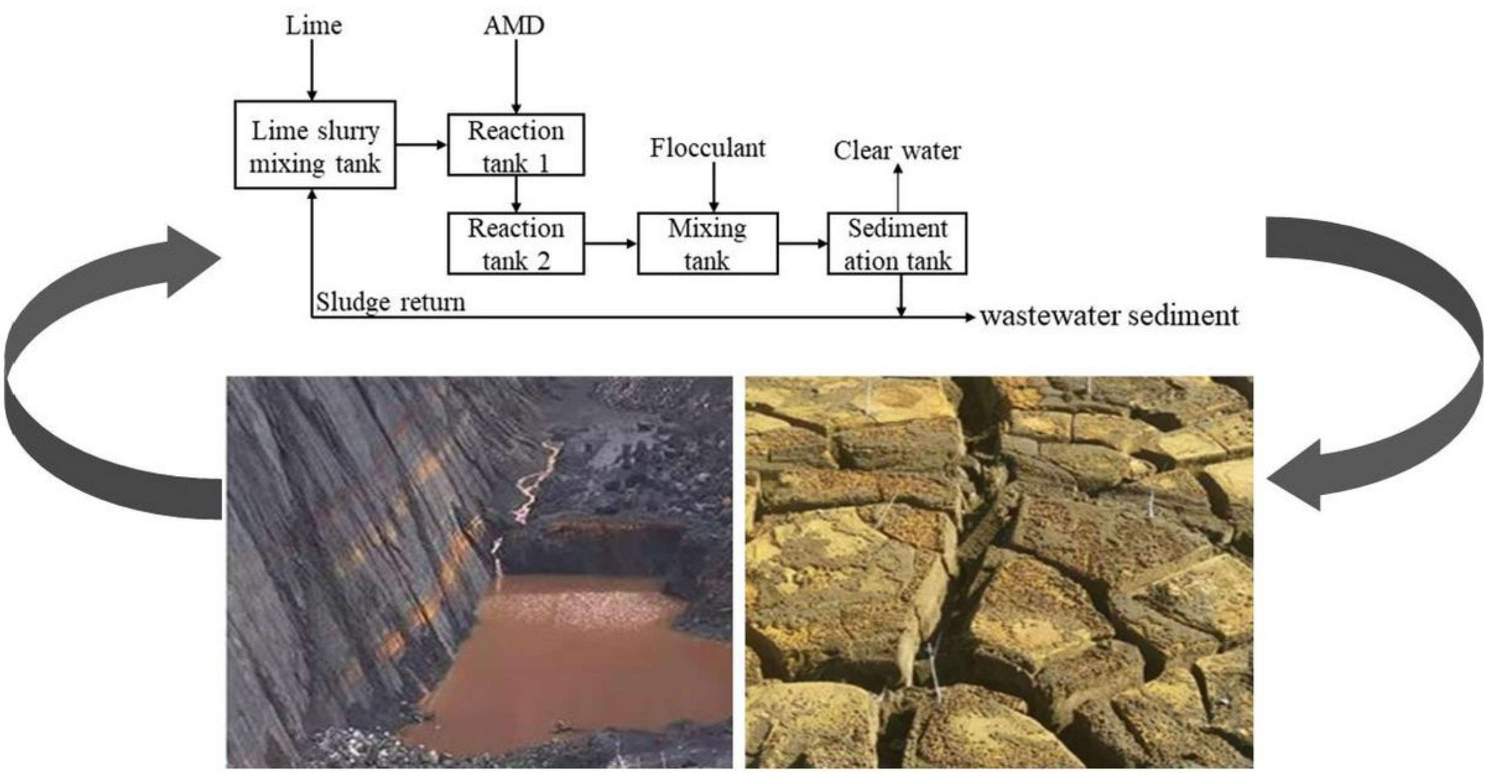

Figure 1

Flow chart of the High-density Sludge process. The acidic mine wastewater is added to the lime mud mixing tank, passes through reaction tanks 1 and 2, and the flocculant is poured into it and flows into the sedimentation tank for precipitation to realize the separation of mud and water. The supernatant is discharged out after overflow, a part of the sedimentation tank bottom sludge is returned to the bottom sludge-lime mixing tank. The excess sediment is discharged to the sludge tank, directly pumped from the bottom of the sedimentation tank to the filter press room for pressure filtration, and then discharged to the dumpsite Pileup.

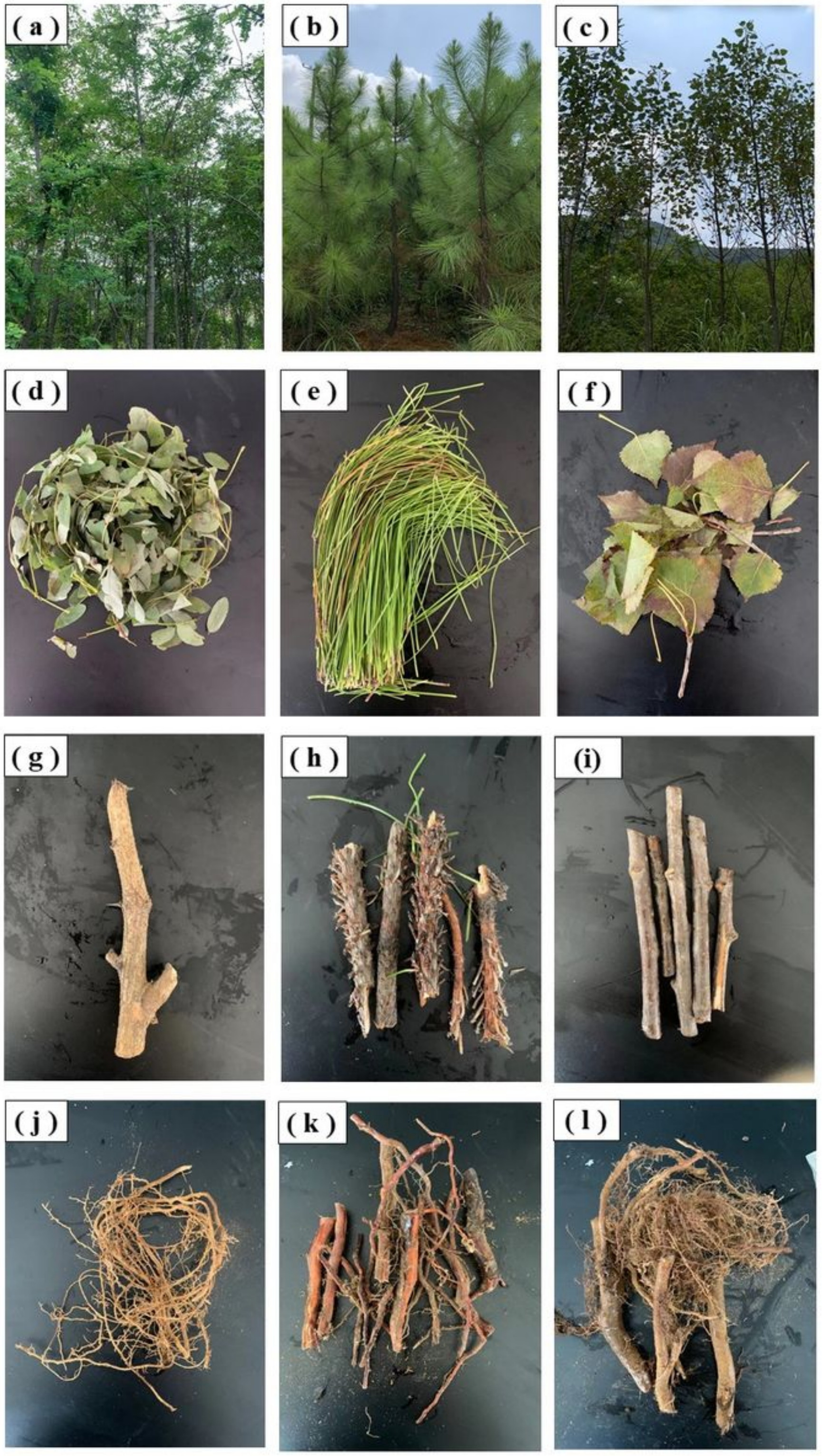

Figure 2

Species planted and plant roots stem and leave samples grown in the experimental area. (a), (d), (g) and (j) are black locust, black locust leaf, black locust stem, and black locust root, respectively. (b), (e), (h), combined with (k) are slash pine, slash pine leaf, slash pine stem, and slash pine root, respectively. (c), (f), (i), (l) are Chinese white poplar, Chinese white poplar leaf, Chinese white poplar stem, and Chinese white poplar root, respectively.

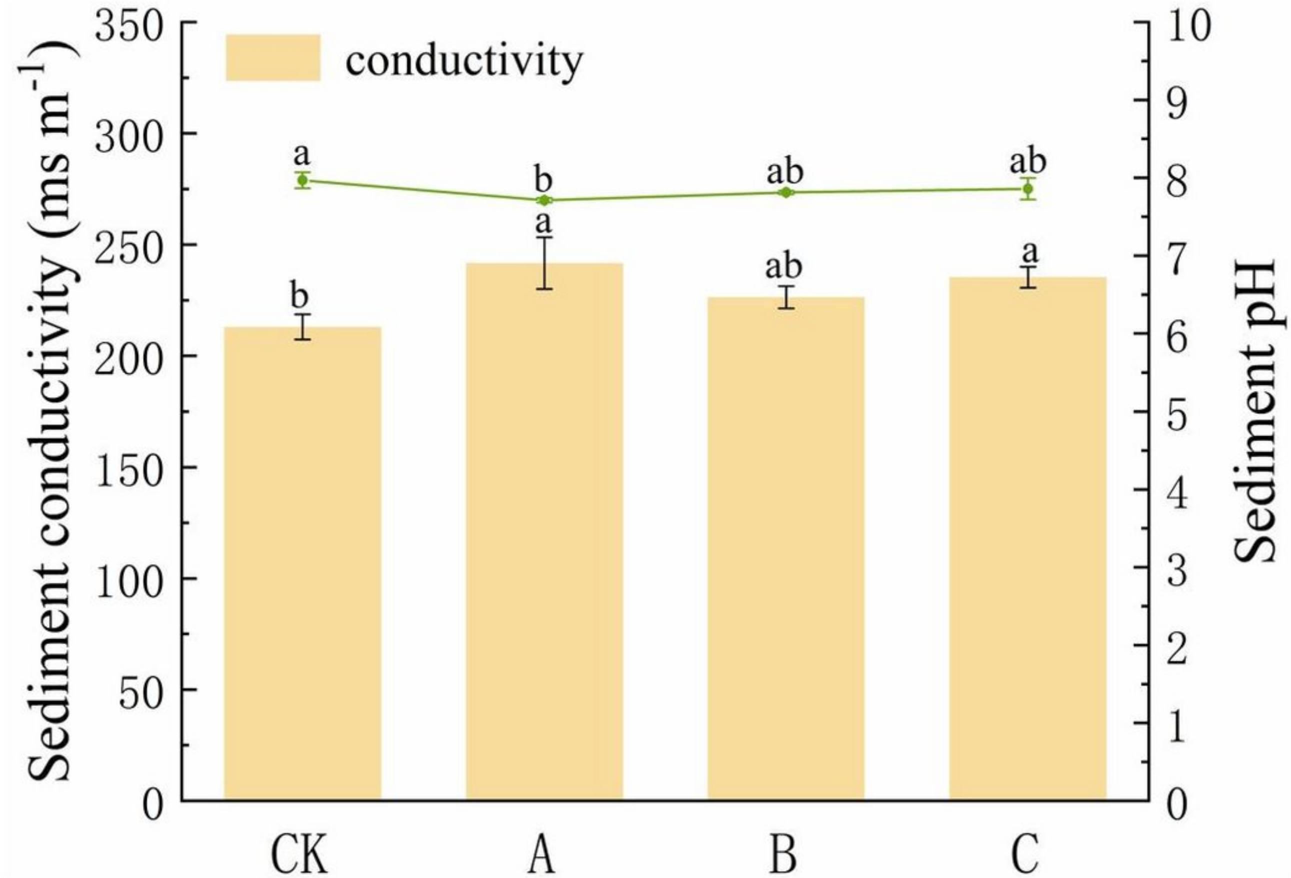

Figure 3

Effects of different phytoremediation on pH value and conductivity of HDS sediment. Values are means ± standard error. According to Duncan's multiple range test, the data followed by a different letter are significantly different (P≤0.05). CK, the sediment without phytoremediation; A, planted black locust; B, planted slash pine; C, planted Chinese white poplar.

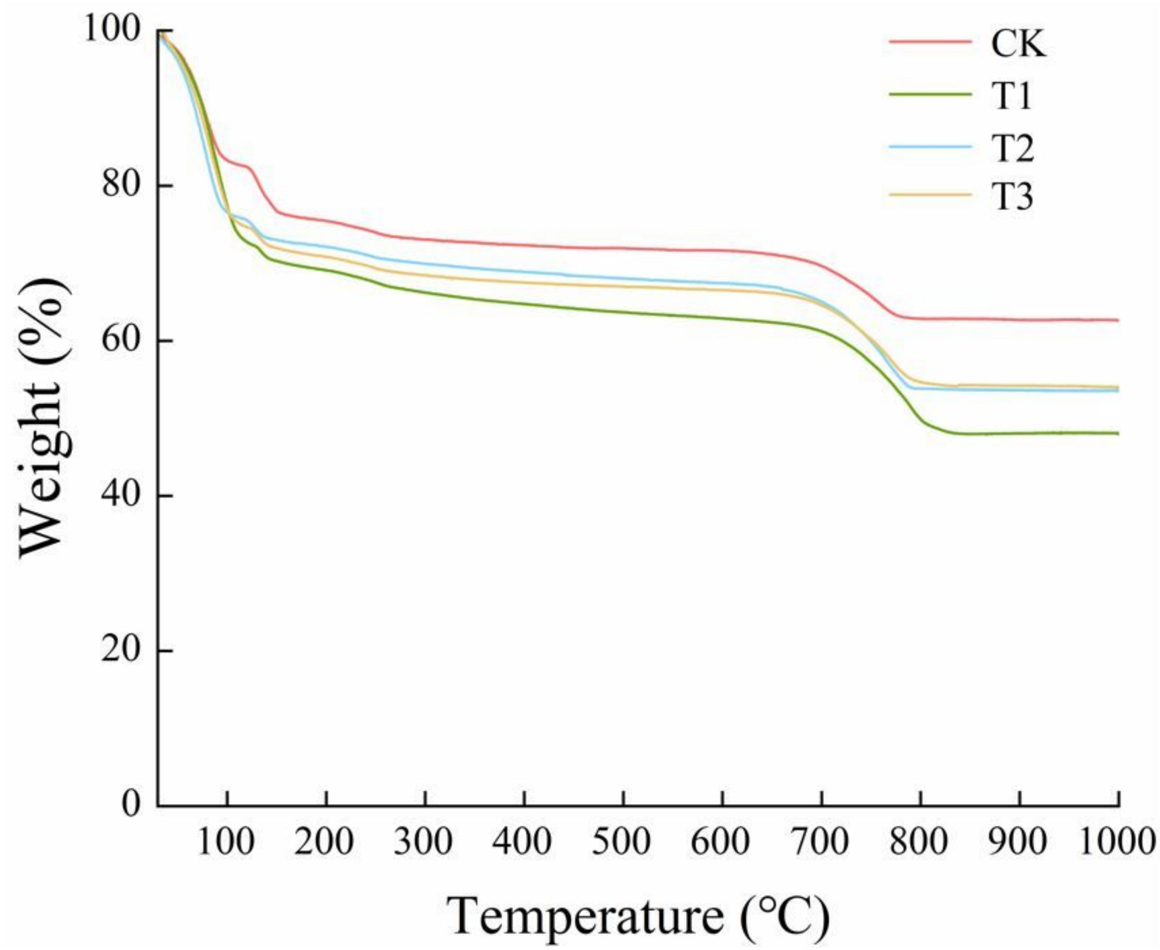

Figure 4

Thermogravimetric (TG) curves of HDS sediment after phytoremediation. CK, the sediment without phytoremediation; T1, planted black locust; T2, planted slash pine; T3, planted Chinese white poplar.

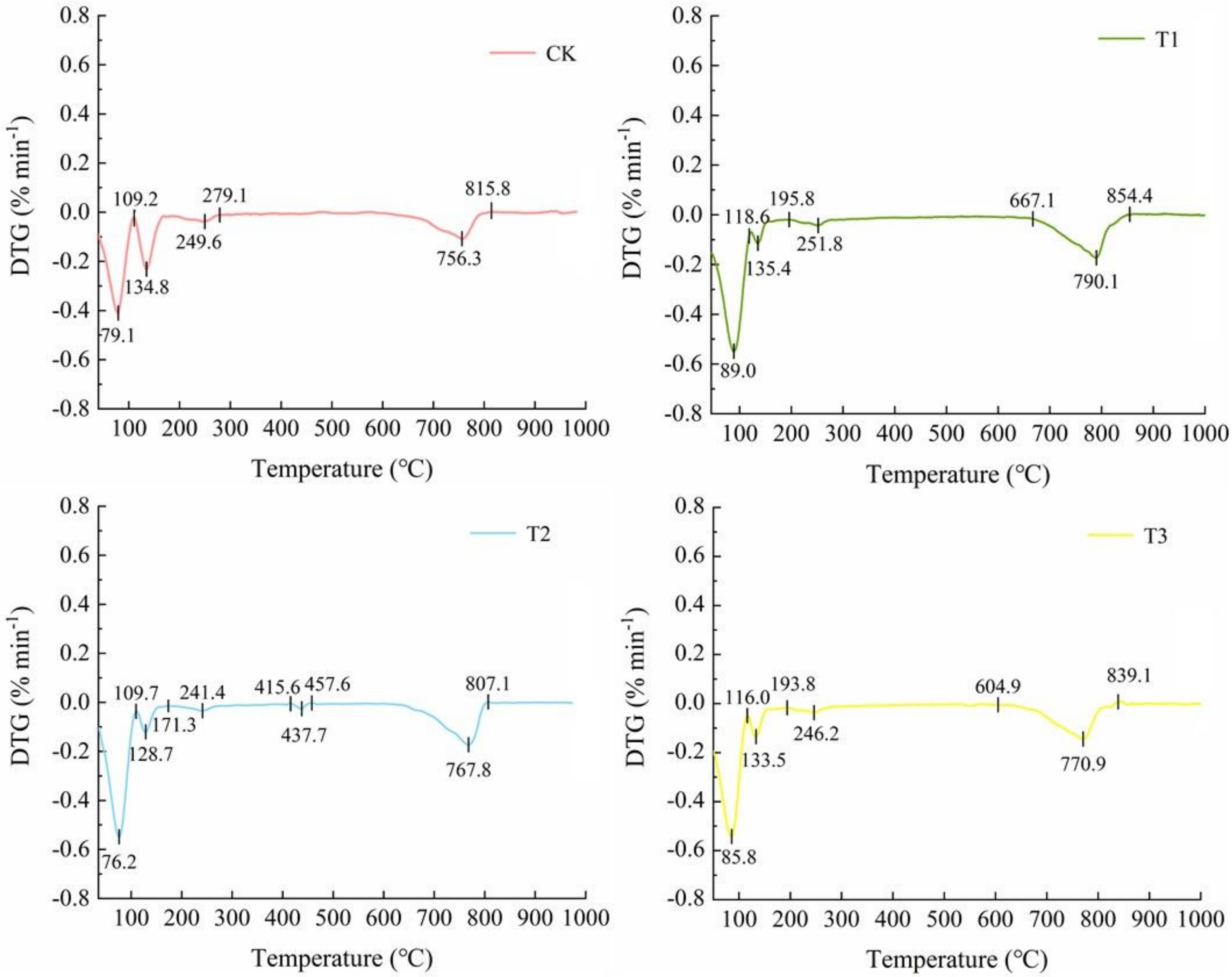

Figure 5

The derivative curves of mass loss (DTG) curves of HDS sediment after phytoremediation. CK, the sediment without phytoremediation; T1, planted black locust; T2, planted slash pine; T3, planted Chinese white poplar.