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Synergistic Remediation of Cd-Contaminated Soil with Pure Natural Adsorption Material and Hyperaccumulator Plant

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Abstract: In recent years, cadmium (Cd) contamination in agricultural soil has emerged as a significant global environmental issue, posing irreversible harm to crops and human health. As a result, efficient soil remediation techniques are urgently needed. For this issue, synergistic remediation by material and plant is an effective approach. In this study, a natural and green adsorption material (starch/montmorillonite composite, SMC) of Cd was prepared, which was further employed in synergistic remediation toward soil Cd contamination with the cadmium hyperaccumulator plant *Bidens bipinnata*. The results of the pot experiment demonstrated that an available Cd removal rate of 77.92 could be obtained, and the results of the field experiments demonstrate that the concentrations of Cd in contaminated soil could be reduced below the risk-screening values for agricultural land. Further analyses, including a microbial community diversity study, changes in soil BCR fraction components, and a TCLP toxicity leaching experiment, unequivocally elucidated that the synergy of SMC and *Bidens bipinnata* enhanced the remediation efficiency of Cd in contaminated soil. This study confirmed the application potential of the synergy of SMC and *Bidens bipinnata* toward Cd-contaminated soil.

Keywords: Cd contamination; available Cd; starch/montmorillonite composites; *Bidens bipinnata*; collaborative remediation



Citation: Guo, J.; Xu, H.; Yin, F.; Cao, J.; Xu, X.; Li, C.; Huang, F.; Chen, F.; Mao, X.; Liao, Q. Synergistic Remediation of Cd-Contaminated Soil with Pure Natural Adsorption Material and Hyperaccumulator Plant. *Agronomy* **2024**, *14*, 1299. <https://doi.org/10.3390/agronomy14061299>

Received: 8 May 2024

Revised: 7 June 2024

Accepted: 11 June 2024

Published: 15 June 2024



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1. Introduction

Synergistic remediation techniques are an efficient and safe approach to addressing heavy metal pollution in agricultural soil [1], which includes microbial–plant synergy, electrokinetic–plant synergy, and chemical or adsorption material–plant synergy [2]. Among various synergistic remediation techniques, the synergy of adsorption material and plants promotes the transfer of the total heavy metal content in soil from large aggregates to small aggregates through passivation control and reduces the available heavy metal content in large aggregates [3]. Furthermore, the synergy of adsorption material and plants could also transform heavy metals in the soil from an unstable state to a stable state, which enhances the vital activity of plants and the tolerance and stability of plants to heavy metals. As a consequence, the synergy of adsorption material and plants occupies a dominant position among all the synergistic remediation techniques [4].

For the synergistic remediation techniques using adsorption material–plant synergy, the adsorption material plays the role of solidification or passivation, which is greatly conducive to the remediation of heavy metals in soil. However, on the other hand, adsorption materials are often synthetic materials, which have adverse effects on soil properties and the surrounding environment after long-term use. Fly ash material and *Jatropha curcas* are used for the synergistic remediation of heavy metal-contaminated soil [5]. Iron oxides in fly ash materials (FeO , Fe_3O_4) can form coordination compounds with heavy metals in the soil, reducing their activity. However, simultaneous use introduces new metal ions (Fe^{3+}), which may lead to other safety issues in the long term. Limestone, red mud composite material, and lettuce are used for the synergistic remediation of As, Cd, Pb, and Zn contamination [6]. The alkalinity of limestone affects the growth and activity of soil microorganisms, thereby influencing the balance of the soil ecosystem [7]. At present, green adsorption materials are urgently needed for the further development of material–plant synergistic remediation techniques.

Montmorillonite is a widely used and inexpensive natural clay mineral. Due to the layered silicate structure, montmorillonite possesses an interlayer space capable of cation exchange and a large specific surface area (up to $800 \text{ m}^2/\text{g}$) [8,9]. As a result, montmorillonite has been increasingly employed as a green and cost-effective adsorption material for heavy metal contaminants [10,11]. In recent years, various organic compounds have been utilized in the modification of montmorillonite to obtain highly efficient montmorillonite passivators. Until now, montmorillonite has been modified with different types of organics, including anionic compounds (such as sodium dodecyl sulfate [12]), cationic compounds (such as quaternary ammonium salt [13]), and neutral compounds (polyacrylamide [14]). However, over time, these compounds will be degraded, resulting in organic or inorganic sulfides and nitrides, which could severely impact the soil property, microbiota, and other ecological factors. In previous studies, we noticed that starch is particularly suitable as an environment remediation material. Starch is a natural polymer and there are almost no heteroatoms except oxygen atoms in the starch molecule. After degradation, the degradation products of starch have little impact on the soil environment. Based on these factors, a natural and green adsorption material (starch/montmorillonite composite, SMC) was proposed to be efficient towards heavy metal contaminants in soil, which was also a perfect adsorption material candidate used in material–plant synergistic remediation techniques.

The use of adsorption material against heavy metals in soil is usually hindered by the interface reactions between the adsorption material and soil, which affects the inherent adsorption capacity of the adsorption material for heavy metals [12]. Therefore, it is difficult for the adsorption material to completely adsorb the heavy metals firmly bound to the soil. In this regard, the material–plant synergistic remediation technique could promote the upper limit of the adsorption material towards heavy metals. The heavy metals in soil (including the parts that are difficult to adsorb) could be gradually released by beneficial microorganisms and organic substances produced by plant growth. Moreover, through mild biological processes, the toxicity of the heavy metals released was reduced. Both aspects are beneficial to the remediation of heavy metals in soil [15]. In this work, the SMC-*Bidens bipinnata* synergistic remediation technique was developed, and the remediation effect was confirmed by pot experiments (in a greenhouse) and field experiments (in a location on the eastern edge of Dongting Lake, Hunan Province, China). In addition, detailed mechanism studies have also been conducted. This study offers insights into the synergy of material–plant synergistic remediation of Cd-contaminated soil and also provides a soil remediation technical for Cd-contaminated sites.

2. Materials and Methods

2.1. Characteristics of Contaminated Soil

The soil samples were collected from a location on the eastern edge of Dongting Lake in Yueyang County, Hunan Province, which is an area with heavy metal pollution in agriculture. The eastern edge of Dongting Lake was divided into nine grids, an area of

10 cm × 10 cm was selected as a representative of each grid, and the depth of soil sampling was 0–18 cm [16]. Soil samples in this interval are representative of heavy metal pollution remediation, and the weight of the samples taken out was approximately 25 kg. These nine samples were mixed well, and 100 g was taken out for testing (Table 1), while the others were evenly divided into three 8 kg portions of soil for subsequent experiments. It is situated in the southwest part of Yueyang County, at 113°02′ east longitude and 29°07′ north latitude (Figure 1). The sampling site is situated in the Zhongzhou levee area on the banks of Dongting Lake. It has a subtropical monsoon climate characterized by hot summers, mild winters, and abundant and concentrated rainfall. Soil sampling revealed severe Cd contamination in the area. Despite heavy metal contamination, the affected area continues to support a diverse range of wild plant species. For the purpose of phytoremediation screening, fifteen representative native plants, noted for their substantial biomass and widespread distribution, were selected. These species include *Chinese brake herb*, *ramie*, *Equisetum hyemale*, *Imperata cylindrica*, *Dandelion*, *Coleseed*, *Bermuda grass*, *Petroselinum crispum*, *Symphiotrichum subulatum*, *Ficus benjamina*, *Aster indicus*, *Wormwood*, *Bidens bipinnata*, *Peacock grass*, and *Black nightshade*.

Table 1. Heavy metal content and pollution level of soil in affected area (mg/kg).

Items	Cu	Pb	Zn	Cd	Cr	As	Ni
Total heavy metal (mg/kg)	52.2	90	126	1.91	98.6	53.9	36.3
Agricultural Soil Risk Screening Standard Value (mg/kg)	150	120	200	0.3	250	30	60
Agricultural Soil Risk Control Standard Value (mg/kg)	-	500	-	1.5	800	200	-
Pi value	0.348	0.75	0.73	6.36	0.394	1.79	0.605
Pollution Level [17]	Clean	Relatively clean	Clean	Heavy pollution	Clean	Slight pollution	Clean



Figure 1. Heavy metal-polluted agricultural area at sampling site.

2.2. Preparation and Characterization of Adsorbent Materials

The experimental procedure commenced with the pulverization of K10-montmorillonite (Macklin, Shanghai, China) particles into a fine powder using a grinder. Subsequently, 5 g of montmorillonite powder (MMT) was suspended in 50 mL of deionized water at 70 °C for 8 h, while in a separate conical flask, 3 g of wheat starch (Macklin, Shanghai, China) was dissolved in 50 mL of deionized water and subjected to agitation in a water bath at 50 °C for 8 h. Following agitation, the starch solution was introduced into the montmorillonite

suspension at a mass ratio of montmorillonite to starch of 1:0.6. The resulting mixture underwent stirring at an ambient temperature for 2 h employing a magnetic stirrer, followed by centrifugation at 9000 rpm, triple washing with deionized water, and subsequent drying at 45 °C. Ultimately, the material was finely ground to a particle size below 200 mesh and stored under desiccation for subsequent analysis.

2.3. Experimental Design of Synergistic Remediation

Upon preparation of the starch/montmorillonite composite (SMC), a certain quantity of the SMC (0.5% to 10%) was uniformly mixed with the soil and left to stand at room temperature for two weeks to adsorb the soil–material blend. Subsequently, the adsorbed material was combined with the selected plants for synergistic remediation potted experiments. Plastic flowerpots measuring 10 cm × 10 cm × 10 cm with trays were utilized. Each pot was filled with 400 g of soil and supplemented with N, P, and K nutrient elements [w(N):w(P):w(K) = 0.10 g/kg:0.10 g/kg:0.20 g/kg] as basal fertilizer. After thorough mixing with water, the pots were left outdoors to equilibrate for one week. Subsequently, 0.2 g of plant seeds were sown in each pot, and three parallel control groups were established. Following sowing, the pots were arranged in the greenhouse according to their numbering, and soil moisture was maintained at approximately 70% through irrigation. After a cultivation period of 120 days, samples of the aboveground and underground parts of the plants, along with rhizosphere soil samples, were collected for subsequent analysis and testing.

2.4. Analysis Method of Plant Samples

After harvesting, plant samples were first measured for plant height using a ruler. Subsequently, the plants were washed with deionized water and air-dried, then divided into shoot and root parts. The wet weight of the shoot and root parts was measured separately using an electronic balance. After measurement, the samples were dried at 65 °C until a constant mass was reached. Biomass was then measured, and the plant moisture content was calculated accordingly.

The dried plant samples were ground into powder. We weighed 0.1 g of plant tissue into a crucible and added 10 mL of aqua regia for digestion. The crucible was placed on a graphite heating plate (HT-250, Guangzhou Gedan Instrument Co., Ltd., Guangzhou, China) and digested at 150 °C for 3 h, followed by digestion at 80 °C for 1.5 h. After digestion, the solution was diluted to a final volume in a 50 mL volumetric flask. The Cd content in the plant samples was determined using ICP-MS (NexION 300X, PerkinElmer, Waltham, MA, USA).

2.5. Analysis Method of Soil Samples

Material morphology analysis: 10 mg of powdered samples was directly adhered onto the conductive adhesive and coated with gold using the Quorum SC7620 sputter coater for 45 s at 10 mA. Surface morphology was examined using the TESCAN MIRA LMS (TESCANL, Brno, Czech Republic) coupled with an EDS analyzer (Xplore) (Oxford Instruments plc, Oxford, UK). During morphology imaging, the acceleration voltage was set to 3 kV, while during energy-dispersive X-ray spectroscopy (EDS) mapping, the acceleration voltage was set to 15 kV, utilizing the SE2 secondary electron detector.

Determination of total Cd content in soil: Roots, stones, and other foreign objects were removed from the soil, which was then air-dried and ground to below 0.15 mm. A 0.1 g soil sample was weighed into a 100 mL conical flask, and 6 mL of aqua regia was added. After ensuring sufficient contact between the soil sample and aqua regia, a glass funnel was placed at the top of the conical flask to facilitate the reflux of aqua regia vapor. The conical flask was heated to a slight boil and maintained for two hours. Once digestion was complete, the conical flask was cooled to room temperature, and the extract was filtered to a fixed volume. The soil Cd content was then measured using ICP-MS (NexION 300X, PerkinElmer, Waltham, MA, USA).

Determination of the available Cd content in soil: After drying, soil samples were crushed to below 2 mm. A 10 g soil sample and 20 mL of DTPA-CaCl₂-TEA buffer solution were added to a 100 mL conical flask. The conical flask was shaken at room temperature for 2 h, followed by centrifugation and filtration. The supernatant was then taken for ICP measurement of the available Cd in the soil.

TCLP (Toxicity Characteristic Leaching Procedure)-extractable Cd content: Processed and dried soil samples were crushed to below 0.85 mm, and 1 g of the soil sample and 20 mL of the extraction solution were weighed and placed in a centrifuge tube, subjected to constant-temperature shaking for 18 h, centrifuged, and filtered, while the Cd toxicity leaching amount in the soil was detected by ICP-MS (the 1 L extraction solution was prepared with acetic acid (17.5 mol/L) and sodium hydroxide (1 mol/L), pH = 2.88 ± 0.5).

Determination of soil pH: 10 g of the air-dried soil sample was weighed into a 50 mL beaker. Twenty-five milliliters of deionized water was added, and the container was sealed with plastic wrap. The mixture was stirred for 2 min on a magnetic stirrer and allowed to stand for 30 min, and the pH was measured within 1 h using a pH meter.

Soil Cd fractionation was determined using the European Community Bureau of Reference (BCR) sequential extraction method, consisting of three steps. The specific steps are as follows:

The bioaccumulation factor (BF) of a plant for a certain element is defined as the ratio of the element's concentration in the plant (C_{Plant} , mg/kg) to its concentration in the soil (C_{Soil} , mg/kg). The translocation factor (TF) represents the ratio of the element's concentration in the aboveground parts of the plant (C_{shoot} , mg/kg) to that in the belowground parts (C_{Root} , mg·kg⁻¹). These formulas are defined as follows:

$$\text{BF} = C_{\text{Plant}} / C_{\text{Soil}}$$

$$\text{TF} = C_{\text{Shoot}} / C_{\text{root}}$$

The removal rate is one of the key indicators for evaluating the effectiveness of remediation materials. The removal rate is defined as the ratio of the amount of heavy metals removed during remediation to the initial concentration of heavy metals before remediation.

$$\text{Removal rate} = C_{\text{Before}} - C_{\text{After}} / C_{\text{Before}}$$

2.6. Total DNA Extraction, 16S rRNA Amplification and High-Throughput Sequencing

Soil microbial quantification: DNA extraction was conducted on soil samples before and after synergistic remediation. After extraction, 0.8% agarose gel electrophoresis was used for molecular size determination, and a UV spectrophotometer (NanoDrop NC2000, Thermo Fisher Scientific, Waltham, MA, USA) was used for DNA quantification [18]. Bacterial 16S rDNA genes in the V3-V4 region were amplified using genomic DNA as a template, employing the forward primer 338F (5'-ACTCCTACGGGAGGCAGCA-3') and the reverse primer 806R. PCR was initiated with denaturation at 98 °C for 30 s, followed by amplification cycles consisting of denaturation at 98 °C for 15 s, annealing at 50 °C for 30 s, and extension at 72 °C for 30 s, for a total of 26 cycles to accumulate ample DNA fragments with a final extension step at 72 °C for 5 min to ensure complete product extension. Amplified fragments were screened via 2% agarose gel electrophoresis and stored at 4 °C. The quantification of PCR products was performed using the Quant-iT Pico Green dsDNA Assay Kit on a Microplate reader (BioTek, FLx800, Winooski, VT, USA), followed by pooling according to the required data volume for each sample. After pooling, libraries were constructed using the TruSeq Nano DNA LT Library Prep Kit (Illumina, San Diego, CA, USA), followed by quality control and quantification of libraries. Qualified libraries underwent paired-end sequencing on the Illumina NovaSeq platform using the NovaSeq 6000 SP Reagent Kit (500 cycles, Illumina, CA, USA). Data analysis was performed using QIIME2 2019.4 [19].

2.7. Statistical Analysis Methods

To eliminate interference from unrelated factors (such as seed germination failure or pest damage), all experiments were conducted with three pots of plants, and each analysis was repeated three times to ensure data reliability. Statistical analysis was performed using IBM SPSS Statistics 26. One-way ANOVA was used to compare intergroup differences in various parameters, with significance set at $p < 0.05$. Post hoc analysis was conducted using Duncan's test, and the results are displayed in figures and tables using letter notation [20].

3. Results

3.1. Characterization of Materials

Following the synthesis of SMC, surface morphology was determined to confirm the deposition of starch onto the montmorillonite surface and investigate the adsorption mechanism between starch and montmorillonite. Experiments performed in aqueous phase systems provided robust evidence that starch modification significantly enhanced the capacity of montmorillonite to adsorb heavy metal cations.

3.1.1. Surface Morphology Characterization of SMC

The morphology of starch, montmorillonite, and SMC is shown in Figure 2. In Figure 2A, starch exhibits a granular or aggregated structure, with loosely arranged particles. Starch particles are circular, elliptical, or irregular in shape, with a smooth and uniform surface and an average particle size of 10 μm . Figure 2B displays the platy or layered structure of montmorillonite, with clear interlayer spacing and well-defined crystal edges, arranged closely. Figure 2C,D depicts the particles of SMC, where it is observed that the starch particles open up into smaller granules and adhere to the surface of montmorillonite, resulting in a smoother and more rounded surface. Figure 2D reveals that the montmorillonite surface has adsorbed numerous starch molecules, indicating the significant adsorption capacity of montmorillonite. Additionally, the elemental analysis of SMC is shown in Figure 2E, where an increase in C, O on the modified montmorillonite surface is evident. The main components include C, O, Si, Al, Fe, K, and Ca, accounting for 46.2 wt%, 31.8 wt%, and 17.2 wt%, respectively.

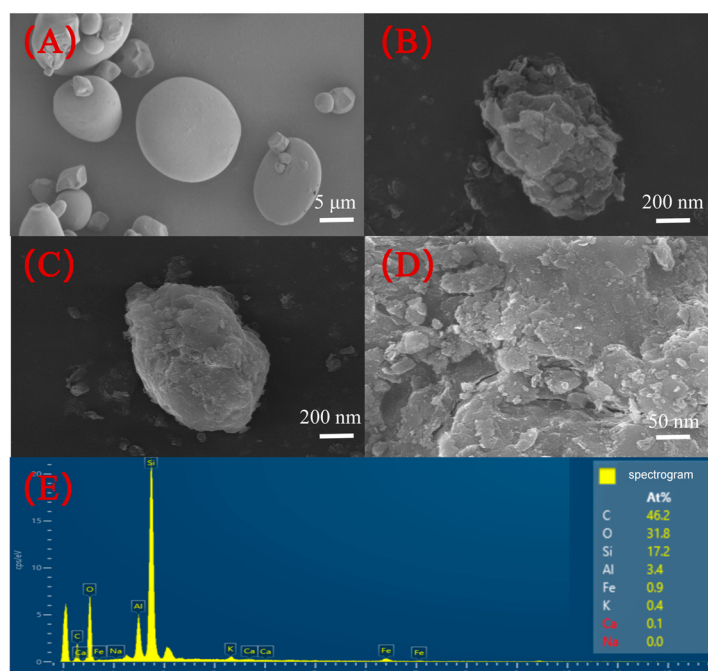


Figure 2. SEM images of unmodified starch (A), montmorillonite (B), modified montmorillonite (C), and magnified view of modified montmorillonite (D). EDS elemental mapping of the modified montmorillonite (E).

3.1.2. Adsorption Efficiency of SMC towards Heavy Metals in Solution

Water is the primary transport medium of heavy metals in soil. Therefore, the adsorption capacity of SMC for heavy metals was first detected in the water phase. Table 2 shows the adsorption capacity of montmorillonite and SMC towards heavy metal ions. Compared to montmorillonite, the adsorption capacity was significantly improved after modification. For Cd^{2+} , Pb^{2+} , and Cu^{2+} , the removal rates of natural montmorillonite were 50.45%, 64.37%, and 74.33%, while the removal rates of SMC increased to 95.31%, 94.12%, and 87.92%. The modification resulted in an increase of 44.86, 29.75, and 13.59 percentage points, respectively. For natural montmorillonite, the comprehensive adsorption capacity for seven heavy metals is due to the cation exchange capacity. For modified montmorillonite SMC, the improved adsorption capacity for seven heavy metals is due to the reserved cation exchange capacity of montmorillonite and the additional chelation capacity of starch [21].

Table 2. Removal rate (%) of heavy metal ions in aqueous phase by montmorillonite and SMC.

Material	Cu	Pb	Zn	Cd	Cr	As	Ni
Montmorillonite (%)	74.33	64.37	50.31	50.45	33.45	28.07	39.66
SMC (%)	87.92	94.12	73.22	95.31	48.23	48.23	51.37

3.2. Screening of Indigenous Hyperaccumulating Plants

In order to develop a candidate remediation plant that is suitable for the eastern edge of Dongting Lake, 15 native plants were collected with the standard of relatively large biomass from the vicinity of the contaminated site, including Peacock grass, Dandelion, Bermuda grass, Bidens bipinnate, and other plants (as shown in Figure 3). The plants were divided into shoot and root parts, and the heavy metal content in the plants was determined. The bioaccumulation factor (BF) and translocation factor (TF) of the plants were calculated as the screening criteria (Table 3).



Figure 3. Fifteen Indigenous hyperaccumulating plants of the Eastern Margin of Dongting Lake (1. Chinese brake herb, 2. ramie, 3. *Equisetum hyemale*, 4. *Imperata cylindrica*, 5. Dandelion, 6. Coleseed, 7. Bermuda grass, 8. *Petroselinum crispum*, 9. *Symphyotrichum subulatum*, 10. *Ficus benjamina*, 11. *Aster indicus*, 12. Wormwood, 13. *Bidens bipinnata*, 14. Peacock grass, and 15. Black nightshade).

Table 3. Cd content, Bioaccumulation Factor (BF), and Transfer Factor (TF) in 15 indigenous hyperaccumulating.

Plant	Cd Content (mg/kg)	BF	TF	Plant	Cd Content (mg/kg)	BF	TF
1 shoot	0.0145	0.0076	0.3713	9 shoot	0.0998	0.0522	0.2791
1 root	0.0391	0.0205		9 root	0.3575	0.1872	
2 shoot	0.0529	0.0277	0.6451	10 shoot	0.0945	0.0495	0.1755
2 root	0.0820	0.0430		10 root	0.5385	0.2819	
3 shoot	0.1729	0.0905	0.6725	11 shoot	0.1885	0.0987	0.2622
3 root	0.2570	0.1346		11 root	0.7189	0.3764	
4 shoot	0.1541	0.0807	0.9862	12 shoot	0.1003	0.0525	0.6524
4 root	0.1563	0.0818		12 root	0.1537	0.0805	
5 shoot	1.1768	0.6161	0.8376	13 shoot	2.2833	1.1954	0.6982
5 root	1.4049	0.7356		13 root	3.2704	1.7123	
6 shoot	1.8418	0.9643	0.7760	14 shoot	0.5077	0.2658	0.6873
6 root	2.3735	1.2427		14 root	0.7386	0.3867	
7 shoot	1.6964	0.8881	1.3830	15 shoot	0.2916	0.1527	0.9119
7 root	1.2266	0.6422		15 root	0.3197	0.1674	
8 shoot	0.3021	0.1581	0.4652				
8 root	0.6493	0.3399					

Different plants exhibit varying degrees of tolerance and response to heavy metals. The aboveground and underground parts of these 15 plants contain different concentrations of heavy metals, indicating their varying abilities to accumulate Cd. Plants 5, 6, 7, and 13 exhibited strong Cd enrichment capacity, with BF values greater than 0.5 for both shoot and root parts. Among them, plant 13, *Bidens bipinnata*, exhibits the highest accumulation capacity, with Cd contents of 2.2833 mg/kg in the aboveground part and 3.2704 mg/kg in the underground part. Apart from these four plants, plants 2, 3, 4, 12, 14, and 15 show relatively high translocation factors, which are conducive to long-term extraction in plant remediation and represent potential remediation plants.

Generally, plants with higher BF and TF values are considered more suitable for remediation, as they can effectively absorb heavy metals from the soil and transfer them to the aboveground parts, thereby reducing the heavy metal content in the soil [22]. By evaluating the BF and TF of 15 native plants, it was determined that plants 2, 3, 4, 5, 6, 7, 12, 13, 14, and 15 have stronger abilities to absorb and transport heavy metals, playing a more significant role in the remediation process. Therefore, these 10 plants were selected for subsequent pot experiments.

3.3. Remediation Effect of SMC in Cd Contaminated Soil

The dosage of adsorption material plays a decisive role in the synergistic remediation process. Therefore, the remediation effect of using different dosages of SMC was tested in contaminated soil with high Cd concentrations (Cd = 10 mg/kg) and low Cd concentrations (Cd = 3 mg/kg). From Figure 4, it can be seen that at high or low Cd concentrations, the optimized dosage of SMC is 2%, and the corresponding reduction rates of available Cd are 37.75% and 21.76%, which is much higher than the previously reported reduction rate obtained by clay mineral passivators (9.54%, 13.9%) [23,24]. Experimental results indicated high remediation efficiency of SMC in soils with varying cadmium concentrations. The optimal dosage is determined to be 2%, while the optimal remediation concentration of Cd²⁺ is 3 mg/kg. Subsequent pot experiments will be conducted based on these conditions for synergistic remediation.

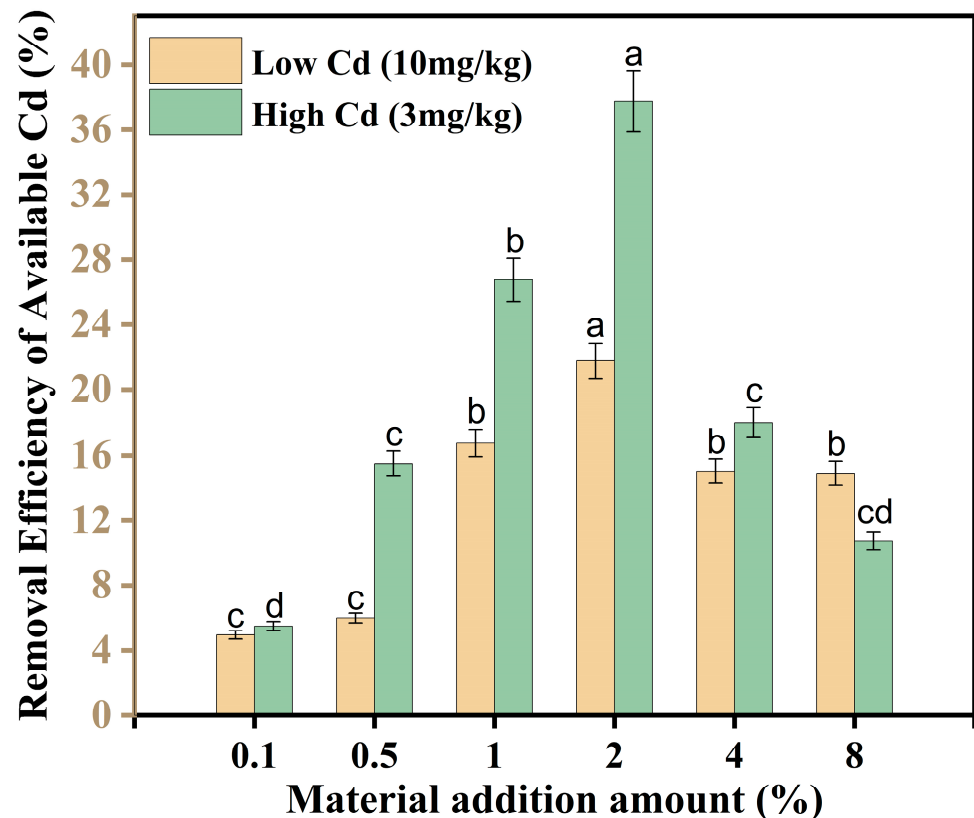


Figure 4. Remediation effect of SMC for Cd in soil with high and low concentrations (different letters above the bars in the bar chart indicate significant differences at the $p < 0.05$ level between different treatments. Error bars represent the standard deviation of the mean, $n = 3$).

3.4. Screening of Remediation Plants by Potted Experiment

Pot experiments were conducted using ten selected remediation plants with higher TF and BF values out of the 15 plant species screened in the remediation site, in artificial synthetic Cd-contaminated soil. The ten plant species were subjected to three treatments: (a) natural conditions without any treatment, (b) the addition of 3 mg/kg Cd^{2+} , and (c) the addition of SMC after Cd^{2+} addition. After 90 days of greenhouse cultivation, photographs were taken and are shown in Figure 5. It was observed that all ten seed species were able to germinate and survive in uncontaminated soil (Figure 5A), while under Cd^{2+} stress (Figure 5B), only seven plant species germinated, with stunted growth and significantly reduced biomass. However, upon the addition of SMC material (Figure 5C), the growth of the plants improved markedly, alleviating the heavy metal stress. Nevertheless, ramie exhibited excessively slow growth and was deemed unsuitable as a remediation plant. Conversely, the other six plant species, namely *Peacock grass*, *Bidens bipinnata*, *Coleseed*, *Bermuda grass*, *Black nightshade*, and *Dandelion*, exhibited robust growth with higher biomass.

Specific measurements of biomass, plant height, and water content were conducted for these six plants (Figure 6). The results indicate that the addition of Cd significantly stressed the growth of all plants. However, with the addition of SMC, toxic Cd in the soil was immobilized, which alleviated growth inhibition caused by the toxicity of Cd and promoted a significant increase in biomass. This is similar to findings from other studies on heavy metal-contaminated soils [25]. Among them, *Bidens bipinnata* had the highest biomass under natural conditions. However, it decreased significantly under heavy metal stress and then recovered to the highest biomass after the addition of SMC. Trends in water content, plant height, and biomass were generally consistent, indicating that heavy metals have a significant impact on plant metabolism. Under metal stress, changes occur in the physiological characteristics and cell structure of plants, such as increased cell wall thickness and vacuole volume, the disruption of internal chloroplast tissues, increased

number of plastids, and the disintegration of primary cell wall fibers [26]. The addition of SMC eliminated these effects, promoting the absorption and transport of substances within plants, thereby establishing tolerance to heavy metals.

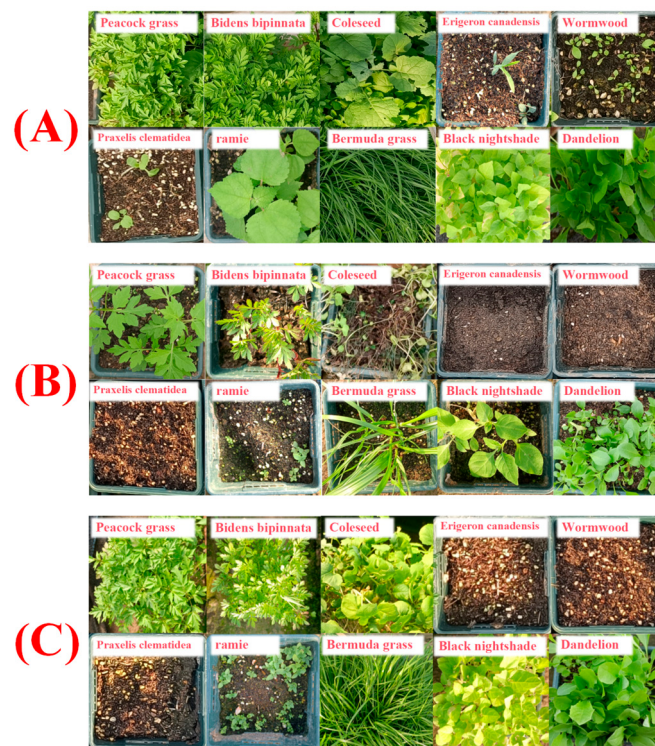


Figure 5. Comparison of growth conditions of 10 plant species before and after material remediation ((A) control group (plant growth status under natural conditions), (B) single premeditation group, (C) SMC–plant synergistic repair group).

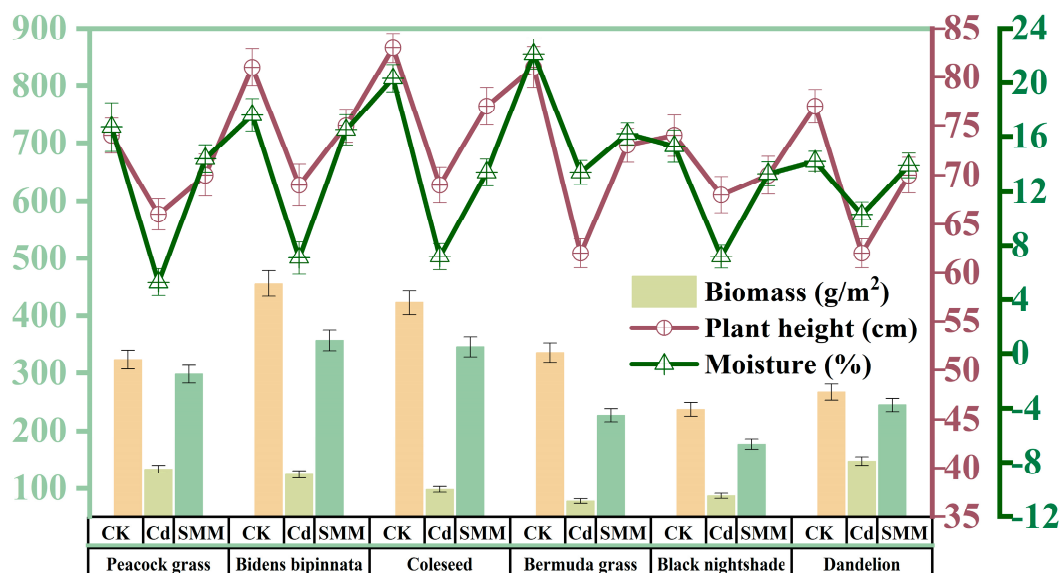


Figure 6. Biomass, plant height, and water content changes in the six selected plants from Figure 5 under natural conditions (CK), Cd ion stress (Cd), and Cd ion stress with the addition of SMC chemical material (SMC).

Figure 7 depicts the heavy metal content in the tissues of six plant species from Figure 6. It can be observed that all six plants exhibit a certain adsorption capacity to Cd. Under Cd stress, plants secrete organic acids, which could chelate with Cd^{2+}

in the soil to reduce the toxicity of Cd^{2+} , and as a result, the damage to various enzymes inside the plant via free Cd^{2+} could be reduced [27]. The sequence of Cd content in the plant tissues in plant remediation without the material is *Bidens bipinnata* > *Peacock grass* > *Coleseed* > *Bermuda grass* > *Dandelion* > *Black nightshade*. For material–plant synergistic remediation, the sequence is similar (*Bidens bipinnata* > *Peacock grass* > *Bermuda grass* > *Black nightshade* > *Coleseed* > *Dandelion*). Furthermore, the amount of heavy metals absorbed by the plants obtained from material–plant synergistic remediation is significantly lower than that from plant remediation, similar to the results of previous research by Li [28]. The largest difference in these two different remediation processes is obtained in *Bidens bipinnata* (1.89 mg/kg), while the smallest difference is in *Black nightshade* (1.42 mg/kg). The responsible reason is that during material–plant synergistic remediation, the Cd that is difficult to dissolve from the soil could be released in the form of chelates by various secretions (such as small organic acids) from the plant roots, and the cadmium complex is further solidified by SMC. In this way, the solubility, transferability, and toxicity of Cd in the soil was substantially inhibited, thereby the bioavailability of Cd in the soil was significantly reduced after material–plant synergistic remediation (the extraction rate of Cd by plants was also reduced). Moreover, there is a significant difference in the adsorption amount of Cd by plants under the same material, indicating that the interaction between plants and materials is not entirely consistent, possibly related to plant secretions. Based on the screening results, *Bidens bipinnata* and *Peacock grass* exhibit relatively high extraction amounts under both conditions, while *Coleseed* performs well in single-plant remediation but is not as effective as *Bermuda grass* after the addition of the material. Combining the results of Figures 6 and 7, three plants were suitable for synergistic remediation (*Bidens bipinnata*, *Peacock grass*, and *Bermuda grass*).

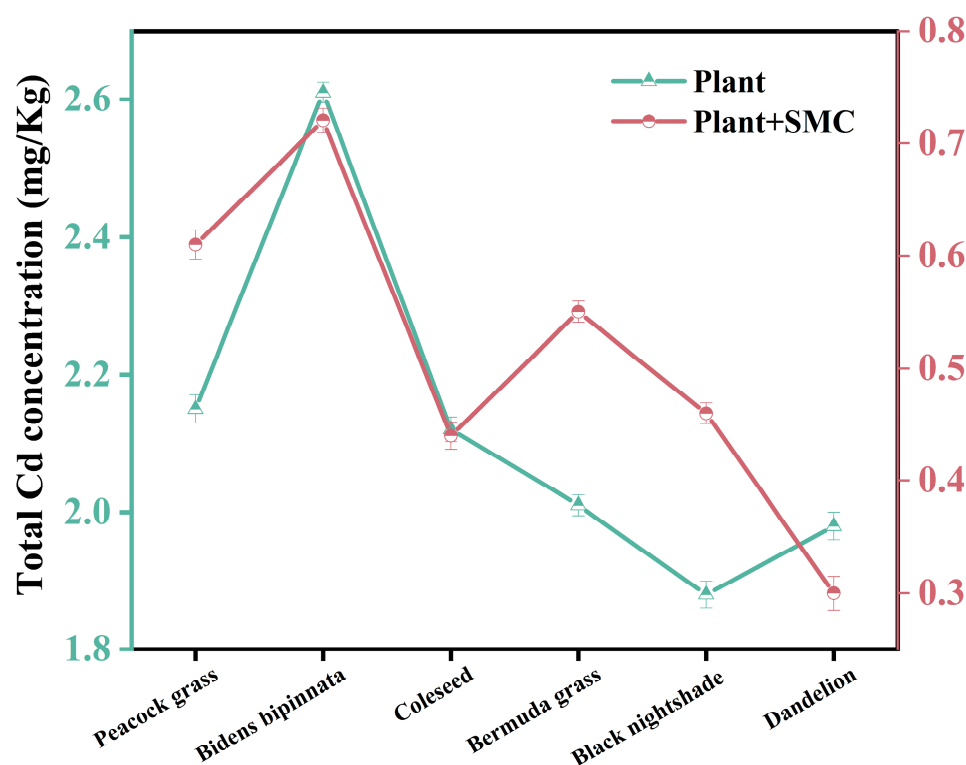


Figure 7. Heavy metal content in the six tested plants.

Figure 8 illustrates the further screening of the optimized plant in material–plant synergistic remediation through the pot experiment. It is evident from the figure that *Bidens bipinnata* performs better than *Bermuda grass* and *Peacock grass* in both plant remediation and SMC–plant synergistic remediation.

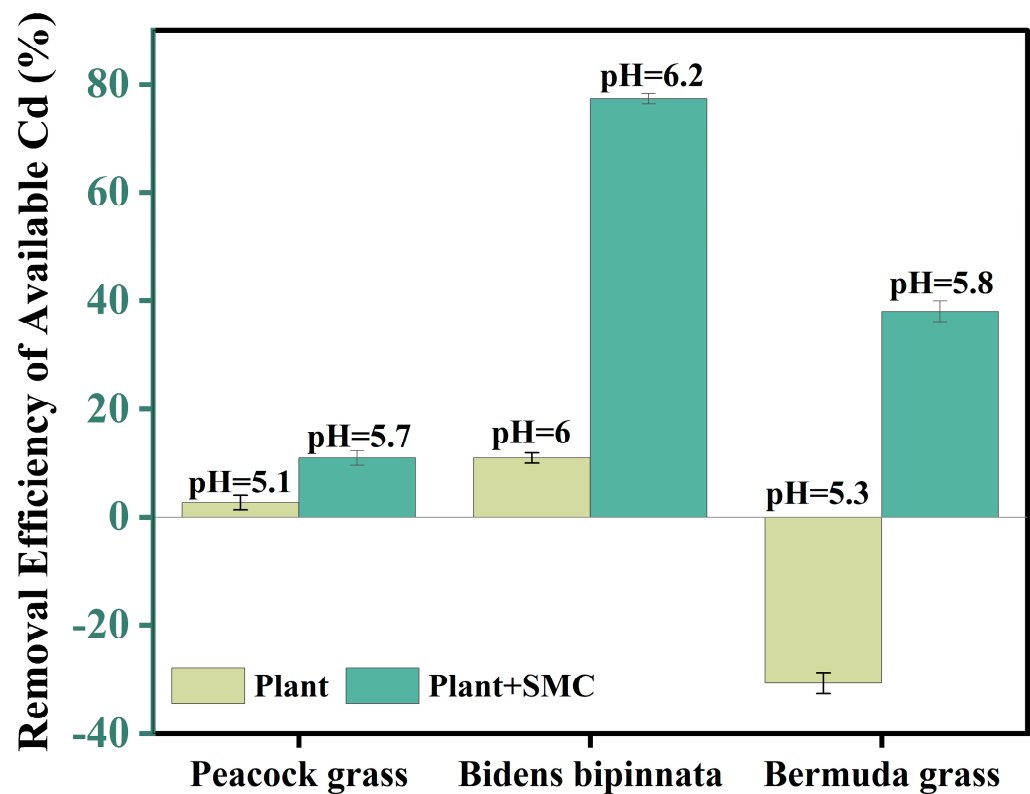


Figure 8. Available Cd changes in SMC–plant synergistic remediation and single phytoremediation.

The removal efficiency of available Cd of *Bidens bipinnata* in plant remediation and synergistic remediation is 11% and 77.33%, respectively. *Bermuda grass* activates Cd during plant remediation and passivates Cd during synergistic remediation, with the removal efficiency of available Cd of −30.67% and 38%, respectively. The passivation effects of *Peacock Grass* during both plant and synergistic remediation are not significant, at 2.67% and 11%, respectively, both lower than the removal efficiency of available Cd in soil treated with *Bidens bipinnata*. The available Cd content of heavy metals is related to the physical and chemical properties of the soil, such as the pH value, texture, and dissolved organic matter [29]. The pH of *Bermuda grass* and *Peacock grass* is significantly lower than that of *Bidens bipinnata*, and the activation of Cd in the soil may be influenced by both pH and the action of rhizosphere microorganisms. After the addition of the material, the pH of the three tested plants increases to some extent. This may be attributed to the weak alkalinity of the modified montmorillonite itself. As the pH value increases, the adsorption and fixation of Cd by the soil gradually increase, weakening the activation effect of plant secretions on Cd and reducing the available Cd content [30]. *Bidens bipinnata* exhibits the highest removal rate, possibly due to its high enzyme activity in the soil (i.e., alkaline phosphatase, dehydrogenase, and urease) [31], which reduces oxidative damage to plants under heavy metals.

3.5. Screening of SMC Dosage by Potted Experiments

It can be observed in Figure 9 that the addition of SMC improves the remediation effect of Cd and the extraction efficiency of heavy metals by *Bidens bipinnata* is greatly enhanced. With the SMC dosage increased, the reduction rate of available Cd in the soil first increased and then decreased. When the SMC dosage was 2%, the available Cd removal efficiency of the synergistic remediation was the highest, reaching 77.92%. However, after the SMC dosage exceeded 2%, there was a significant decrease in the reduction rate of available Cd. The reason for this is that excessive SMC changes the pH value of the soil, which affects the solubility of Cd and the absorption capacity of plants. Cd^{2+} is less soluble under alkaline

conditions, thereby the extraction rate of Cd by *Bidens bipinnata* was reduced [32,33]. On the other hand, excess SMC may alter the soil structure and aeration, thereby affecting the growth and development of plant roots. If the soil structure becomes too dense, roots may not be able to fully extend and absorb nutrients, leading to restricted plant growth.

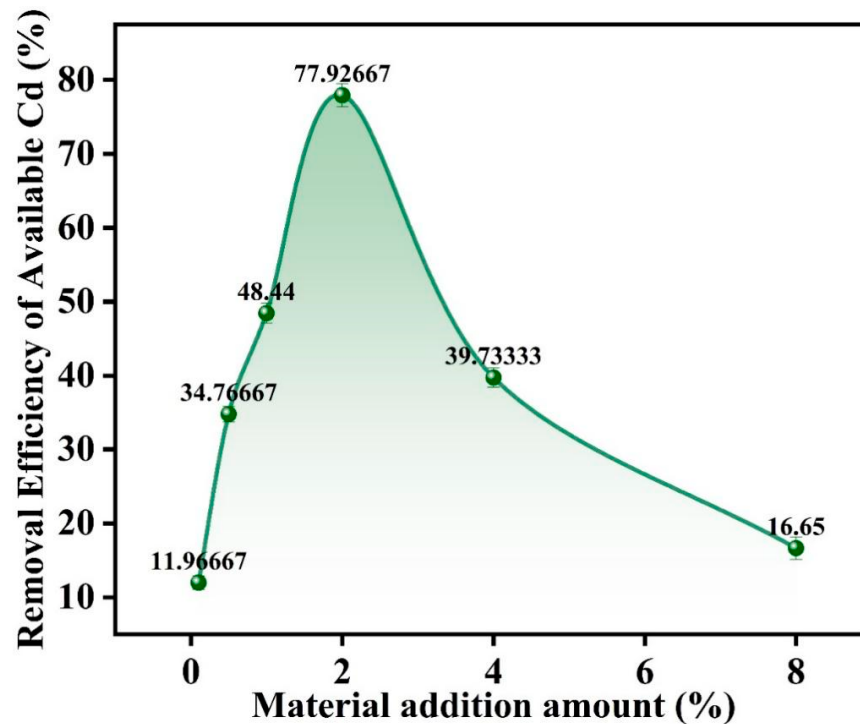


Figure 9. The removal efficiency of available Cd in soil during the synergistic remediation of SMC-*Bidens bipinnata* under different material dosages.

3.6. Application of SMC-*Bidens bipinnata* Synergistic Remediation Technology in Field

In practical field applications, the efficacy of synergistic remediation technology was evaluated. The optimized plant *Bidens bipinnata*, along with the optimal dosage (2%) of SMC, was implemented in contaminated soils located on the eastern edge of Dongting Lake, Yueyang City. Initial soil assessments revealed that the Cd content in the soil of the appointed field was 1.91 mg/kg, which was categorized as “heavy pollution”, while that of the As content was 53.9 mg/kg, which was categorized as “slight pollution”. Other heavy metal concentrations were within acceptable limits (“Relatively clean” range).

Therefore, the object of field experiments was focused on the reduction in total Cd and As in field soil (Figure 10). The results in Figure 10 indicated that synergistic remediation exhibited a notable passivation effect on both Cd and As, with the passivation effect increasing gradually over time. After 60 days, the concentration of Cd in remediated soil decreased to 0.29 mg/kg (Table 4), which was lower than the agricultural soil pollution risk screening value of 0.3 mg/kg (stipulated in GB15618-2018 [34]). Similarly, the concentration of As in remediated soil dropped to 28.4 mg/kg, which was also lower than the screening value of 30 (stipulated in GB15618-2018 [34]). For synergistic remediation with an extended period (60–120 days), the variations in the concentration of Cd and As in the soil became relatively minor, possibly attributed to the saturation of coordination between the oxygen-containing functional groups in the passivator with Cd and As ions [35]. In summary, Cd and As in the contaminated soil of the eastern edge of Dongting Lake were effectively inhibited below the screening value for agricultural land risk by the application of synergistic remediation.

In the process of synergistic remediation with materials and plants, microorganisms play a crucial role in the restoration of soil ecosystems and the remediation of heavy metal pollution. A deeper understanding of the changes in local microbial communities could elucidate the synergistic effects of SMC-*Bidens bipinnata* [36]. Therefore, high-throughput

sequencing analysis of microbial DNA (16s V3V4) extracted from the soil was conducted to investigate the changes in microbial population diversity before and after remediation. Figure 11 illustrates the relative abundance of species at the genus level in soil obtained from potting and field experiments before and after synergistic remediation.

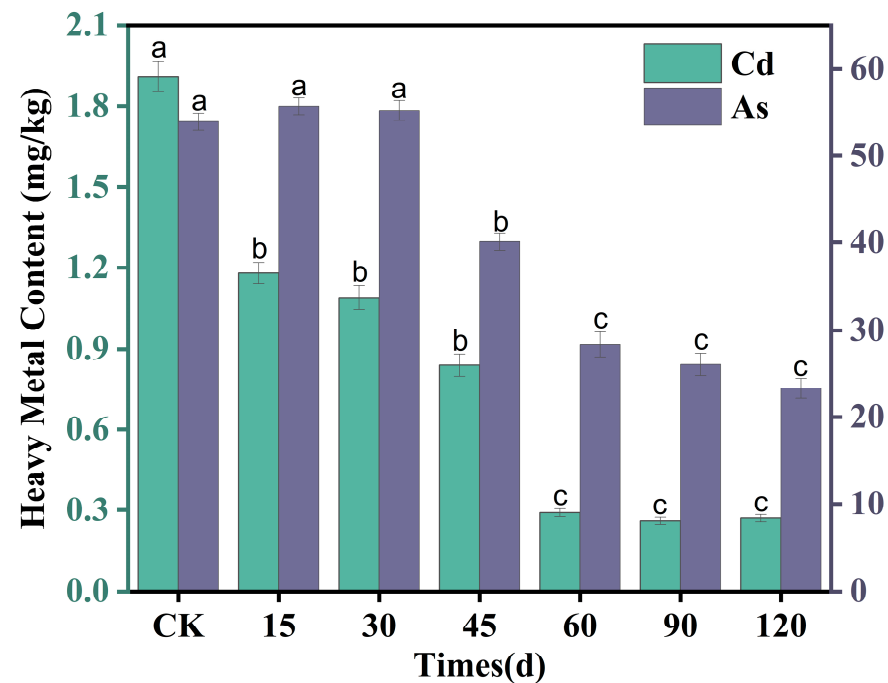


Figure 10. Influence of synergistic remediation on Total Cd and As contents in soil in the field conditions (different letters above the bars in the bar chart indicate significant differences at the $p < 0.05$ level between different treatments. Error bars represent the standard deviation of the mean, $n = 3$).

Table 4. Heavy metal content and pollution level in soil after remediation (mg/kg).

Items	Cd	As
Total heavy metal (mg/kg)	0.29	28.4
Agricultural Soil Risk Screening Standard Value (mg/kg)	0.3	30
Pi value	0.94	0.94
Pollution Level	Relatively clean	Relatively clean

A1 and A2 represent soil samples from the potting experiment. There were significant differences in dominant bacterial communities before and after remediation. In sample A1, the dominant bacterial taxa were Subgroup_10, Arenimonas, and S0134_terrestrial_group. Among these, only Arenimonas exhibited certain environmental remediation capabilities. In sample A2, dominant bacterial taxa included S0134_terrestrial_group, Nocardioideae, Hydrogenophaga, Candidatus_Kaiserbacteria, Pseudomonas, and Bacillus subtilis. Notably, the relative abundance of Candidatus_Kaiserbacteria increased from 4% to 9%, indicating its role in promoting plant growth and soil nutrient cycling [37,38]. Bacillus subtilis, with its relative abundance increasing from 3% to 21%, secretes β -galactosidase, which can be used to assess heavy metal biotoxicity. Bacillus subtilis cultured in high-concentration Cd environments secretes extracellular polymeric substances (EPSs) and cell enzyme proteins, enhancing its resistance to heavy metals [39]. Furthermore, Bacillus subtilis produces auxins, promoting plant growth and enhancing the synergistic effects of synergistic remediation.

B1 and B2 represent soil samples from the actual field. Before remediation, the dominant bacterial taxa in B1 included Saccharimonadales, Pelagibius, AKYG1722, Candidatus_Kaiserbacteria, S0134_terrestrial_group, Chryseolinea, and Truepera. After remediation, the dominant taxa were Chryseolinea, Cellvibrio, Flavobacterium, Hafnia alvei, and Truepera. Flavobacterium and Hafnia alvei were virtually absent in other soils. Hafnia alvei contains

dipeptidase, conferring Cd resistance [40]. The *Devosia* genus secretes organic compounds that chelate heavy metals, converting them into more stable organic forms [41]. Overall, the addition of materials enhances the robustness of soil microbial communities and selects for microorganisms with stronger resistance to heavy metals. Through the combined adsorption of materials, plants, and microorganisms, more heavy metal ions in the effective state are chelated.

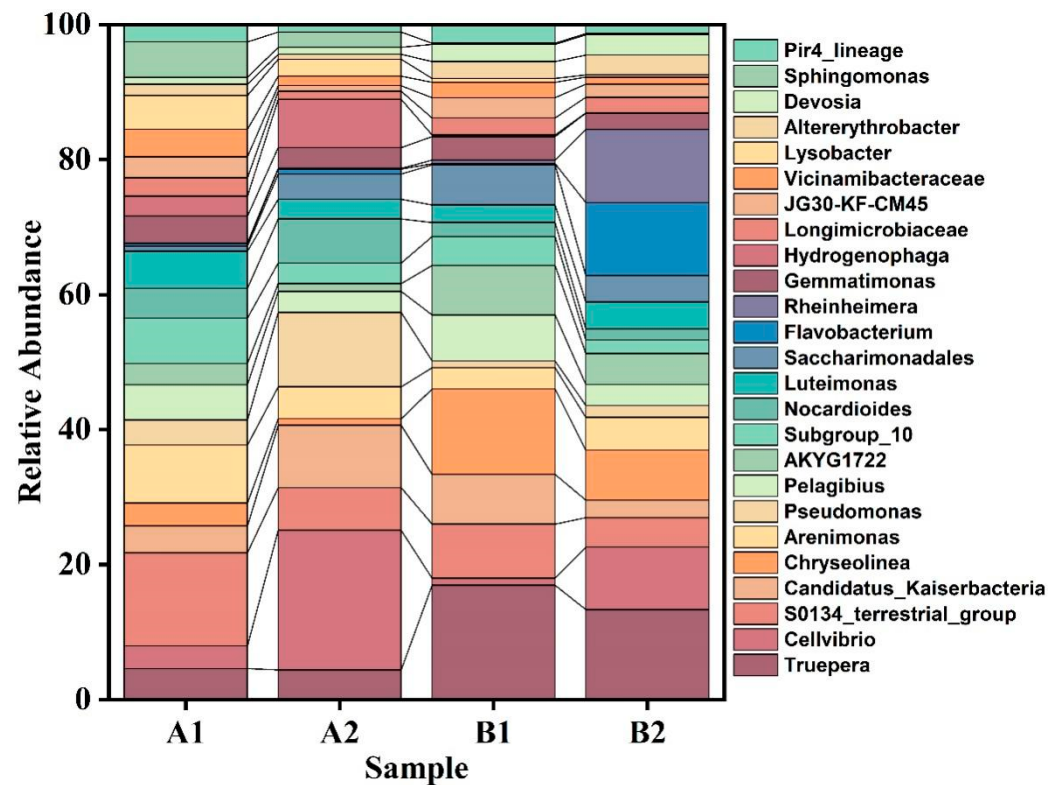


Figure 11. Genus-level species abundance composition stacked bar chart. A1: soil before pot experiment remediation; A2: soil after pot experiment remediation; B1: soil before field experiment remediation; B2: soil after field experiment remediation.

There are significant differences between the microorganisms in the soil obtained from potting and field experiments, possibly due to the effects of soil composition and properties. The pH value of the potting soil was 6.2, while that of the actual soil was 5.21. The higher acidity of actual soil inhibits bacterial nutrient uptake and reduces bacterial activity. H^+ ions react with extracellular bacterial secretions, competing for heavy metal ion binding sites, reducing microbial adsorption of heavy metals. Additionally, H^+ ions increase the activity of heavy metals, leading to an increase in the effective state of Cd. This may be one of the reasons why the available Cd removal rate of *Bidens bipinnata* is higher than that of other plants. The addition of materials promotes a pH increase, mitigating the effects of H^+ ions on microorganisms, facilitating better synergy between microorganisms and plants, and thereby significantly improving the efficacy of synergistic remediation.

3.7. Changes in Soil BCR Fraction Components

Due to the close relationship between the available content of heavy metals and their distribution and binding states in the soil, sequential extraction experiments were conducted to assess the changes in the forms of Cd in the soil after synergistic remediation. As shown in Figure 12, all six plants facilitated the transformation of oxidizable and reducible forms into residual forms. In CK, the residual form in soil accounted for 40%, which could reach up to 63% after synergistic remediation. The oxidizable and reducible forms decreased to 4% and 5%, respectively, while the weak acid-soluble form remained

relatively unchanged. Among all metal components, the residual form was almost impossible to extract from the soil, while the reducible and weak acid-soluble forms were more easily absorbed by plants. All six plants could transform Cd from forms available for plant uptake and utilization into stable residual forms, reducing its activity. Among them, *Bidens bipinnata* transformed the most residual forms, resulting in the lowest bioavailability of Cd in the soil. This may be attributed to the combined effects of its secretions and enzymatic degradation, as well as the cooperative metabolism and degradation of rhizospheric microorganisms.

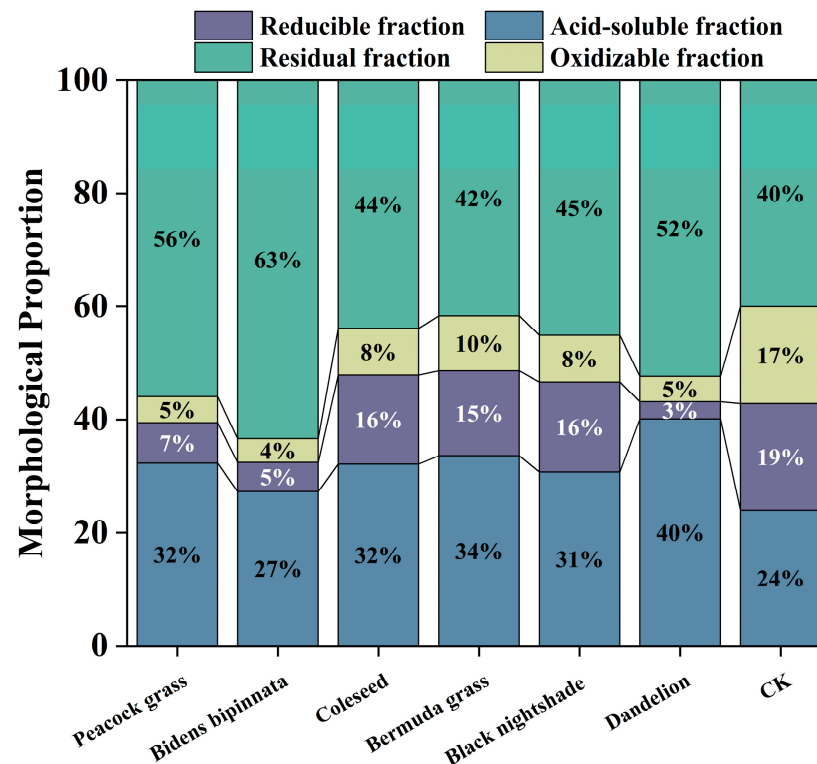


Figure 12. BCR fraction components of Cd in synergistic remediation soil.

3.8. TCLP Toxicity Leaching Experiment

Figure 13 presents the results of the TCLP leaching test for Cd after synergistic remediation with materials and plants. As depicted in Figure 13a, all treatments effectively reduce the migration of Cd, and except for the blank control CK, all values are below the threshold of 1 mg/L set by the US Environmental Protection Agency [42]. When the amount of material added is low, the concentration of Cd decreases with increasing addition, similar to the trend observed in the effective removal rate mentioned earlier. When the material addition reaches 2%, the release of Cd is minimal at 0.229 mg/L, representing an 83% reduction compared to the control group. However, when the material addition exceeds 2%, excessive material may potentially affect plant growth and soil fertility. It could also inhibit the activity and diversity of soil microorganisms, leading to deterioration of the soil ecosystem and a loss of biodiversity, thereby reducing the adsorption of heavy metals by microorganisms and plants and increasing the migration and desorption of heavy metals in the soil. As shown in Figure 13b, Cd toxicity leaching gradually decreases with time, reaching a stable level around 60 days, indicating that the Cd^{2+} adsorbed by the remediation material has reached saturation. Since the remediation material is green and non-polluting, the concentration of TCLP toxicity leaching in the soil changes relatively little over time, indicating that the remediation effect is well-maintained.

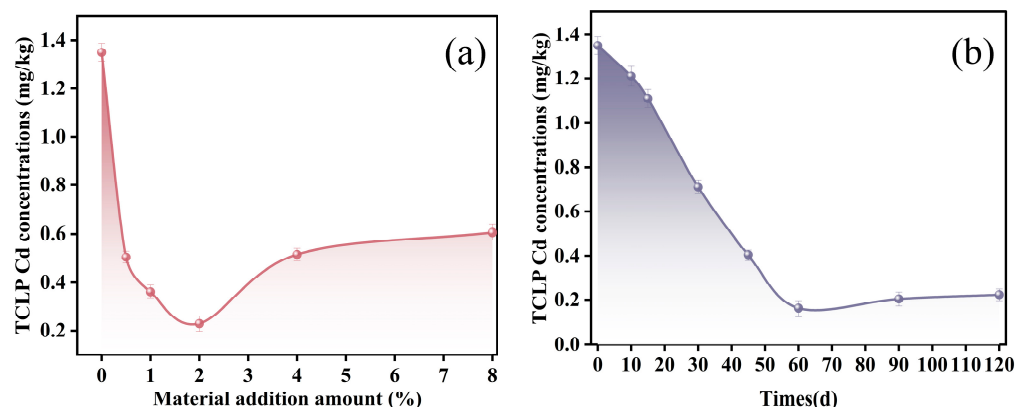


Figure 13. TCLP toxicity leaching amount of Cd in soil after synergistic remediation: the change in toxicity leaching amount with the amount of material added; (a) the change in toxicity leaching amount with time (b).

4. Conclusions

Aiming at the remediation of Cd contaminated soil, a pure natural mineral material (starch-modified montmorillonite) was designed and synthesized and a hyperaccumulator plant (*Bidens bipinnata*) was screened. On this basis, a synergistic remediation technique was developed, and a satisfactory reduction rate of available Cd content in the remediated soil was achieved in pot and field experiments. The detailed mechanisms of the synergistic remediation technique were studied using a series of verification tests. The main conclusions are as follows:

1. Remediation material was synthesized using natural montmorillonite and starch, and the remediation plant was screened from native plants. Hence, this synergistic remediation technique is high in environmental safety. Meanwhile, the reduction rate of the available Cd content in the remediated soil in the pot experiment was able to reach 77.92% and the total Cd concentration in soil in field experiments could be reduced to 0.29 mg/kg. Hence, this synergistic remediation technique is of high efficiency.
2. In this synergistic remediation technique, the synergistic effect is pronounced. Starch-modified montmorillonite significantly enhances the transport capacity of plants for cadmium. On the other hand, beneficial microorganisms were released in the plant growth process, which significantly promoted the solidification effect of starch-modified montmorillonite towards Cd in soil.
3. For cadmium-contaminated soil, this synergistic remediation technique has great application potential.

The findings indicate that, on one hand, the chelating effect of plant root exudates promotes microbial metabolism, enhancing microbial activity and material solidification. On the other hand, the material increases soil pH, promoting plant growth and microbial reproduction, reducing Cd leaching toxicity, and facilitating the conversion of Cd into a residual state. This study demonstrates the remediation potential of the synergistic technique employing an environmentally friendly natural adsorbent material, modified montmorillonite, and the hyperaccumulating plant *Bidens bipinnata*, while elucidating the mechanism underlying material–plant synergistic remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy14061299/s1>, Table S1: Classification standard of heavy metal pollution in soil; Table S2: Extraction order according to BCR method.

Author Contributions: Conceptualization, J.G. and H.X.; methodology, J.G., J.C. and F.Y.; formal analysis, J.G., F.Y. and C.L.; investigation, Q.L., X.M. and F.C.; data curation, F.H. and F.Y.; writing—original draft preparation, J.G. and F.Y.; writing—review and editing, H.X., J.C. and J.G.; supervision,

H.X., X.X. and J.C.; funding acquisition, J.G. and X.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the open project program in Hunan Provincial Key Laboratory of Geochemical Processes and Resource Environmental Effects, Geophysical and Geochemical Survey institute of Hunan (NO.GRE202309G); the Natural Science Foundation of Hunan province (2024JJ7620); the China Geological Survey Programs [DD20230478, ZD20220213]; the Key Research and Development Program of Hunan Province [2023SK2066].

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of 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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