

Article

Enhanced Stabilization of Lead in Soil Using Novel Biochar Composites Under Simulated Accelerated Aging Conditions

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Abstract: Straw biochar (BC) and four innovative biochar environmental materials (AFFA/BC) were synthesized via oxygen-limited pyrolysis at different ratios and applied for the remediation of lead (Pb)-contaminated soils. Accelerated aging, which mimics the effects of natural aging on heavy metal fixation properties, was induced through alternating dry and wet conditions. Two models, which are based on conditional probability-induced failures, were developed to characterize the aging process more effectively. The results indicated that the novel biochar material presented elevated Si, Al, and Na contents, increased specific surface area, pore volume, and yield, and the formation of chemical bonds such as T-O-T and T-O (T = Si or Al). Simultaneously, synchronous and asynchronous spectral analysis methods were used to demonstrate that fly ash leads to the formation of new chemical bonds and protects the functional groups of biochar from the destructive effects of high temperatures. Compared with the original biochar, the application of the new biochar material to Pb-contaminated soil increased the soil pH, cation exchange capacity (CEC), and soil organic matter (SOM) content while reducing toxic Pb leaching, resulting in conversion to a more stable residual state. Throughout wet-and-dry cycles, the Pb leaching concentration from the soil gradually increased, with AFFA/BC-2 resulting in a lower aging rate. This study provides a method for preparing low-cost and green soil amendments, which have great potential for repairing HM-contaminated soil and achieving value-added utilization of coal-based solid waste and agricultural waste.

Keywords: biochar; lead; soil; conditional probability theory



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1. Introduction

The contamination of soils in China by heavy metals (HMs) currently presents one of the major environmental issues, and owing to the high toxicity, persistence, and non-biodegradability of HMs, this issue has garnered significant public attention [1]. In the absence of an effective remediation program, prolonged contamination by HMs can result in substantial soil damage and potential threats to human health [2]. While the total concentration of HMs serves as an indicator of soil contamination, the potential toxicity of HMs is influenced by their toxic leaching concentrations and chemical forms [3]. Among

the various technologies available for remediating HM-contaminated soil, chemical stabilization technology offers advantages such as low cost, minimal labor requirements, and large coverage area. This technology can rapidly diminish the mobility of toxic metals in contaminated soil and protect the ecological environment and agricultural plants from the adverse effects of toxic metals by applying effective remediation materials [4]. Therefore, the key to chemical stabilization technology lies in identifying an environmentally friendly, low-cost soil remediation material.

Biochar (BC), derived from biomass, is a carbon-rich solid product formed by the thermal conversion of biomass raw materials in anaerobic conditions, involving processes like dehydration, aromatization, and aldol condensation [5]. It effectively decreases the mobility and availability of HMs in contaminated soils, thereby reducing HM uptake by crops [6]. The strong passivation of metal ions occurs primarily through surface adsorption, complexation, ion exchange, precipitation, and coprecipitation [7]. However, the remediation efficiency of untreated biochar for HMs is limited, requiring higher application rates to achieve desired outcomes [8]; hence, chemical modification of BC is necessary to enhance its remediation performance and practical effectiveness. The physicochemical properties of BC typically depend on the biomass source and preparation method [9]. Incorporating minerals has been shown to modify the structure, composition, and physicochemical properties of biochar, enhancing HM ion passivation [10]. Additionally, metal oxide fractions can enhance aromatization efficiency during biomass pyrolysis, though few studies have investigated the potential effects of mineral-induced changes in biochar's physicochemical properties on soil HMs.

Fly ash (FA), a typical representative of mineral-derived materials, is a major byproduct of coal-fired power plants, comprising SiO_2 and Al_2O_3 , along with other components such as Fe_2O_3 , CaO , MgO , SO_3 , Na_2O , and other metal oxides [11]. These components can be utilized to synthesize materials like zeolite and alum. As a soil stabilizing material, FA offers advantages over other materials, including low cost, easy availability, soil texture improvement, acidity reduction, and minimal risk of secondary pollution [12]. It has been demonstrated that the copyrolysis of fly ash with biomass can introduce ring structures, rigid groups, or large side groups to biochar, thereby enhancing its thermal stability [13]. Due to the limited adsorption capacity of raw FA for HMs in soil, FA requires modification to enhance the activity of its main components and improve its adsorption and immobilization capacity for HMs. For instance, the addition of sodium hydroxide to molten FA stimulates the activity of components such as SiO_2 and Al_2O_3 [14]. Copyrolysis of alkali-fused fly ash (AFFA) and biochar for the preparation of novel biochar materials not only enhances FA's ability to passivate HMs in soil but also improves biochar's adsorption efficiency [15]. This approach enables the resourceful utilization of FA and reduces the cost of soil treatment for HMs. Soil remediation materials undergo natural processes post-application, leading to changes in soil fertility, contaminant fixation, and carbon storage. These changes are influenced by soil type, remediation techniques, local climate, natural rainfall events, temperature fluctuations, ultraviolet irradiation, and microbial colonization, all of which contribute to the post-application aging process [16]. Most studies to date have focused on relatively short timeframes. However, over prolonged remediation periods, soil remediation materials undergo aging processes after application, leading to changes in soil physicochemical properties and the chemical morphology of heavy metals, affecting their leaching toxicity [17]. These aging processes are influenced by various factors, including soil type, remediation techniques, local climate conditions, natural rainfall events, temperature fluctuations, ultraviolet irradiation, and microbial colonization. After stabilizing and remediating the HM-contaminated soil, the main aging factors are selected according to the environmental conditions at the remediation site. For

instance, in areas with abundant rainfall, alternating wet and dry methods can be used to simulate changes in the toxicity of heavy metal leaching to stabilize and repair [18]. Two conditional probability-based models have been established to elucidate the gap between biochar materials and uncover their aging characteristics.

The study aimed to (1) compare the physicochemical properties of newly developed biochar materials derived from copyrolysis of alkali-molten fly ash and biomass at varying straw-to-ash ratios, (2) assess alterations in leaching toxicity and morphology of the biochar materials concerning heavy metal Pb in soil, (3) analyze the impact of wet and dry alternation on the stabilization of HMs in biochar-treated soils, and (4) employ two conditional probability-based models to delineate different soil amendments and unveil their aging traits. These findings will provide suitable stabilizing materials for the remediation of lead-contaminated soil and offer a theoretical basis for the application of biochar in the long-term remediation of heavy metal-contaminated soil.

2. Materials and Methods

This study investigated the effectiveness of alkali-fused fly ash biochar (AFFA/BC) in stabilizing lead (Pb) in contaminated soil through a series of laboratory experiments. The study consisted of three main steps: (1) Synthesis of biochar materials—preparing AFFA/BC composites via copyrolysis of corn stover and alkali-fused fly ash; (2) Soil treatment and incubation—applying the biochar materials to Pb-contaminated soil and allowing stabilization over a controlled period; and (3) Aging simulation and evaluation—subjecting the treated soil to wet–dry cycling to assess long-term stabilization performance. Key parameters such as soil pH, cation exchange capacity (CEC), and Pb leaching toxicity were analyzed to evaluate the remediation efficiency and aging resistance of AFFA/BC.

2.1. Experimental Reagents and Soil Samples

The primary reagents utilized in this study comprised sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$), sulfuric acid (H_2SO_4), hex ammonium cobalt chloride ($H_{18}ClCoN_6$), hydrogen peroxide (H_2O_2), and hydroxylamine hydrochloride (H_3NOHCl), all of which were of analytical purity. Additionally, nitric acid (HNO_3), perchloric acid ($HClO_4$), hydrofluoric acid (HF), and acetic acid ($C_2H_4O_2$) were of high-grade purity. Fly ash was obtained from a coal-fired power plant in Shanxi Province, China. After drying in an 85 °C oven, the sample was sieved through an 18-mesh sieve and stored in a sealed self-sealing bag at room temperature. Corn straw biomass was harvested from the cover soil of a coal gangue yard in Changzhi, Shanxi. The fly ash required for the experiment was sourced from a coal-fired power plant in Shanxi Province, China. Both samples were air-dried, crushed through an 18-mesh sieve, dried in an 85 °C oven, and then stored in self-sealing bags for future use. Deionized water was used throughout the experiment.

The soil utilized in this study was gathered from a lead–zinc mine in Inner Mongolia. The 0–20 cm surface soil was air-dried, then crushed and sieved through a 2 mm mesh to remove stones and visible debris before use. The fundamental physical and chemical properties of the soil were determined prior to the experiment, as outlined in Table 1. According to the Soil Pollution Risk Control Standards for Agricultural Land, the Pb content in the soil exceeded the risk screening value by approximately 1.19 times.

Table 1. The physical and chemical parameters of the soil used in the experiment.

Parameter	Soil
pH	7.03
CEC ($\text{cmol}^+ \text{kg}^{-1}$)	9.17
moisture content (%)	7.31
Soil bulk density (g cm^{-3})	1.39
SOM (g kg^{-1})	2.13
The total of Pb (mg kg^{-1})	263

2.2. Preparation of Biochar Materials

2.2.1. Preparation of the AFFA

Ten grams of pretreated fly ash and 15 g of sodium hydroxide were weighed at a 1:1.5 mass ratio, grounded, and evenly mixed in an agate mortar. The mixture was then placed in a 50 mL nickel crucible and baked for 2 h in a box-type resistance furnace at 350 °C. Upon completion of calcination, the product was removed and allowed to cool to room temperature. Subsequently, the sample was ground into a powder using an agate mortar and sieved through an 18-mesh sieve to obtain alkali-melted fly ash, designated as AFFA.

2.2.2. Preparation of Biochar Composites

A specific quantity of AFFA and BM was weighed according to the mass ratio of different stovers to alkali-melted fly ash, and a blank control group was established. To ensure thorough mixing of alkali-melted fly ash with biomass, a small volume of deionized water was added to the mixture. After stirring for 2 h on a magnetic stirrer, the sample was dried and ground in an 85 °C blast drying oven. Subsequently passing through a 35-mesh sieve, it was spread flat in a nickel boat and placed in a box-type resistance furnace with continuous nitrogen gas flow. Pyrolysis was conducted as per Table S1. The heating rate of the box-type resistance furnace was set to 10 °C·min^{−1}, with the final temperature reaching 500 °C for pyrolysis for 2 h. Throughout this duration, nitrogen gas was continuously introduced, and the furnace was subsequently cooled under a nitrogen gas flow before removing the nitrogen. The resulting product was ground through a 60-mesh sieve and transferred to a plastic bag for storage, resulting in four types of biochar materials.

2.2.3. Simulation of Natural Aging Processes

Following 12 days of soil stabilization and remediation, the stability of Pb in the treated soil was assessed through accelerated aging via wet–dry alternation. Wet–dry alternation involved adding deionized water to achieve a moisture content of 55%, ensuring soil saturation with excess moisture. After 12 h of incubation in darkness, the container underwent drying in a 40 °C oven for 12 h. Subsequently, deionized water was added again to restore the initial moisture content. The experiment included 2, 4, 6, 8, 10, and 12 cycles of wet–dry alternation for all treated soils. After the respective number of cycles, the soil was naturally air-dried, and an appropriate soil sample was extracted and ground through a 2 mm sieve. The sample was then stored in a sample bag and refrigerated for future use. Analytical tests included pH, cation exchange capacity, and soil organic matter content analysis. The leaching toxicity of the samples was evaluated using the “Identification Standard for Hazardous Waste Leaching Toxicity Identification”. The three-step BCR extraction method was employed to extract various forms of HMs for analysis, with ICP-MS used to analyze HM content in the filtrate.

2.2.4. Aging Method Establishment

The performance of materials during accelerated aging can be described by the fixed rate $IR(t)$:

$$IR(t) = \frac{c_n - c_t}{c_n} \times 100\% \quad (1)$$

In the formula, c_n represents the concentration of unmodified Pb leachate ($\mu\text{g L}^{-1}$), and c_t represents the concentration of leachate after adding biochar material for t years ($\mu\text{g L}^{-1}$).

To better describe the aging characteristics of BC and AFFA/BC, all IR values were normalized to the reliability value $R(t)$:

$$R(t) = \frac{IR(t)}{IR(t_0)} \quad (2)$$

In the formula, $IR(t)$ and $IR(t_0)$ represent the immobilization rates in year t and year 0, respectively.

To depict the aging characteristics, two models were formulated based on different aging rate assumptions [19]. Both models presuppose that (1) the acceleration of wet–dry alternation results in the disruption of porous structures, a reduction in the mineral content of coprecipitation, and an elevation in dissolved organic matter content, thereby facilitating the migration of HMs in the soil. (2) The interaction between HMs and soil materials can be simplified as the binding of Pb at the “active fixation point” of the material. (3) In the initial stage of non-aging, all binding points are valid with a reliability of 1. As aging progresses, the reliability of the fixation effectiveness of biochar materials tends to diminish, approaching zero after an extended period. Assuming that the fixed HMs of biochar material operate well at time t but at time $t + \Delta$ are invalid after t , the aging process can be described as a conditional probability:

$$\text{Aging rate} = \lim_{\Delta t \rightarrow 0} \frac{P((t \leq T \leq t + \Delta t) | T > t)}{\Delta t} \quad (3)$$

The random variable T in the equation represents a fixed effective time.

Model 1—The aging rate a_0 (year^{−1}) of the soil amendments remains constant:

$$\lim_{\Delta t \rightarrow 0} \frac{P((t \leq T \leq t + \Delta t) | T > t)}{\Delta t} = a_0 \quad (4)$$

In this case, the cumulative distribution function (CDF) and reliability can be expressed as:

$$CDF = P(T \leq t) = 1 - e^{-a_0 t} \quad (5)$$

$$R(t) = \frac{IR(t)}{IR(t_0)} = P(T > t) = 1 - CDF = e^{-a_0 t} \quad (6)$$

Model 2—The aging rate of the soil amendments increases with time:

$$\lim_{\Delta t \rightarrow 0} \frac{P((t \leq T \leq t + \Delta t) | T > t)}{\Delta t} = at^b \quad (7)$$

In the formula, $b > 0$ (a : year^{− b −1}, b : dimensionless) indicates an increase in the aging rate.

The cumulative distribution function (CDF) and reliability can be expressed as:

$$CDF = P(T \leq t) = 1 - e^{-\frac{a}{b+1} t^{b+1}} \quad (8)$$

$$(t) = \frac{IR(t)}{IR(t_0)} = P(T > t) = 1 - CDF = e^{-\frac{a}{b+1}t^{b+1}} \quad (9)$$

For simplification and comparison, new parameters $a'_0 = \frac{a}{b+1}$ (year^{-b-1}) and $b'_0 = b + 1$ ($b'_0 > 1$, dimensionless) are adopted.

$$CDF = P(T \leq t) = 1 - e^{-a'_0 t^{b'_0}} \quad (10)$$

$$(t) = \frac{IR(t)}{IR(t_0)} = P(T > t) = 1 - CDF = e^{-a'_0 t^{b'_0}} \quad (11)$$

2.3. Characterization and Analysis Methods

This study employed the potentiometric method (HJ962-2018) to determine soil pH and referenced the cobalt hexachloride leaching spectrophotometric method (HJ889-2017) for assessing soil cation exchange capacity (CEC), as well as the potassium dichromate oxidation spectrophotometric method (HJ615 2011), for measuring soil organic matter (SOM).

Various methods were used to reveal the physicochemical properties of soil amendments and test the effectiveness of FA doping. Surface morphologies and elemental compositions were analyzed with a Japanese Rigaku Ultima IV X-ray diffractometer. Specific surface areas and porous structures were determined using N2 adsorption–desorption at 77 K (ASAP2460, McMurdoch, Micromeritics Instrument Corporation, Norcross, GA, USA). Functional groups of the amendments were examined with FTIR (TSN iS5, Thermo Fisher, Waltham, MA, USA) (resolution 4 cm⁻¹, wavenumber ranging from 4000 cm⁻¹ to 400 cm⁻¹). The mechanisms of long-term metalloid immobilization were also explored with XRD under the same 2θ range and scanning speed (Japanese Ultima IV X-ray diffractometer, Rigaku Corporation, Tokyo, Japan).

2.4. Two-Dimensional FTIR Correlation Spectroscopy (2D-FTIR-COS)

2DCOS was a technique used to analyze simultaneous or sequential changes in spectral signals by observing peak changes in the spectrum. Noda's rule states that if the peak or zone signals in the generalized synchronous or asynchronous mapping are identical, the spectrum change at variable v1 occurs before the change at variable v2. Conversely, if the signs are different, the order of changes is reversed. When the synchronization signal is zero, the sequence order becomes uncertain. FTIR data were first normalized, and then the 2D-FTIR-COS spectra were plotted using the 2D Correlation Analysis plugin (Originlab Corporation, Northampton County, PA, USA) in OriginPro 2018.

2.5. Statistical Analysis

All experiments were conducted in triplicates, with standard errors presented as error bars in the Figures. One-way analysis of variance was used to test the differences among each group using the Fisher LSD test (significant level 0.05). Modeling and plotting were conducted with OriginPro 2018. XRD analysis was conducted with the Jade 6 software.

3. Results and Discussion

3.1. Characteristics of the Biochar Composites

3.1.1. Characteristics of AFFA

SEM analyses were conducted on both virgin fly ash (FA) and alkali-fused fly ash (AFFA), with specific findings depicted in Figure S1. FA appeared as a gray powder, while AFFA exhibited a lighter color after alkali-fused roasting, presenting as an off-white powder. The observations revealed that FA possessed a loose structure predominantly comprising relatively uniform glassy spherical particles with smooth surfaces, varying

in size, with small powder particles adhering to their surfaces. Additionally, elongated and sharp edges, along with large gaps between the glass beads, were evident. Upon modification with NaOH, the glassy phase structure within the coal dust was disrupted, leading to the surface being adorned with numerous fine particles characterized by rough surfaces. Furthermore, irregularity, multichannel, and mesh structures were augmented, accompanied by an increase in specific surface area. These rough, cavity-like surfaces facilitated a larger surface area compared to that of FA.

The BET results of FA and AFFA revealed an increase in the specific surface area of modified FA from $7.08 \text{ m}^2 \text{ g}^{-1}$ to $23.47 \text{ m}^2 \text{ g}^{-1}$, indicating an augmentation in FA's specific surface area due to water evaporation during the roasting process. Pore size distributions of FA and AFFA depicted in Figure S2a–c illustrated that FA's pore size was primarily distributed between 1.5 and 25 nm, with a minor presence of micropores, whereas AFFA exhibited a similar pore size distribution, with main pores ranging from 1.6–25 nm. This suggests that high-temperature roasting led to the collapse of the internal large pore structure, albeit with the formation of a small quantity of mesopores on the surface. Notably, the pore volume content of AFFA surpassed that of FA significantly. Generally, adsorbent samples possessing a high pore structure exhibit elevated specific surface area, ion exchange performance, and superior adsorption capacity [20].

Based on the FTIR spectra, the two materials exhibit distinct peak characteristics, with both similarities and differences in their functional group assignments. Unlike FA, AFFA exhibited a robust and broad peak around 3510 cm^{-1} , attributed to the stretching vibration and antisymmetric superposition of the -OH group, primarily due to the addition of -OH to FA's surface via NaOH modification [21]. Additionally, the bending vibration of H-O-H was identified in AFFA at 1662 cm^{-1} . This likely resulted from the modification process, during which roasting caused the loss of bound and surface water in the structural skeleton. As a result, the adsorption resistance of the original water film was reduced, facilitating the diffusion of adsorbate molecules. This, in turn, enhanced the adsorption capacity of FA. [22]. The peak near 459 cm^{-1} represented the T-O (T = Al/Si) bending vibration, with the asymmetric stretching vibration peaks of T-O on FA shifted towards 459 cm^{-1} and 462 cm^{-1} . Moreover, the peak attributed to the asymmetric stretching vibration of O-T-O on FA shifted from 1102 cm^{-1} to 989 cm^{-1} , while the peak at 699.19 cm^{-1} denoted the symmetric stretching vibration of O-T-O, signifying successful modification of FA by NaOH. Thus, the reaction between SiO_2 , Al_2O_3 , and Fe_2O_3 from FA with NaOH during low-temperature alkali modification reduced the SiO_2 and Al_2O_3 polymerization of FA, leading to gradual breakage of Si-O and Al-O bonds during the modification process, releasing Si and Al [23].

The XRD patterns of FA and AFFA are displayed in Figure 1b. Mullite ($\text{Al}_6\text{SiO}_{13}$) and quartz (SiO_2) constitute the primary crystal phases of FA. Subsequent to modification with NaOH, the surface of AFFA is characterized by the presence of sodium salt ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$), sodium silicate (Na_2SiO_3), and thermal sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). Prominent packet peaks at 24 and 34° indicate the amorphous state of Si. Similarly, the large peak at 34° denotes the amorphous state of Si, while the peaks of quartz and mullite essentially diminish, suggesting a gradual disruption of the ordered glassy phase structure of FA mullite and quartz during the modification process. This leads to the dissolution of active groups in FA and the transformation of crystalline substances into amorphous substances, as NaOH activates stabilized substances such as SiO_2 and Al_2O_3 to form amorphous Si-O and Al-O. Additionally, the introduction of alkali metals induces the replacement and depolymerization of network aggregates [24]. Furthermore, under the influence of alkali flux, alkali can interact with silica–alumina oxides to release amorphous SiO_2 and Al_2O_3 [25], thereby increasing the number of available adsorption

sites, which promotes enhanced fly ash activity and subsequently improves the adsorption performance and remediation capacity of the soil. In summary, alkali modification significantly increases the specific surface area and pore volume of fly ashes, enhancing their adsorption capacity and chemical activity for heavy metal ions. In addition, the new chemical bonds generated during the modification process improve their interaction with pollutants, enhancing the effectiveness and persistence of fly ashes in soil remediation. The modified fly ashes also exhibit better aging resistance, which helps maintain their remediation effect under environmental changes.

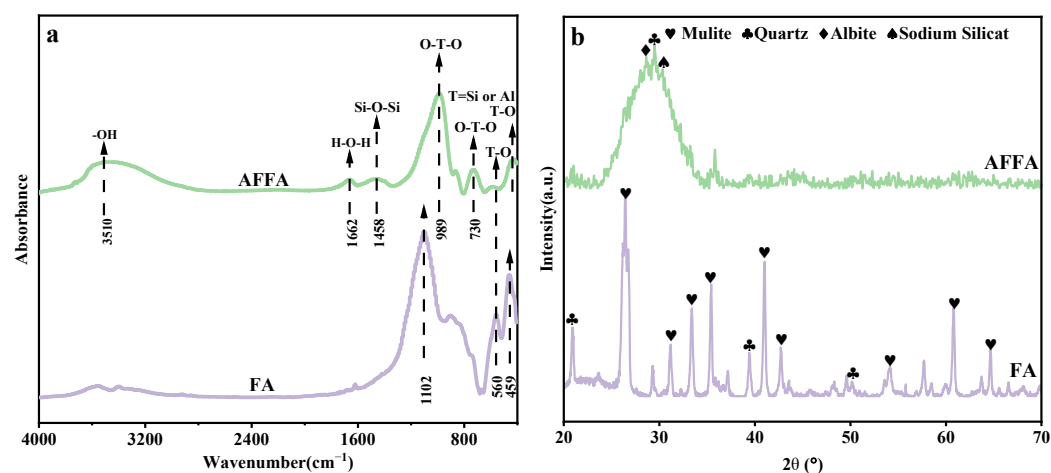


Figure 1. (a) Fourier transform infrared spectroscopy (FTIR) characterization of FA and AFFA. (b) X-ray diffraction patterns of FA and AFFA.

3.1.2. Characteristics of AFFA/BC

The fundamental parameters of raw biochar (BC) and biochar material (AFFA/BC) are presented in Table 2. The yields of AFFA/BC exceed those of BC, ranging from 22.41 to 39.77%, with a greater straw-to-ash ratio (BM:AFFA) resulting in higher yields due to the presence of cationic Na⁺ in AFFA/BC and chemical bonds like Al-O and Si-O, introduced during copyrolysis. Additionally, Na⁺ and O that were introduced during copyrolysis form new stabilizing chemical bonds, such as C-Si and C-Al, augmenting the specific gravity of the prepared biochar material [26]. The pH is influenced by metal oxide composition, such as calcium oxide and magnesium oxide, and the content of alkaline minerals like calcite and dolomite in AFFA/BC, resulting in a pH increase above 7.

Table 2. Basic characteristic parameters of BC and AFFA-BC.

Adsorbents	Yield (%)	pH	SBET (m ² g ⁻¹)	Vtotal (cm ³ g ⁻¹)	Dap (nm)
BC	22.42	10.17	25.50	0.0156	2.432
AFFA/BC-1	24.31	9.79	6.33	0.0076	4.806
AFFA/BC-2	26.89	9.76	50.60	0.0315	2.491
AFFA/BC-3	34.81	9.24	42.22	0.0384	3.635
AFFA/BC-4	39.77	9.46	8.23	0.0482	23.371

The varying amounts of fly ash added exhibit different effects on the modification of biochar, with the specific surface area of AFFA/BC-2 reaching 50.60 m² g⁻¹. However, the specific surface areas of AFFA/BC-1 and AFFA/BC-4 in this study are relatively small compared to pristine biochar, likely due to pore clogging or collapse induced by the modified materials [27]. AFFA/BC-2 and AFFA/BC-3 increased by 614.4% and 496.1% compared to alkali-fused fly ash, respectively, with the high specific surface area and

porosity favoring adsorption, as confirmed in prior studies [28,29]. Nevertheless, when the BM:AFFA ratio reached 10:5, the specific surface area started to decline, suggesting that the proportion of modified materials should be carefully considered when preparing fly ash composites with large specific surface areas and pore volumes, as excessive AFFAs may lead to pore clogging or collapse. Overall, these findings suggest that the modified biochar material exhibits greater adsorption capacity compared to both alkali-fused fly ash and unmodified biochar.

The SEM images of BC and AFFA/BC (Figures 2 and S3) reveal distinct characteristics. BC exhibits a porous structure with smooth surfaces and clear channels. In contrast, AFFA/BC displays rough surfaces, the presence of fine mineral particles, and significant pore clogging and disruption, where minerals adhere directly to the pores, leading to pore blockage. Considering the XRD spectra of AFFA (Figure S1), this observation is hypothesized to be related to the aluminum silicates present in AFFA.

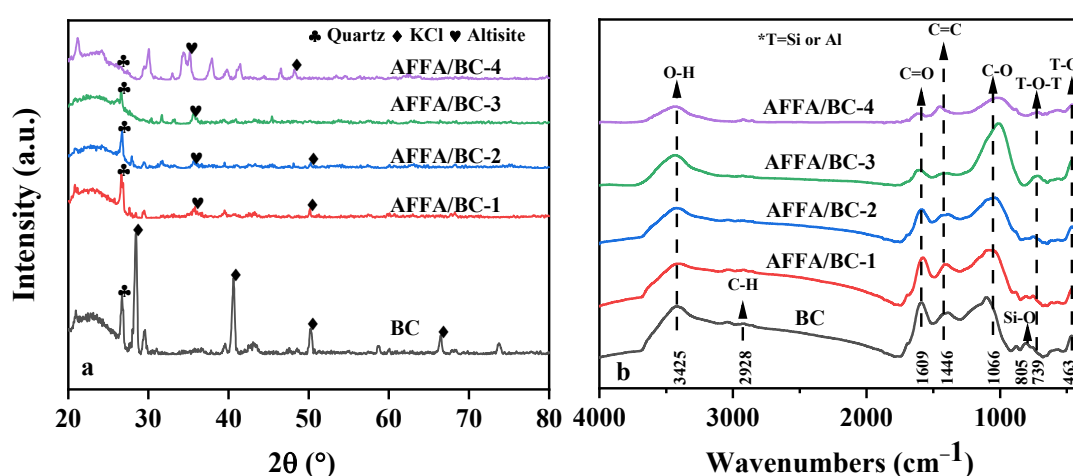


Figure 2. (a) XRD patterns for BC and AFFA/BC. (b) Fourier transform infrared spectroscopy (FTIR) characterization of BC and AFFA/BC, * stands for the Si and Al elements.

The interaction between C and Si was quantitatively assessed by analyzing the elemental content and the amount of C and Si in all biochar materials using EDS spectra combined with elemental mapping. The EDS results indicate that the content of C surpasses that of Si on the BC surface, indicating that the BC surface is dominated by carbon. Additionally, inorganic mineral elements like Si, Al, Na, and Mg, often involved in ion exchange and precipitation reactions of pollutants, were detected on the surface of a small portion of biochar. This suggests that the primary constituent elements of AFFAs were effectively integrated into the biochar material, thereby enhancing the ion exchange performance of AFFA/BC for HMs in soil.

Figure 2a displays the XRD pattern of BC. The surface of the BC material primarily comprises quartzite and potassium chloride. The presence of KCl indicates the pyrolytic decomposition of typical cellulose fractions associated with corn stover, and the transformation of intrinsic K elements in the original fly ash into KCl components is evident at 2θ values of 28, 41, 50, and 62. Quartz is reflected at 2θ of 27.

The surface of the AFFA/BC reveals the presence of quartz, calcite, and sodium feldspar ($\text{Na}(\text{AlSi}_3\text{O}_8)$), along with complex salts of silica and alumina ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and calcium and magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$). This suggests that pyrolysis facilitates the binding of elemental silica, aluminum, calcium, magnesium, and iron. It implies that the components of AFFA were effectively incorporated onto the biochar surface, potentially offering active sites for binding with Pb and As ions.

The surface functional groups of BC with four copyrolyzed biochar materials were identified by FTIR spectroscopy, and the results are shown in Figure 2b. Compared with those of BC, functional groups or chemical bonds such as T-O and T-O-T (T = Si/Al) at 739 cm^{-1} and 463 cm^{-1} newly appeared on the surface of AFFA/BC, respectively. This phenomenon proved that the reactive SiO_2 or Al_2O_3 components of AFFA were successfully loaded onto the surface of the copyrolyzed biochar, enhancing the potential adsorption capacity of the modified biochar material, which could be adsorbed by the interactions of the π -bonds between the T-O-T and the HMs [29]. As the proportion of AFFA increases, the T-O-T peak becomes more pronounced, and the T-O-T bonds are enhanced by the AFFA modification, protecting the functional groups of the biochar from the destructive effects of high temperatures. The protection and enhancement of functional groups by modification can account for the high adsorption capacity of AFFA/BC, and modification of AFFA can generate more adsorption sites and increase the number of aromatic functional groups or chemical bonding structures. Biochar materials produced through copyrolysis can adsorb HMs through the precipitation and complexation of functional groups and chemical bonds such as alcohol/phenol-OH, T-O, and O-T-O (T = Si/Al), thereby improving the potential adsorption capacity of biochar materials [15].

The chemical structure of the biochar material underwent significant changes after pyrolysis treatment. Specifically, the broad peak at approximately 3425 cm^{-1} was primarily generated by the -OH expansion vibration of intermolecular hydrogen bonding, which was significantly weakened by pyrolysis with the addition of AFFA, indicating that the hydroxyl groups in cellulose are easily decomposed at high temperatures. The aliphatic C-H expansion vibration of the BC meso-biomass near 2928 cm^{-1} was almost completely decomposed after pyrolysis, and the disappearance of the peaks indicated that the cellulose and hemicellulose fractions underwent $-\text{CH}_3$ and $-\text{CH}_2$ fracture [30]. With the addition of fly ash, some of the aliphatic C-H in AFFA/BC was preserved, proving that fly ash could protect the functional groups of biochar from high temperatures. In contrast, the wavenumbers 1609 cm^{-1} , 1446 cm^{-1} , and 1066 cm^{-1} represent the expansion and contraction vibrations of C=O, aromatic C=C, and aliphatic C-O caused by the vibration of the aromatic ring skeleton of lignin, respectively. The preservation of the vibration of the aromatic ring skeleton of lignin is better among the five kinds of biochar materials, indicating that lignin has greater thermal stability than the cellulosic component in the pyrolysis process [31].

In summary, the characterization analysis results show that AFFA-BC has significant advantages over BC. Specifically, the specific surface area and pore volume of AFFA-BC significantly increase, which gives it a stronger ability to adsorb heavy metal ions. In addition, AFFA-BC's chemical structure has also been improved, with new chemical bonds formed on the surface, enhancing its interaction with pollutants. These characteristics enable AFFA-BC to exhibit superior performance in soil remediation, effectively immobilizing and stabilizing heavy metals and improving soil environmental safety.

3.1.3. Reaction Order of Functional Groups in BM with Different AFFA Additions

The reaction sequence of the complexation sites is elucidated by analyzing synchronous and asynchronous spectra and evaluating the positive and negative cross peaks, as shown in Figure 3 and Table S2. A comparative analysis of the infrared characterization results presented in Figure 2 was conducted, focusing on the identification and evaluation of 21 cross peaks. A comparison of Figure 3a,b shows that the synchronous and asynchronous spectral features of these cross-peaks are reversed, indicating that the changes at specific complexation sites on the y-axis occur prior to those on the x-axis, which aligns with Noda's rule. Therefore, it was determined that when the ratio of BM ash-to-fly ash is

10:1, the reaction sequence of fly ash at the biomass binding sites is as follows: aliphatic C-H $\rightarrow$ T-O $\rightarrow$ aliphatic C-O $\rightarrow$ aromatic C=C $\rightarrow$ -OH $\rightarrow$ C=O $\rightarrow$ T-O-T (Table S2). For the composite site identification at a ratio of 5:1, the cross peaks are shown in Figure 3c. The changes in the values of the cross-peaks observed in the synchronous and asynchronous spectra indicate that the reaction sequence at the complexation sites is as follows: T-O $\rightarrow$ aliphatic C-O $\rightarrow$ T-O-T $\rightarrow$ -OH $\rightarrow$ aliphatic C-H $\rightarrow$ aromatic C=C $\rightarrow$ C=O (Table S2). For the composite site identification at a ratio of 2:1, the cross peaks show that the π bond between T-O, T-O-T, and biomass have the same sign, and the specific reaction sequence at the complexation sites is as follows: T-O $\rightarrow$ T-O-T $\rightarrow$ aliphatic C-O $\rightarrow$ -OH $\rightarrow$ C=O $\rightarrow$ aliphatic C-H $\rightarrow$ aromatic C=C (Table S2). For the composite site identification at a ratio of 1:1, three cross peaks, (3425 cm^{-1} , 1446 cm^{-1}), (2928 cm^{-1} , 1446 cm^{-1}), and (1609 cm^{-1} , 1446 cm^{-1}), display positive values in both the synchronous and asynchronous spectra (Figure 3g,h), while the other cross peaks show the same patterns as those at the 5:1 ratio. The reaction sequence is as follows: T-O $\rightarrow$ T-O-T $\rightarrow$ aliphatic C-O $\rightarrow$ aromatic C=C $\rightarrow$ -OH $\rightarrow$ C=O $\rightarrow$ aliphatic C-H (Table S2). With the addition of fly ash, new functional groups or chemical bonds such as T-O and T-O-T (T = Si/Al) emerged on the surface of biochar materials. Moreover, as the fly ash content increases, the reaction sequence of T-O and T-O-T functional groups becomes more advanced, indicating that AFFA modification can enhance the T-O-T bond and also protect the functional groups of biochar from the destructive effects of high temperatures [15].

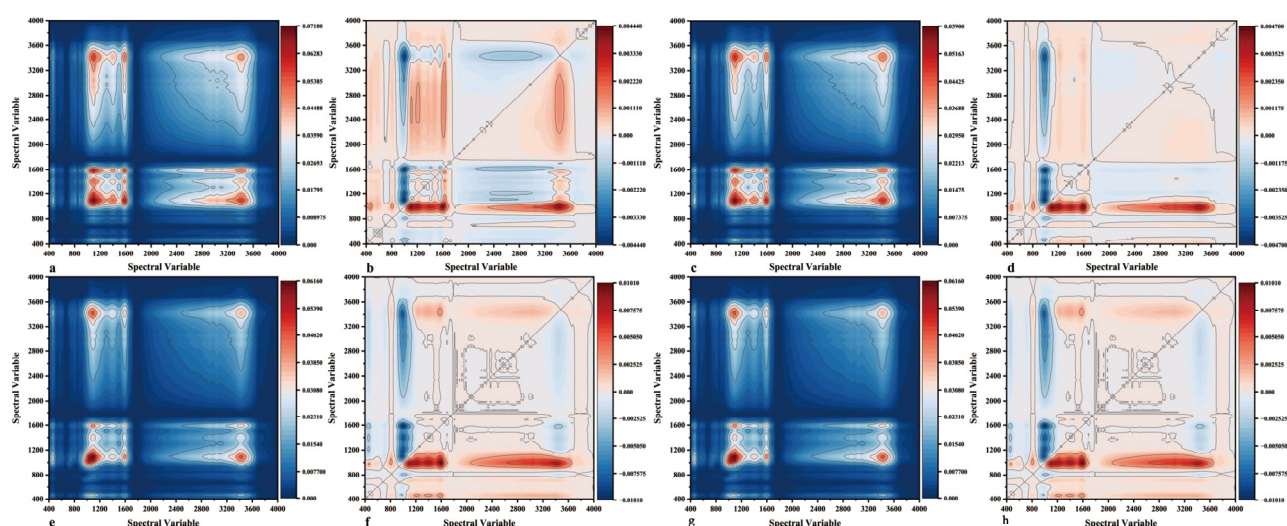


Figure 3. Synchronous (left) and asynchronous (right) maps generated from the FTIR spectra for AFFA/BC (a,b): AFFA/BC-1; (c,d): AFFA/BC-2, (e,f): AFFA/BC-3, (g,h): AFFA/BC-4.

3.2. Long-Term Stability of Biochar Conditions on Heavy Metals in Soil

3.2.1. Changes in Soil Physicochemical Properties

Changes in soil pH can alter the charge of soil colloids and the solubility of HMs in the soil, thus influencing the storage, migration, and transformation patterns of HMs [32]. The effects of different BC and AFFA/BC treatments on soil pH during stabilization are presented in Table 3. The results indicate that the addition of BC and AFFA/BC led to an increase in soil pH, with a higher percentage of fly ash in AFFA/BC resulting in a greater increase in soil pH after application. It has been observed that an elevation in soil pH facilitates the transformation of HMs into more stable components, thereby stabilizing them. With an increase in the number of wet/dry cycles, the pH of the soil fluctuates but remains relatively stable overall. Generally, wet/dry cycles elevate soil pH, and the pH of stabilized soil shows relative stability with an increasing number of wet/dry cycles.

Table 3. Soil SOM, CEC, and pH contents under different treatments after 12 cycles of stabilization.

Cycles	Materials	SOM (g kg ⁻¹)	CEC (cmol ⁺ kg ⁻¹)	pH
Dry wet cycles	CK	2.08	8.54	7.64–8.02
	BC	5.97	9.05	7.88–8.02
	AFFA/BC-1	6.24	10.3	8.38–8.51
	AFFA/BC-2	4.87	9.8	8.62–8.76
	AFFA/BC-3	4.86	9.0	9.21–9.33
	AFFA/BC-4	4.39	9.2	9.68–9.79

The effects of different treatments on changes in SOM after soil incubation are also depicted in Table 3. Following 12 rounds of stabilization involving dry–wet cycles, the SOM content tended to increase with the addition of various doses of BC and AFFA/BC to the contaminated soil. After the 12 rounds of wet and dry cycle stabilization, the SOM value of the soil with BC was 5.97, marking a 187.0% increase compared to that of the CK, while the SOM values of the soil with AFFA/BC were 6.24, 4.87, 4.86, and 4.39, with increases of 200.0%, 134.1%, 133.7%, and 111.1%, respectively, compared to those of the CK. The most substantial increase in soil SOM induced by the biochar material was observed in the AFFA/BC-1 treatment, attributed to its higher proportion of biochar, which had a more significant impact on the SOM content of the contaminated soil. This aligns with previous findings where researchers modified biochar with 2% iron-containing compounds, resulting in an increase in soil SOM by a maximum of 17.98%. Additionally, Jiang et al. demonstrated that the addition of fresh biochar to soil effectively sequestered carbon, increasing soil SOM, an effect that persisted even after biochar aging, albeit at a slower rate than fresh biochar [33]. Biochar's high carbon content enables it to augment total soil organic carbon (SOC), while its highly aromatic and carboxylic esterified structure aids in further immobilizing SOC, reducing its susceptibility to decomposition in the soil [34]. Conversely, the formation of mineral–organic assemblages plays a crucial role in controlling the protection and stabilization of SOM. Biochar facilitates mineral–organic interactions through adsorption and ligand exchange, thereby enhancing soil SOM. Additionally, biochar can adsorb organic molecules in the soil onto its surface, potentially leading to their polymerization to form SOM [35]. Changes in soil SOM can indirectly influence the stabilization of HMs. Increased soluble organic matter (DOM) in the soil may weaken the stabilization effect of heavy metals as DOM binds with heavy metal ions, forming more reactive and mobile complexes, thereby increasing their bioefficacy. However, the stabilization effect of heavy metal ions can be enhanced when they are adsorbed and immobilized on the surfaces of clay minerals or solid-phase macromolecules of organic matter in the soil [36]. In summary, biochar can elevate soil SOM levels while contributing to the stabilization of heavy metal ions.

The effects of different treatments on soil CEC changes after soil incubation are presented in Table 3. After 12 rounds of alternating wet and dry stabilization, various additions of BC and AFFA/BC to the contaminated soil led to varying increases in CEC. After 12 rounds of cycling, the soil CEC value in the BC-amended soil was 9.05, reflecting a 7.1% increase compared to that of the CK. In contrast, the soil CEC values in the AFFA/BC-amended soil were 10.3, 9.8, 9.0, and 9.2, representing increases of 21.9%, 14.8%, 5.4%, and 7.7%, respectively, relative to those of the CK. The order of CEC increase was AFFA/BC > BC, suggesting that AFFA/BC had a more pronounced effect on the CEC of contaminated soil than BC. Cui et al. observed that the addition of corn stover biochar to soil incubated for 156 days significantly increased soil CEC, with increases of 87%, 120%, and 142% observed when 20, 40, and 60 g kg⁻¹ were added, respectively, aligning with the findings of this paper [37]. The rise in soil CEC primarily stems from the gradual oxidation

of biochar, the oxidation of some surface functional groups to form organic–inorganic composite minerals, and the augmentation of cation attachment sites on the surface of soil colloidal particles, leading to enhanced soil CEC and, consequently, improving the stabilization of cationic heavy metals. Furthermore, the high negative charge and expansive specific surface area of biochar can stimulate cation exchange activity, amplifying soil CEC and intensifying the adsorption of cationic heavy metals in the soil [38].

3.2.2. The Leaching Concentration of Heavy Metals and the Aging Characteristics of Biochar Materials

The toxic leaching concentrations of Pb increased in soils stabilized with the five biochar species under alternating wet and dry conditions. However, the rate of increase in the toxic leaching concentrations of Pb was relatively high in the early stages of wet and dry alternation and gradually decreased to zero as the cycle progressed. The study demonstrated that wet and dry alternation had a significant effect on the migration and leaching concentration of HMs in soil [39,40]. Lu et al. illustrated that wet–dry alternation has the potential to facilitate the release and migration of HMs from slag particles. Li et al. implemented wet–dry alternation on Pb-contaminated soils after silicate-curing treatment and observed that wet–dry alternation expedited the leaching of Pb from treated soils [39]. Han et al. performed wet and dry treatments on Cd-contaminated agricultural soils and reported that alternating wet and dry conditions promoted Cd release [41].

Comparing the remediation effect of the various materials on Pb after 12 rounds of wet and dry alternation, the new biochar materials fixed more HMs than the original biochar, among which AFFA/BC-2 was the best for the remediation of Pb in soil, and the leaching concentration of Pb decreased by 17.4%. The introduced fly ash significantly improved the immobilization performance of the biochar material for HMs, which was mainly due to the increased surface precipitation and surface complexation effects of the introduced mineral fraction, while the larger specific surface area and pore volume of AFFA/BC-2 were the reasons that it was a better material for immobilizing Pb passivation in soil. According to the results of the morphological analysis of HMs after 12 rounds of wet and dry alternation, the biochar materials prepared under different conditions had a certain ability to passivate and immobilize Pb. The acid-extractable Pb decreased slightly, the reducible Pb decreased, and the oxidizable and residual Pb increased. In the AFFA/BC samples prepared under different conditions, compared with those in the soils without and with BC, the content of Pb in the more unstable acid-extractable and reducible states was lower, which was consistent with the results of the toxic leaching experiment of the TCLP and proved that the remediation effect of AFFA/BC on heavy metal Pb in soil was excellent and had long-term stability, among which the acid-extractable and reducible states of Pb in the soil remediated with AFFA/BC-2 were the lowest, indicating that AFFA/BC-2 was the best material in AFFA/BC for the remediation of Pb in soil. The acid extractable and reducible states of Pb in the soil remediated by AFFA/BC-2 were the lowest, indicating that AFFA/BC-2 is the best material in AFFA/BC for the remediation of Pb in soil. The addition of biochar can promote the transformation of soil Pb from active acid-extractable and reducible states to more stable oxidizable and residual states.

The curing rate and immobilization properties of the biochar materials during 12 rounds of alternating dry and wet aging are depicted in Figure 4c,d. It is observed that the immobilization properties of the biochar materials gradually decreased over time. However, even after 12 rounds of alternating dry and wet aging, the immobilization properties of the biochar materials remained above zero. Compared with virgin biochar without added fly ash, the new biochar material with added fly ash exhibits a greater immobilization rate of HMs, and the addition of fly ash enhances the aging resistance of the biochar material (Table S3). The curing rate of AFFA/BC-2 after 12 rounds of wet/dry

alternation was 44.70%, the highest among the tested materials, whereas the curing rate of BC after the same number of rounds was only 12.31%. Additionally, the aging coefficients of AFFA/BC-2 were the lowest compared to those of the other biochar materials (aging rate constant: 0.07, aging rate change: 0.12). AFFA/BC-2 demonstrated stability with a lower aging rate than the other materials, possibly due to its higher specific surface area and pore size volume. This stability suggests that AFFA/BC-2 is a superior soil remediation material with long-term effectiveness [42].

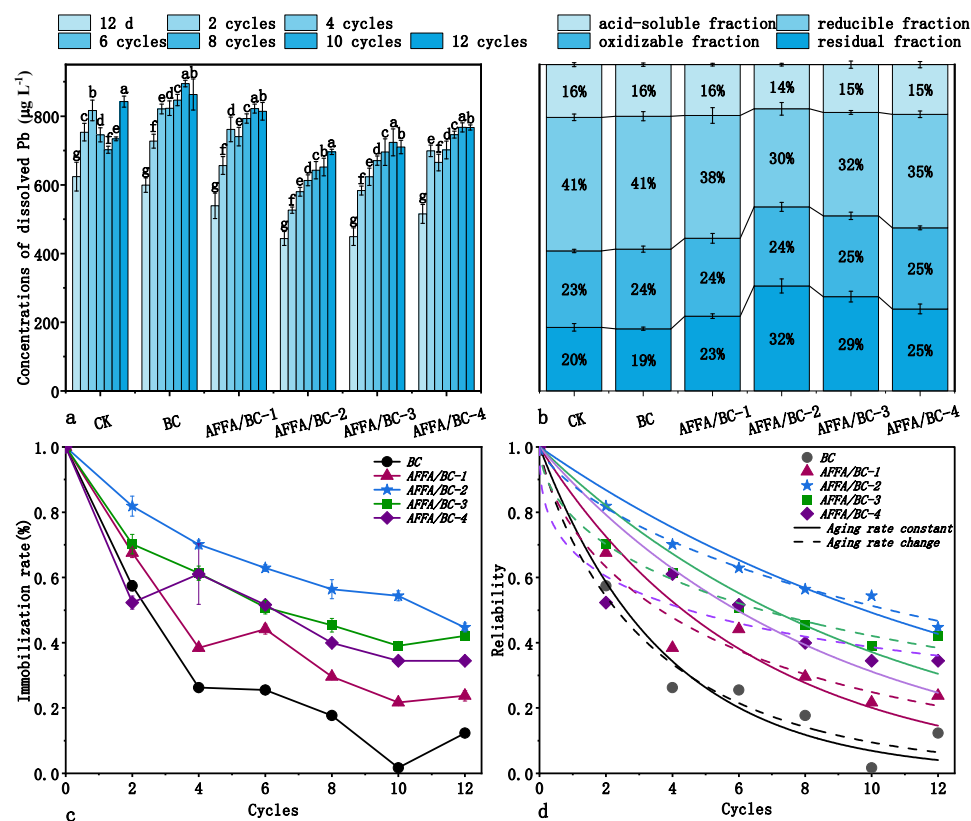


Figure 4. (a) Pb bioavailability of soil in control and BC- and AFFA/BC-treated soils during dry-wet cycling. The significant differences of different treatments were marked by different letters above each bar ($p < 0.05$). (b) Effects of dry-wet cycles on the occurrence of Pb in compound-contaminated soil. (c,d) Immobilization rate and reliability of the soil amendments during the dry-wet cycles of simulated aging.

After 12 cycles of wet-dry alternation, a Pearson correlation analysis quantified the relationships between biochar, various fly ash materials, soil physicochemical properties, and As leaching concentrations, as shown in Figure S4. The analysis indicates a strong correlation between Pb leaching concentrations and BCR acid-extractable and residual fractions under wet-dry conditions, suggesting that fly ash promotes the transformation of heavy metals to more stable residual forms, enhancing soil stability. Furthermore, Pb leaching concentrations correlate significantly with soil pH, CEC, specific surface area (SSA), and pore volume, demonstrating that fly ash improves soil physicochemical properties, thereby stabilizing heavy metals. The fitting results of Pb leaching with soil pH ($R^2 = -0.69$ and -0.71) reveal that increasing soil pH through fly ash reduces Pb toxicity and leaching. Additionally, soil pH positively correlates with CEC, SSA, and pore volume, confirming that fly ash enhances these properties, improving metal stabilization. Notably, fly ash addition and SSA show a negative correlation with aging rate constants, indicating improved anti-aging performance of biochar.

3.2.3. Effect of Changes in the Physicochemical Properties of Biochar Induced by Fly Ash on the Long-Term Immobilization Performance of Heavy Metals

The surface functionality, surface acid–base and electrical properties, chemical composition, and pore structure of the novel biochar are the main factors affecting its immobilization performance. In this study, AFFA/BC composites were prepared using a copyrolysis method to enhance the long-term remediation of HMs in contaminated soil.

After pyrolysis, the decomposition of cellulose in the biomass occurred, leading to a significant decrease in the amount of oxygen-containing hydroxyl and carboxyl functional groups on the BC surface, while the incorporation of AFFAs protected the functional groups of the biochar from high temperatures (Figure 2b). The surface complexation produced by oxygen-containing functional groups in AFFA/BC was more robust compared to that in BC for metal immobilization, and the inclusion of fly ash bolstered the prolonged immobilization of heavy metals by biochar. Conversely, the retention of the lignin fraction in biomass remained significant following pyrolysis (Figure 2b), and biochar derived from lignin could bind to heavy metals via robust noncovalent interactions [43]. This interaction is defined as a “cation- π interaction”, a π - π^* donor–acceptor interaction, and is a coordination force between the metal cation and the π -electron [44]. Cation- π interactions are prevalent in polycondensed aromatic structures, wherein the bonding is more robust than hydrogen bonding and corresponds to both internal and external surface complexation effects [43]. Additionally, cation exchange, surface precipitation, and electrostatic attraction have significant effects on metal immobilization in biochar [45]. Throughout the immobilization process, the alkali/alkaline earth metals K, Ca, Na, and Mg, present in the biochar, underwent replacement by heavy metals via electrostatic attraction, inner and outer sphere complexation, and precipitation. Moreover, with the addition of AFFA, the contents of elements such as Si and Al increased, which strengthened the ion exchange properties of the biochar material and stabilized the adhesion of HMs to the biochar. The addition of AFFAs increased PO_4^{3-} , and the addition of AFFAs increased the PO_4^{3-} and CO_3^{2-} contents of the biochar (Figure 2a), which could react with metals to form highly insoluble precipitates and significantly reduce the mobility of HMs in the contaminated soil. Previous studies have indicated that biochar materials produced through pyrolysis were found to be conducive to Pb immobilization within the temperature range of 400–500 °C, forming highly insoluble precipitates. AFFA/BC, created by incorporating alkali-fused fly ash, exhibits a larger specific surface area and higher pH compared to BC. Furthermore, AFFA/BC-2, boasting the highest specific surface area and pore volume, demonstrates superior resistance to aging (Figure 4c,d). Hence, the inclusion of AFFA amplified the surface complexation, cation exchange, surface precipitation, and electrostatic attraction of the biochar material, potentially resulting in the stable adsorption of additional heavy metals onto the biochar. Concurrently, the outstanding aging-resistant characteristic of AFFA/BC bolstered its long-term immobilization of heavy metals. Soil-biochar interactions also play important roles in metal immobilization. The incorporation of fly ash biochar material raised soil pH (Table 3) and facilitated metal stabilization by forming MeCO_3 , $\text{Me}_3(\text{PO}_4)_2$, and $\text{Me}(\text{OH})_2$ precipitates. Moreover, the humic-like components of soluble organic carbon (DOC) can bind metals via robust cation- π interactions. Over the incubation period, DOC undergoes oxidation and becomes notably more responsive to heavy metals. Consequently, the introduction of biochar material considerably aided metal immobilization through the creation of stable DOC organometallic complexes.

In summary, the immobilization of HMs by AFFA/BC and BC can be divided into the following steps: (1) Initially, biologically available HMs in pore water migrate from solution to the soil near-surface driven by significant physical gravitational forces (including electrostatic attraction, hydrogen bonding, and Van der Waals forces); (2) Subsequently, HMs

adsorb onto the biochar's inner and outer surface active sites; and (3) Finally, adsorbed metals are transported to the soil near-surface through precipitation/coprecipitation (PO_4^{3-} , CO_3^{2-} , CaCO_3 , and MgCO_3), surface complexation (Si-O bonding), cation- π interactions (π electrons in lignin- and humus-like DOC components), and cation exchange (K, Ca, Na, and Mg ions), forming stable metal-biochar complexes.

4. Conclusions

In this study, we developed a novel alkali-fused fly ash biochar composite (AFFA/BC) for the stabilization of lead (Pb) in contaminated soil and evaluated its long-term performance under simulated accelerated aging conditions. Compared with conventional biochar, AFFA/BC exhibited superior physicochemical properties, including increased specific surface area, enhanced chemical stability, and improved immobilization capacity for Pb. The copyrolysis process led to the formation of new functional groups and stable mineral phases, which contributed to the transformation of Pb into less bioavailable forms. The results demonstrated that AFFA/BC significantly reduced Pb leaching toxicity and maintained its immobilization effectiveness even after multiple wet-dry cycles.

The aging analysis revealed that the addition of alkali-fused fly ash not only enhanced biochar's heavy metal adsorption capability but also improved its structural integrity, reducing the rate of functional group degradation over time. AFFA/BC-2 exhibited the highest stability and lowest aging rate, making it a promising material for long-term soil remediation. Furthermore, the modeling approach based on conditional probability provided a quantitative assessment of biochar aging characteristics, offering valuable insights into its long-term application potential. These findings suggest that AFFA/BC is an effective, low-cost, and sustainable soil amendment for remediating heavy metal-contaminated soils while also promoting the resource utilization of coal-based solid waste and agricultural byproducts. Future studies should focus on field-scale validation and the interactions between AFFA/BC and other soil contaminants under varied environmental conditions.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su17062563/s1>. Figure S1: SEM characterization of FA (a) and AFFA (b); Figure S2: Evidence showing that alkali modification improves the adsorption properties of fly ash. (a) N₂ adsorption-desorption isotherms for FA and AFFA; aperture distribution of FA (b) and AFFA (c). The pore volume content of alkali-modified AFFA was significantly greater than that of FA, and the adsorbent samples with high pore structures had greater specific surface areas, greater ion exchange properties, and excellent adsorption capacities; Figure S3: (a) SEM images of BC and AFFA/BC b-e: AFFA/BC-1, AFFA/BC-2, AFFA/BC-3, AFFA/BC-4; Figure S4: Correlation analysis results revealing pivotal factors affecting the aging performances; Table S1: Preparation conditions of biochar materials; Table S2: Summary of the 2D-FTIR-COS synchronous/asynchronous spectra of biochar-derived AFFA complexed with metal ions. The symbol '○' indicates that the positive and negative values of the cross peaks in the synchronous/asynchronous spectra are the same, while the symbol '□' indicates that the sign of the cross peaks in the synchronous/asynchronous spectra is different.; Table S3: Aging parameters of BC and AFFA-BC.

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